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Water quality monitoring- Introduction

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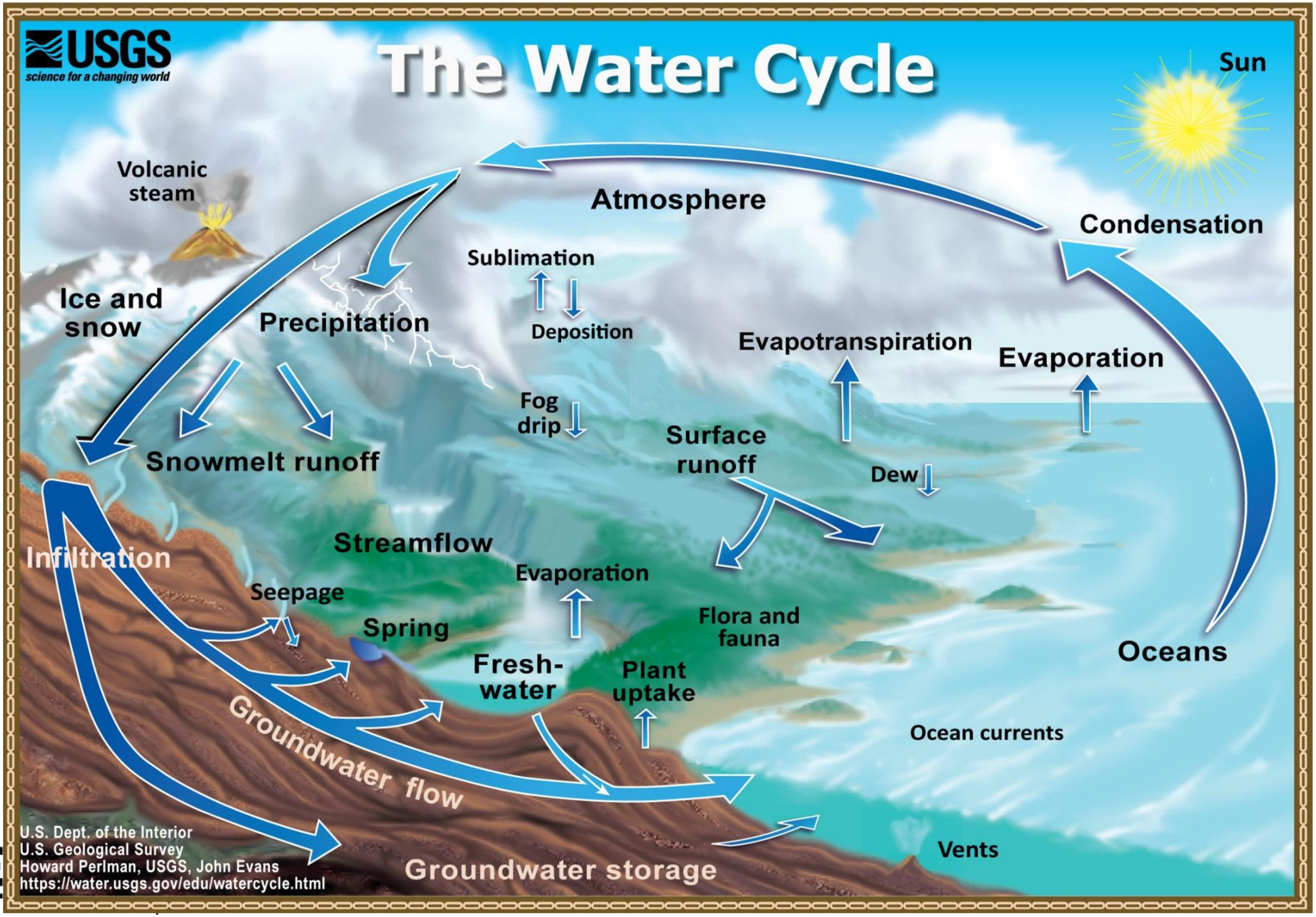
Hydrological cycle



U.S. Dept. of the Interior
U.S. Geological Survey
Howard Perlman, USGS, John Evans
https://water.usgs.gov/edu/watercycle.html

What happens to the water quality in the hydrological cycle?

- Water compositions change through reactions with environment
  - host rock, oxygen contribution, etc.
- Water quality may yield information about environments through which water has circulated
- Chemical reactions are *time* and *space* dependent - can provide info on residence times, flow paths and aquifer characteristics

Why care about the water chemistry?

- Helps us understand the hydrogeologic system
- Indicates mixing of GW and SW
- Helps us interpret GW / SW flow dynamics
- Delineates GW/ SW contamination

Factors controlling water chemistry

1. Rock type

- Waters draining igneous and metamorphic rocks (BUT there will always be exceptions – these are generalisations)
  - Total dissolved solids (TDS) <500mg/l
  - bicarbonate is the major anion
  - sodium and calcium are the major cations
- Waters draining limestones and dolomites
  - limestones weather more rapidly than igneous rocks, so generally limestone waters are more concentrated
  - TDS between 100 and 600 mg/l
  - calcium, magnesium, bicarbonate are the only significant solutes
- Waters draining sandstones, shales
  - most minerals unreactive in weathering environment

Factors controlling water chemistry

2. Relief

- as relief increases, rate of chemical weathering generally decrease
- difficult to evaluate importance of relief alone (correlate with rock type, climate, vegetation, etc.)

3. Climate

- more recharge, more dilution
- high temperature, more evaporation

4. Vegetation

- effect complex - not independent of climate, rock type, relief
- vegetation supplies CO_2 and organic acids to soil = increased rate of chemical weathering

Concentrations

- Amount of the solute in the solvent
  - e.g., the amount of chloride dissolved in water
  - Mass of solute per volume of solution
    - most often expressed as mg/l or μg/l
  - Mass of solute per mass of solution
    - parts per million (ppm) or parts per billion (ppb); sometimes reported as mg/kg
  - Moles per volume (molarity) or moles per mass (molality)
  - Equivalents – moles x charge of the atom

Concentration and unit conversion

Mass concentrations

Water analyses are most commonly expressed in terms of the mass contained in a liter of solution (mg L^{-1}, µg L^{-1}, ng L^{-1})

$$\text{mg } l^{-1} = \frac{\text{mass of solute (mg)}}{\text{volume of solution (l)}}$$

Closely related to mg l^{-1} is parts per million (ppm) or mg kg^{-1}

$$\text{mg kg}^{-1} = \frac{\text{mass of solute (mg)}}{\text{mass of solution (kg)}}$$

These two units are related through the density of the solution (ρ) or mass per unit volume.

Concentration units

Mass concentrations (continued)

The conversion factor between mg L^{-1} and ppm is:

$$\text{mg kg}^{-1} = \text{mg L}^{-1} \times \frac{1}{\rho}$$

Because the density of many natural waters is near 1 kg L^{-1}, it is often a sufficiently good approximation that mg L^{-1} and ppm are numerically equal.

Concentration units

Mass concentrations (continued)

Ambiguity can arise for some components of natural waters. For example, we can express the concentration of sulphate as mg L^{-1} SO_4^{2-} or mg L^{-1} sulphate-S. The relationship among these is:

$$\text{mg L}^{-1}\,\text{SO}_4^{2-} \times \frac{32.066}{96.06} = \text{mg L}^{-1}\ \text{sulphate} - \text{S}$$

Atomic weight S= 32.066 and O = 16

Concentration units

Molar concentrations

In most geochemical calculations, it is necessary to use molar concentrations rather than mass concentrations.

Molarity (*M*) = moles of solute/liter of solution

Molality (*m*) = moles of solute/kg of solvent

If the density of the solution is significantly different from 1 kg L^{-1}, then molality and molarity will be quite different; however, in most natural waters, these quantities are nearly equal and the difference between them can be neglected.

Concentration units

Molar concentrations (continued)

Conversion from mol L^{-1} (*M*) to mg L^{-1} is accomplished using the formula:

$$\text{mg L}^{-1} = \text{mol L}^{-1} \times \text{FW}\left(\text{g mol}^{-1}\right) \times \frac{1000\ \text{mg}}{\text{g}}$$

where FW is the formula weight of the substance in g mol^{-1}. The reverse conversion is accomplished using:

$$\text{mol L}^{-1} = \frac{\text{mg L}^{-1}}{\text{FW} \times 1000}$$

Concentration units

Equivalents and Normality

- Equivalents (eq) are similar to moles, but take into account the valence of an ion. For example,
- 0.002 mol L^{-1} of Ca^{2+} = 0.004 eq L^{-1} Ca^{2+}
- 0.001 mol L^{-1} of Na^{+} = 0.001 eq L^{-1} Na^{+}
- $\text{meq L}^{-1} = \text{mg L}^{-1} / \text{eq.wt}$
- $\text{meq L}^{-1} = \text{mg L}^{-1} /(\text{atomic weight/valence})$
- Normality (*N*) is another name for eq L^{-1}
- Alkalinity is an important solution parameter that is expressed as eq L^{-1} or meq L^{-1}. Hardness too.

Calculating Equivalence

Parameter	Sandstone Aquifer	
	mg/L	meq/L
Na^+	19	0.827
Cl^-	13	0.367
SO_4^{2-}	7	0.146
Ca^{2+}	88	4,391
Mg^{2+}	7.3	0.6
HCO_3^-	320	5.245
Total Anions		5.758
Total Cations		5.818
% Difference		1%

The atomic wt. of Sodium (valence of one) = 22.989

And its charge is one

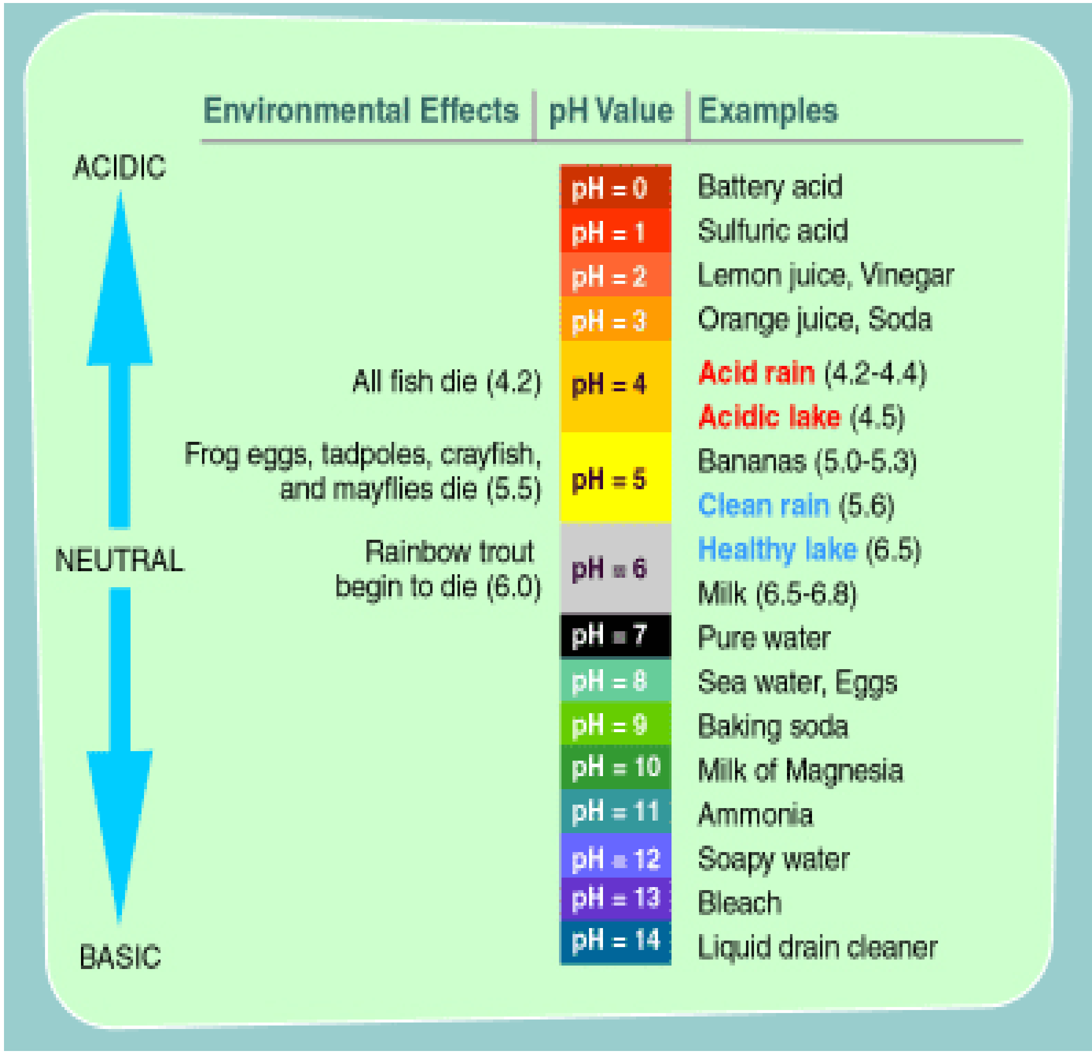
$$Equivalent\ Concentration = \frac{Concentration}{\left(\frac{Formula\ Weight}{Charge}\right)} = \frac{19}{\left(\frac{22.989}{1}\right)} = 0.827$$

Basic chemical Parameters

- pH
  - Inverse log of hydrogen ion activity in the water
- Alkalinity
  - Ability of the water to neutralize an acid
- Specific conductance or Elec. conductivity
  - Ability of the water to conduct electricity
  - Increases with increasing TDS
- Total dissolved solids (TDS)
  - Everything dissolved in the water
- Hardness
  - Sum of the divalent cations, expressed as equivalent $CaCO_3$

pH

- pH = -log [H^+] , based on dissociation of water where [H^+] x [OH^-] = 10^{-14}
- Measures hydrogen ion concentration
- Logarithmic scale, from 0 (acidic) to 14 (basic)
- Influences the solubility of many elements - important in surface and ground water
- Most aquatic species sensitive to pH with limited range that they can live in



Environmental Effects	pH Value	Examples
	pH = 0	Battery acid
	pH = 1	Sulfuric acid
	pH = 2	Lemon juice, Vinegar
	pH = 3	Orange juice, Soda
All fish die (4.2)	pH = 4	Acid rain (4.2-4.4) Acidic lake (4.5)
Frog eggs, tadpoles, crayfish, and mayflies die (5.5)	pH = 5	Bananas (5.0-5.3) Clean rain (5.6)
Rainbow trout begin to die (6.0)	pH = 6	Healthy lake (6.5) Milk (6.5-6.8)
	pH = 7	Pure water
	pH = 8	Sea water, Eggs
	pH = 9	Baking soda
	pH = 10	Milk of Magnesia
	pH = 11	Ammonia
	pH = 12	Soapy water
	pH = 13	Bleach
	pH = 14	Liquid drain cleaner

Alkalinity

- Alkalinity is a measure of the ability of water to neutralise acids
- It is the sum of the anions capable of pairing with hydrogen ions
- For most natural waters these are:
  - Bicarbonate, Carbonate and Hydroxide
- Under most environmental conditions CO_3^{2-} and OH^- can be ignored, so
- Alkalinity = HCO_3^- as mg $CaCO_3$ /l

Electrical Conductivity

- The electrical conductivity of water estimates the total amount of solids dissolved in water (TDS)
- TDS can be estimated in the field by measuring the electrical conductivity of the water
- Unit µS/cm (micro Siemens/cm)

dS/m   (deciSiemens/m)

Where: 1000 µs/cm = 1 dS/m

- **TDS (mg/l) = 0.64 X EC (µS/cm) = 640 X EC (dS/m)**

Some studies use 0.65 as the constant

This relation provides an appox. estimate only!

Total Dissolved Solids (TDS)

- The TDS is the total amount of salts dissolved in the water
- TDS is measured in ppm (parts per million) or in mg/l
- At least 99.99% of the TDS comes from just 7 major ions:
- Nitrogen-based ions may also be present in significant quantity but are considered separately here, as they derive from biological and not geological sources

Hardness

- Hardness is the sum of the divalent cations, expressed as equivalent $CaCO_3$
- The major divalent cations are:
  - Calcium, Ca^{2+} and magnesium, Mg^{2+}
- Though there may also be a minor contribution from:
  - Iron, Fe^{2+} and divalent manganese Mn^{2+}
- Hardness = (Ca^{2+} + Mg^{2+}) as mg $CaCO_3$ /l
  - Occasionally it may be expressed as: mg Ca /l

Descriptions of water hardness

Hardness (mg $CaCO_3$ /l)	Description
0 - 50	soft
50 - 100	moderately soft
100 - 150	slightly hard
150 - 200	moderately hard
200 - 300	hard
> 300	very hard

Primary Constituents

- Primary cations and anions
  - Concentrations generally > 5 mg/L
  - Make up about 99% of the typical groundwater sample (by weight)
    - Bicarbonate
    - Calcium
    - Chloride
    - Magnesium
    - Silicon
    - Sodium
    - Sulphate

Minor/Trace Elements

- Minor constituents
  - Concentrations generally ranging from 0.1 –10 mg/L
    - Boron
    - Fluoride
    - Iron
    - Nitrate
    - Strontium
- Trace elements
  - Concentrations generally < 0.1 mg/L
    - Arsenic, Cobalt, Cadmium, Manganese, Nickel, Lead, Zinc

Sampling and Analysis Plan

Document written in advance of sampling that defines:

- Sampling locations and frequency
- How field parameters are measured
- How samples are collected
- Quality control and assurance measures

Do NOT go to the field without a plan!

Groundwater Sampling

- Important Points
  - Be sure to take a representative sample
  - Take field measurements with proper equipment
  - Make sure water bottles are properly rinsed
  - Filter and preserve samples in the field
  - Store on ice at 4^o C
  - Try to analyse in laboratory within 24 hours of sampling
  - Have a quality control program with duplicates, blanks, field blanks, or spiked samples

WELL SAMPLING

- Calculate Well Volume:
  - – Determine static water level
  - – Calculate volume of water in the well casing
- Purge the well:
  - – A minimum of three casing volumes is recommended.

Analysis of Water Samples

- **Field:**
  - pH, specific conductance, temperature, dissolved oxygen, and alkalinity
- **Laboratory:**
  - **Cations:** sodium, calcium, magnesium, potassium, and iron
  - **Anions:** bicarbonate, carbonate, sulfate, and chloride
  - **Trace Metals, Radioactivity**

Ion Balance Error

- Aqueous solutions must be electrically neutral. In other words, the sum of all negative charges must equal the sum of all positive charges.
- One check on the quality of a water analysis is the ion-balance error (IBE) or charge balance error (CBE) is calculated.

(1) Charge balance: $\sum \text{cations} = \sum \text{anions}$

(2) IBE/ CBE = $\dfrac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \; x \; 100$

Ion Balance Error

- There is always some error in the measurement of cation and anion concentrations.
- Thus, we cannot expect a charge-balance error of zero for any analysis.
- The I.B.E. may be positive or negative, depending on whether cations or anions are more abundant.
- A reasonable limit for accepting an analysis as valid is ±5%.

Reasons for IBE values greater than ±5%

- An important anion or cation was not included in the analysis
    - Sometimes this can point out the presence of a high concentration of an unusual anion or cation.
- A serious error has occurred in the analysis
- One or more of the concentrations was recorded incorrectly
- Using *unfiltered* samples that contain particulate matter which dissolves upon addition of acid (for preservation purposes)

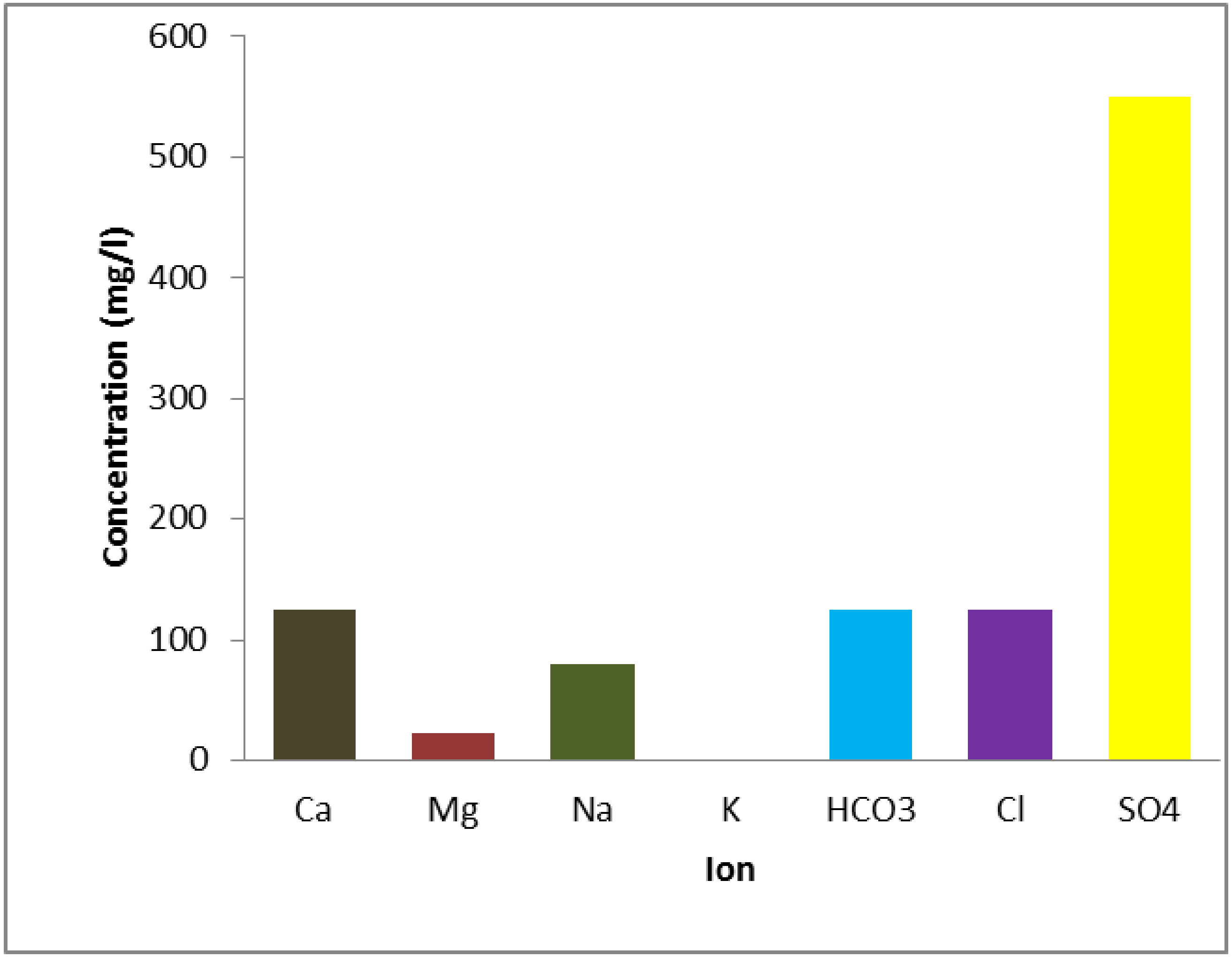
Water Classification

- Why?
  - Helps define origin of the water
  - Indicates residence time in the aquifer
  - Aids in defining the hydrogeology
  - Defines suitability

Water Classification

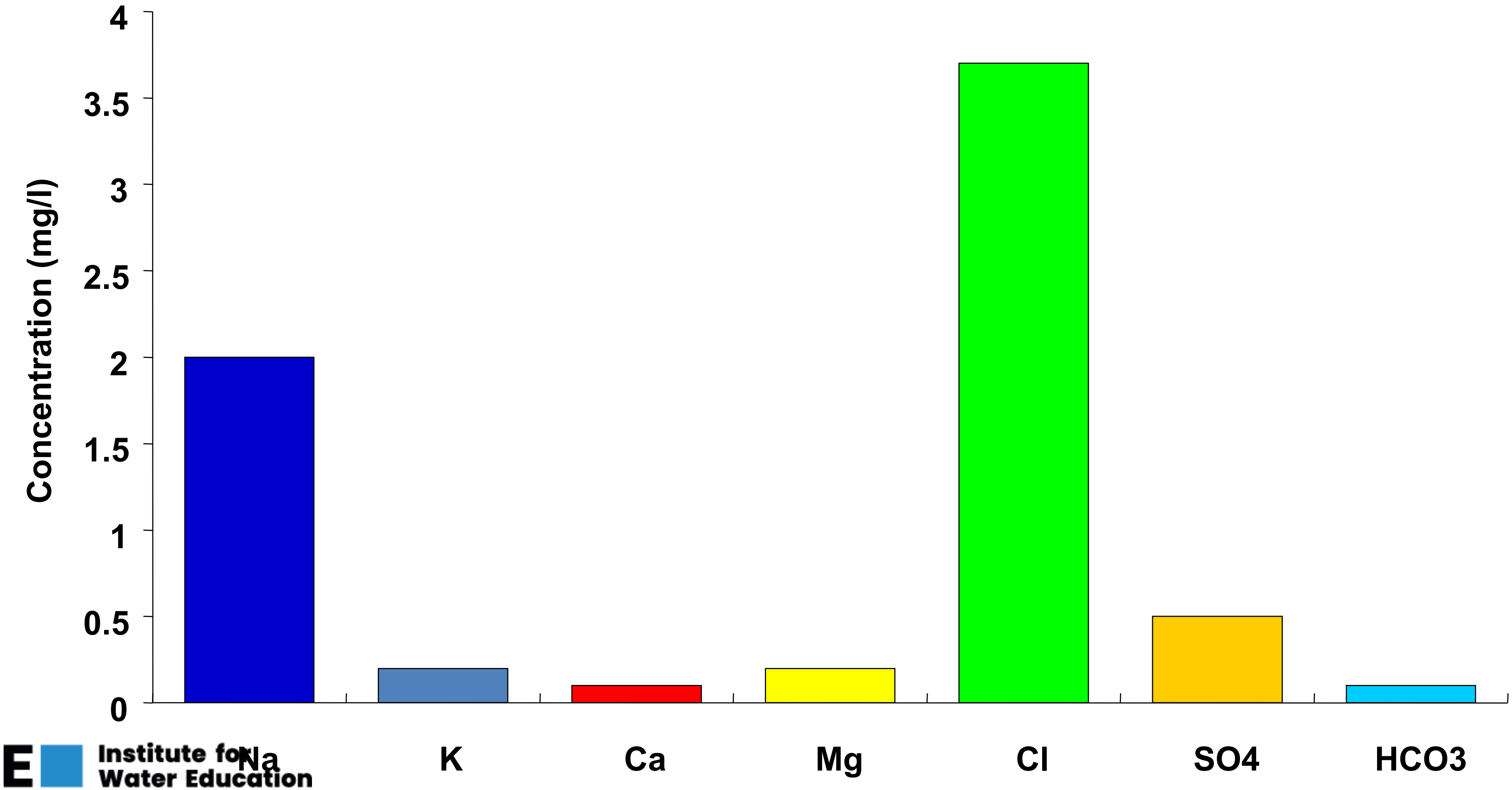
- How?
  - Compare ions with ions using chemical equivalence
  - Making sure anions and cations balance
  - Use of diagrams and models

Graphical representations of water geochemistry



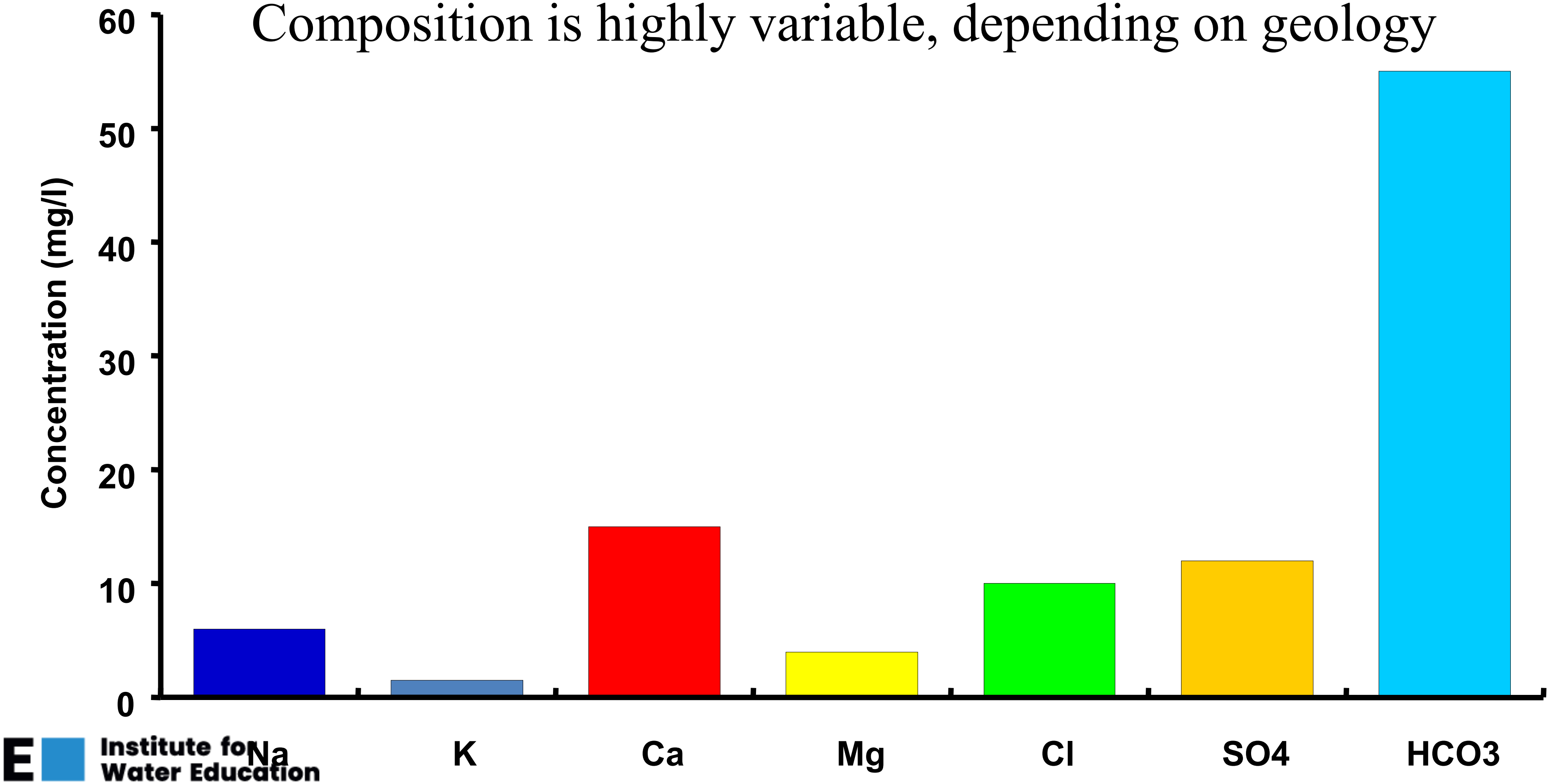
Major ion composition of rain water

pH = 5.7,
TDS = 7 mg/l



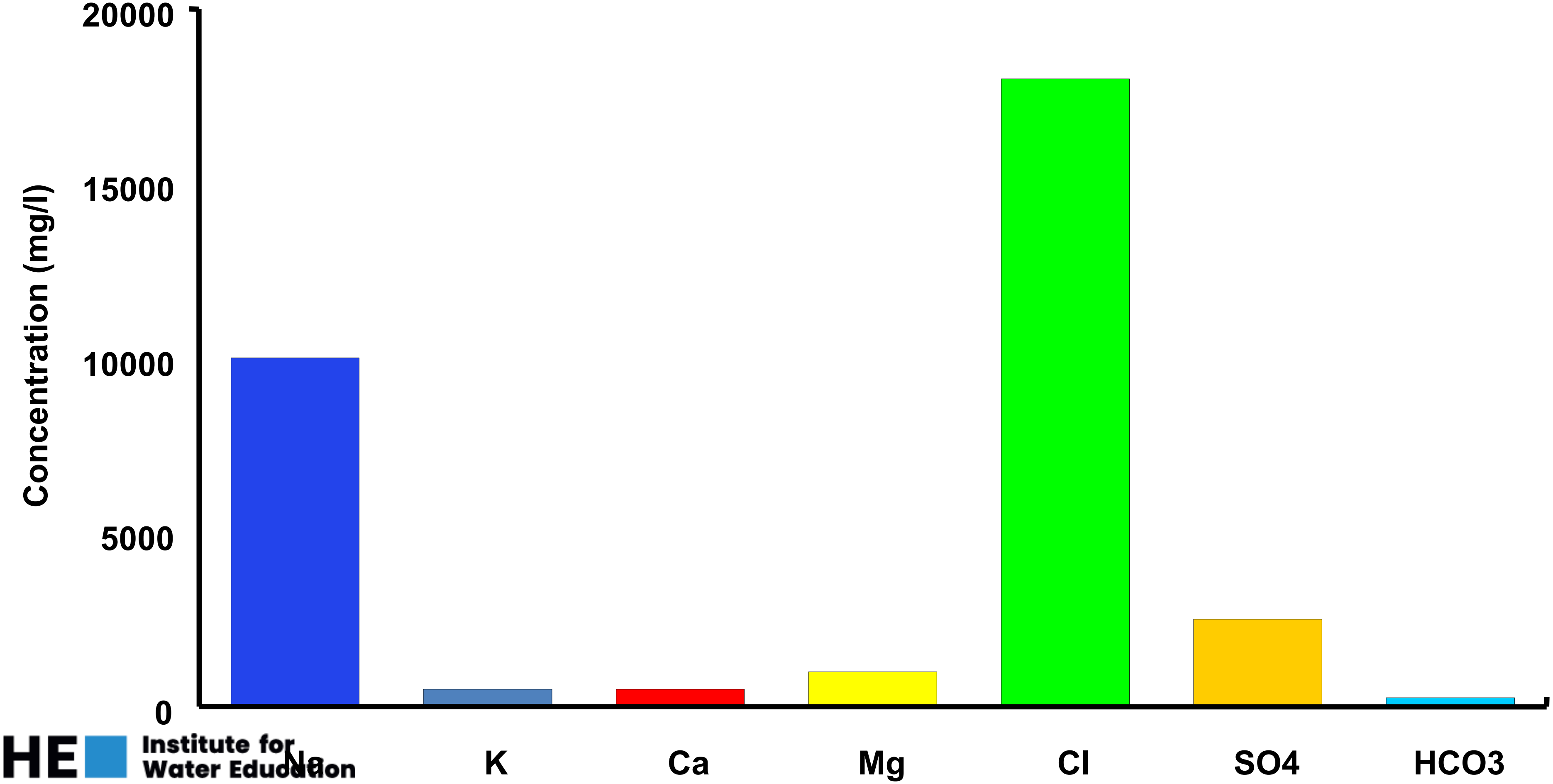
Major ion composition of groundwater

pH = 6 - 8,
TDS = 100 - 300 mg/l
Composition is highly variable, depending on geology

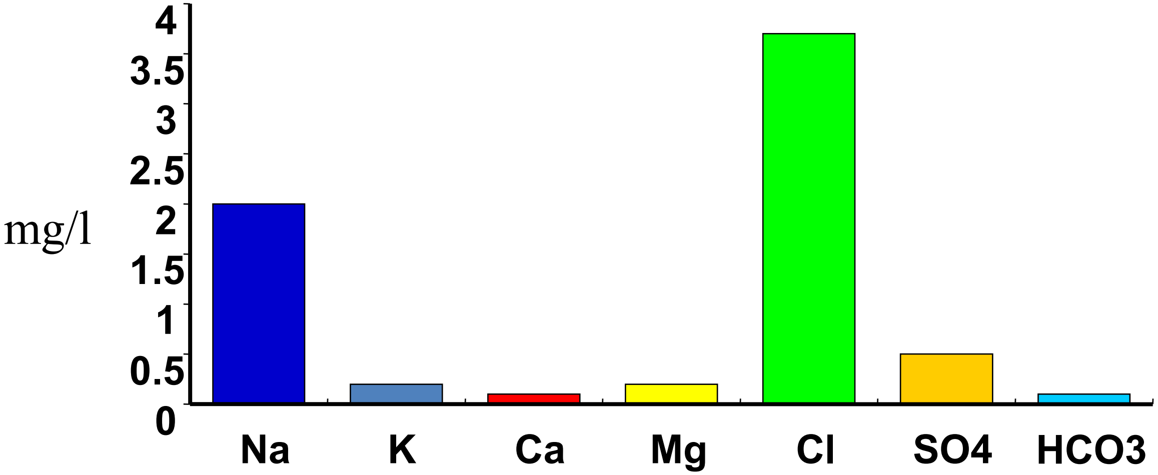


Major ion composition of seawater

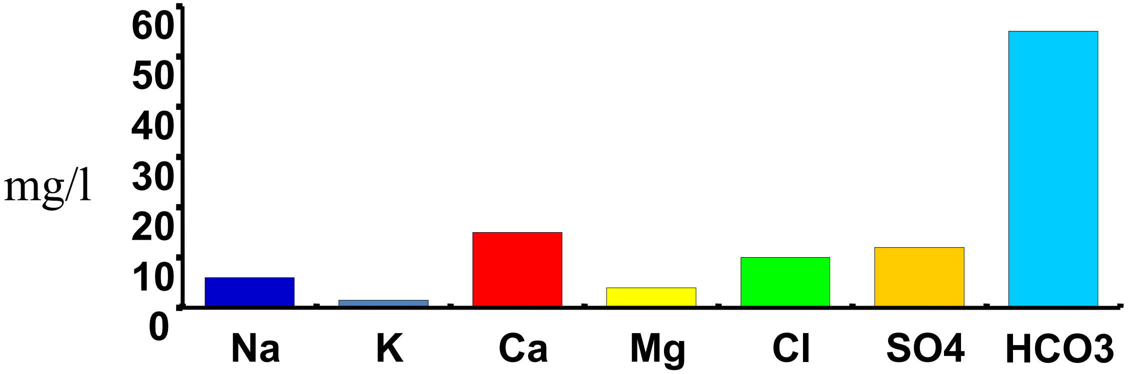
pH = 8.2,
TDS = 34,400 mg/l



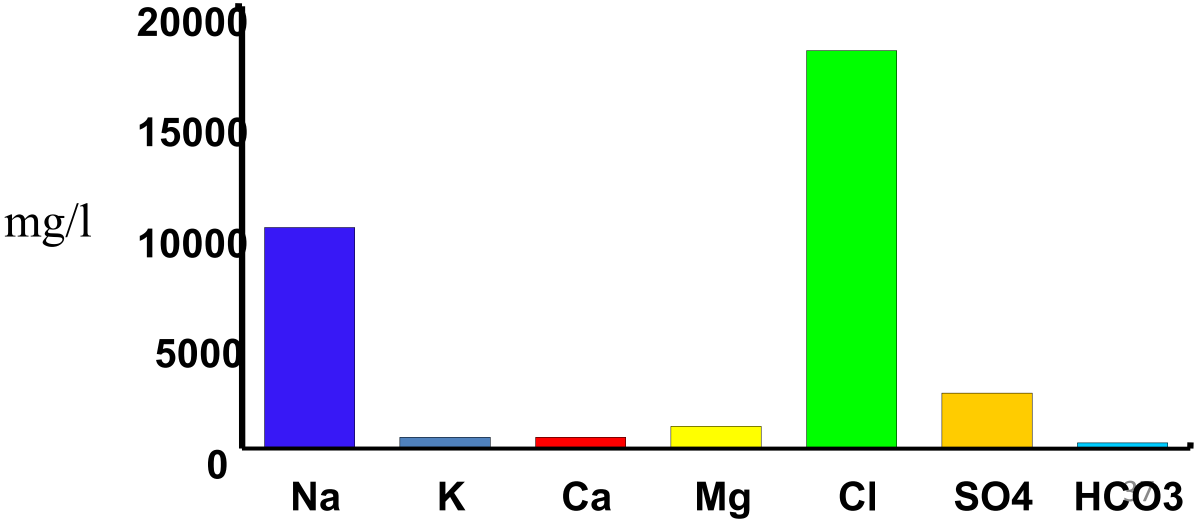
- Rain water



- Groundwater



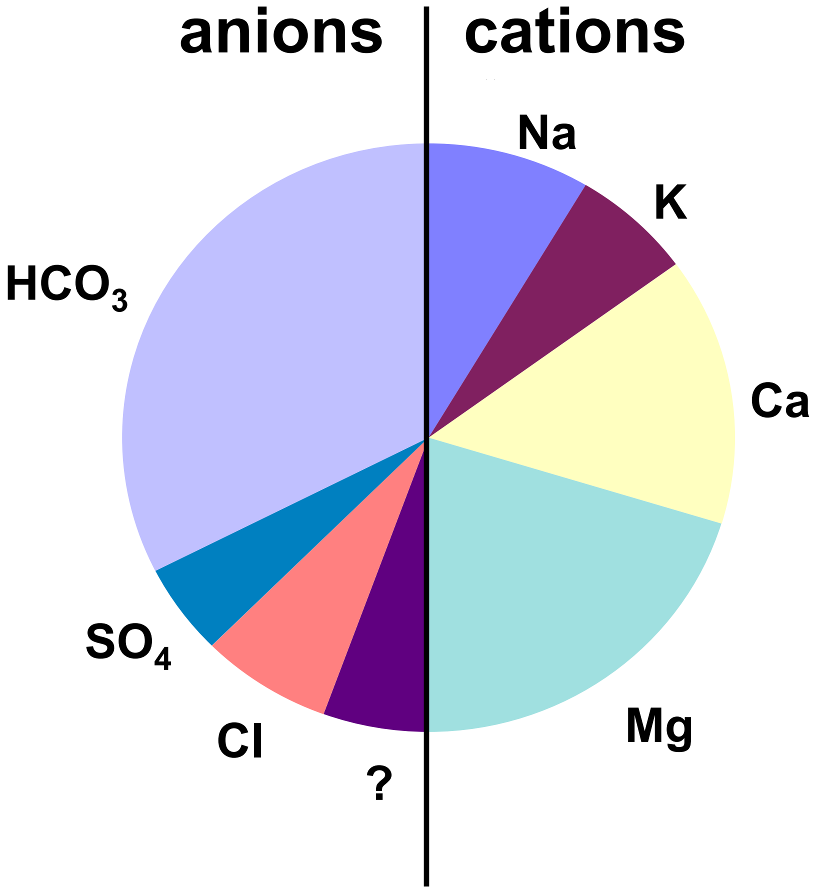
- Seawater

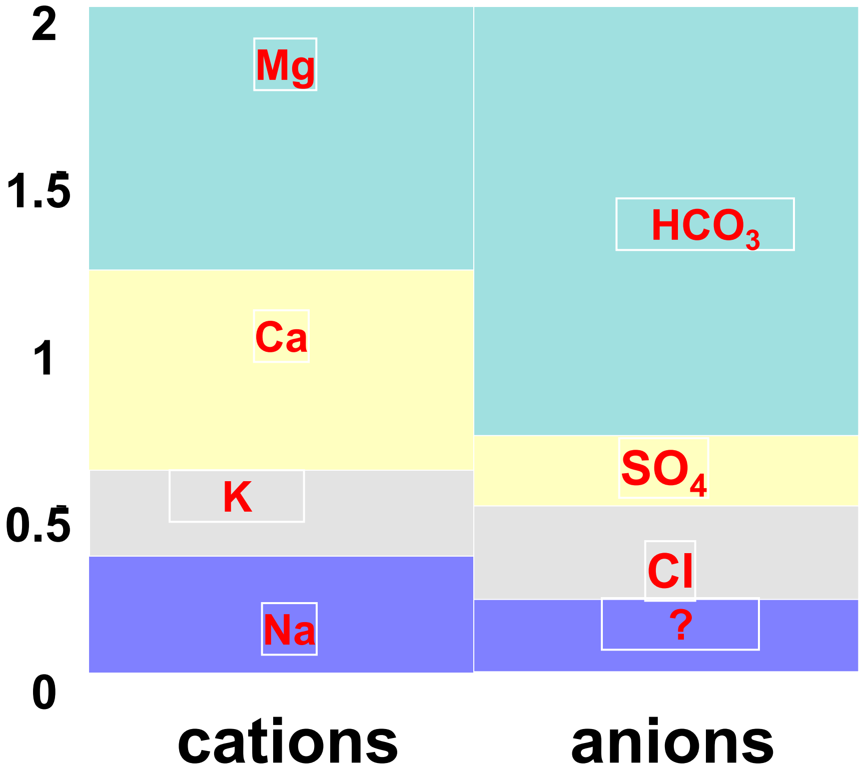


Graphical representations of water geochemistry

- Rather than providing just a list, or table, of laboratory results, it is useful to view the geochemical composition in graphical form
- Techniques include:
  - Pie and bar charts
  - Stiff patterns (Kite diagrams)
  - Piper diagrams (ternary graphs)
- First it is necessary to express concentrations in terms of ionic strengths

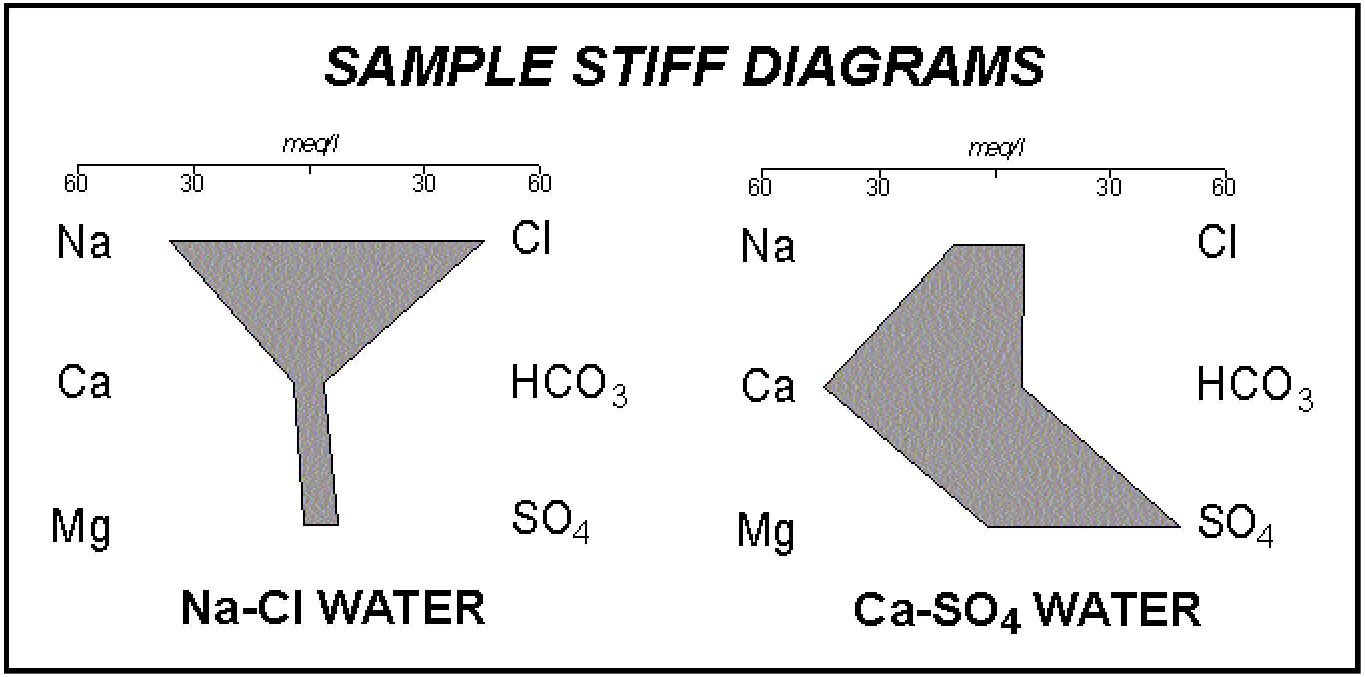
Pie and bar charts





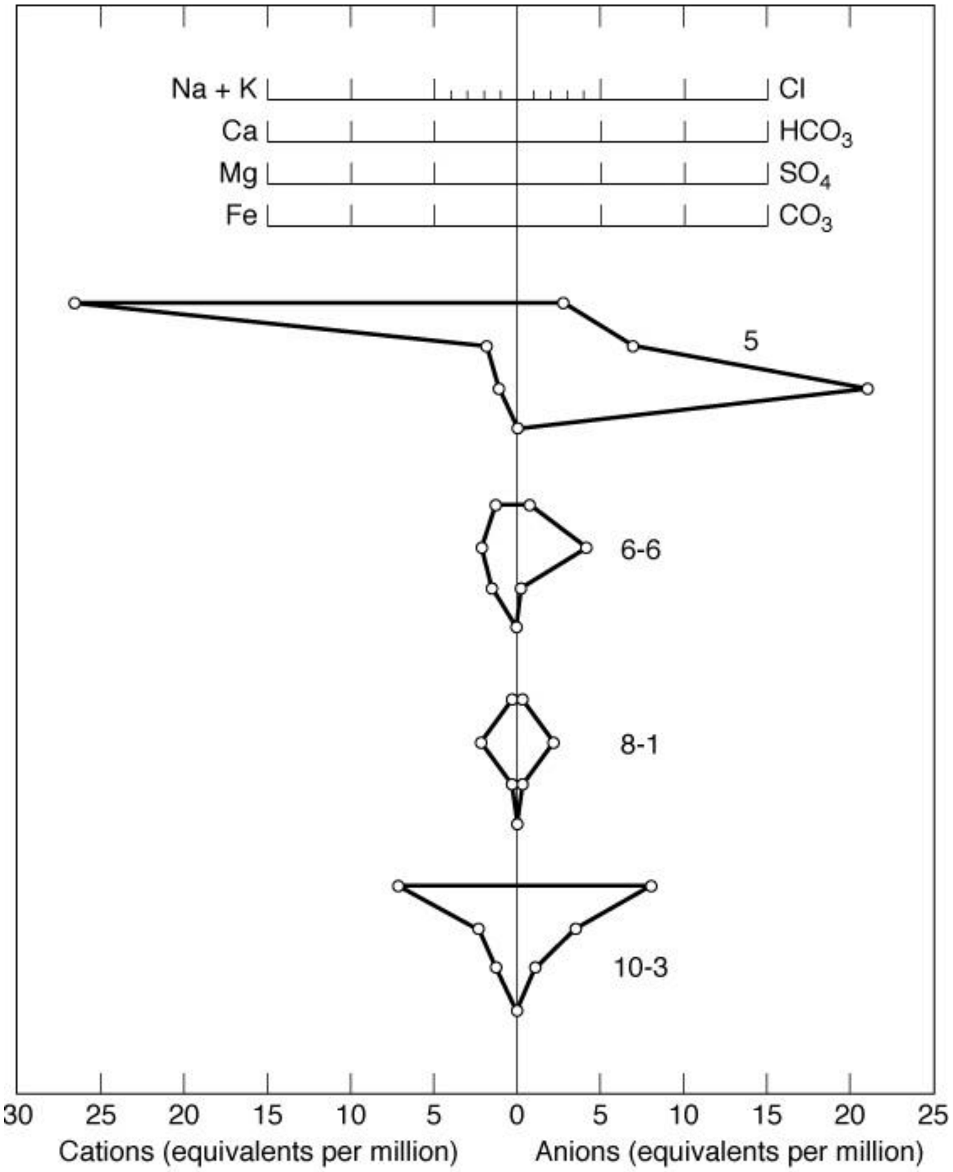
Stiff Diagrams

- Graphic representation of the water chemistry of a single sample



Stiff Diagrams

- Concentrations of cations are plotted to the left of the vertical axis and anions are plotted to the right (meq/L)
- The points are connected to form a polygon
- Waters of similar quality have distinctive shapes



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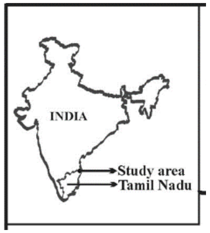
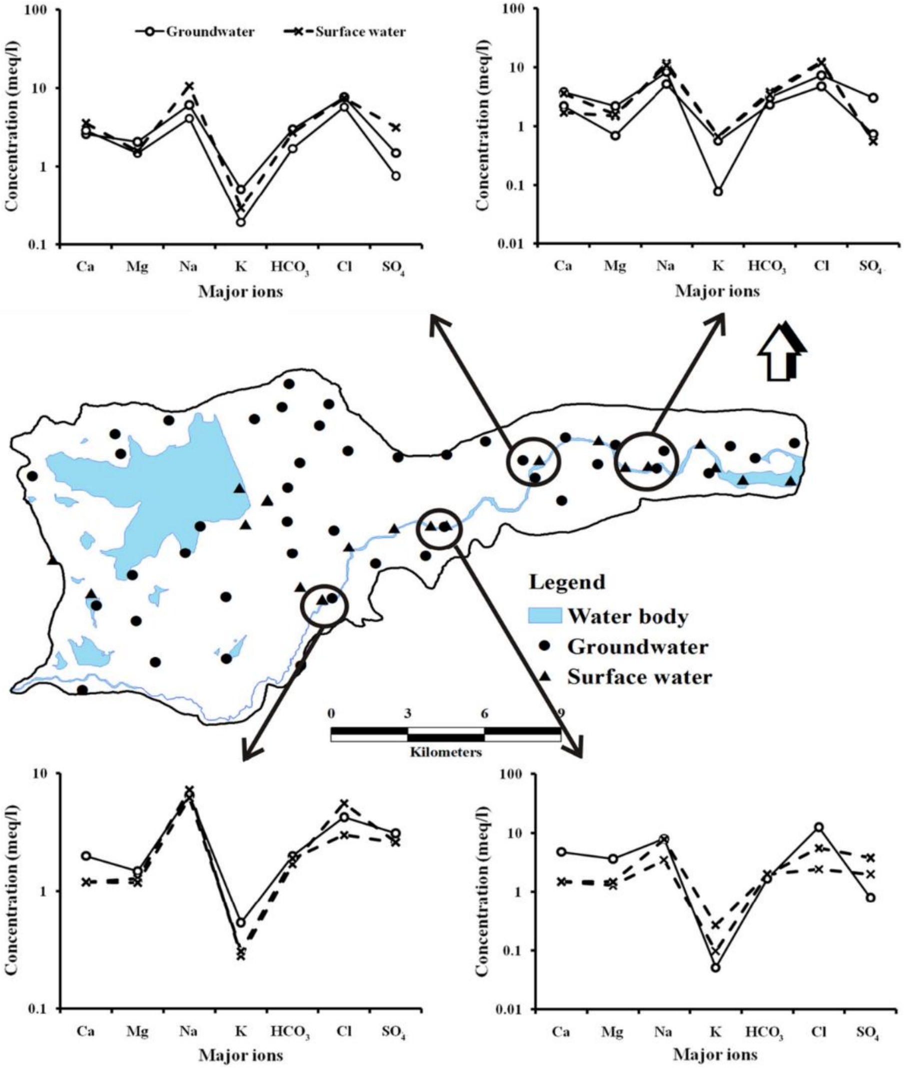
Schoeller Diagrams



- Graph of concentrations of major ions
- Each sample has a specific shape to the curve; can be used to compare to other samples

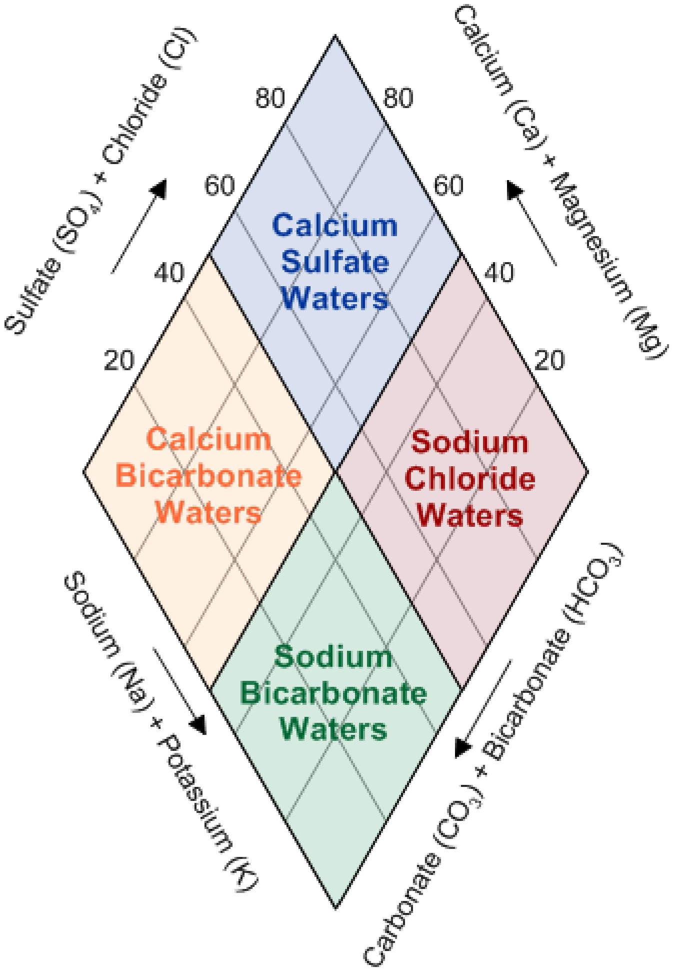


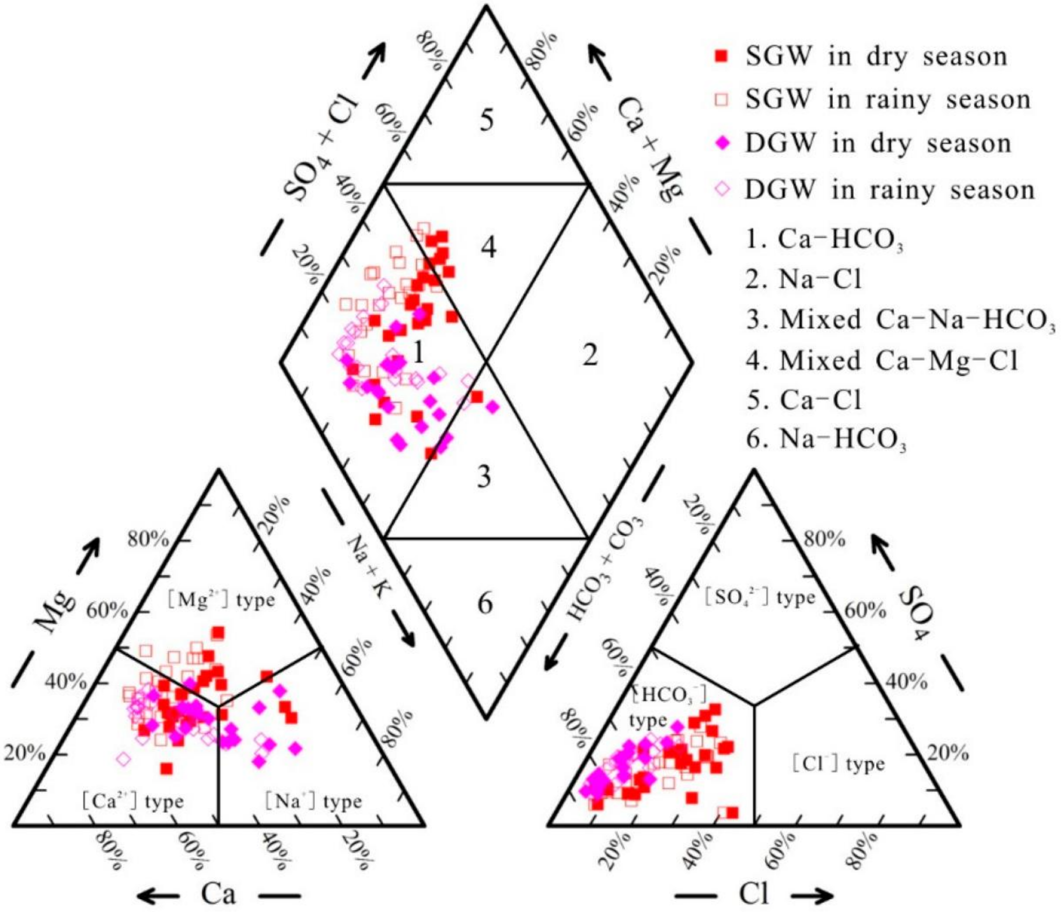
Brindha et al. 2014

Piper diagram

- Piper diagrams are tri-linear graphs representing the ionic strengths of the cations and anions.
- Plotting the data onto the tri-linear graphs takes a little practice
- Again, Na and K are plotted together
- There is no room on a Piper diagram for NO_3 as it is a purely geochemical method
- Plots each ion as a value normalized to 100%
- Data on the 2 triangles is projected on the quadrilateral

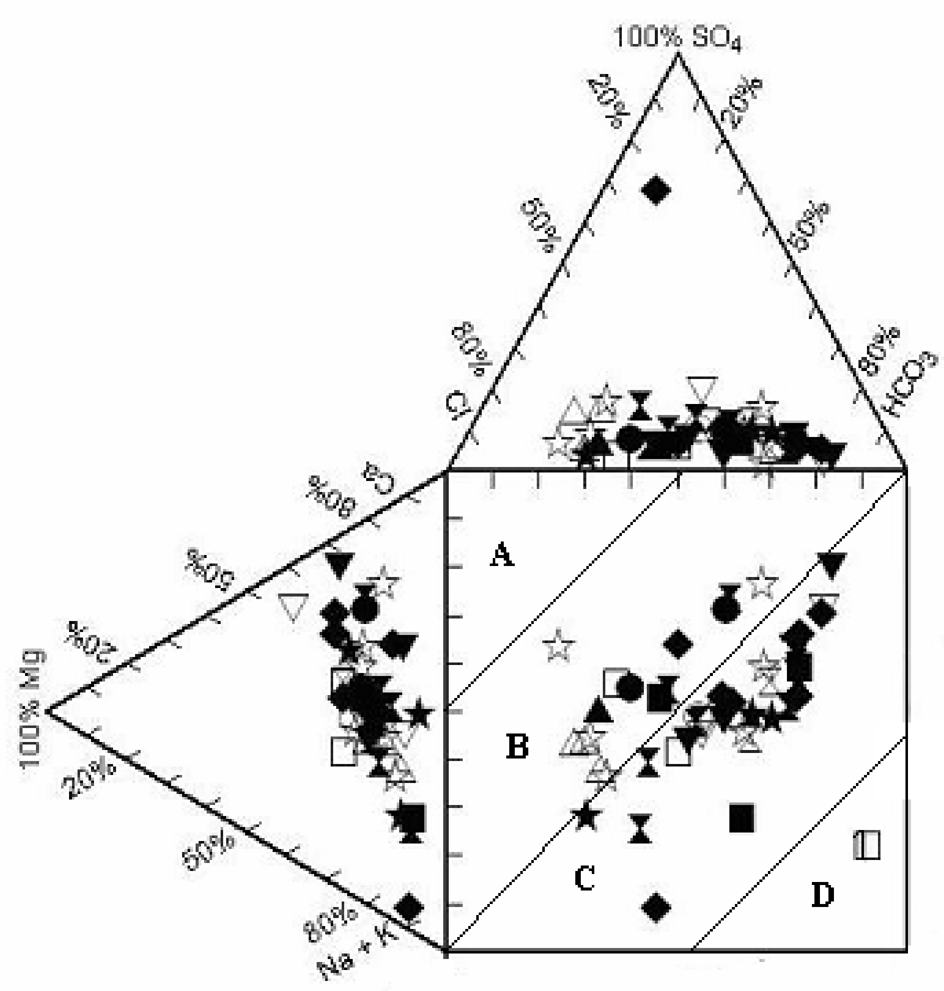
Piper diagrams





https://support.goldensoftware.com/hc/en-us/articles/115003101648-What-is-a-piper-plot-trilinear-diagram-

Durov Diagram



Literature

- Geochemistry, groundwater and pollution- C.A.J. Appelo and D. Postma
- Applied Hydrogeology- C.W. Fetter
- Groundwater- R.A. Freeze and J.A. Cherry

You can download this here: http://hydrogeologistswithoutborders.org/wordpress/original-groundwater-by-freeze-and-cherry-1979-now-available-online/

Answers

- Slide 10

Molecular weight of SO_4^{2-}= 32.066 + 16x4 = 96.066

200 mg/l SO_4^{2-} x (32.066/96.06) = 66.8 mg/L sulphate-S

- Slide 39

Identify the missing ion: could be carbonate or nitrate