COMPOSITION OF NATURAL WATERS

Natural waters contain dissolved and suspended materials that affect and are affected by water chemistry. The presence of these species is largely dependent on the source of the water.

1. Rain Water

Relatively low concentrations of total dissolved solids. (TDS < 15 ppm). Depends of air pollution an geography. For example, coastal rains often contain sea spray salts up to 15 ppm.

Typical rainfall:

Ion	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
Conc (ppm)	2	8	0.5	4	0.3	0.3	2
Conc (meq/L)	0.021	0.22	0.001	0.17	0.008	0.012	0.050

Low dissolved organic carbon (DOC < 1 mg/L)

Relatively high concentrations of dissolved gases. (**O_2**, **CO_2**, **SO_3**, **NO_2** etc).

→ oxidizing conditions (high pe)

Gases may be natural (photosynthesis, volcanoes etc) or anthropogenic (industry, transportation etc).

Natural rainwater has pH ~ 5.6

Acid rain pH < 5

Other Gases:

2. Rivers and Streams

Composition depends on:

1. rain constituents
2. soil/mineral substrate
3. plant/animal life
4. human activity

TDS ~ 20 – 150 mg/L
DOC ~ 1- 10 mg/L

major cations: **Ca^{2+}. Mg^{2+}, Na^{+}, K^{+}**

major anions: **HCO_3^-/CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3-, PO_4^{3-}**

dissolved gases: **O_2**(aq)
CO_2(aq)/**H_2CO_3**

dissolved organic matter: fulvic and humic acids

suspended solids:

human activity:

agriculture logging mining pulp food processing urbanization

- fertilizers
- treated wastewater
- oils/hydrocarbons
- heavy metals

3. Lakes and Resevoirs

1. composition depends on:
2. inflow constituents
3. residence time
4. plant/animal activity
5. human activity

Lake stratification characteristic of deep temperate lakes. Effects chemical specieation and chemical/biological processes.

Epilimnion - high O_2(aq)

→ high pe favours high oxidation states

e.g.,

Thermocline

Hypolimnion – low O_2(aq)

→ low pe favours low oxidation states

e.g.,

classification system

oligotrophic → mesotrophic → eutrophic

4. Groundwaters

composition depends largely on soil and rock type

- filtered through soil, sand and clay
- usually low in micro-organisms
- low oxygen content (ORP < -200 mV), low pe ('reducing' conditions)

TDS > 100 mg/L
DOC < 1 mg/L

typically higher concentrations of **Ca^{2+}, Mg^{2+}, HCO_3^-** than in surface waters

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

e.g.,

Fe^{2+}

Mn^{2+}

Mineral Content in Hotsprings (ppm):

Ion	**SO_4^{2-}**	**HCO_3^-**	**$Na^{+/}$ K^+**	**Mg^{2+}**	**Ca^{2+}**
Banff	572	138	5	36	205
Fairmount	1000	700	40	105	480

5. Marine and Ocean Waters

Concentration of all ions much higher than freshwater, but major ions in seawater are **Na^+** and **Cl^-** rather than those in fresh surface water, which are **Ca^{2+}** and **HCO_3^-**

TDS ~ 35,000 ppm (i.e., 3.5 % or 35 $^{o}/_{oo}$)

Na^+ ~ 12,000 ppm
Cl^- ~ 18,000 ppm

pH = 8.2
typical DOC ~ 1 mg/L C

Density ~ 1.035 g/mL

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

Ionic Strength = $0.5 \Sigma c_i Z_i^2 = 0.71$ (for seawater)

The ionic strength (*I*) of a solution is a measure of the total amount of dissolved ions and is defined below. The ionic strength affects equilibrium conditions due to ion pairing, a transient and weak association between cations and anions, which reduces their 'effective' concentration to become involved in other processes

Activities reflect 'effective concentrations' of species in solution

{Activity} = Activity Co-efficient x [Molar Concentraion]

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

Activity coefficients range from ~0.8 – 1.0 freshwater and ~0.1 – 0.8 in seawater

Table: Typical concentrations of inorganic ions in oceans

	ppm ≡ g/kg	M	meq/L	
Anions				
Cl^-	19.4	0.55		
SO_4^{2-}	2.7	0.03		
HCO_3^-	0.14	0.002		
Br^-	0.07	0.001		
BO_3^{3-}	0.024	4×10^{-4}		
CO_3^{2}-	0.012	2×10^{-4}		
PO_4^{3}-	0.0014	1.5×10^{-5}		
F^-	0.0013	7×10^{-5}		
NO_3^-	0.0012	2×10^{-5}		$\sum -ve$
Cations				
Na^+	10.8	0.47		
Mg^{2+}	1.3	0.05		
Ca^{2+}	0.4	0.01		
K^+	0.4	0.01		
Sr^{2+}	0.0088	1×10^{-4}		
Al^{3+}	0.0011	4×10^{-5}		
Li^+	0.00014	2×10^{-5}		$\sum +ve$