An Introduction to Groundwater Chemistry

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NORAD supported project in MRRD:
Capacity Building and Institutional Cooperation in the field of Hydrogeology for Faryab Province , Afghanistan

NORPLAN

Hydrochemistry of Groundwater

Each groundwater has a unique chemical fingerprint, derived from:

Rainfall / snowmelt recharge:

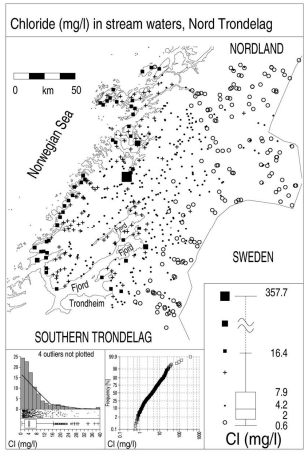
- H and O isotopes
- Nitrate, sulphate
- Chloride
- Oxygen

Soil Zone:

- Evapoconcentration
- Removal of nutrients by plants (K, NO_3^-)
- Respiration => CO_2

Influence of recharge chemistry.
Marine aerosols.

Concentrations of marine salts increase with proximity to the coast.

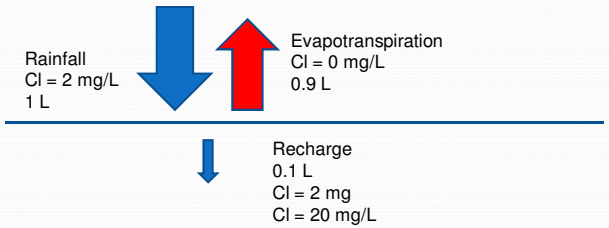


Chemistry of Precipitation in Faryab

Precipitation (mg/L)

		Cl^-	SO_4=	NO_3-
Maimana	Snow	0.10	0.58	0.46
Maimana	Rain	0.48	3.25	1.67
Maimana	Rain	1.74	2.46	0.64
Gurziwan	Snow	0.60	0.75	0.38
Gurziwan	Rain	0.56	0.88	0.49
Andkhoi	Snow	15.6	25.1	16.4
Andkhoi	Rain	2.04	6.94	6.76
Andkhoi	Rain	1.36	3.91	1.04

Evapo-concentration of rainfall



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Groundwater (mg/L)

		Cl^-	Up-concentration
Kohistan	Groundwater	Typically 2-5	4-9
Gurziwan	Groundwater	Typically around 20	30-40
Andkhoi	Groundwater	Typically 600-1000	300-500

If taken at face value....this could imply that:
Rainfall recharge in Kohistan is 50-100 mm/a
Rainfall recharge in Gurziwan is c. 10 mm/a
Rainfall recharge in Andkhoi is < 1 mm/a

Hydrochemistry of Groundwater (II)

Water Rock Interaction
- Consumption of O_2 and CO_2
- Increase in pH, alkalinity
- Release of base cations

Mixing
- E.g., with deep, saline formation water
- With intruding sea-water

Water Rock Interaction

1. Dissolution

When many inorganic chemicals dissolve in water, they form electrically charged species called "ions"

- $NaCl \Leftrightarrow Na^+ + Cl^-$
  Halite
- $CaSO_4.2H_2O \Leftrightarrow Ca^{++} + SO_4^{=} + 2H_2O$
  Gypsum
- $CaF_2 \Leftrightarrow Ca^{++} + 2\ F^-$
  Fluorite

Water Rock Interaction

2. Ion Exchange

- $Ca\text{-clay} + 2Na^+ \Leftrightarrow Na_2\text{-Clay} + Ca^{2+}$
- $F\text{-Apatite} + OH^- \Leftrightarrow OH\text{-Apatite} + F^-$

Water-Rock Interaction – Acid Base Reactions

3. Acid Base Reactions

Note CO_2 is regarded as an acid

$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$

- $CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$
- $2NaAlSi_3O_8 + 2CO_2 + 3H_2O \Leftrightarrow$
  $2Na^+ + 2HCO_3^- + Al_2Si_2O_5(OH)_4 + 4SiO_2$

Feldspar + carbon dioxide + water = dissolved cations + alkalinity + silica + clay

Water Rock Interaction – Redox Reactions

4. Redox reactions

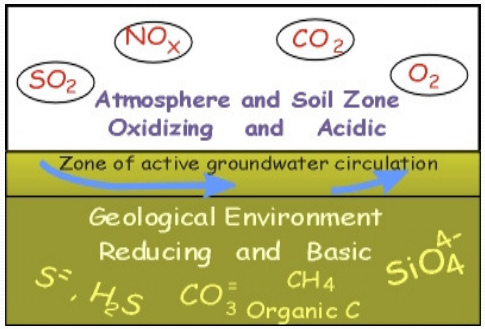
Oxidation of organic matter

- $CH_2O + O_2 \Leftrightarrow CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$

Oxidation of pyrite

- $2FeS_2 + 2H_2O + 7O_2 \Leftrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$

Groundwater as the reaction zone between atmosphere and geosphere



Water Rock Interaction

In most groundwater systems, carbonate and silicate hydrolysis are the dominant reactions:

- consuming protons and CO_2
- generating base cations
- generating alkalinity

Thus, most groundwaters:

- are circum-neutral
- are dominated by Ca^{++}, Mg^{++}, Na^{+}, (K^{+}) – major cations
- are dominated by HCO_3^{-}, ($SO_4^{=}$, Cl^{-}, NO_3^{-}) – major anions

Major Ion Composition

In young, fresh groundwaters, typically, bicarbonate is the dominant anion

$$CO_2 + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^{-}$$

- sulphate may be prominent in deep saline waters, in marine areas, where sulphides or gypsum are present in the rock or in brines in arid areas
- chloride may be prominent in deep saline waters or marine areas, where halite is present in the rock, or in brines in arid areas
- nitrate may be prominent in areas of agricultural or latrine / sewage / refuse pollution