Properties of Natural Waters

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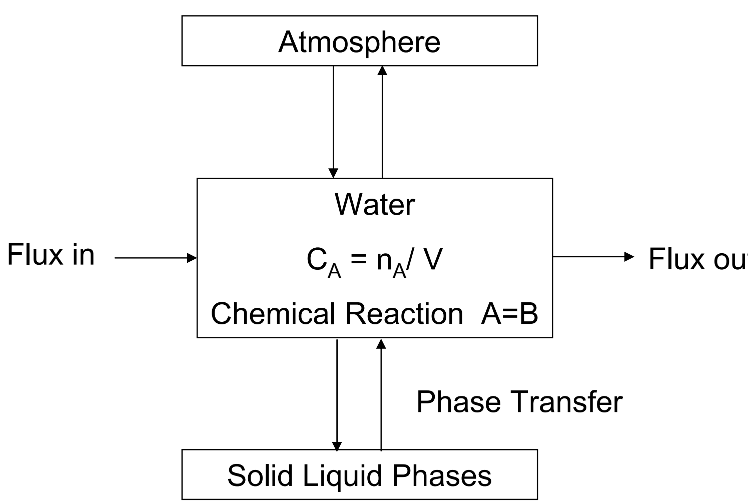

Figure: General Representation of a Natural Water System

C_A = concentration of a constituent resulting from chemical reactions

Properties of Natural Waters

Important Natural Processes occurring at the Interfaces

Process	Interface	Examples
Weathering	Solid-liquid (rock-water)	Dissolution of rock, erosion, soil formation
Gas exchange	Liquid-gas (water-atmosphere)	evaporation of sediment
Crystallization, Precipitation	Liquid-solid (water-sediment)	Formation of sediment
Adsorption	Liquid-solid	Adsorption of cations, anions and weak acids on surface
Absorption	Liquid-liquid	Dissolution of lipophillic substances
Aerosol formation	Solid-gas	Emission of industrial and smoke particles, erosion of soil dust.

Properties of Natural Waters

Physico-chemical parameters

a. Discharge ($m^3\ s^{-1}$)
b. Alkalinity ($mEq\ L^{-1}$)
c. Calcium ($mEq\ L^{-1}$)
d. pH
e. Conductivity ($\mu S\ cm^{-1}$ at $25^{o}C$)
f. $EpCO_2$ (CO_2 pressure)

→ $$EpCO_2 = \frac{\text{partial pressure of } CO_2 \text{ in natural water}}{\text{equilibrium partial pressure of } CO_2}$$

g. Air temperature (^{o}C)
h. Nutrient and trace metal concentrations
i. Turbidity
j. Suspended and dissolved solids

Properties of Natural Waters

Suspended Solids – empirical estimate of water quality

→ measures the amount of suspended matter present

→ determined by taking the weight gain of the filter after drawing a known volume of H_2O through it.

Dissolved Solids – material that cannot be removed by the filter (0.45 mm).

→ Inorganic salts, weak organic acids

→ measure by conductivity

Density – often used in substance identification

→ the greater the density in above H_2O (pure) the greater the amount of dissolved solids.

TDS (mg L^{-1}) = (density of solution – density of pure H_2O)(1000 mg g^{-1})(1000mL L^{-1})

Properties of Natural Waters

Physico-chemical parameters (Significance)

pH ⟶ -log [H^+]

-Measurement of pH provides a useful indicator of some biogeochemical effect that has caused the buffer capacity of water to be exceeded.

Process	Alkalinity	pH change
Nitrification $NH_4 + 2O_2 \longrightarrow NO_3 + H_2O + 2H^+$	Decrease	Decrease
Sulfide Oxidation $HS^- + 2O_2 \longrightarrow SO_4^{2-} + H+$	Decrease	Increase

-pH measured by potentiometry using a glass electrode and suitable reference electrode.

-Increases in pH caused by algal growth and denitrification

-Decreases in pH caused by acidic waste, acid rain, bacterial nitrification or sulfate reduction.

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<u>Electrical Conductivity</u>

-Measurement related to the concentration of dissolved ions present.

-Estimates dissolved solids (freshwater) and salinity (marine).

Potability	Range ($\mu S\ cm^{-1}$)	Use
Fresh	<325	Potable Water
Marginal	>325 but <975	Watering livestock, irrigation
Brackish	>975 but <3250	Selective irrigation, livestock
Saline	>3250	Course industrial processes

Note: Strong conductivity: TDS relationship (at pH 4-9)

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Dissolved Oxygen

-Important in determining water quality (biological & biogeochemical)

-Measured by galvanic or voltammetric membrane sensors; depends on temperature, salinity and altitude.

$>$6 mg L^{-1} or 80-90% saturation ideal for biological growth.

Turbidity

-Small particles and colloidal material in suspension affect clarity

-Determined by the amount of light scattering at 90^{o} from an incident beam with a photocell in the wavelength range of 400-600 nm.

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Redox Potential

-Plays a crucial role in the behavior of inorganic and biogeochemical processes.

Eh = the oxidation-reduction potential of the system in volts

Ex: $Fe^{3+} + e \longrightarrow Fe^{2+}$

$$Eh = E^{o} + \frac{Rt}{nF} \ln \frac{a_{Fe3+}}{a_{Fe2+}}$$

At 298 K:

$$Eh = E^{o} + \frac{0.0592}{n} \log \frac{a_{Fe3+}}{a_{Fe2+}}$$

Where E^{o} = standard reduction potential, R = gas constant (8.13143 J K^{-1} mol^{-1}), *n*= # electrons transferred (How many?), F = Faraday's constant (96,487 J V^{-1} mol^{-1}), T= temperature

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Activity Diagrams

- Redox potential-pH diagrams are very useful as a way to visualize and summarize the aqueous speciation of redox-sensitive elements.

Ways to Express Redox Conditions:

Eh (electrode potential of a half-cell reaction with reference to standard hydrogen electrode);

pe (electron activity in aqueous solution);

f_{O_2} (fugacity of oxygen)

f_{H_2} (fugacity of hydrogen)

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Activity Diagrams

- High values of log f_{H_2} indicate reducing conditions; whereas low log f_{H_2} values indicate oxidizing conditions.

$f_{H_2} - \mathrm{pH}$ plot is a type of activity diagram that indicates both oxidation-reduction and acid-base conditions.

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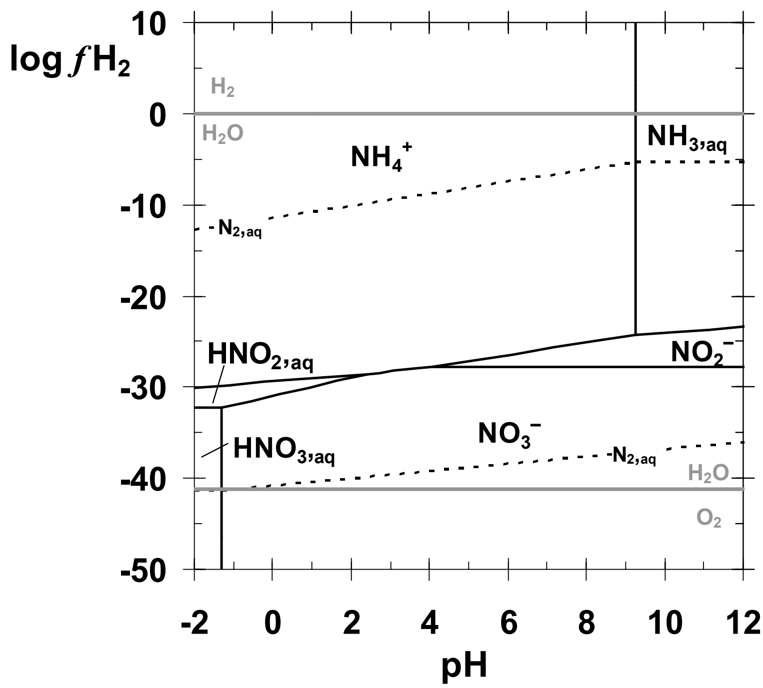
N-O-H system at 25°C and 1 bar



Properties of Soils & Sediments

<u>Properties</u>:

-Soil is made up of ground up fragments of rock, decaying organic matter, water, and air.

-Fine particle transport and particle-bound processes.

-Interactive processes (sorption/desorption, precipitation)

-Binding intensities and capacities for soil/sediment components

-pH a factor

-Any others?

-How does this relate to element cycling in the environment?

Properties of Soils & Sediment

Sediments

1) Provide a substrate for organisms;

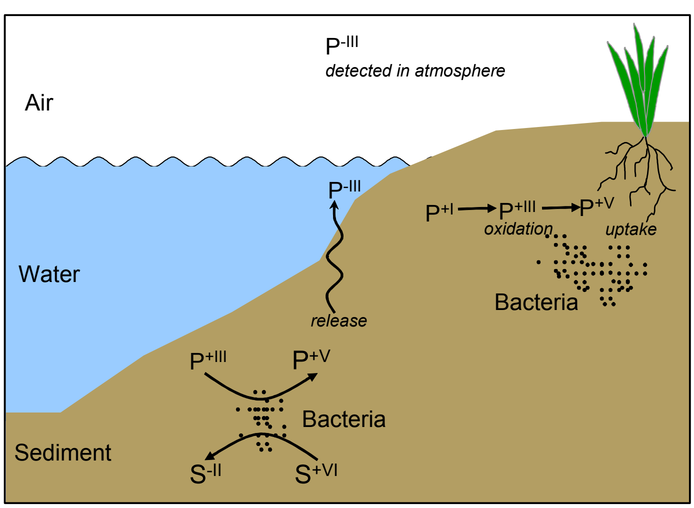
2) Interactions with the overlying waters (e.g. nutrient and trace metal cycling);

3) Left as deposits of fertile soil after flooding;

4) Carrier and possible source of contaminants in natural waters (bioaccumulation and food chain transfer);

5) More complex than water quality assessment (sorption kinetics)

Properties of Soils & Sediment



Biogeochemical Processes

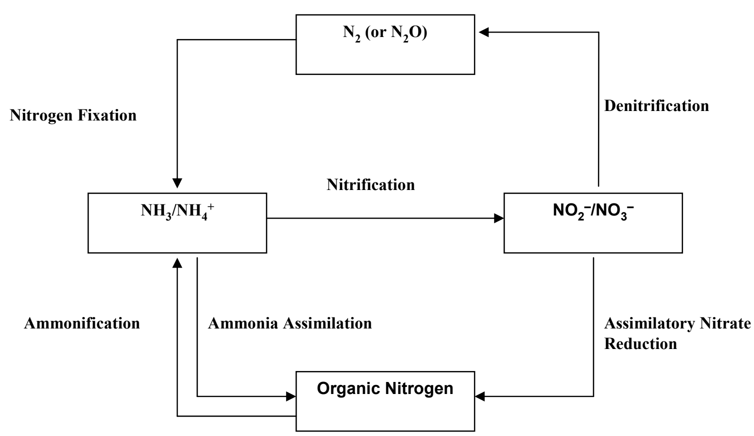
Ex: Nitrogen Speciation

-The activity diagram is constructed for the N-H_2O system, and in it, fields separated by lines essentially map out the predominant nitrogen species over ranges of pH and redox potential in f_{H_2}

- Each field defines the redox and pH conditions in which a particular nitrogen species predominates.

- Such diagram can then be used as *biogeochemical maps* to illustrate nitrogen speciation and a variety of biological and geochemical transformations.

Biogeochemical Processes



All of these processes are mediated by various types of microorganisms with some processes being energy producing and others occurring symbiotically with other organisms.

Biogeochemical Processes

Nitrogen Fixation

Process by which nitrogen is taken from its molecular form (N_2) in the atmosphere and converted into nitrogen compounds useful for other biochemical processes.

$$N_2 + 16\ ATP + 8e^- + 8H^+ \rightarrow 2NH_3 + 16\ ADP + 16\ P_i + H_2$$

Nitrification

Oxidation of NH_3 or NH_4^+ to NO_2^- or NO_3^- by organisms:

$$NH_4^+ + O_2 \rightarrow NO_2^- + H_2O + 2H^+$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$

Biogeochemical Processes

Processes Operating within a Water Body

Process	Spatial or Temporal Scale
Hydrological (Rainfall run-off)	
Urban	Hours
Rural	Days
Physical	
Particle Settling silt/rock	Meter/hr
Oxygen diffusion	One cm/day
Chemical	
Iron oxidation	Minutes
Biological	
Bacterial growth	Hours
Algae growth	Days
Mass Transport	
Non-point sources	Catchment wide
Point sources	Meters to kilometers

Water Quality + Monitoring Guidelines

1. Drinking Water
   a) Microorganisms (e.g. pathogenic bacteria, viruses)
   b) Inorganic Chemicals (e.g. nitrates, heavy metals)
   c) Organic Chemicals (e.g. pesticides)
2. Agricultural Water
   a) Microbiological Indicators (e.g. human and animal pathogens)
   b) Salinity
   c) Inorganic and Organic Contaminants
3. Recreational Water
   a) Microbiological Stressors (e.g. pathogens and viruses)
   b) Nuisance Organisms (e.g. algae)
   c) Physical and Chemical Stressors (e.g. color, clarity, pH)