Introduction

Water Contaminants

- Instructor: Yongju Choi, 35-307, ychoi81@snu.ac.kr

- Course material/textbook:
  1. Lecture notes: uploaded on eTL prior to the class
  2. Schwarzenbach, Gschwend, Imboden, Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, 2003

Office hour

- 5:00-5:30 pm Mon & 9:00-9:30 am Fri
- Via Zoom
- With the instructor
  - Announcement will be made for cancellation; use emails for Q&A when office hour is cancelled

Zoom link:

https://snu-ac-kr.zoom.us/j/8675573197

(Meeting ID 867 557 3197)

Water Contaminants

- Study different types of water contaminants and their fate in various settings of water environment
- Some background on environmental organic chemistry
- Focus on organic contaminants and the physicochemical mechanisms involved in their fate

Student presentation & paper discussion

- Only one exam for this class? But…
- Four students lead 1 class
- Topic & paper selection & posting
  - Select a topic & a paper (relevant to the class!) and submit a brief presentation plan at least **3 business days prior to the class assigned**

    (Mon class → Wed; Wed class → Fri)
  - Post the paper link to eTL at least **2 business days prior to the class assigned**

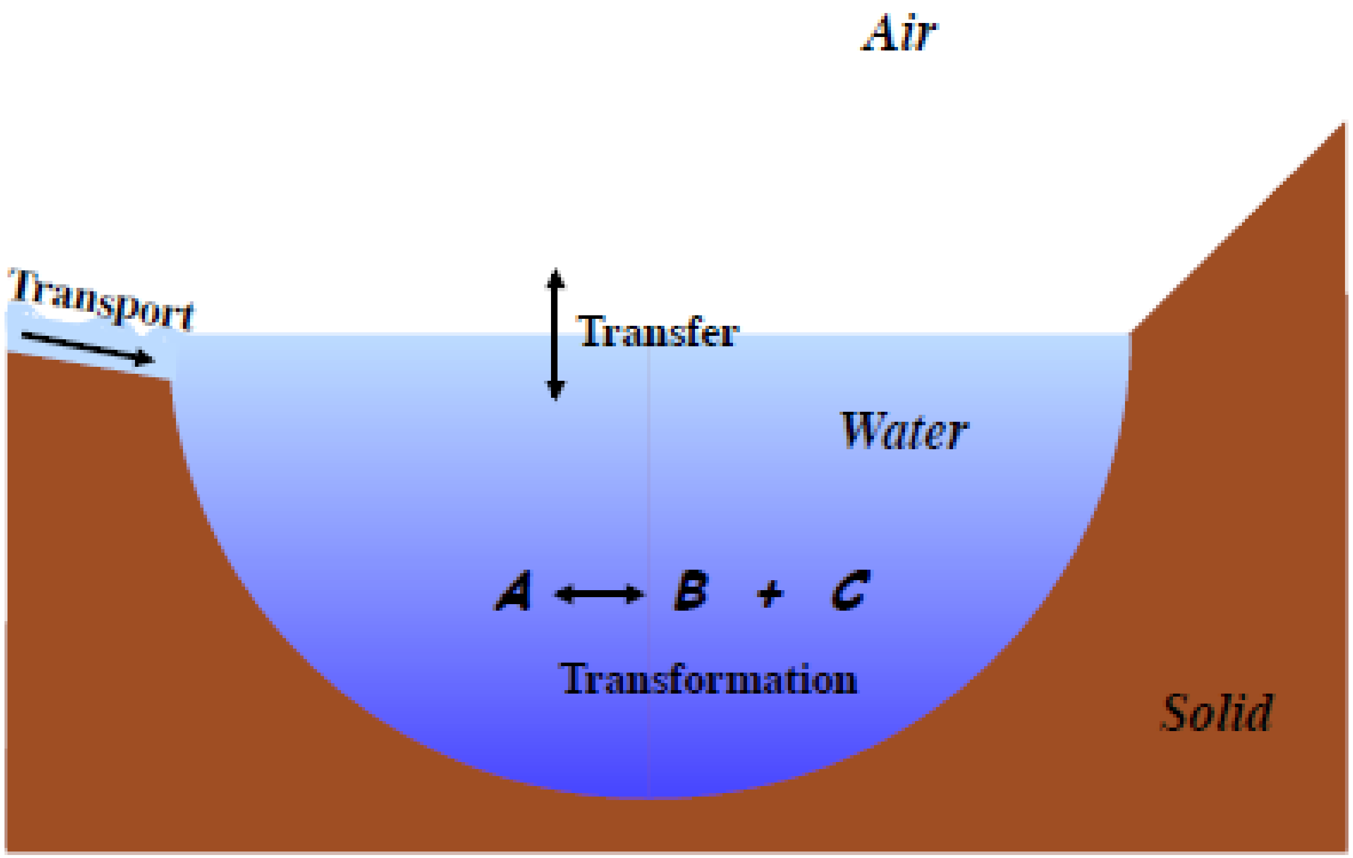
    (Mon class → Thu; Wed class → Mon)

Student presentation & paper discussion

- Contents
  - Brief background on the selected topic
  - **CRITICAL** review of the selected paper
  - Presentation (10 min) + Discussion (5-10 min)

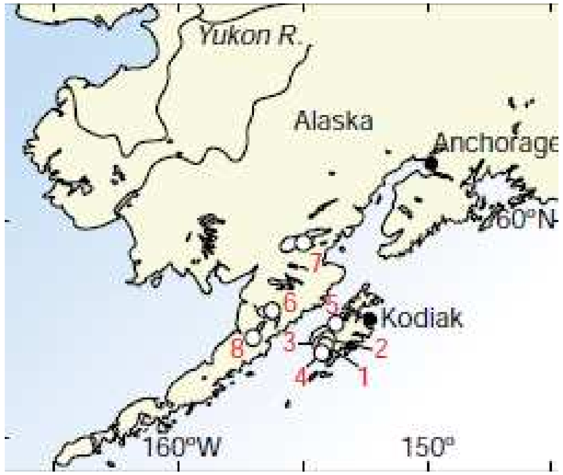
- Construct your presentation in a way that can promote student discussion
  - e.g., throw out questions to your colleagues
  - Note that **YOU** are the discussion leader for your presentation

Transport, phases, interphases



Contaminant fate?

http://www.virginmedia.com/science-nature/wildlife

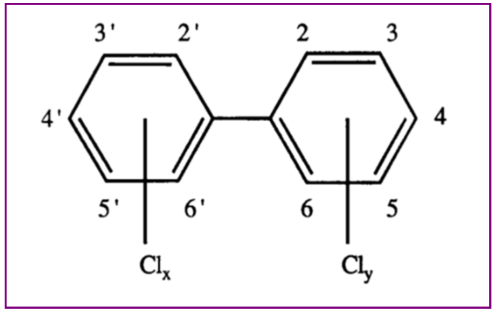


- Sediment PCB conc. proportional to # salmon spawning/km^2
- PCB congener distribution in <u>salmon lakes' sediments similar</u> to distribution in salmon; <u>different</u> from distribution in <u>no-salmon lakes' sediments</u>
- Pacific salmon
  - Amadramous: move from salt to freshwater to breed or spawn
  - Semelparous: die after spawning

Krummel et al., 2003, Nature, 425:255-256

Transport against hydraulic gradient

- Salmons concentrate PCBs (biovectors)



PCB molecular structure

Bioconcentration of PCBs in Lake Ontario

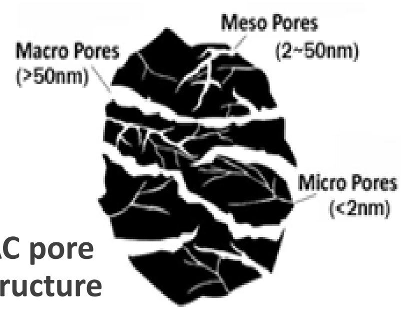
	microgram PCB per *		
PCB congener	52	66	153
MW	291.97	291.97	360.71
dissolved	6.3E-0.5	3.1E-0.5	5.0E-0.5
bottom sediment	25	46	25
suspended sediment	15	27	23
plankton	2.4	1.6	2.2
mysids	3.5	15	30
amphipods	22	30	45
oligochaetes	6.3	8.3	7.5
small smelt	7.6	2.7	64
large smelt	18	72	130
trout/salmon	62	160	430

*liter for dissolved; kg dry wt. for sediments; kg wet wt. for organisms

Oliver & Nilmi, 1988, ES&T, 22:388-397

Water Quality & Environment Lab.

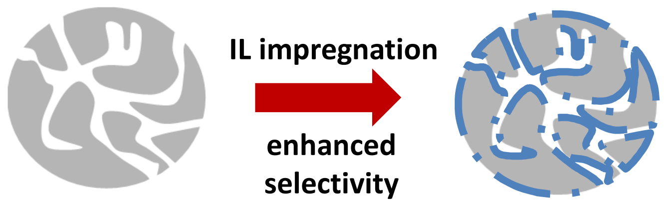
Sorption processes for water & wastewater treatment



AC pore structure

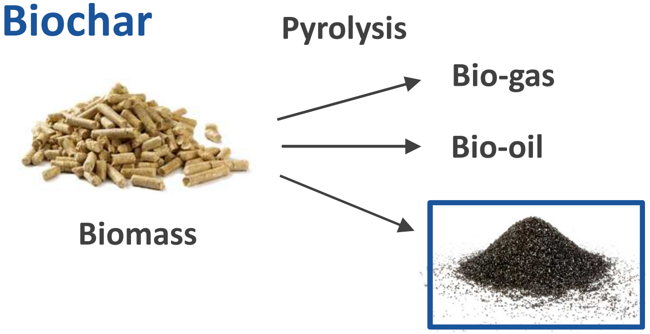
Activated carbon (AC)

Ionic liquid (IL)-impregnated AC

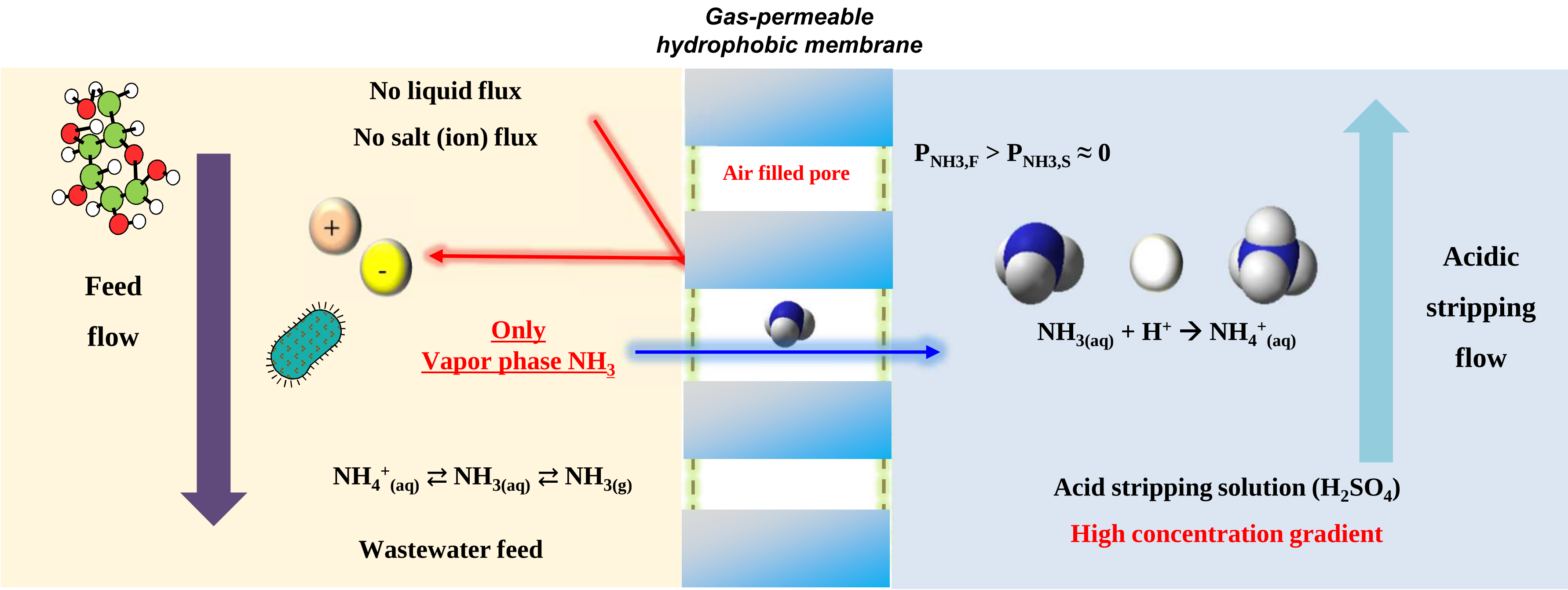


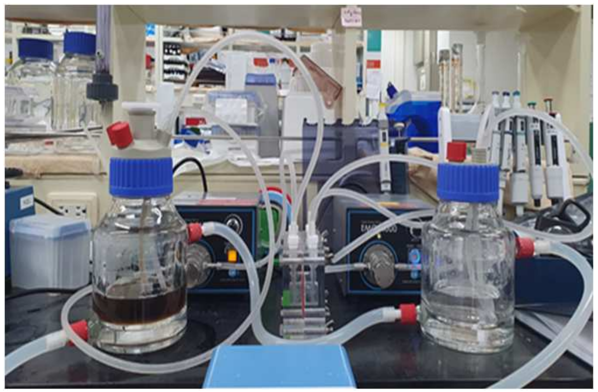
Zeolite

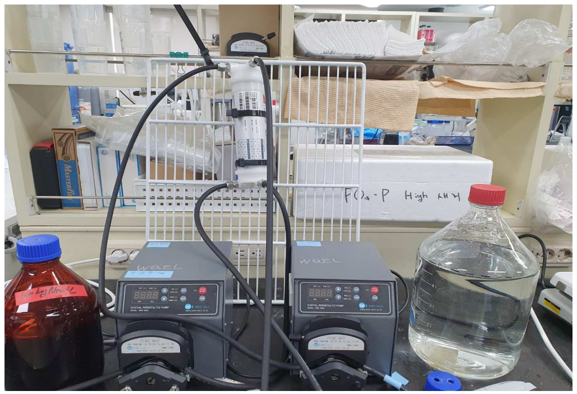
Biochar



Resource recovery from wastewater using gas-permeable membrane

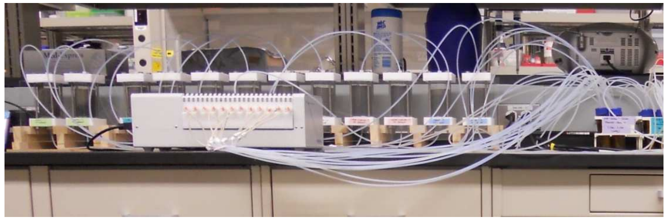


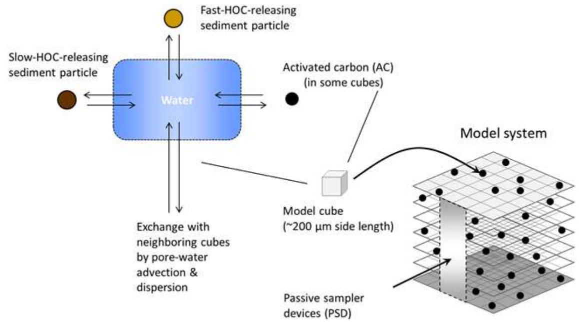




Treatment of sediment impacted by hazardous chemicals

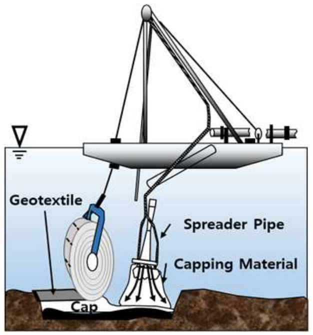
In-situ sorbent amendment

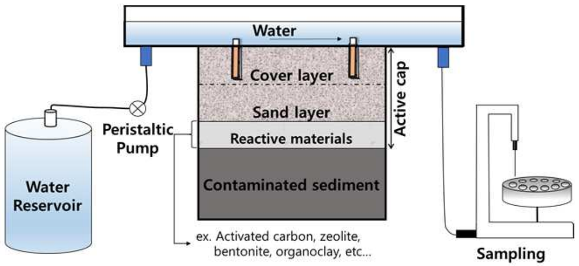


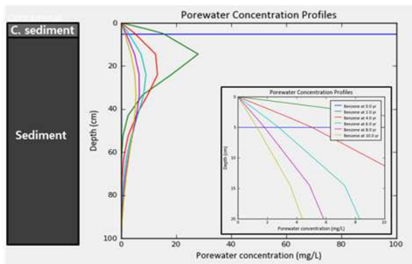


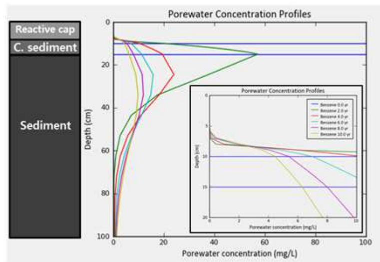
Field ------------------------------ Lab exp. ------------------------------------ Model simulation

In-situ capping







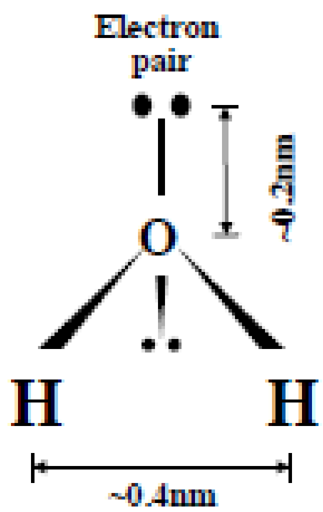


Field -------------------------- Lab exp. ------------------------------------ Model simulation

Uniqueness of water

Water – a unique solvent

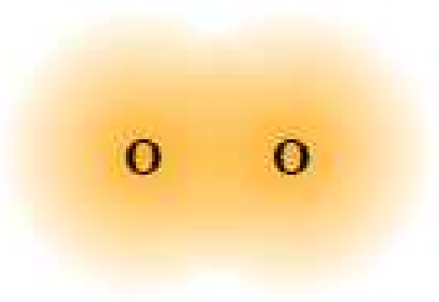
Property	H_2O	H_2S	CH_4	CH_3OH
Molecular weight	18	34	16	32
Dipole moment (Debyes)	2.0	0.9	0.0	1.7
Boiling point (°C)	100	-60	-161	65
Enthalpy of vaporization (kJ/g)	2.30	0.55	0.88	1.10
Melting point (°C)	0	-85	-181	-94
Enthalpy of fusion (kJ/g)	0.33	0.07	0.06	0.10



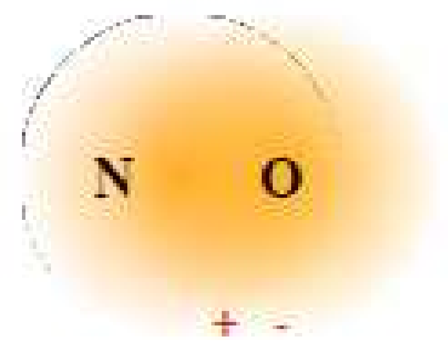
Dipole moment

A molecule has a dipole moment if the center of the molecule's positive charges is not at the same spot as the molecule's negative charges

O_2 – no dipole moment

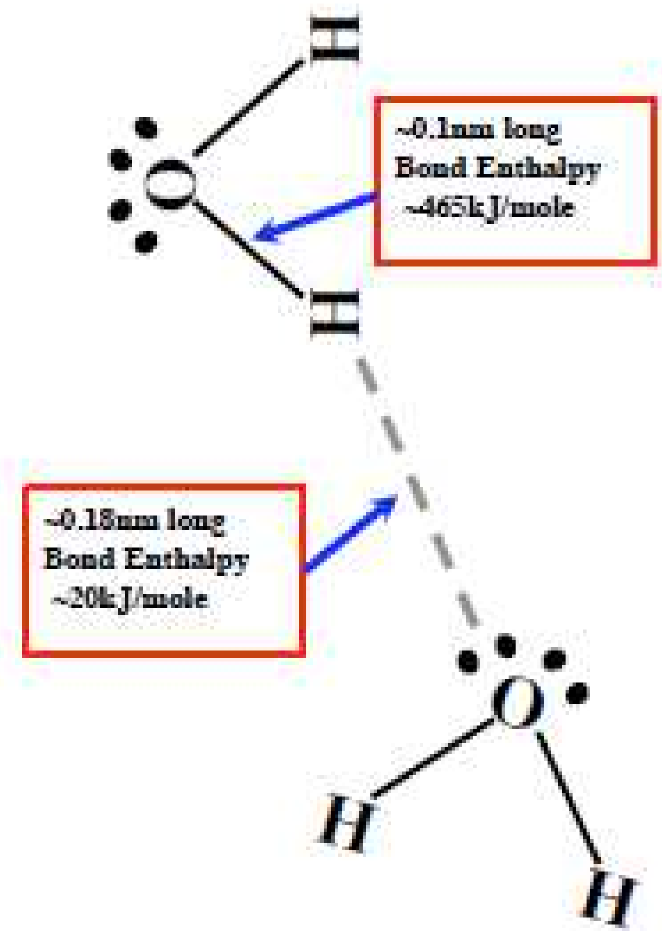


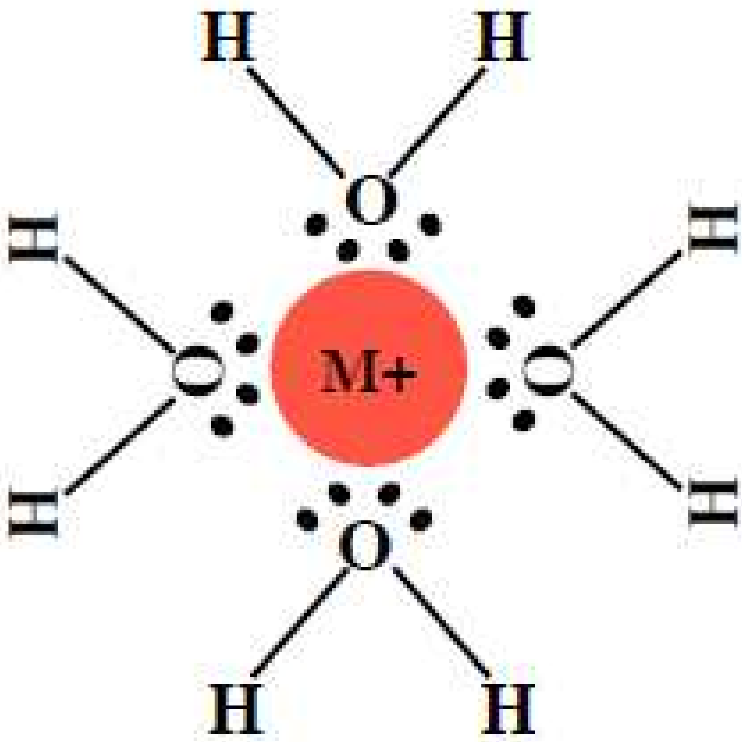
NO – dipole moment



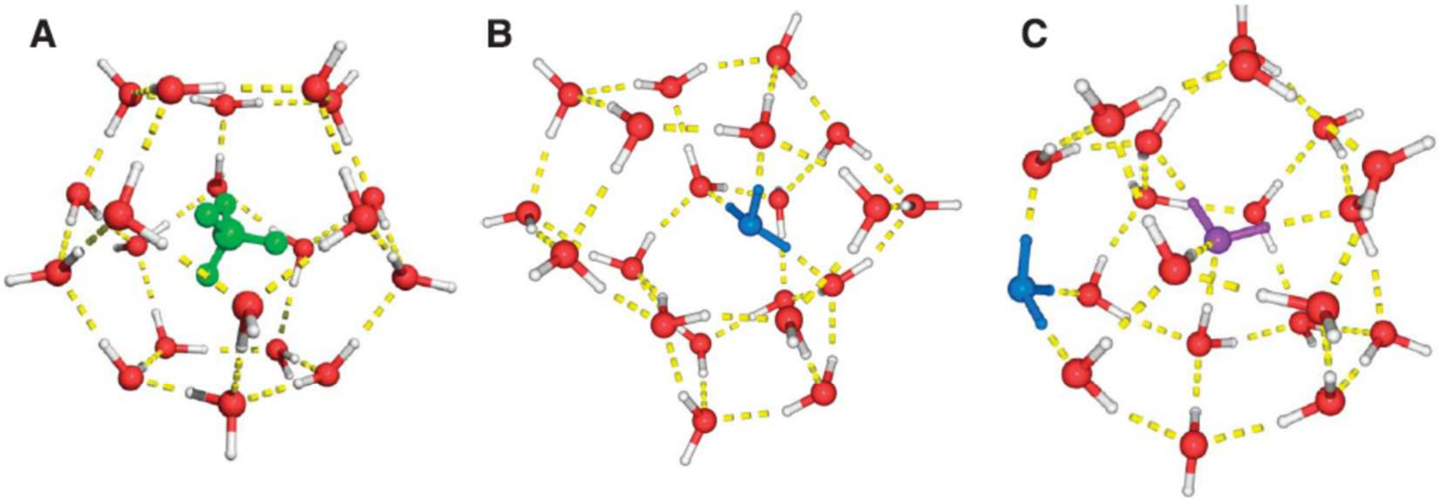
Electron density shifted to oxygen

Water – hydrogen bonding & dipole moment





Hydrogen bonding



Stable water clusters. (**A**) Methane clathrate consists of a dodecahedral water cage surrounding a methane molecule (green). The $n = 21$ protonated water cluster suggested by analogy has the H_3O^+ ion (blue) taking up a position inside the clathrate cage (**B**) or on its surface (**C**), displacing a neutral water molecule (purple) to the cage interior. The hydrogen bonds are indicated by the dashed lines in yellow.

Zweir, 2004, Science, 21:1119

- H_2O structure promotes incorporation of hydrogen bonding, polar, ionic entities
- Non-hydrogen bonding, non-polar, non-ionic entities disrupt water's structure

Basics of basics of water chemistry

Ionic strength, activity, molarity

- **Ionic strength**

$$I = \frac{1}{2}\sum_i (C_i \times z_i^{\,2})$$

C_i = concentration of ionic species i (M)

z_i = charge of ionic species i

  - Significance: in dilute solutions (I ~< 10^{-3} M) the ions behave independently of each other, but as ion concentration increases, ion interactions become significant, decreasing the activity of the ions

- **Activity vs. molarity ({ } vs. [ ])**

$$\{i\} = \gamma_i[i]$$

  - $\gamma_i \cong 1$ in dilute solutions (for most natural waters except for seawater, this would be acceptable for crude calculations)
  - Güntelberg equation (for $I < 0.1$):

$$log_{10}\,\gamma_i = -\frac{0.5 z_i^{\,2} I^{0.5}}{1 + I^{0.5}}$$

Electroneutrality principle

$$\sum cations\ (in\ eq/L) = \sum anions\ (in\ eq/L)$$

** equivalent [eq] of an ion:*

(eq) = (mole) x (valence)

- **May use the following condition to determine the accuracy of water ion content analysis**

$$\left|\sum anions - \sum cations\right| \leq \left(0.1065 + 0.0155 \sum anions\right)$$

** ∑ values in meq/L*

Aqueous chemistry parameters

- **Units**
  - Mass/vol — kg/m^3, mg/L, …
  - #/vol — mole/L, # of organisms/mL
  - Transferable electrons or protons/vol — eq./L, meq./L
  - Mole fraction — mole/∑mole

- **Why different units?**
  - Engineers vs. chemists
  - Specific needs of the problem

Aqueous chemistry parameters

- **Aggregate parameters**
  - Characterize important properties of mixtures
    - __OD (oxygen demand)
    - TO__ (total organic carbons (C), halides (X))
    - Total hardness, Alkalinity, …
    - Total PCBs, Total PCTs, …
  - Conduct one analysis instead of many
- **__per__as__**
  - mg/L as $CaCO_3$ (for alkalinity & hardness)
  - mg/L as N
  - % as P_2O_5 or K_2O

Measures of (oxidizable) organic matter

- **BOD – Biochemical Oxygen Demand**
  - Measure of a water's biologically oxidizable constituents
    - Analyze [DO] in a water sample before & after controlled incubation
    - 5 day incubation is common
- **COD – Chemical Oxygen Demand**
  - Measure of a water's chemically oxidizable constituents
    - 2-3 hour reaction time
    - Generates liquid hazardous wastes
  - Does not oxidize organic N
- **TOC, DOC – Total/Dissolved Organic Carbon**
  - Measure of a water's organic carbon content
    - Analyze mass/concentration of CO_2 produced after chemical oxidation of a sample
    - Sampling time – a few minutes

BOD_5 vs COD vs TOC

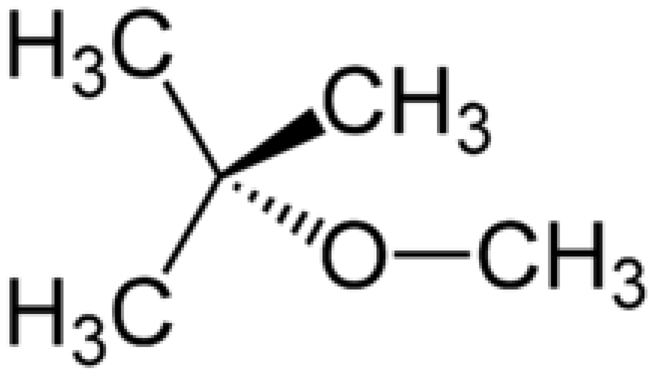
Compound	Formula	MW	BOD_5	COD	TOC	COD/TOC	TOC/MW	COD/MW
Methane	CH_4	16	??	64	12	5.3	0.75	4.0
MTBE	$C_5H_{12}O$	88	~0	240	60	4.0	0.68	2.7
Benzene	C_6H_6	78	??	240	72	3.3	0.92	3.1
Glucose	$C_6H_{12}O_6$	192	~192	192	72	2.7	0.38	1.0

$$CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$$

$$C_5H_{12}O + 7.5O_2 \Leftrightarrow 5CO_2 + 6H_2O$$

$$C_6H_6 + 7.5O_2 \Leftrightarrow 6CO_2 + 3H_2O$$

$$C_6H_{12}O_6 + 6O_2 \Leftrightarrow 6CO_2 + 6H_2O$$



[MTBE]

pH

$$pH = -\,log_{10}\,\{H^+\} \;\approx\; -\,log_{10}\,[H^+]$$

- For most natural waters, $5 < pH < 9$
  - Most aquatic life adapted for this range

- Self ionization constant of water, K_w

$$K_w = \{H^+\}\{OH^-\} = 10^{-14}$$

$$pK_w = pH + pOH = 14$$

@ 25 °C

- Chemical speciation can be highly pH dependent

$$ROH \;\Leftrightarrow\; RO^- + H^+$$

$$K_a \approx \frac{[RO^-][H^+]}{[ROH]}$$

  - If pH < pK_a, protonated (associated)
  - If pH > pK_a, deprotonated (dissociated)