Regional Online Training Course on the Relationship Between Ocean Environment Variability and Marine Resource Abundance and Oceanographic Sampling

Introduction to Marine Chemistry

Penchan Laongmanee

Faculty of Marine Technology

Burapha University, Chanthaburi Campus

Marine chemistry

- study of the chemical composition and chemical processes of the world's oceans.
- Key processes studied are the cycling of: inorganic and organic carbon; nutrients, such as nitrogen and phosphorus; and trace elements, such as iron.

https://www.nature.com/subjects/marine-chemistry

Chemical Oceanography

- understand the distribution and reactivity of chemical components
  - within the ocean
  - earth-ocean,
  - sediment - ocean,
  - atmosphere - ocean interfaces.

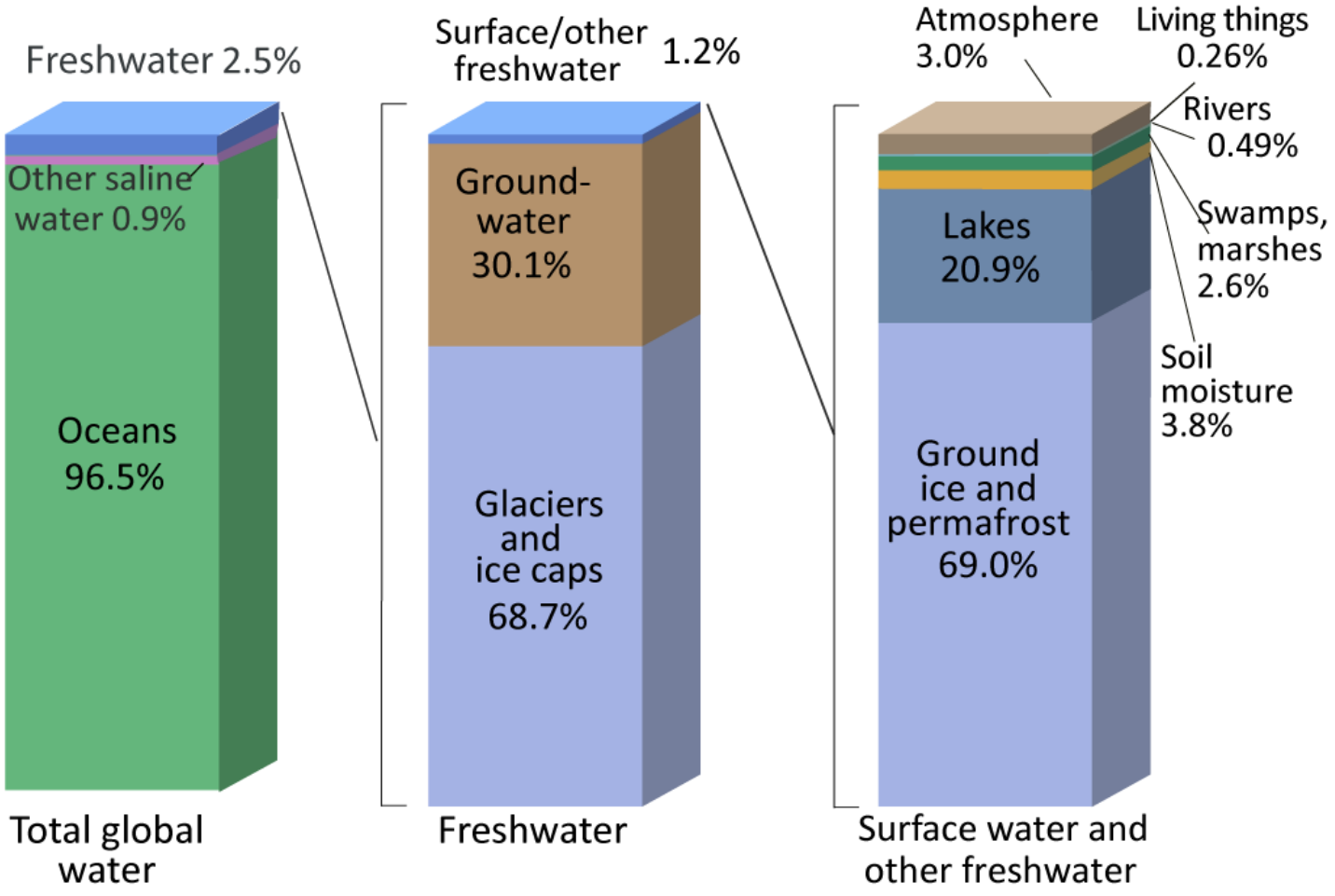
Luther & Boyle (2007) Chemical Reviews, Vol. 107, No. 2

Course objective:

- Improve the knowledge of human resource of the relationship between ocean environment variability and fisheries resource abundance
- Enhance the capacity of human resources to carry out oceanographic survey focusing on sampling methods.
- To establish the network of fishery officers/researchers on oceanography and fisheries resources in the Southeast Asia region.

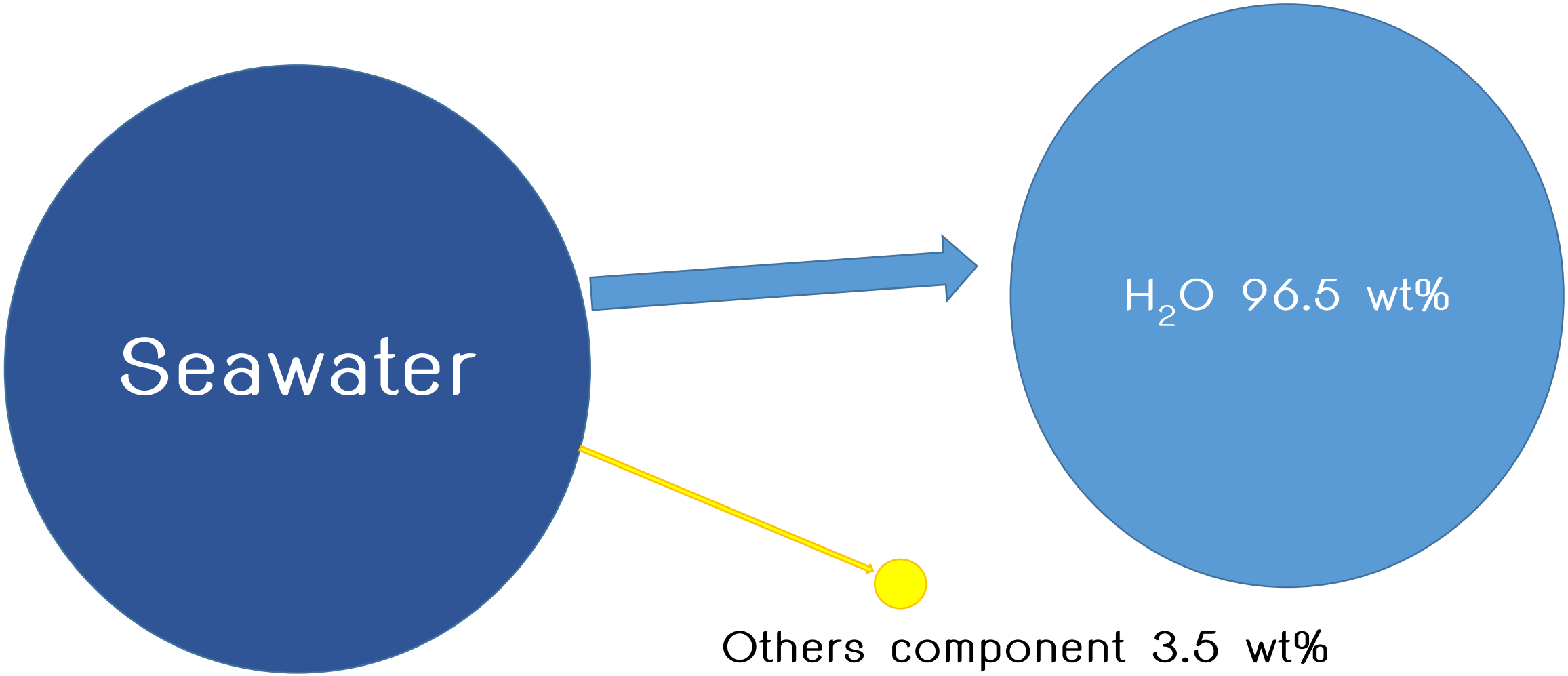
Chemical Oceanography -- > Fishery

Where is Earth's water?



Source: Igor Shiklomanov's chapter "World fresh water resources" in Peter H. Gleick (editor), 1993, Water in Crisis: A Guide to the World's Fresh Water Resources. (Numbers are rounded).

Composition of seawater



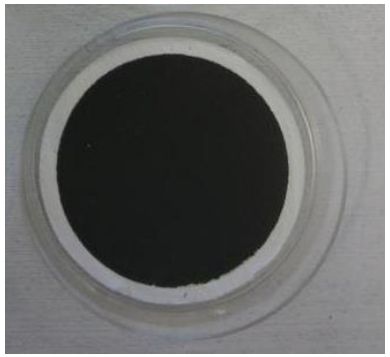
Composition of seawater

- 1. Solids (material that does not pass through a 0.45-µm filter)
- 2. Gases
- 3. Colloids (passes through a 0.45-µm filter but is not dissolved)
- 4. Dissolved solutes

Composition of seawater

1. Solids
   (material that does not pass through a 0.45-µm filter)
   a. Particulate organic material (plant detritus, living organisms & remains)

   b. Particulate inorganic material (minerals)

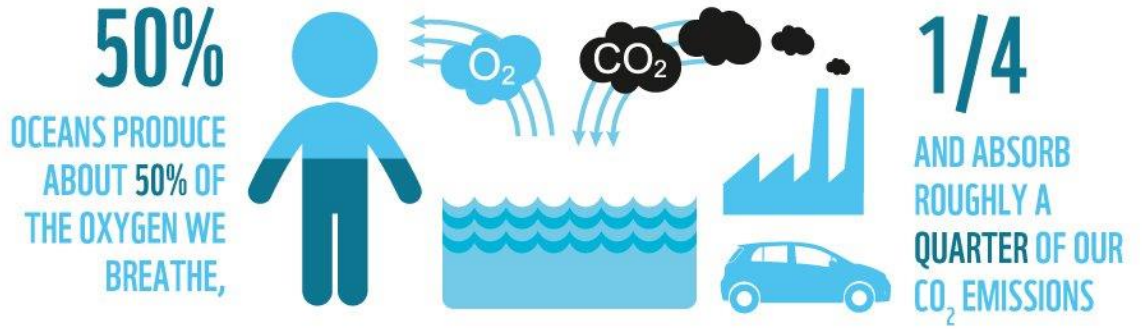


Composition of seawater

2. Gases

a. Conservative (N_2, Ar, Xe)
   - less react with water/other element
   - Less involved in biological process

b. Non-conservative (O_2 and CO_2)
   - react with water/other element
   - Involved in biological process



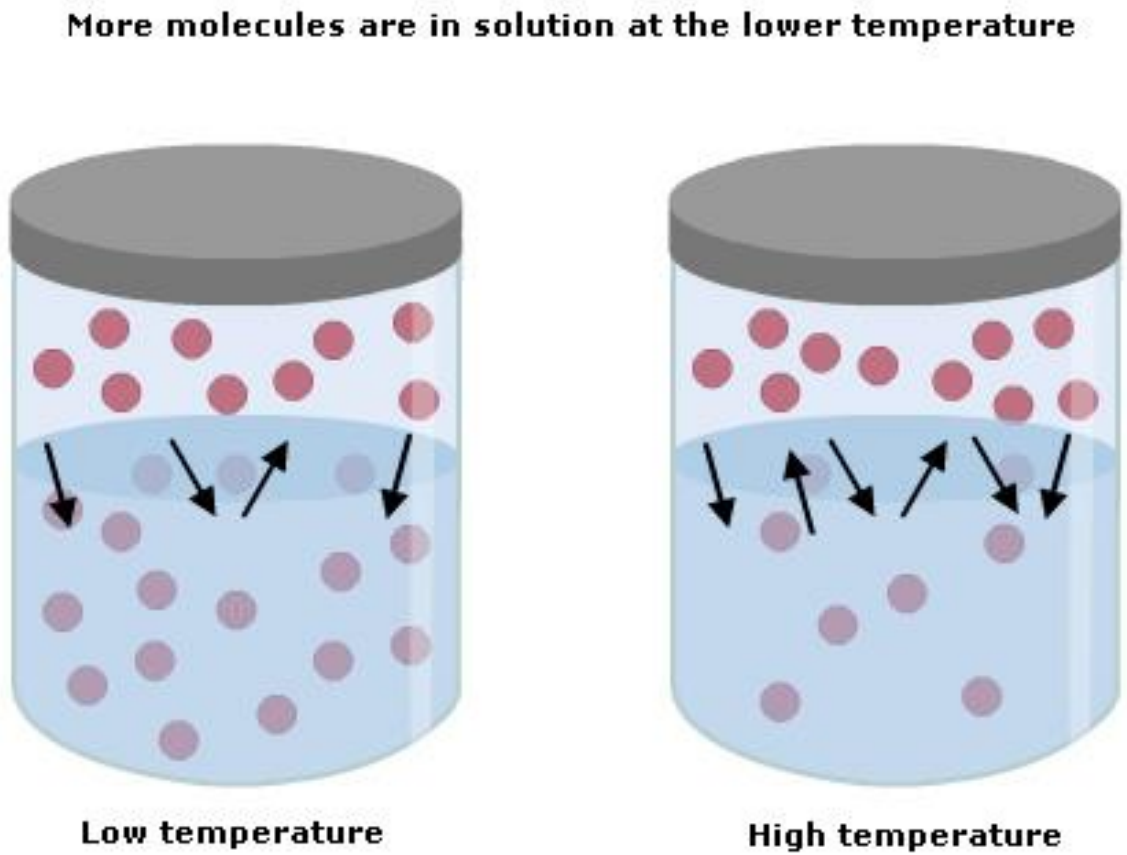
https://texanbynature.org/2019/08/5-ways-to-help-save-our-ocean/

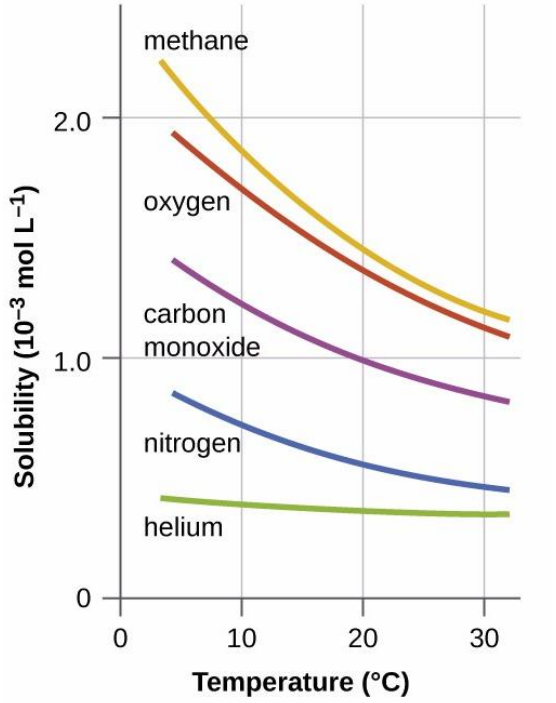
Solubility and Saturation Value of Gases

- Solubility - tendency to dissolve and go into solution
- Saturation value - equilibrium amount of gas dissolved in water at an existing temperature, salinity and pressure
- Solubility and Saturation value increase as
    - Temperature (T) decrease
    - Salinity (S) decrease and
    - Pressure (P) increases

Concentration of Dissolved Gases

- Increases with decreasing T (cold water holds more dissolved gas)



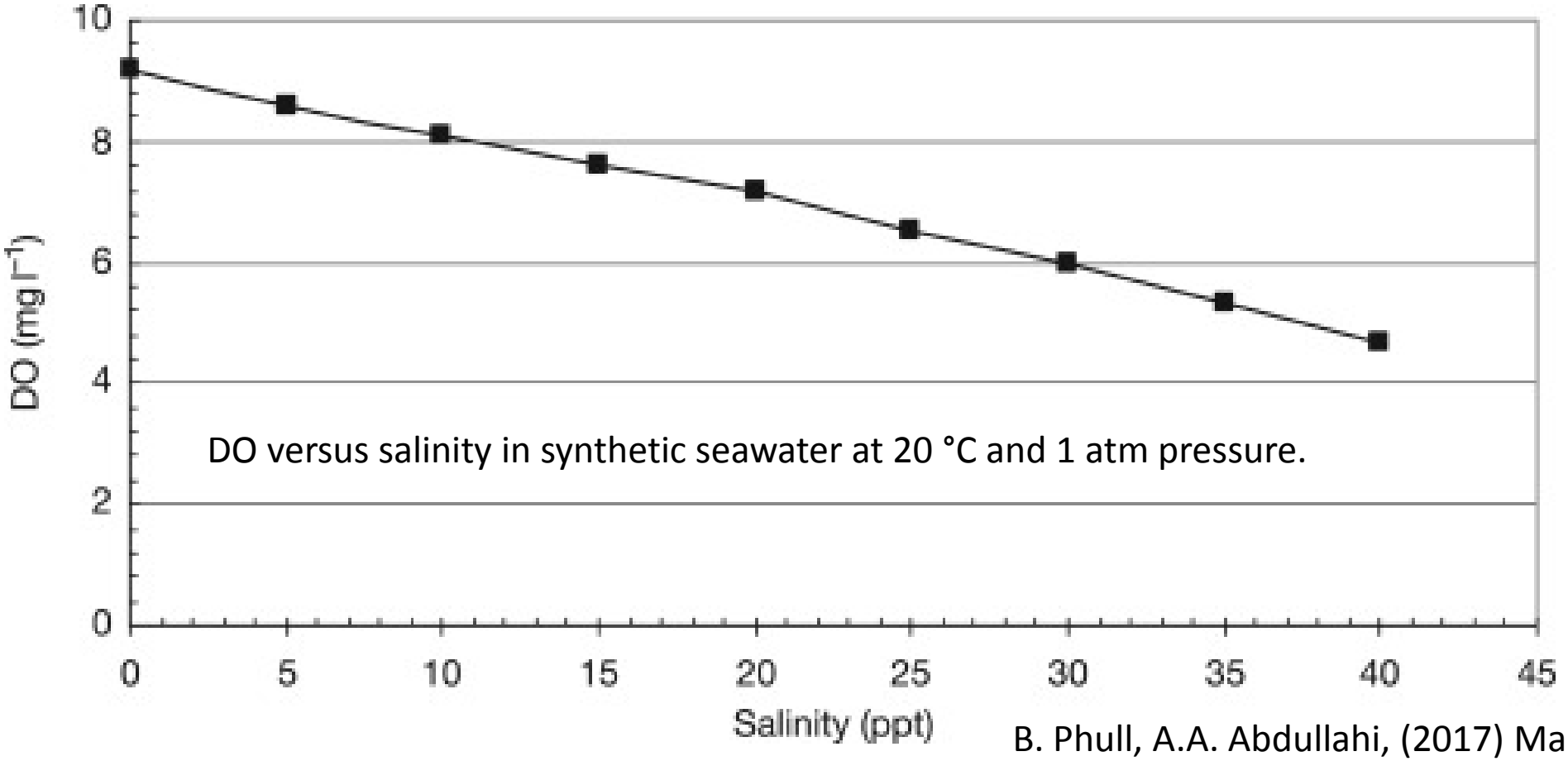


http://kolibri.teacherinabox.org.au/

https://e-safe-anaesthesia.org/

Concentration of Dissolved Gases

- Increases with decreasing S

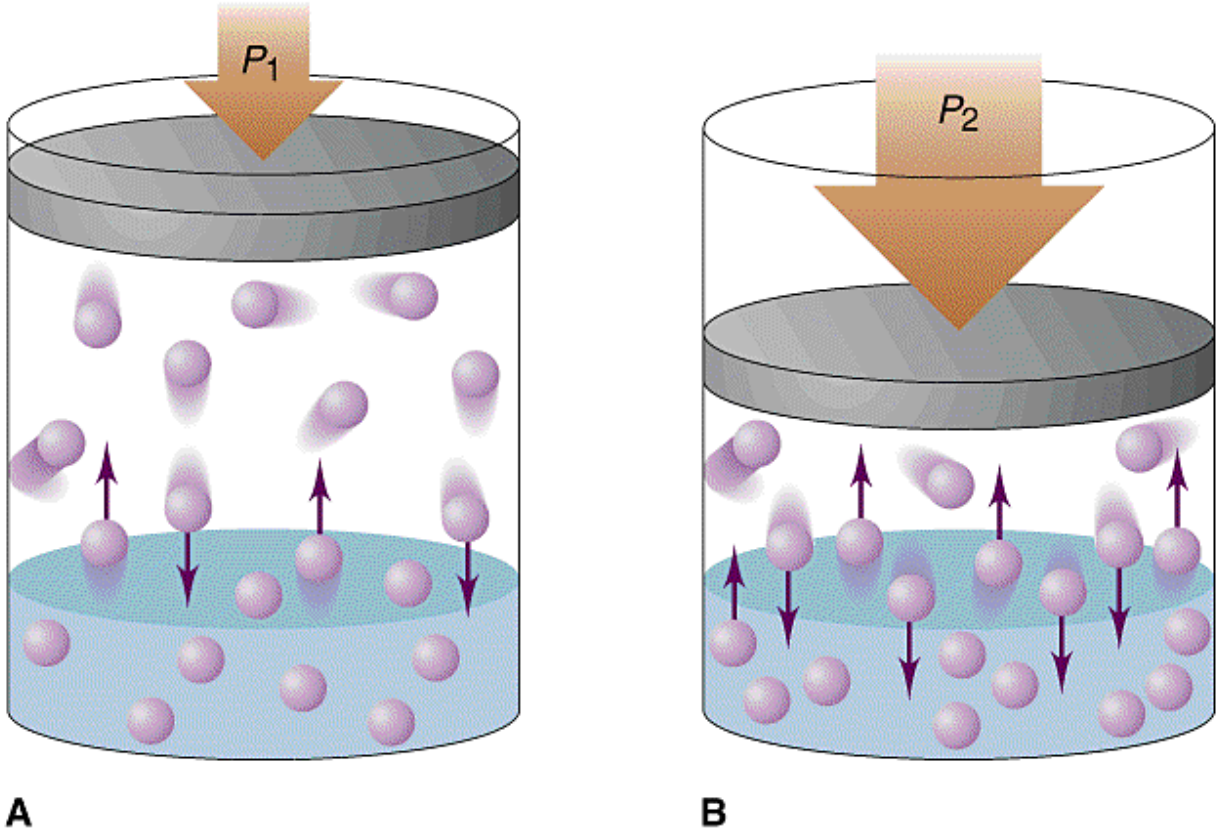


DO versus salinity in synthetic seawater at 20 °C and 1 atm pressure.

B. Phull, A.A. Abdullahi, (2017) Marine Corrosion, Reference Module in Materials Science and Materials Engineering,

Concentration of Dissolved Gases

- Increases with increasing P



http://ch302.cm.utexas.edu/

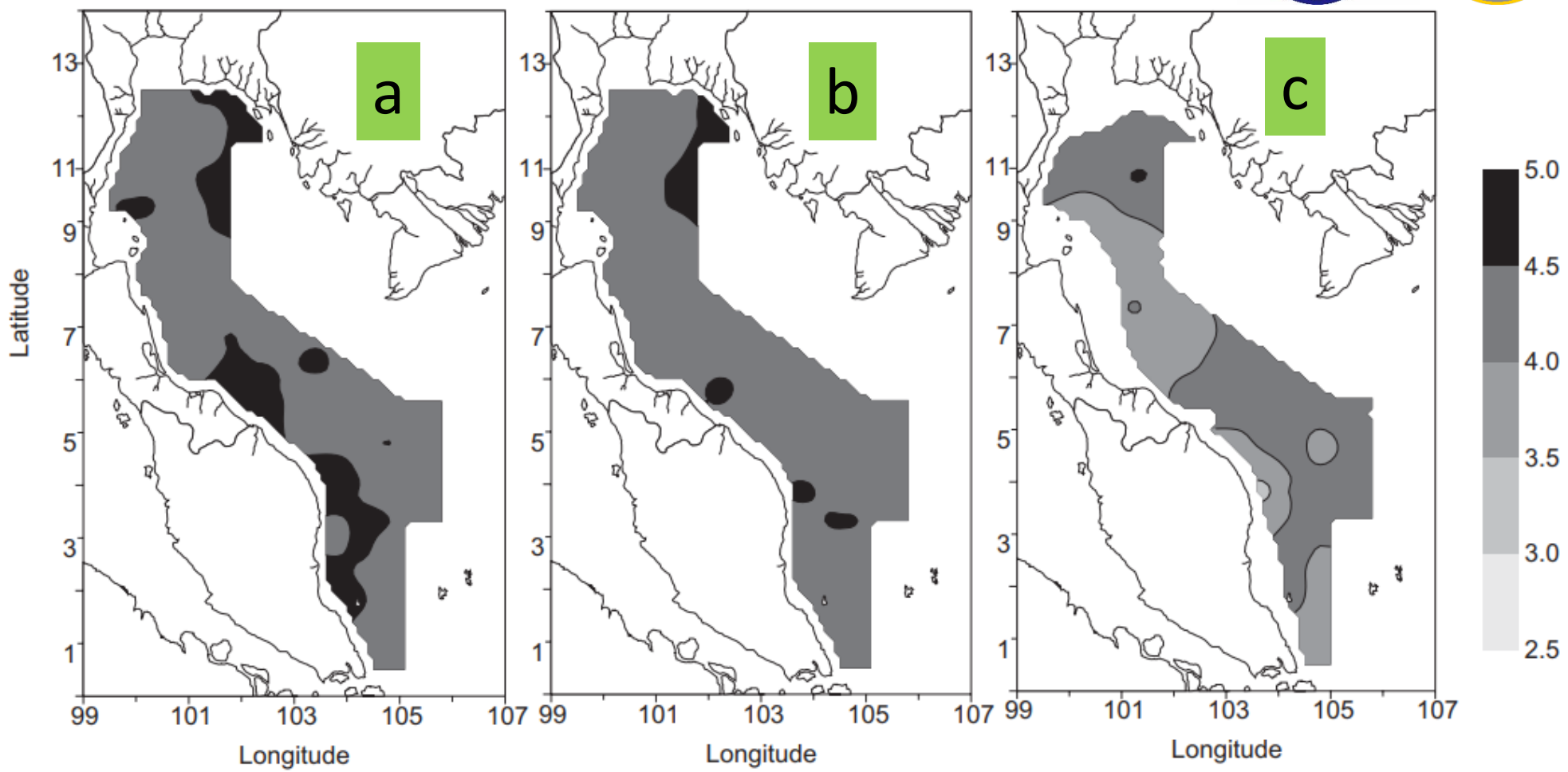
Gas in sea water

- Undersaturation - contains less than maximum amount of dissolved gas
- Saturation - maximum amount of gas
- Supersaturation - contains more gas than saturation value (excess gas comes out of solution)

  - Surface layer - usually saturated due to gas exchange with the atmosphere

  - Below surface layer -gas content reflects respiration, photosynthesis, decay and input from volcanic vents

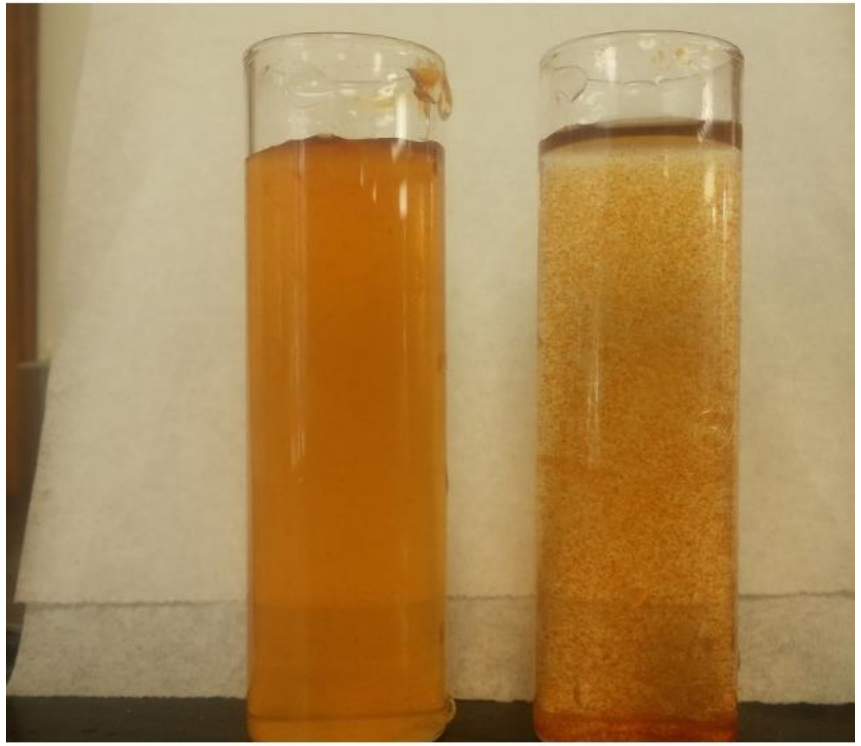
Dissolved oxygen (ml/l)



Dissolved oxygen (ml/l) in the western Gulf of Thailand and eastern Peninsular Malaysia in September 1995;
a) Surface level (0-10m), b) Mid-depth level (10-40m), c) Sub pycnocline level (>40m) (Rojan-anawat&Snidwong,1997)

Composition of seawater

- 3. Colloids (passes through a 0.45-µm filter but is not dissolved)
  - a. Organic (complex sugars)
  - b. Inorganic (iron hydroxides)



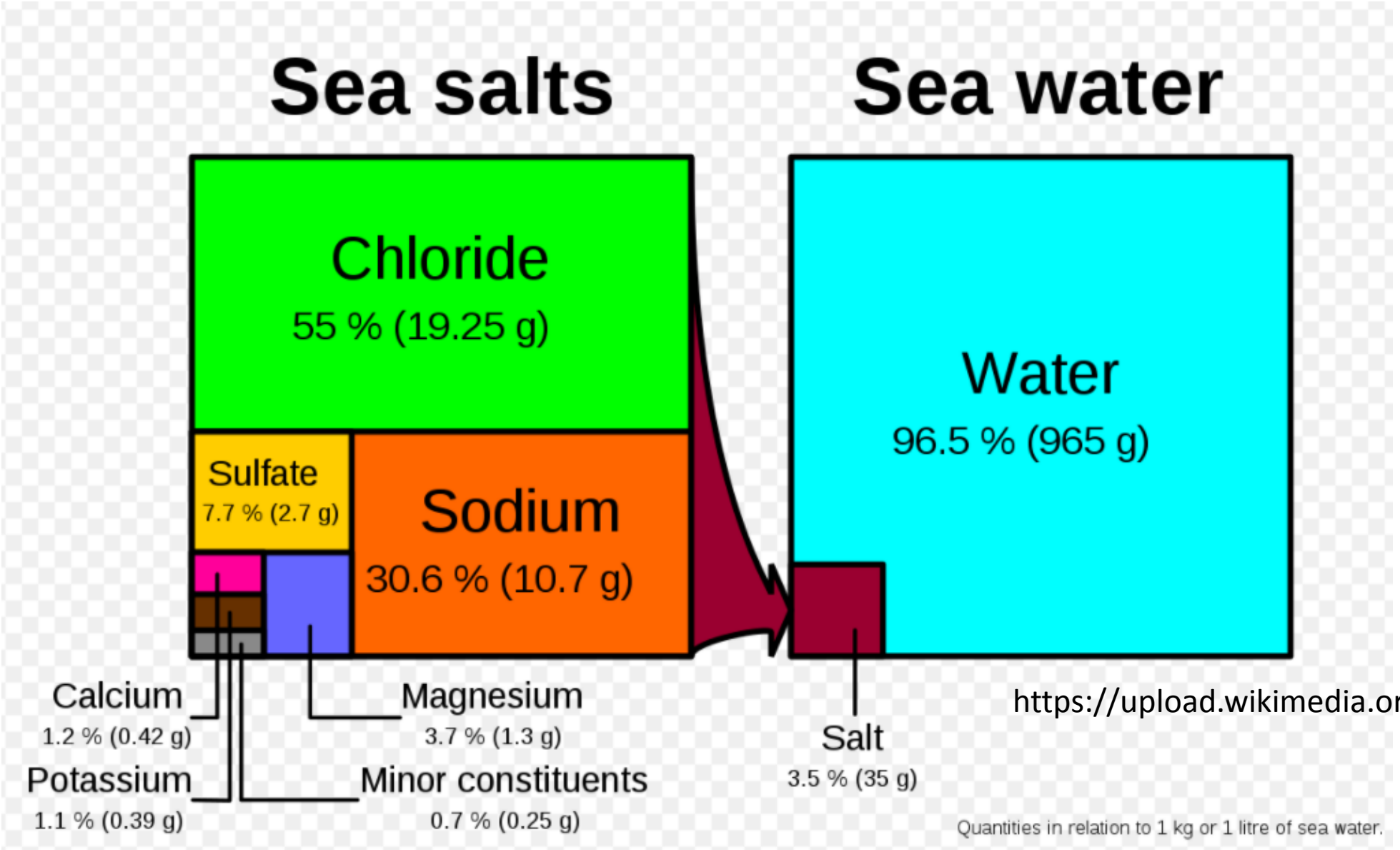
Reaction of Iron(III) with hydroxide ion
https://chemistry.stackexchange.com/

Composition of seawater

4. Dissolved solutes

- a. Inorganic solutes
  - 1. Major (>1 ppm) (Conservative , long residence time) 99.7%
    - less react with water/other element
    - Less involved in biological process
  - 2. Minor (<1 ppm) 0.3%
    - Nutrient
    - Trace element
- b. Organic solutes

Dissolved solutes: (inorganic)

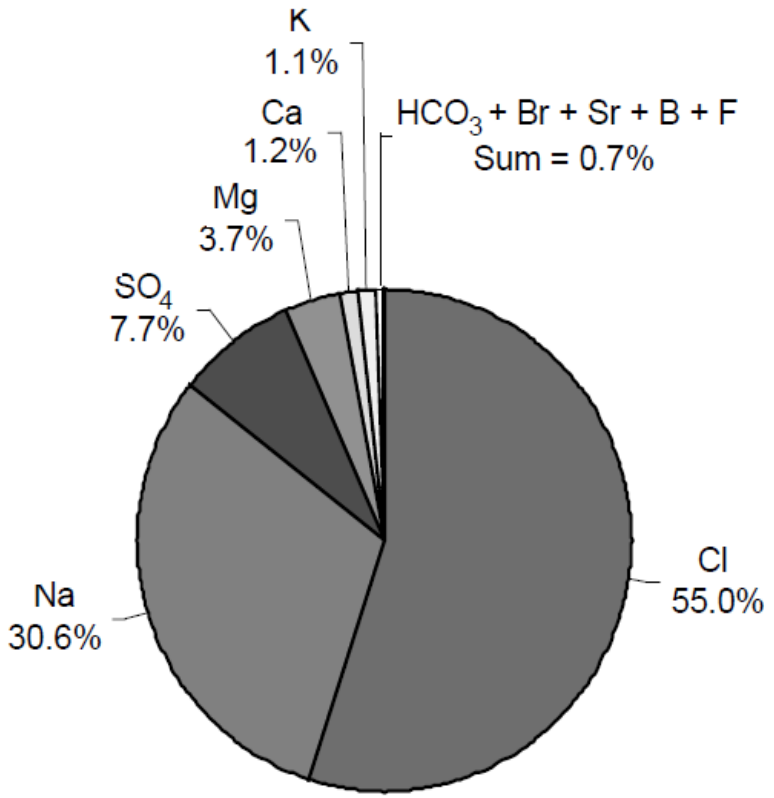


https://upload.wikimedia.org/

Major ion -- > Salinity

The **major ions** (>1mg/kg seawater) at S = 35.000 (from Pilson)

Ion	Formula	g/Kg	mmol/Kg
Sodium	Na^+	10.781	468.96
Magnesium	Mg^{2+}	1.284	52.83
Calcium	Ca^{2+}	0.4119	10.28
Potassium	K^+	0.399	10.21
Strontium	Sr^{2+}	0.00794	0.0906
Chloride	Cl^-	19.353	545.88
Sulfate	SO_4^{2-}	2.712	28.23
Bicarbonate	HCO_3^-	0.126	2.06
Bromide	Br^-	0.067	0.844
Borate	$H_3BO_4^-$	0.0257	0.416
Fluoride	F^-	0.00130	0.068
Totals	11	35.169	1119.87



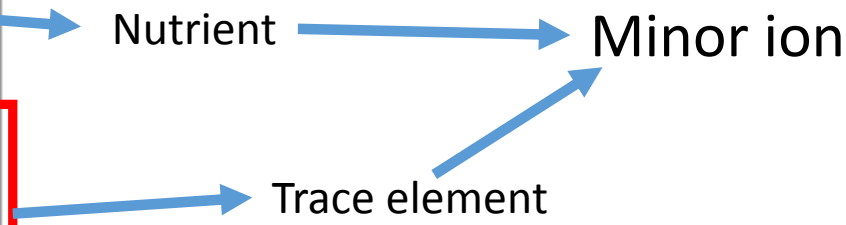
Weight% of Major Ions

Residence time

Constituent	Residence Time (years)
Chloride (Cl^{2})	100,000,000
Sodium (Na^{1})	68,000,000
Magnesium (Mg^{21})	13,000,000
Potassium (K^{1})	12,000,000
Sulfate (SO_4^{22})	11,000,000
Calcium (Ca^{21})	1,000,000
Carbonate (CO_3^{22})	110,000
Silicon (Si)	20,000
Water (H_2O)	4,100
Manganese (Mn)	1,300
Aluminum (Al)	600
Iron (Fe)	200

Sources: Data from Broecker and Peng, 1982; Bruland, 1983; Riley and Skirrow, 1975.

Residence time- Average length of time that an ion or element remains in solution in the ocean

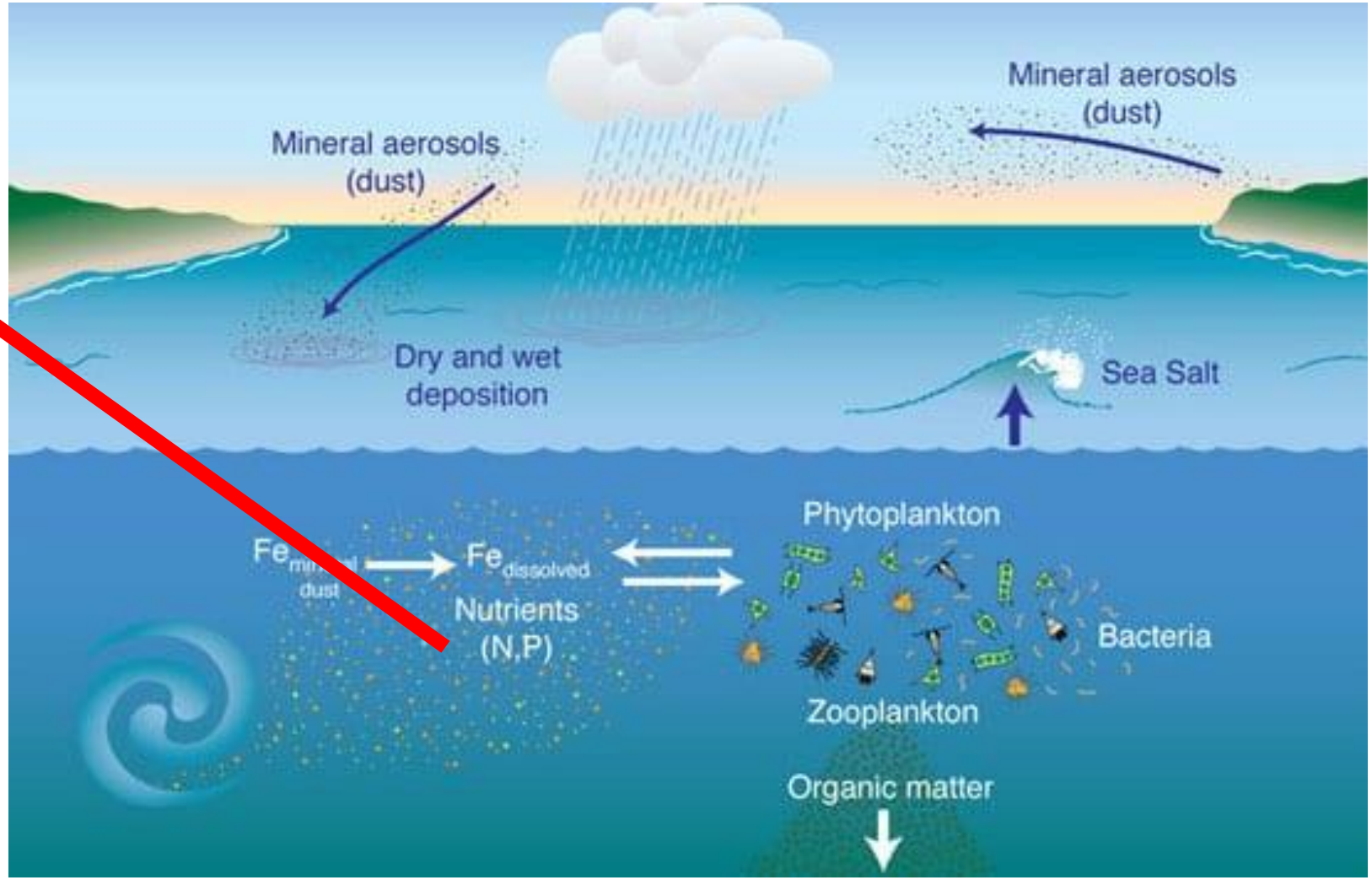


Minor ion -- > Nutrient

- Phosphate
- Nitrate
- Silicate

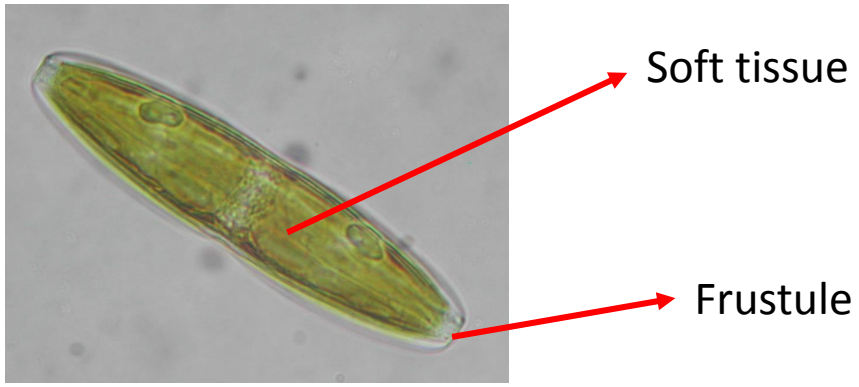
Soft part

Hard part

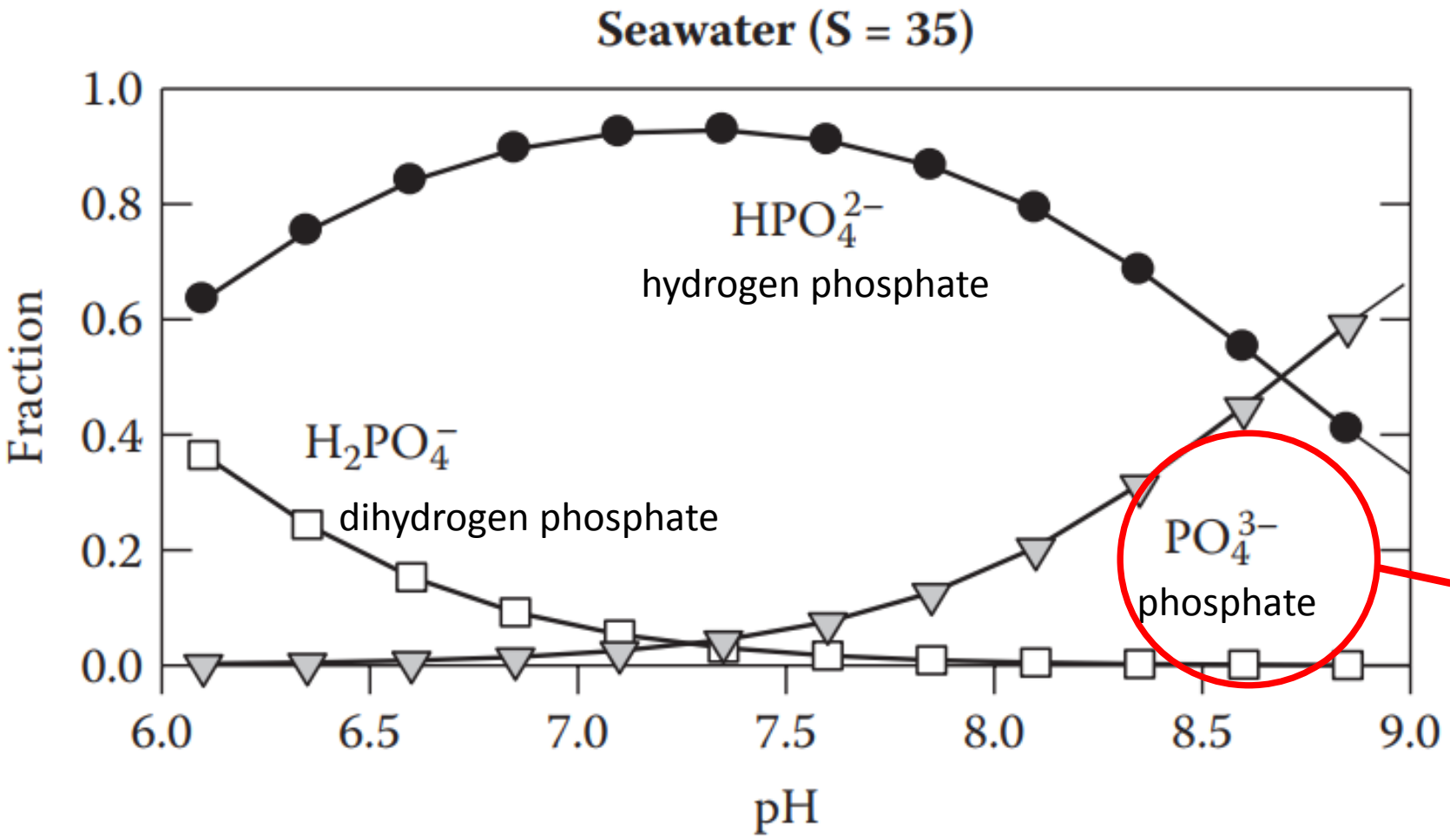


Chemical composition of phytoplankton (ratio)

		P	N	Si	Ca	C
Phytoplankton	Soft tissue	1	16	0	0	106
	Frustule	0	0	50	26	26
	Both	1	16	50	26	132
Sea water	Deep water	1	15	50	5,000	1,000
	Surface	0	0	0	4,974	868

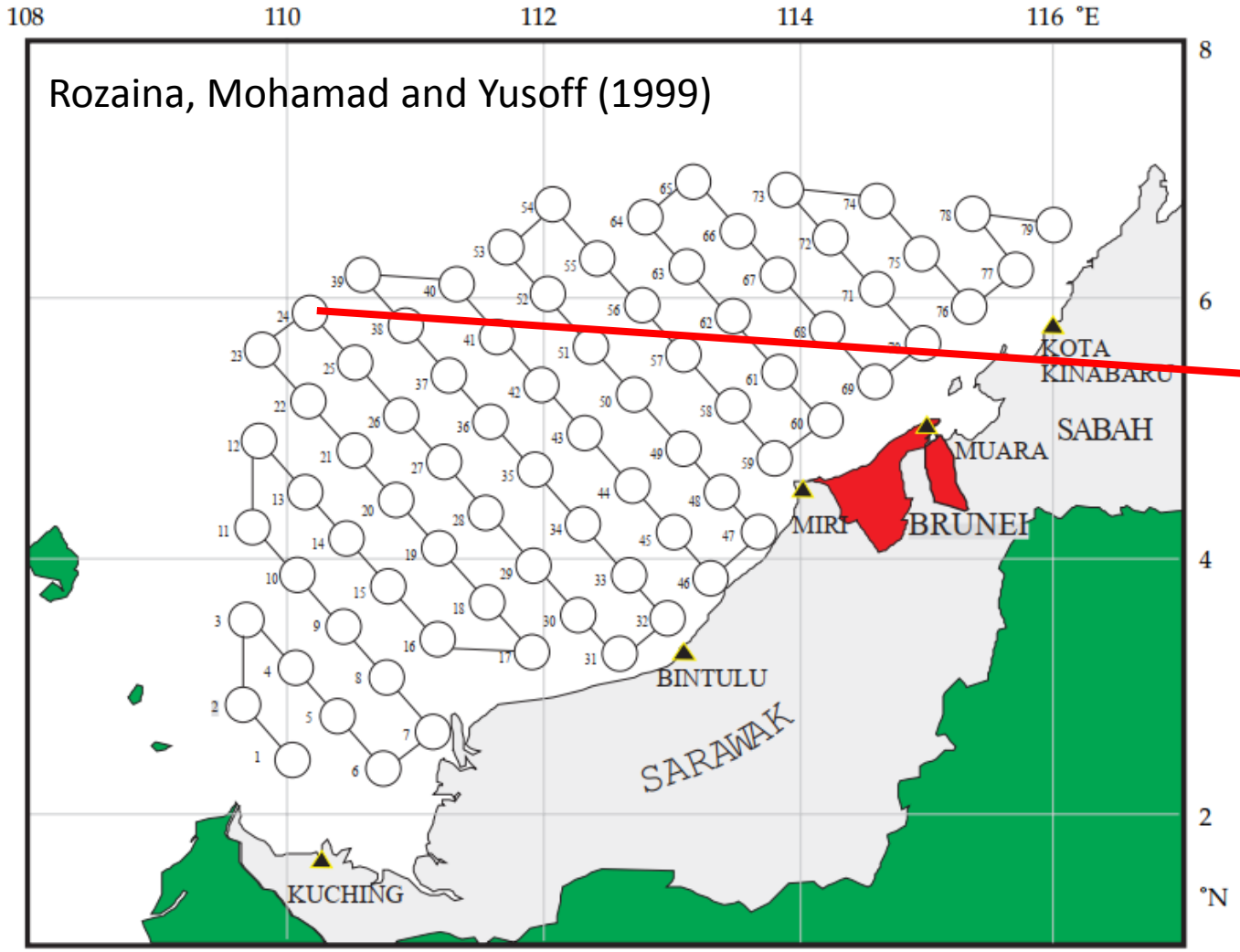


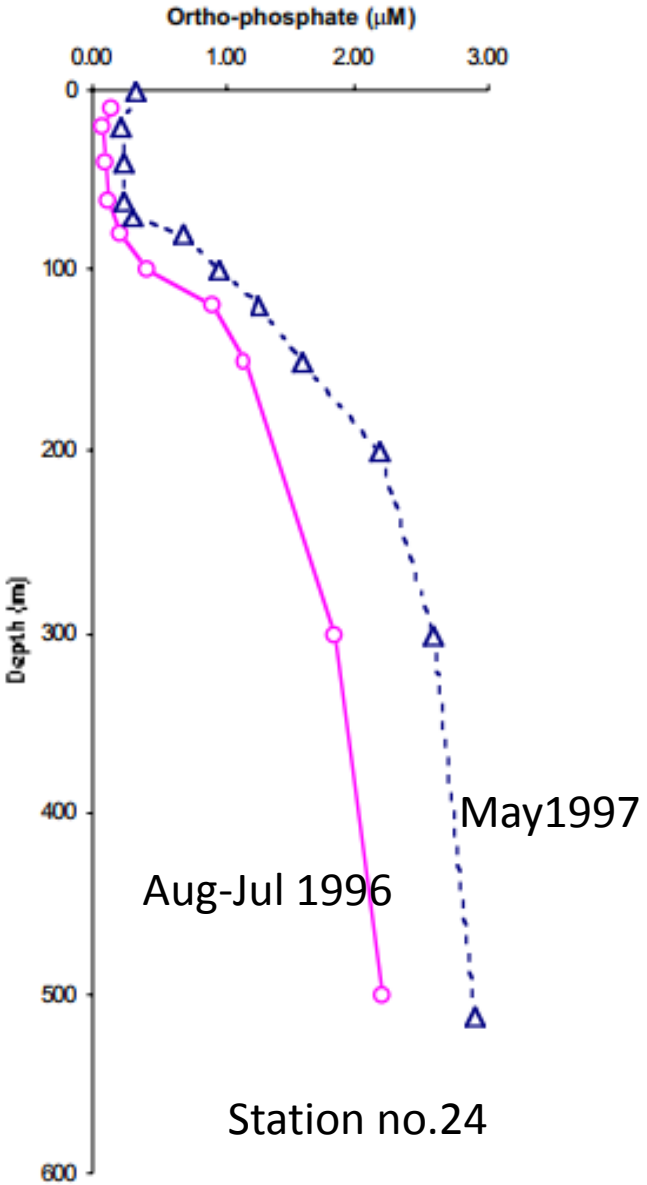
Forms of phosphoric acid in sea water



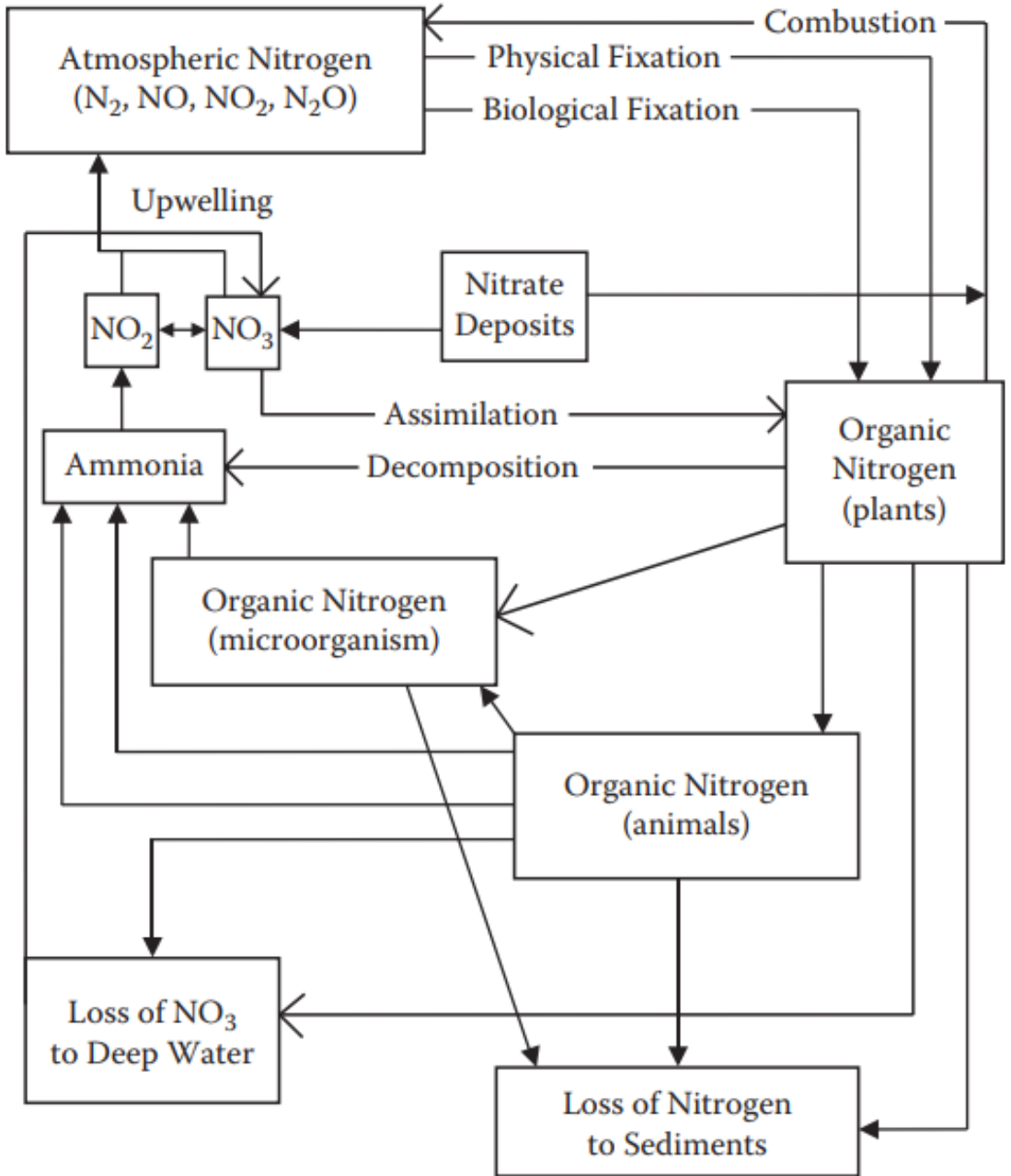
Phytoplankton

Vertical profile of phosphate





Nitrogen cycle in ocean waters



Inorganic nitrogen

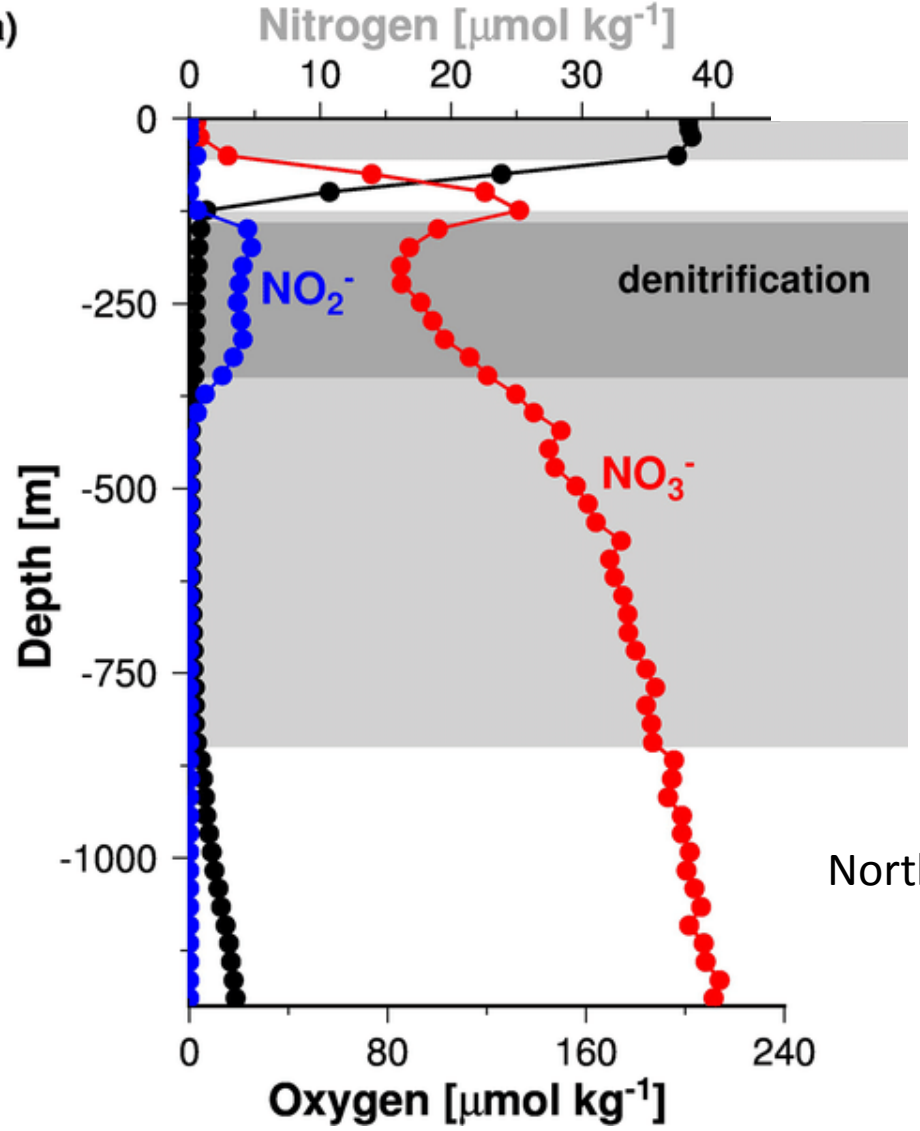
Principal inorganic forms:

NO_3^- (1 to 500 µM),

NO_2^- (0.1 to 50 µM), and

NH_3^+ & NH_4^+ (1 to 50 µM).

Vertical profiles of nitrite, nitrate, and dissolved oxygen



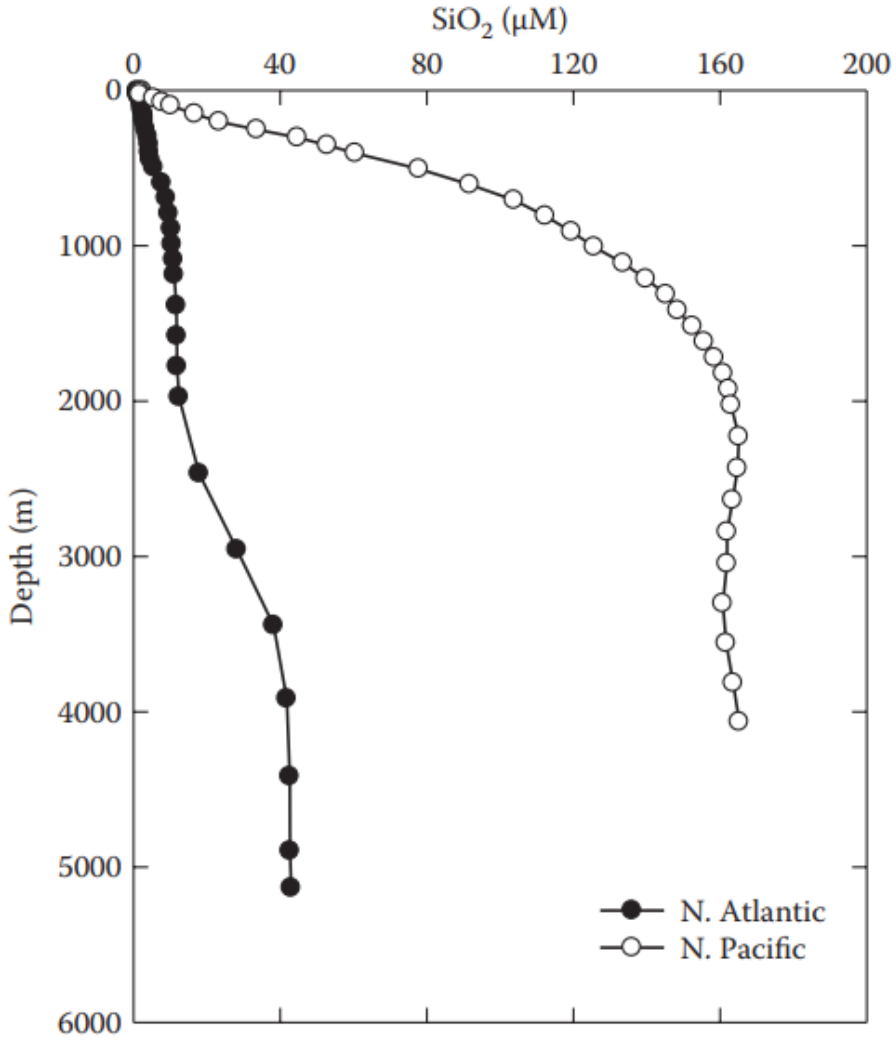
Rixen, et al,. (2020). Reviews and syntheses: Present, past, and future of the oxygen minimum zone in the northern Indian Ocean. Biogeosciences. 17. 6051-6080.

Northern indian ocean

Silicate

- SiO_2 vary from 0 to 200 µM in seawater.
- Essential part of the solid structure of diatoms, radiolarians, and sponges.
- Up to 60% of the inorganic material in diatoms is SiO_2.

Vertical profile of silicate



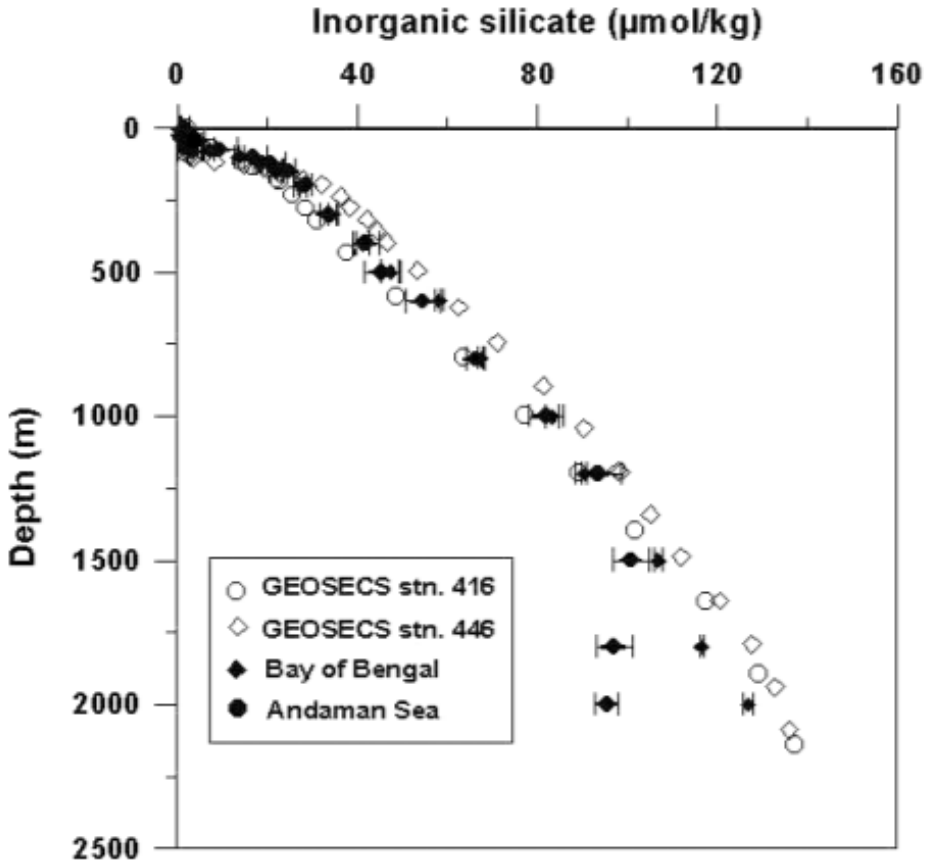
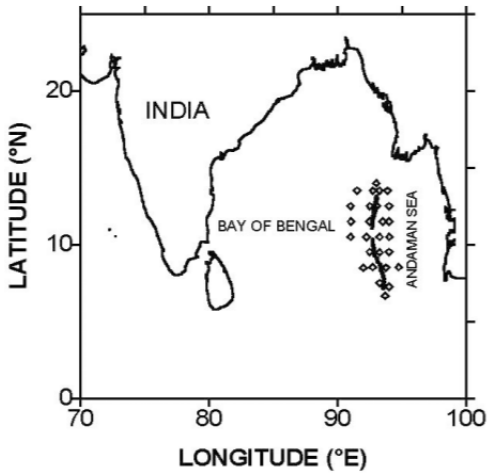


Figure 4. Depthwise averaged vertical distribution of inorganic silicate in the eastern Bay of Bengal, Andaman Sea and Geosecs stations 416 (Arabian Sea) and 446 (Bay of Bengal).



SARMA & NARVEKAR (2000)
OCEANOLOGICA ACTA ·
VOL. 24 – No. 2

Minor ion -- > Trace element

- In recent years, there has been a rapid increase in our knowledge of the distribution of minor trace elements (mostly metals) in the oceans.
- Major advances in instrumentation and the elimination or control of contamination during sampling, storage, and analysis. Bruland (1983)

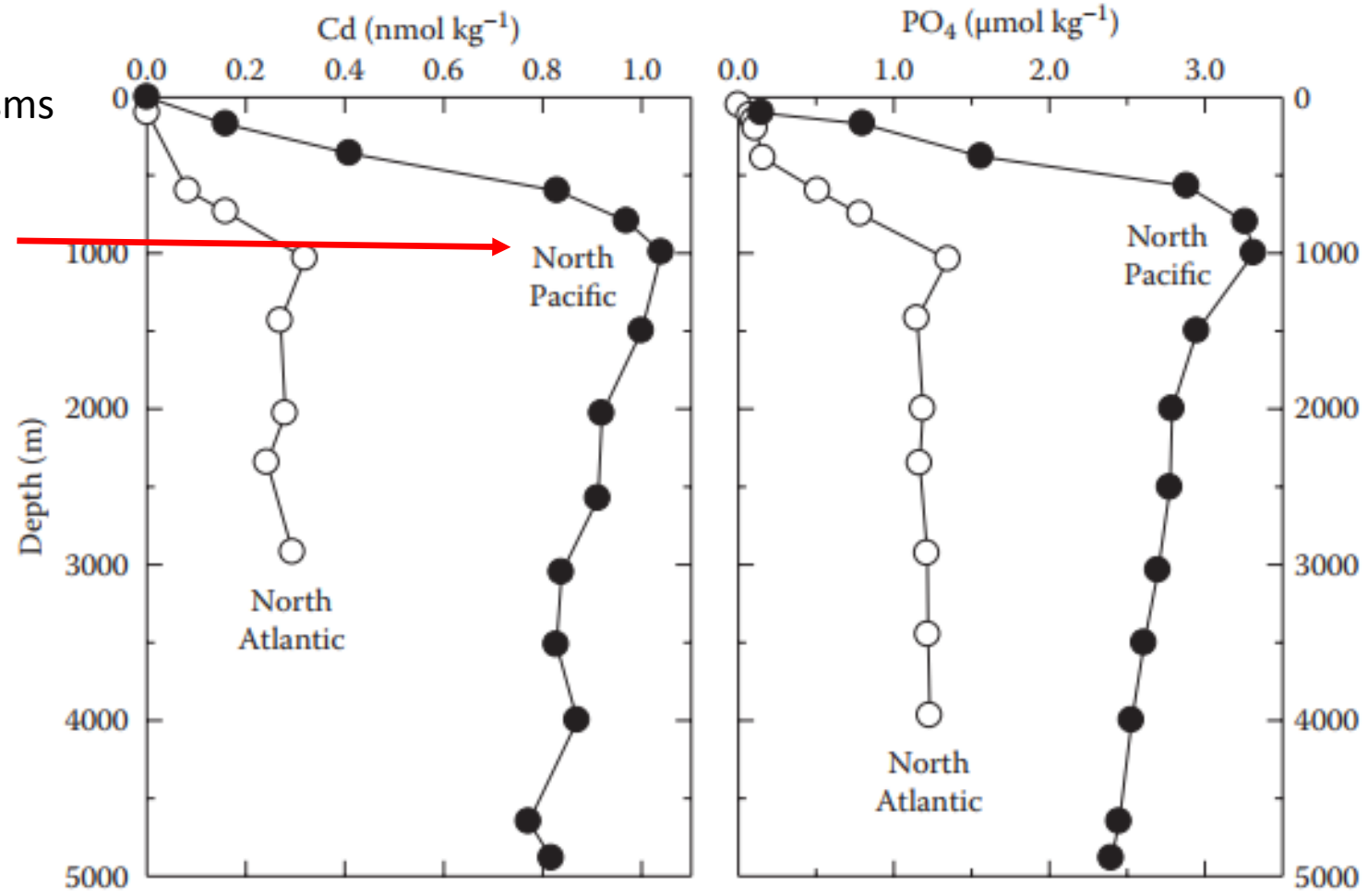
Minor ion -- > Trace element

- Trace elements: 0.05 to 50 n*M*
- Mn, Cu, Cd, Ni, Fe, Pb, Hg, Ni, Zn
- Vertical profile -- > source & behavior (Nutrient like, scavenger)

Nutrient type profile

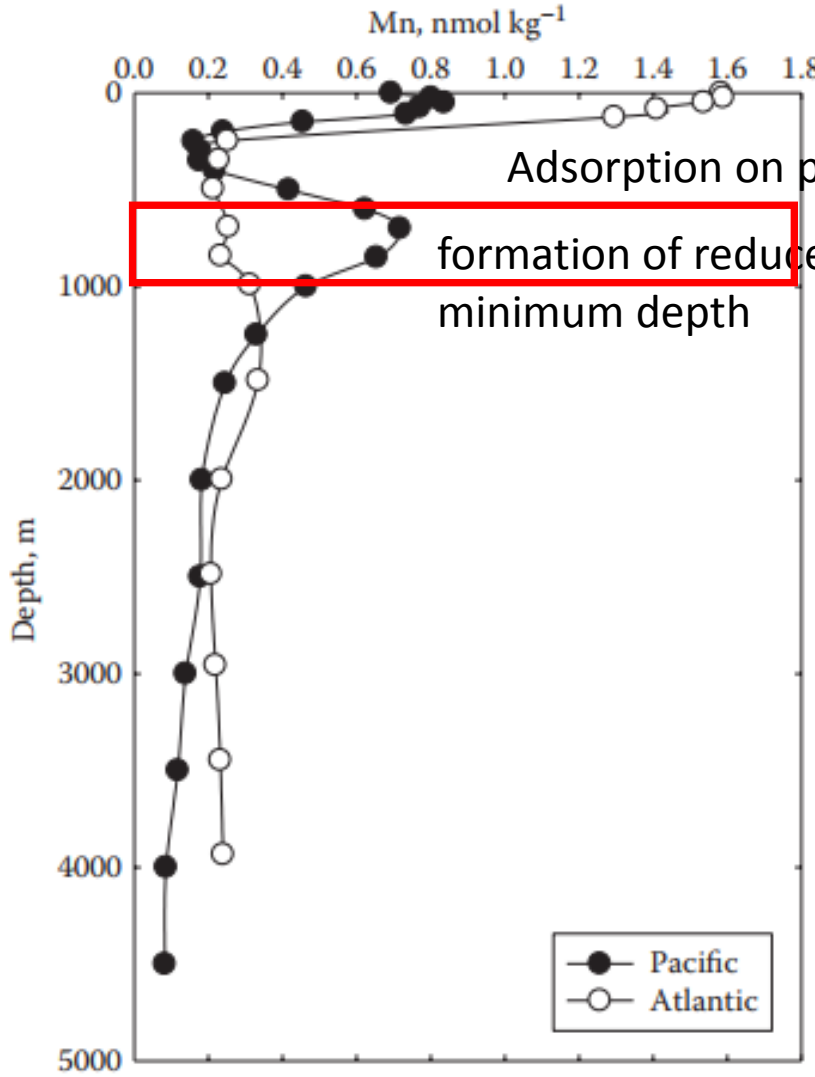
Passive uptake by organisms

Regeneration from dead organism



Profiles of cadmium (Cd) and phosphate (PO_4) in the Atlantic and Pacific Oceans.

Surface enrichment and depletion at depth



Source from air

Adsorption on particulate matter

formation of reduced forms of these metals near the O_2 minimum depth

Profiles of Mn in the Atlantic and Pacific Oceans.

Dissolved solutes: (organic)

- Varity of type
- Low concentration
- Most of the dissolved organic matter in the sea is included within the operationally defined fraction called dissolved organic matter (DOM), usually measured as dissolved organic carbon (DOC)
- DOC -- > derived from living organisms that produce primary production (Phytoplankton)

Table 11.5 Partial list of naturally occurring volatile organic substances detected in seawater, along with representative concentrations, in pM ($= 10^{-12}$ M)

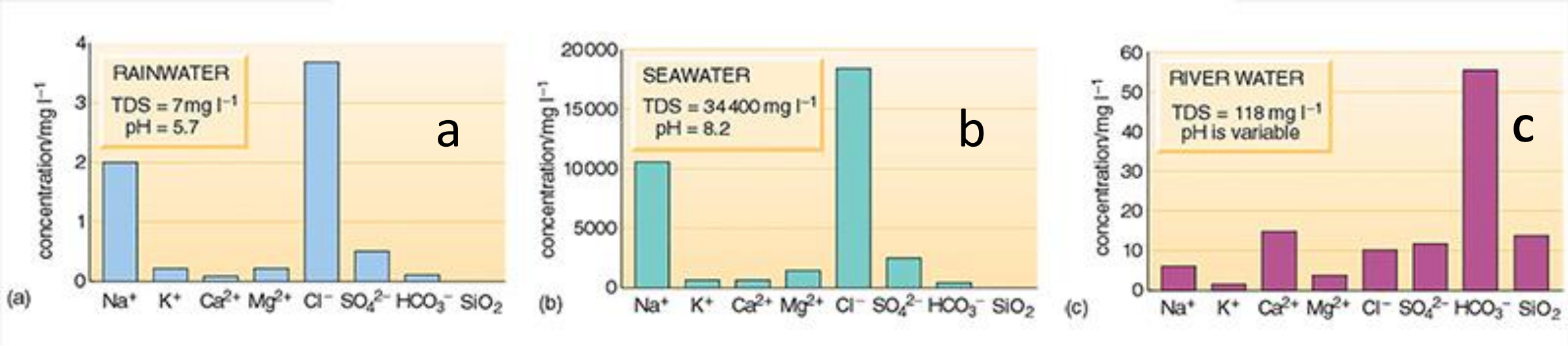
Name	Formula	Surface	Deep
Methane	CH_4	2000	1000
Ethane[a]	$CH_3\ CH_3$	15	
Propane[a]	$CH_3\ CH_2CH_3$	8	4
Butane[a]	$CH_3\ CH_2CH_2CH_3$	3	
Ethene (Ethylene)[a]	$CH_2{=}CH_2$	100	
Propene[a]	$CH_2{=}CHCH_3$	25	14
1-Butene[a]	$CH_2{=}CHCH_2CH_3$	20	
Isoprene[b]	$CH_2{=}C(CH_3)CH{=}CH_2$	5	
Acetylene[a]	$CH{\equiv}CH$	10	
Carbon monoxide[c]	CO	12 800	
Carbonyl sulfide[d]	COS	30	
Dimethyl sulfide[e]	$CH_3{-}S{-}CH_3$	2600	100
Bromoform[f]	$CHBr_3$	8	4
Dibromochloromethane[f]	$CHBr_2Cl$	0.5	1
Bromodichloromethane[f]	$CHBrCl_2$	0.6	1
Dibromomethane[f]	CH_2Br_2	3	1
Chloroiodomethane[f]	CH_2ICl	2	0.5
Methyl iodide[f]	CH_3I	3	0.5
Diiodomethane[f]	CH_2I_2	2	0.5

PILSON (2013) An Introduction to the Chemistry of the Sea

Seawater composition was control by??

- River composition ??

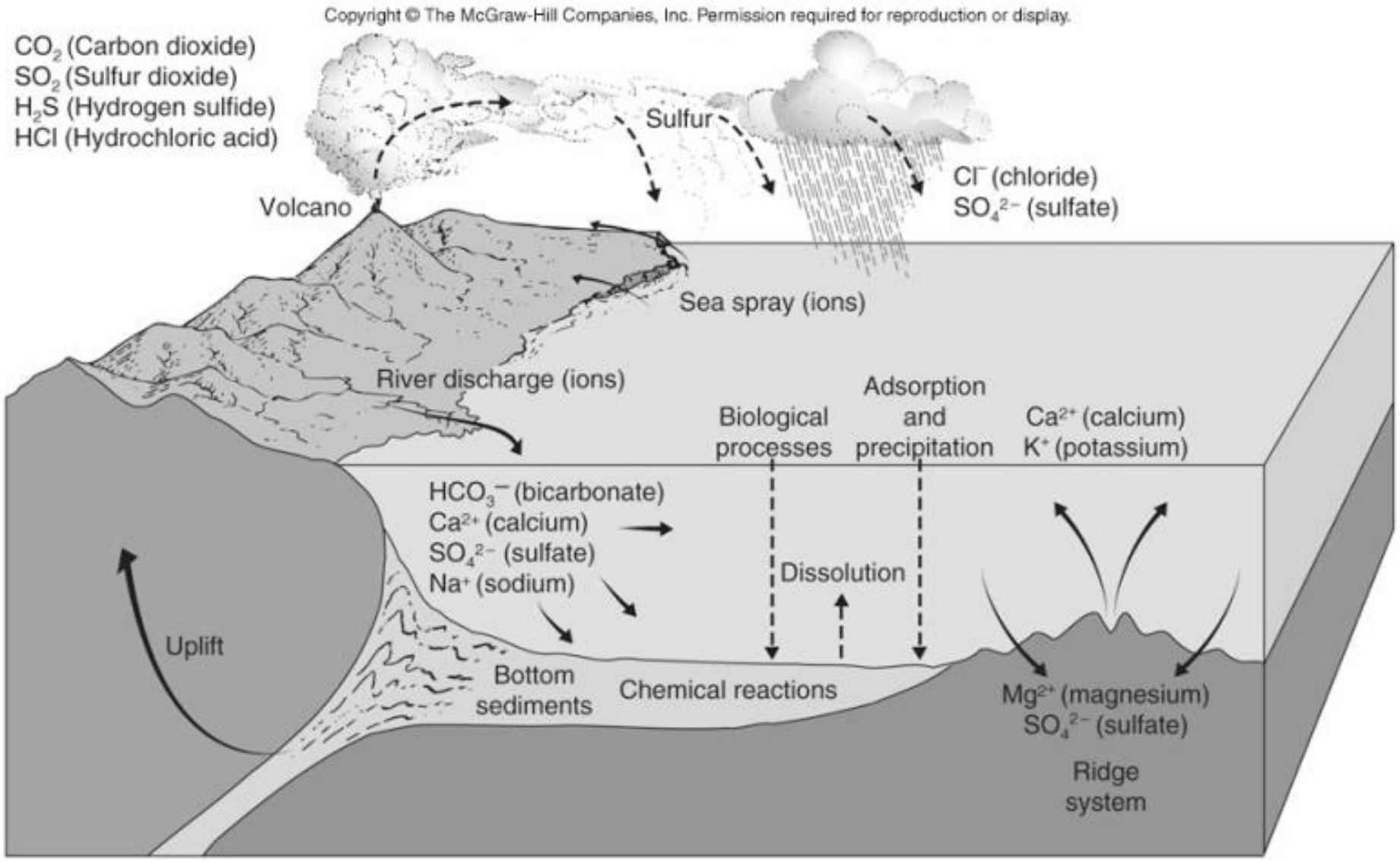
Major ion -- > Salinity



https://www.open.edu/

The average major dissolved chemical compositions of (a) rainwater, (b) seawater and (c) river water

Processes Affecting Seawater Composition



Processes Affecting Seawater Composition

- River discharge
- Air-Sea interaction (sea spray, dissolved gas)
- Biological process
- Sediment – seawater interaction (Dissolution ,absorption and precipitation)
- Ridge system (hydrothermal vent)
- Water cycle (evaporation, precipitation)
- Etc.

Thank you