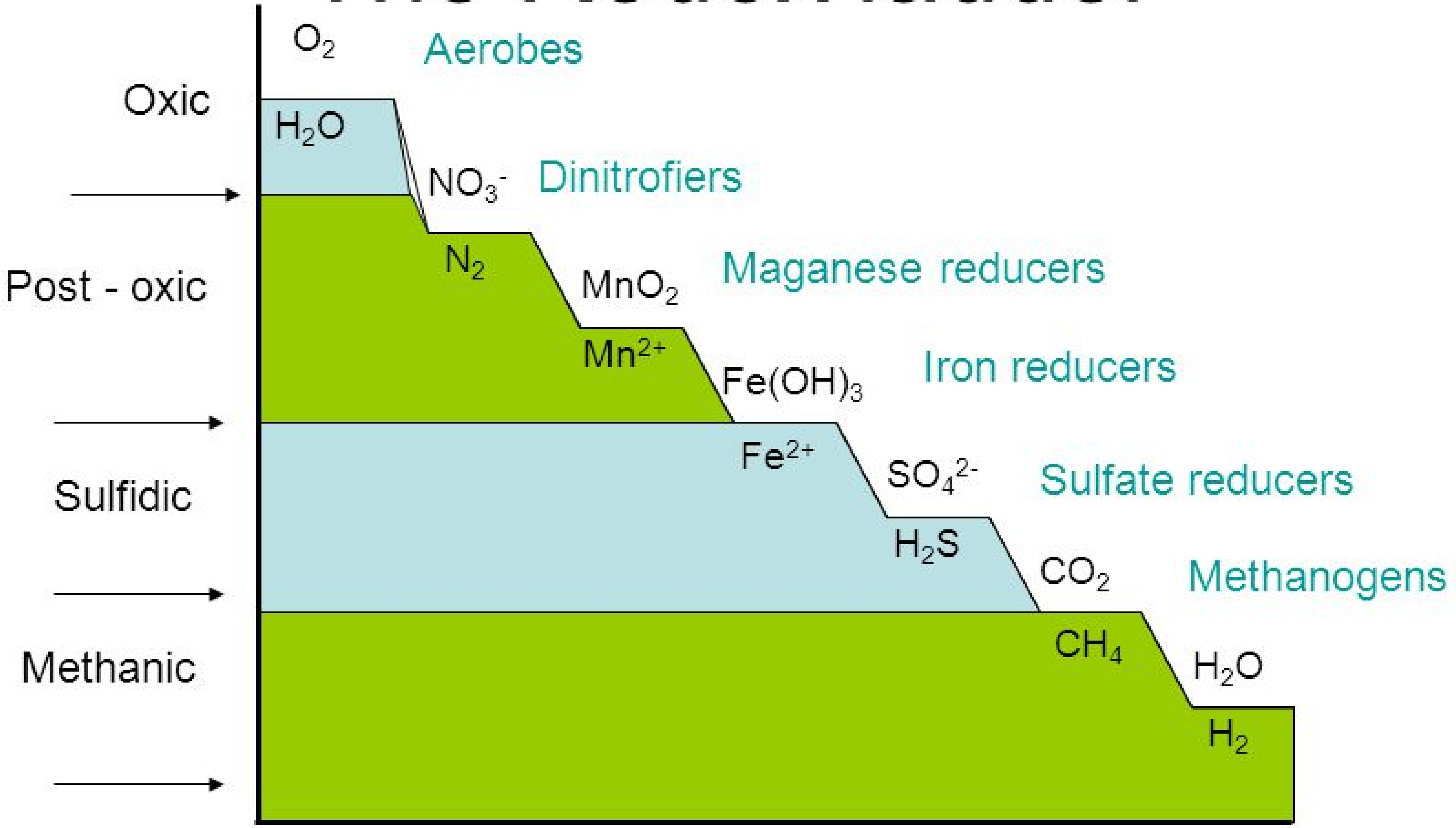
Today’s agenda

- Nitrogen cycle in groundwater
- Geochemistry in groundwater
- Piper plots

The Redox ladder



The redox-couples are shown on each stair-step, where the most energy is gained at the top step and the least at the bottom step. (Gibb's free energy becomes more positive going down the steps)

Nitrogen Cycle

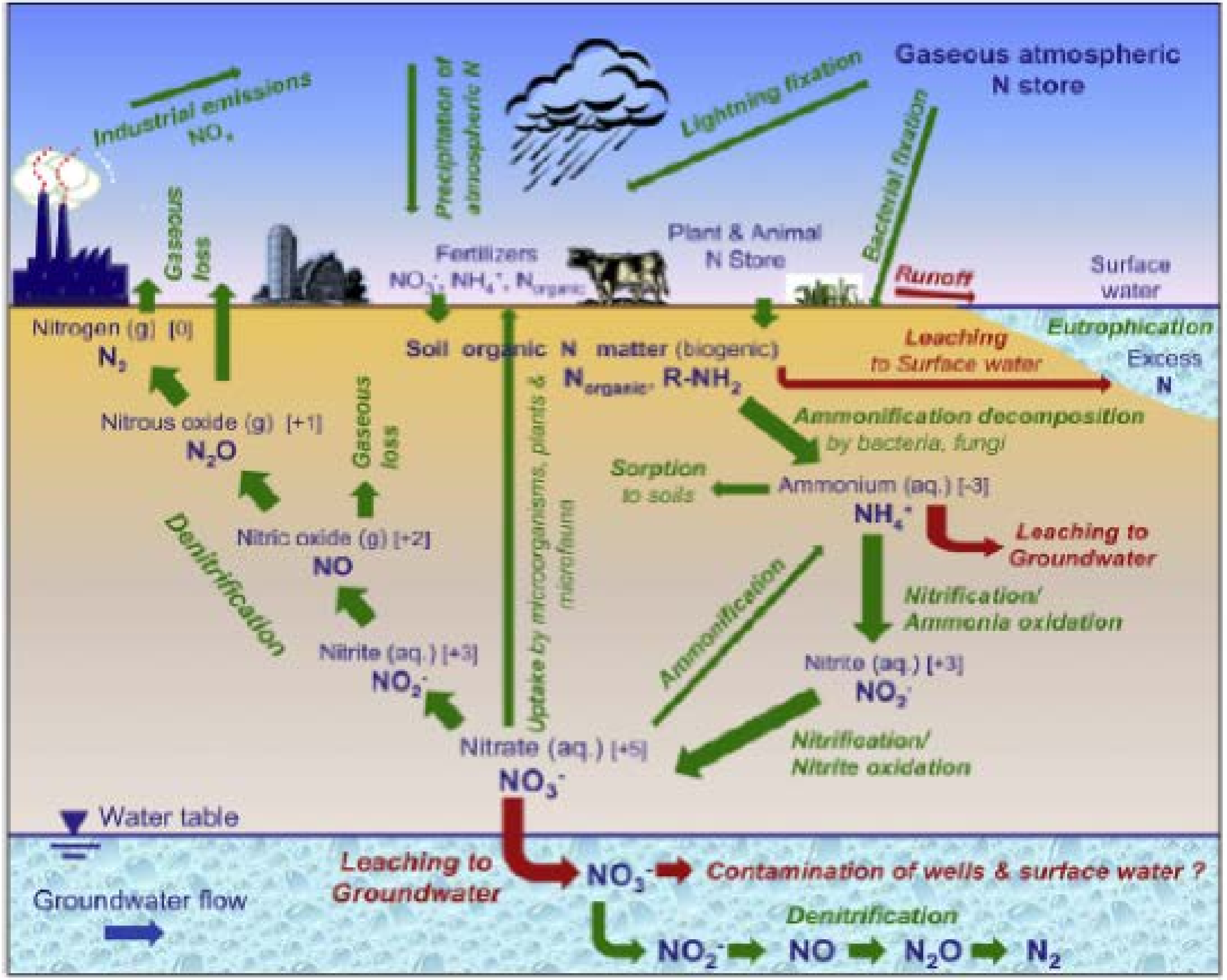
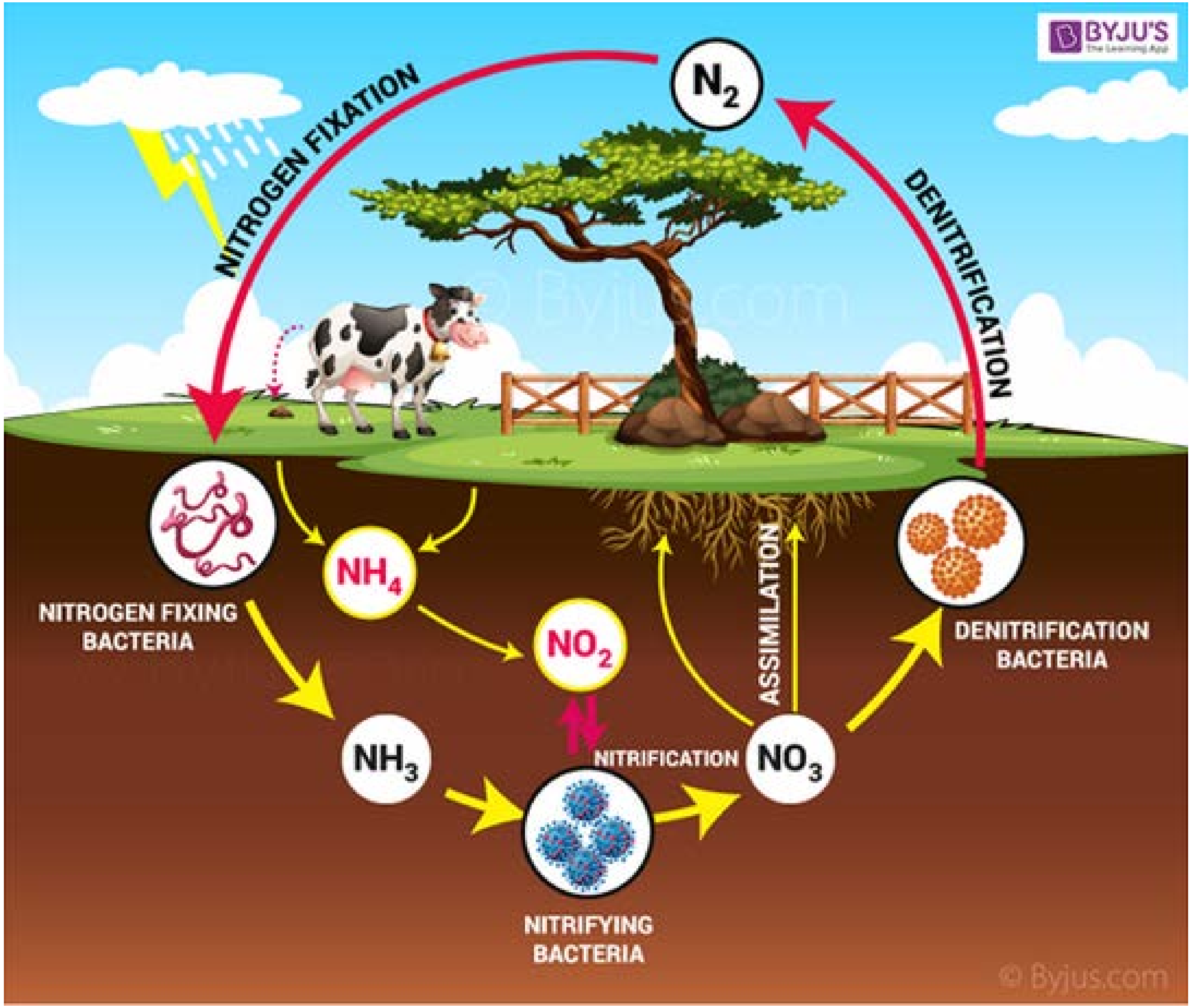


Figure 1. Microbial nitrogen cycle and its influence upon the water environment.
Source: Rivett *et al.* (2008).

Nitrogen Cycle



Nitrogen Cycle

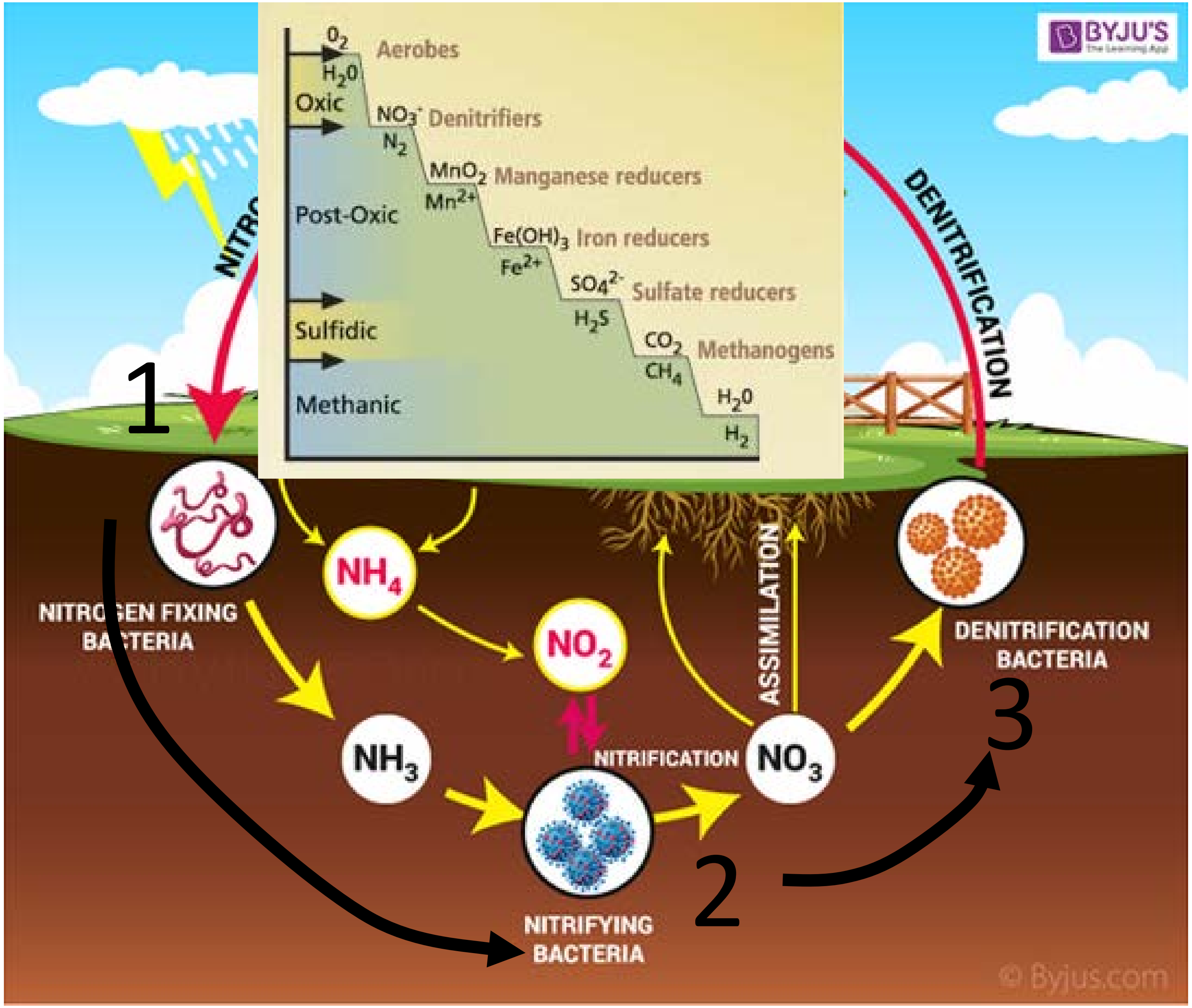
1. Nitrogen enters groundwater through **fertilizer** and **nitrogen fixation** as **ammonium**
   - Ammonium (NH_4) is unusable by plants

2. Ammonium is converted to **nitrate** (NO_3) though **nitrification**
   - Nitrate is usable by plants

3. Once there is no dissolved oxygen left in the groundwater, microbes are forced to respire nitrate instead
   - This respiration is **denitrification**

Denitrification

- Occurs in low oxygen (anoxic) groundwater
- Nitrate + DOC → N_2



Sampling porewater for biogeochemical analysis

The goal is to preserve samples for analysis. Why?

1) Nalgene sample bottles

2) Keep it cold! Put it on ice.

3) Acidify to <2 pH using nitric acid

Measures of concentration

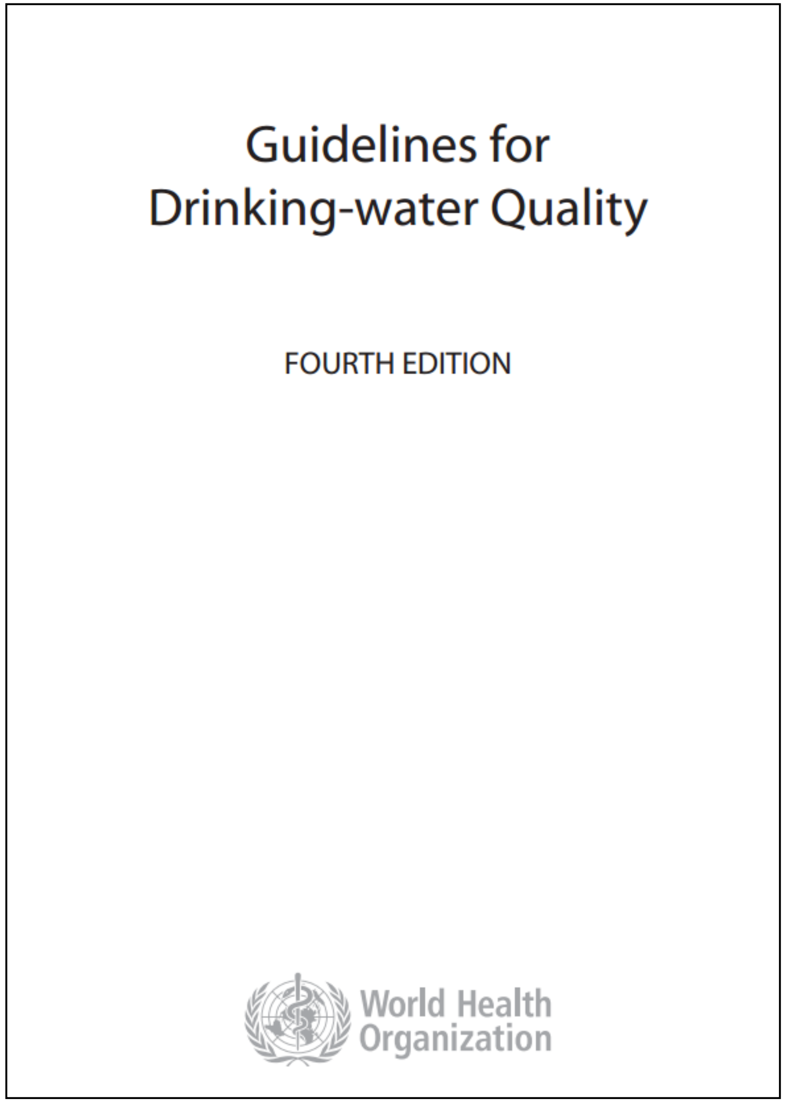
- Total dissolved solids (TDS)
  - Total amount of solids (mg/l) remaining after evaporation

Water Type	TDS (mg/l)
Fresh	0-1,000
Brackish	1,000-10,000
Saline	10,000-100,000
Brine	>100,000

Measures of concentration

- **Electrical conductivity (EC)**
  - Conductance (S or µS) per length (cm or m)
  - EC is temperature dependent (so be careful)

Some water quality guidelines



Arsenic (0.01 mg/L)

Big issue in Bangladesh. Also aquifer storage and recovery systems can cause the release of Arsenic. Natural groundwater concentrations 1-2 µg/L.

Nitrate (NO_3^-, 50 mg/L)

Primarily from agriculture (e.g. fertilizer run off). This value expressed as concentration of NO_3^-. Excess Nitrate can cause 'blue baby syndrome'

Cholera and diarrheal diseases to diarrheal diseases, heart disease, cancer, skin lesions (below)

Common Reactions in Natural Waters

- Dissolution of Carbonate Minerals (limestone, dolostone)

$$(Ca,Mg)CO_3 \rightarrow \mathbf{Ca^{2+}} + \mathbf{Mg^{2+}} + CO_3^{2-}$$
$$CO_3^{2-} + H_2O + CO_2 \rightarrow 2\ \mathbf{HCO_3^-}$$

- Ionic Dissolution of Salts

Halite: $NaCl \rightarrow \mathbf{Na^+} + \mathbf{Cl^-}$

Gypsum: $CaSO_4 \rightarrow \mathbf{Ca^{2+}} + \mathbf{SO_4^{2-}}$

- Ion Exchange with Clays

$$\text{Na-clay} + Ca^{2+} \rightarrow \text{Ca-Clay} + \mathbf{2Na^+}$$

You Can Graphically Classify the Waters

- Based on relative concentrations

The Four Major Water Types:

Ca-Mg-HCO_3	Associated with limestone
Ca-SO_4-HCO_3	Associated with gypsum
Na-HCO_3	Associated with ion-exchange
Na-Cl	Associated with halite or brines

Piper Plot

- Combination of two tri-linear (ternary) diagrams and an xy scatter
    - One tri-linear plot of anions (Cl, SO_4, HCO_3)
    - One tri-linear plot of cations (Ca, Mg, Na+K)

- Concentrations are plotted as a percentage of the total number of cations (or anions)
    - i.e. 50% Ca, 40% Mg, 10% Na+K

- Locations on triangles are projected onto a diamond – point is plotted where they meet

- Sometimes the circle shows the relative total ion concentrations (TDS)

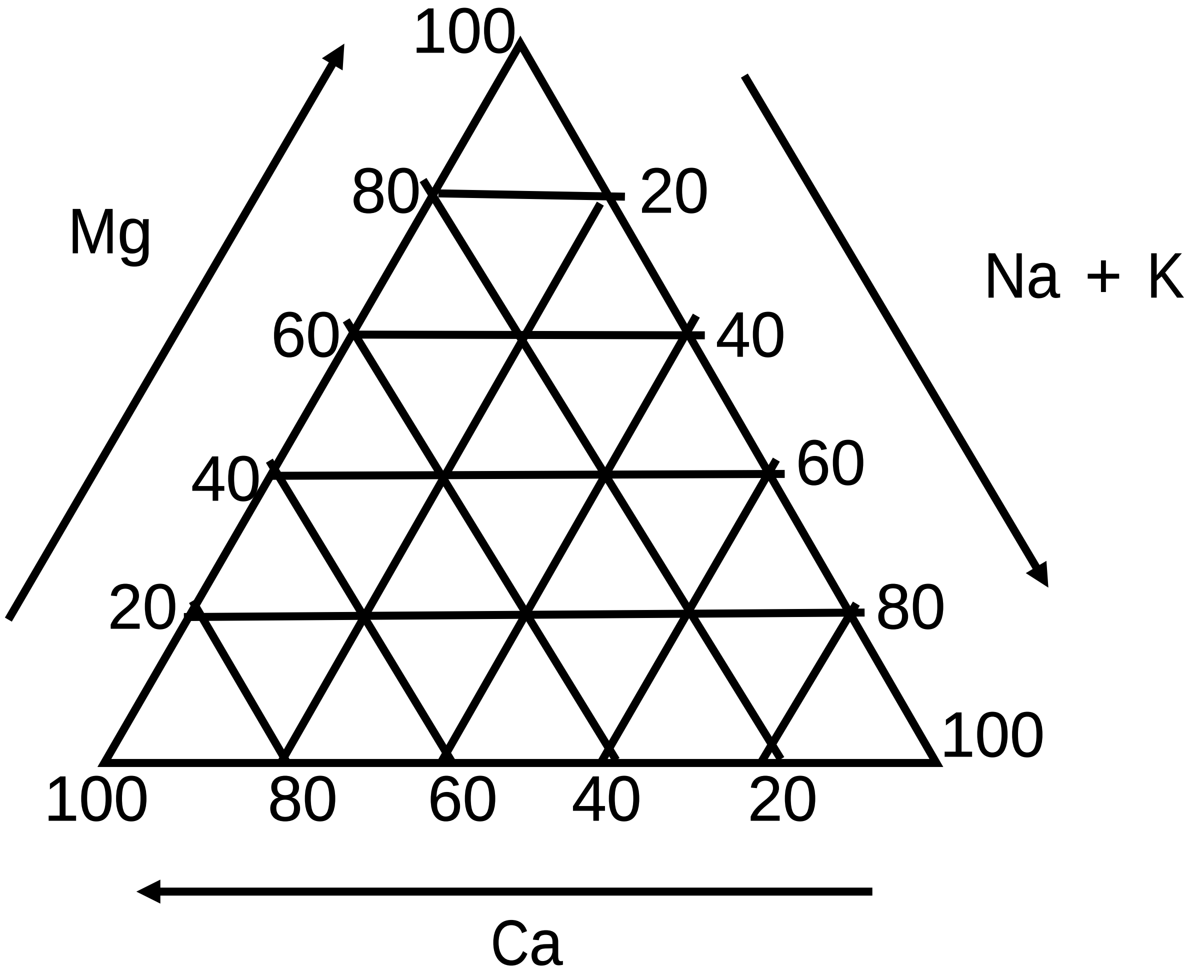
Tri-linear Plot

Mg, Ca, Na+K

100, 0, 0

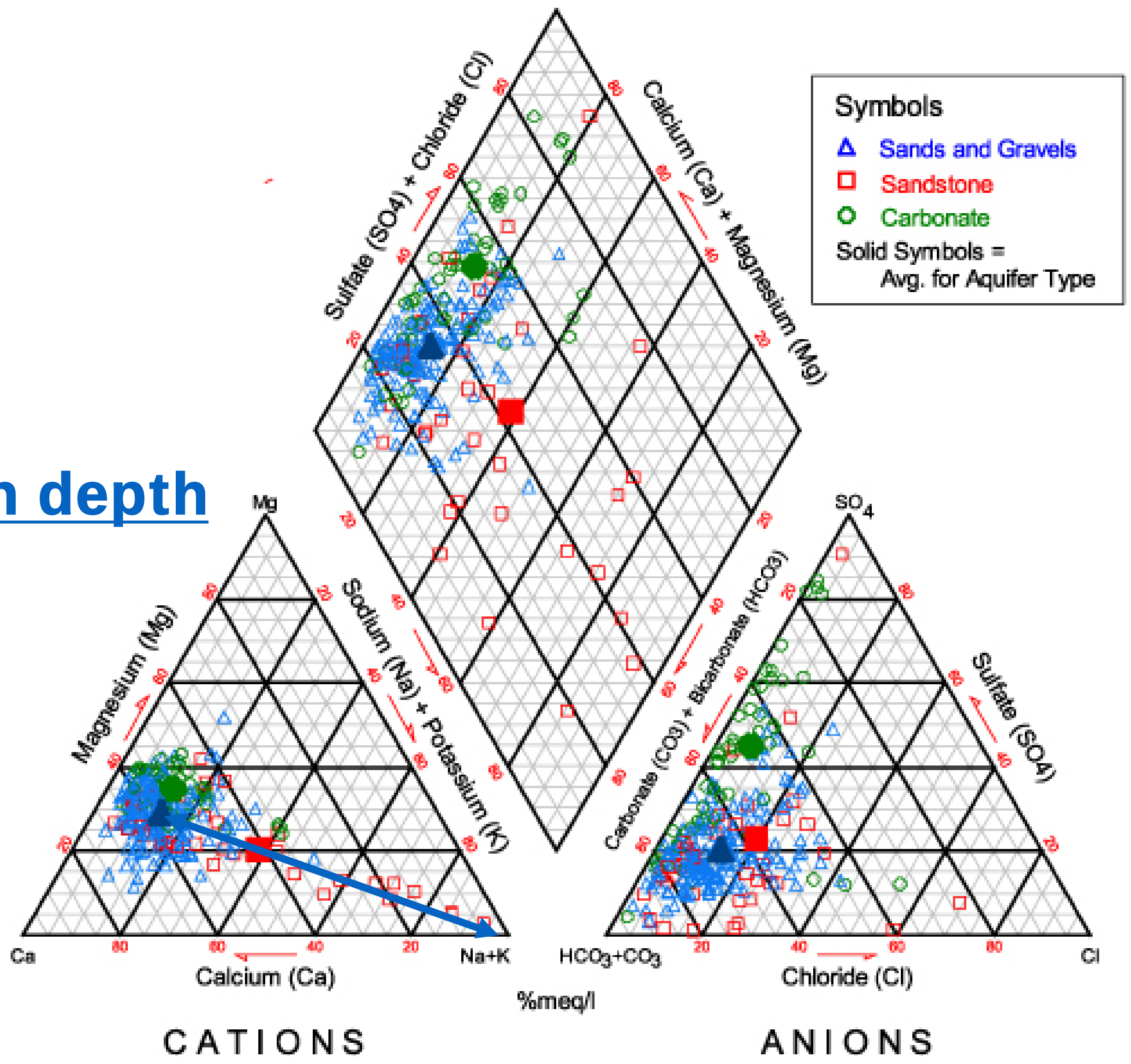
0, 50, 50

33, 33, 33



Compare aquifers and Sources

Mixing with depth

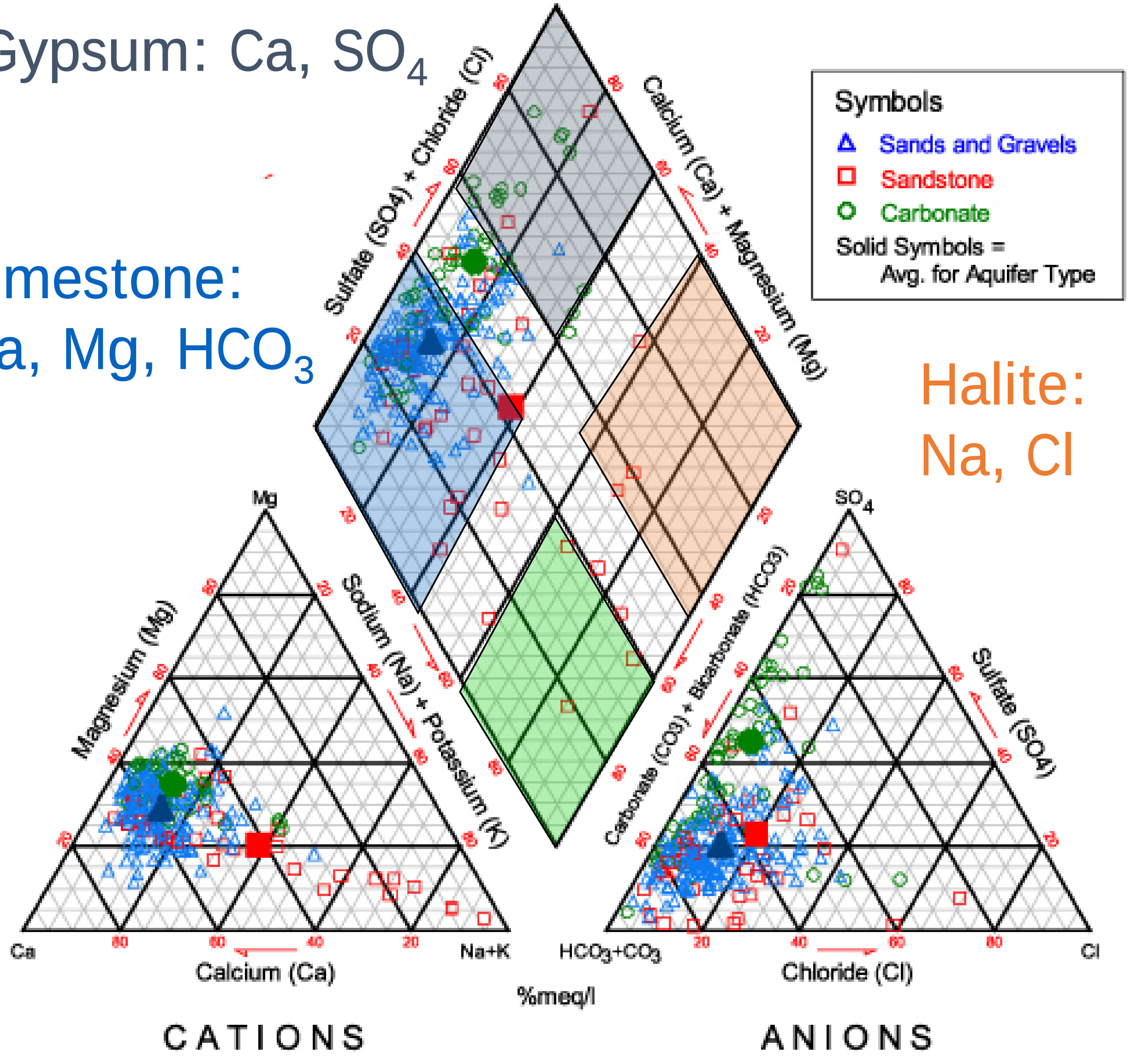


http://epa.ohio.gov/ddagw/gwqcp.aspx#115412887-water-quality-data-distribution

Compare aquifers and Sources

Gypsum: Ca, SO_4

Limestone:
Ca, Mg, HCO_3



Halite:
Na, Cl

Piper plots
can indicate mixing

Ion
Exchange:
Na, HCO_3

http://epa.ohio.gov/ddagw/gwqcp.aspx#115412887-water-quality-data-distribution