Analytical hydrogeochemistry

1. Water on Earth

Outline

- The Hydrologic Cycle
- Precipitation
- Groundwater
  - Hydrogeological zonation (vertical)
    - Groundwater table
    - Piezometric levels
  - Groundwater flow
    - Unsaturated zone
    - Saturated zone
    - Darcy's Law
    - Diffusion
    - Dispersion
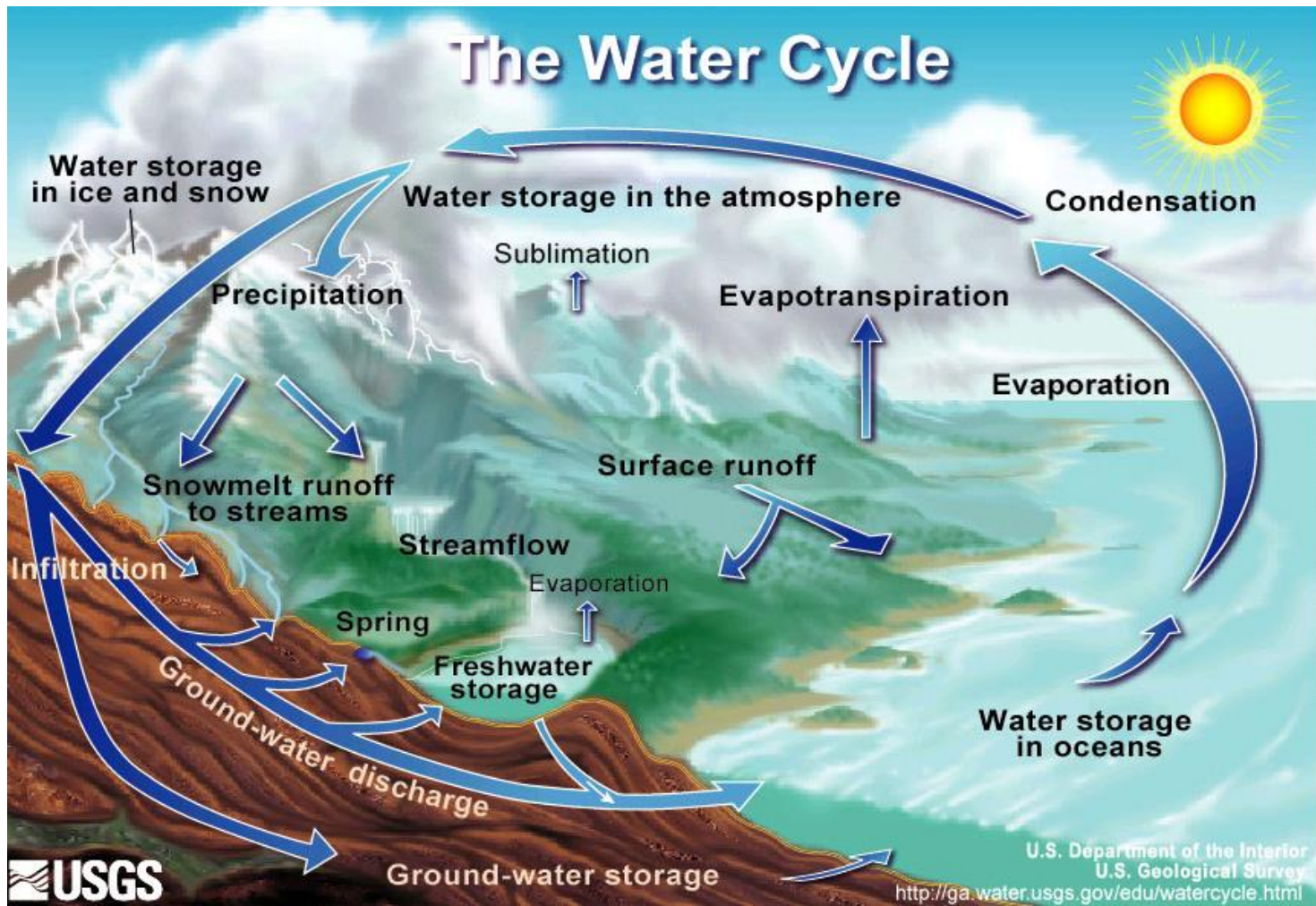   - Retardation
- Sorption and cation exchange

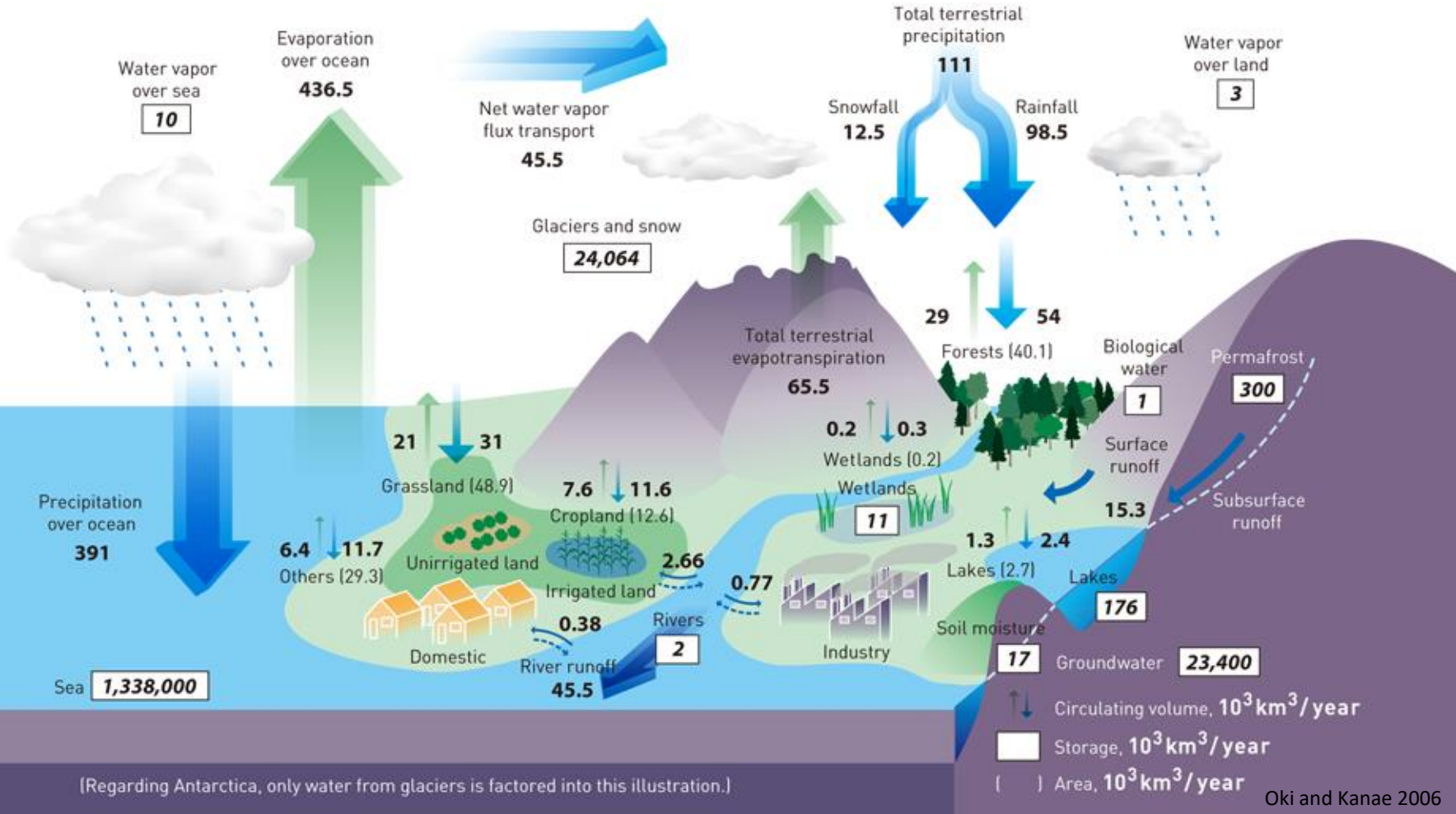# THE HYDROLOGIC CYCLE

The Hydrologic Cycle

- Draw a scheme of the hydrologic cycle
    - Highlight the main reservoirs
    - Highlight the main flows
    - Compare the relativ sizes of individual fluxes

The Hydrologic Cycle

Main flows and reservoirs:

Hydrological cycle

Oki and Kanae 2006

Retention times

Ocean 39,000 years	Groundwater (underground runoff) 9,500 years
Atmosphere 10 days	Groundwater (river runoff) 270 years

Hydrosphere

- Water on (and near) the Earth's surface – liquid, gaseous and frozen
- **Reservoirs:**
- ocean 97.5%
- fresh water 2.5%
  - 1.85% (74% of fresh water) permanently frozen polar cover
  - 0.64% (98.5% of residue) groundwater
- atmosphere, surface water (streams, lakes) 0.01%

The Hydrologic Cycle

1. How does The Hydrologic Cycle influence the chemical properties of Groundwater?
   - How different would be properties of water in individual reservoirs?

The Hydrologic Cycle

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   – How different would be properties of water in individual reservoirs?

2. What forces cause movement of water in the hydrologic cycle?

The Hydrologic Cycle

1. How does The Hydrologic Cycle influence the chemical properties of Groundwater?

   – How different would be properties of water in individual reservoirs?

2. What forces cause movement of water in the hydrologic cycle?

3. Which water contains the least solubles?
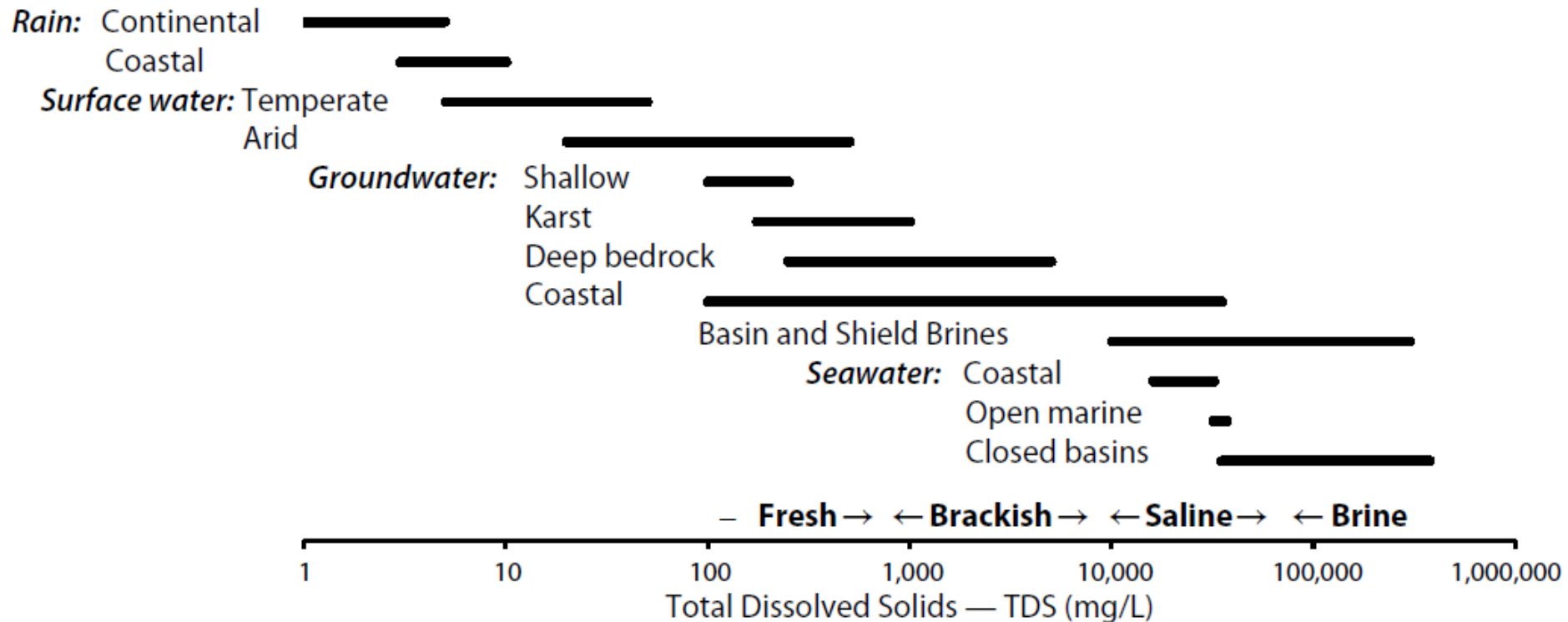
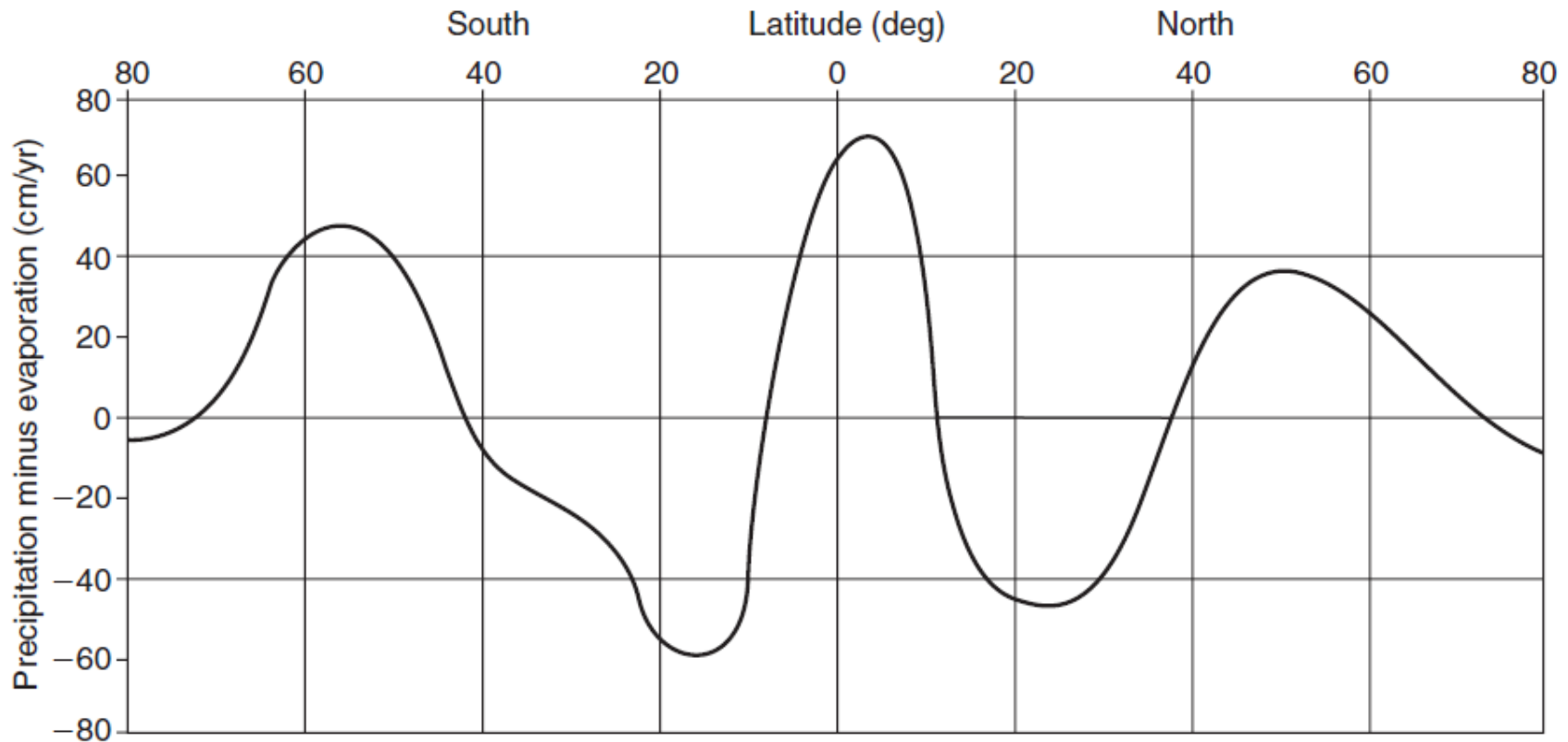# Total dissolved solids in different waters

FIGURE 1.3 Typical range for total dissolved solids in different waters.

Rain and snow

ATMOSPHERIC PRECIPITATION

Net precipitation distribution

Figure 2.3.   Net precipitation (precipitation minus evaporation) as a function of lattitude. Positive values indicate net infiltration and negative values potential evaporation (Peixóto and Keitani, 1973).

What are the consequences of this distribution?

Composition of precipitation

- The composition of the rain is very variable
- Natural and anthropogenic sources
- In a clean environment
  - N_2, O_2, CO_2 + SO_3, NO_x and Na-Cl
- Above the oceans the composition of dilute sea water
- Solid aerosols
- Washing dust from vegetation

Fractionation

- It expresses the ratio in the content of elements
  - Enrichment / depletion (eg. against Na)

$$F_{Na} = \frac{(Cl/Na)_{rain}}{(Cl/Na)_{seaw.}}$$

Table 2.1. Fractionation factors, given as a range, of seawater elements in marine aerosols. Fractionation factors expressed with respect to Na (F_{Na}). (Data from Duce and Hoffman, 1976.)

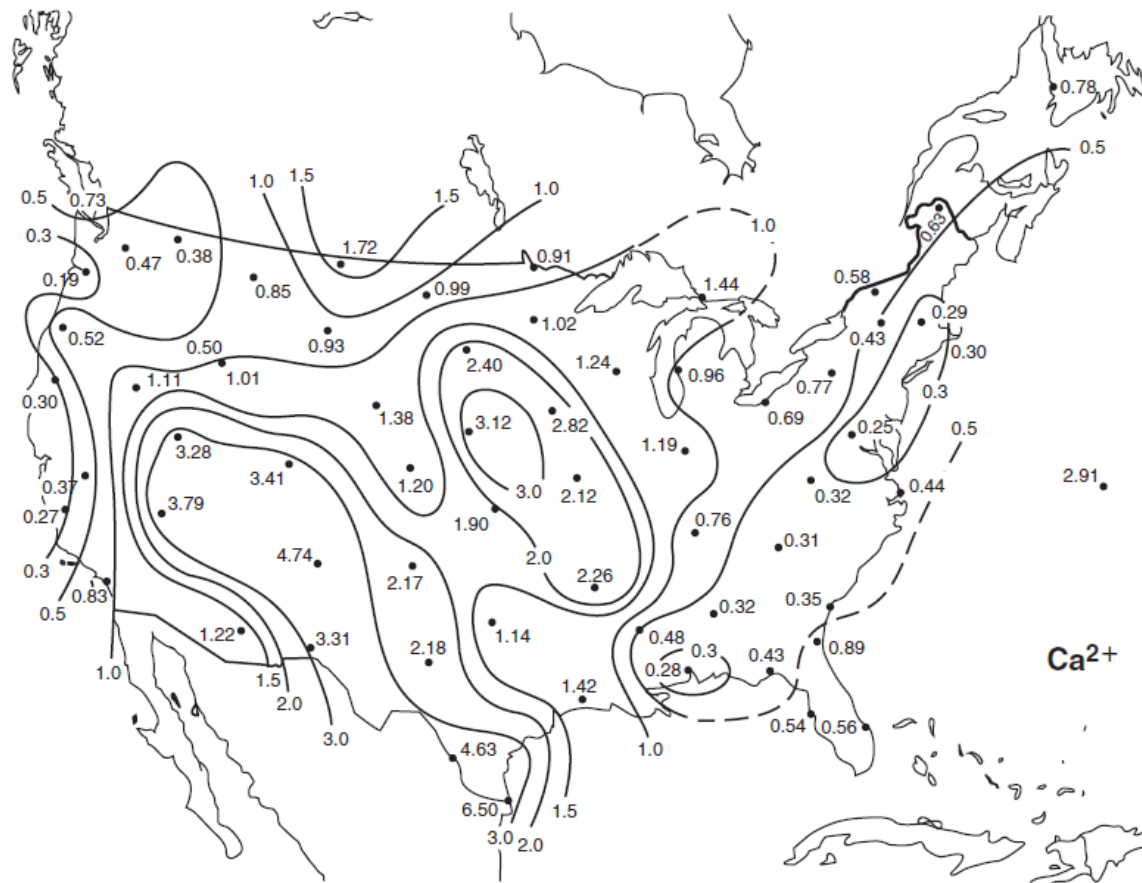|		Mg^{2+}	Ca^{2+}	K^+	Sr^{2+}	Cl^-	SO_4^{2-}	Br^-	Org.N
F_{Na}	upper limit	1.07	1.22	1.05	0.89	1.0	?	12	1×10^6
	lower limit	0.98	0.97	0.97	0.84	0.93	1	1	2×10^4

Appelo & Postma 2005

Composition of precipitation – chlorides
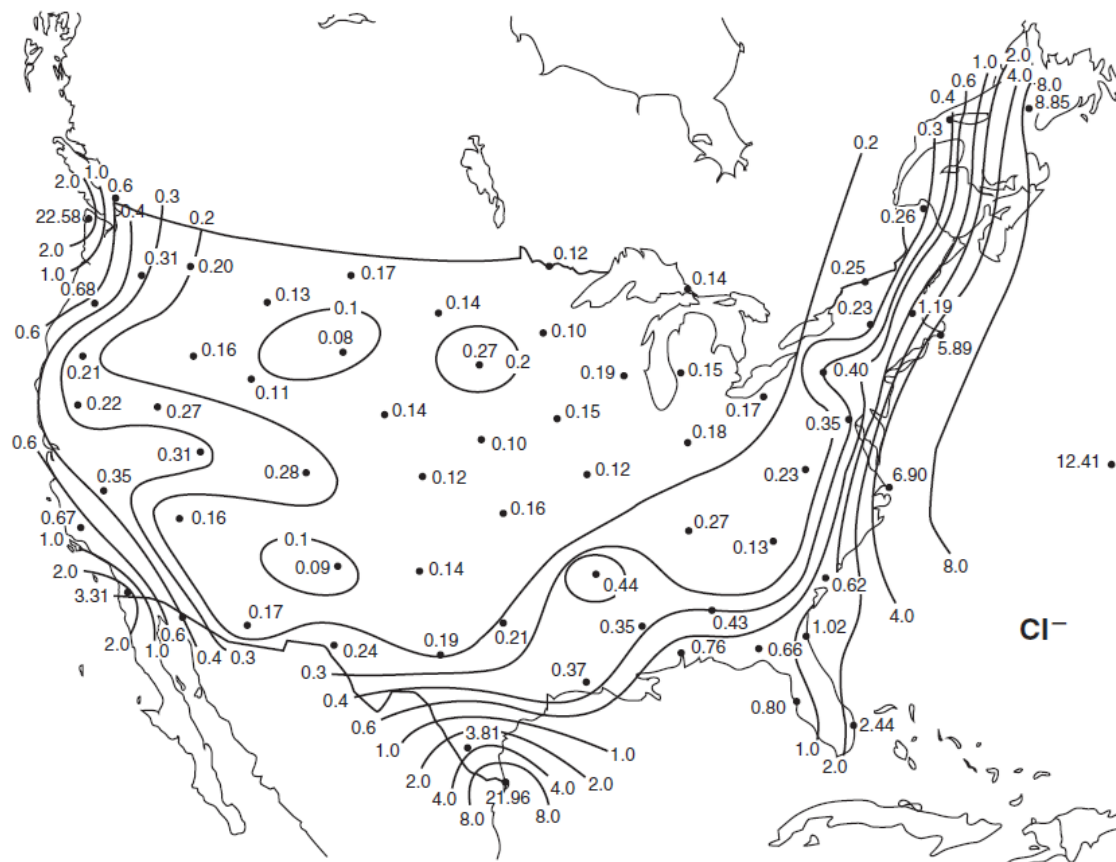
Figure 2.4. Average chloride concentrations (mg/L) in precipitation over the United States (Junge and Werby, 1958).

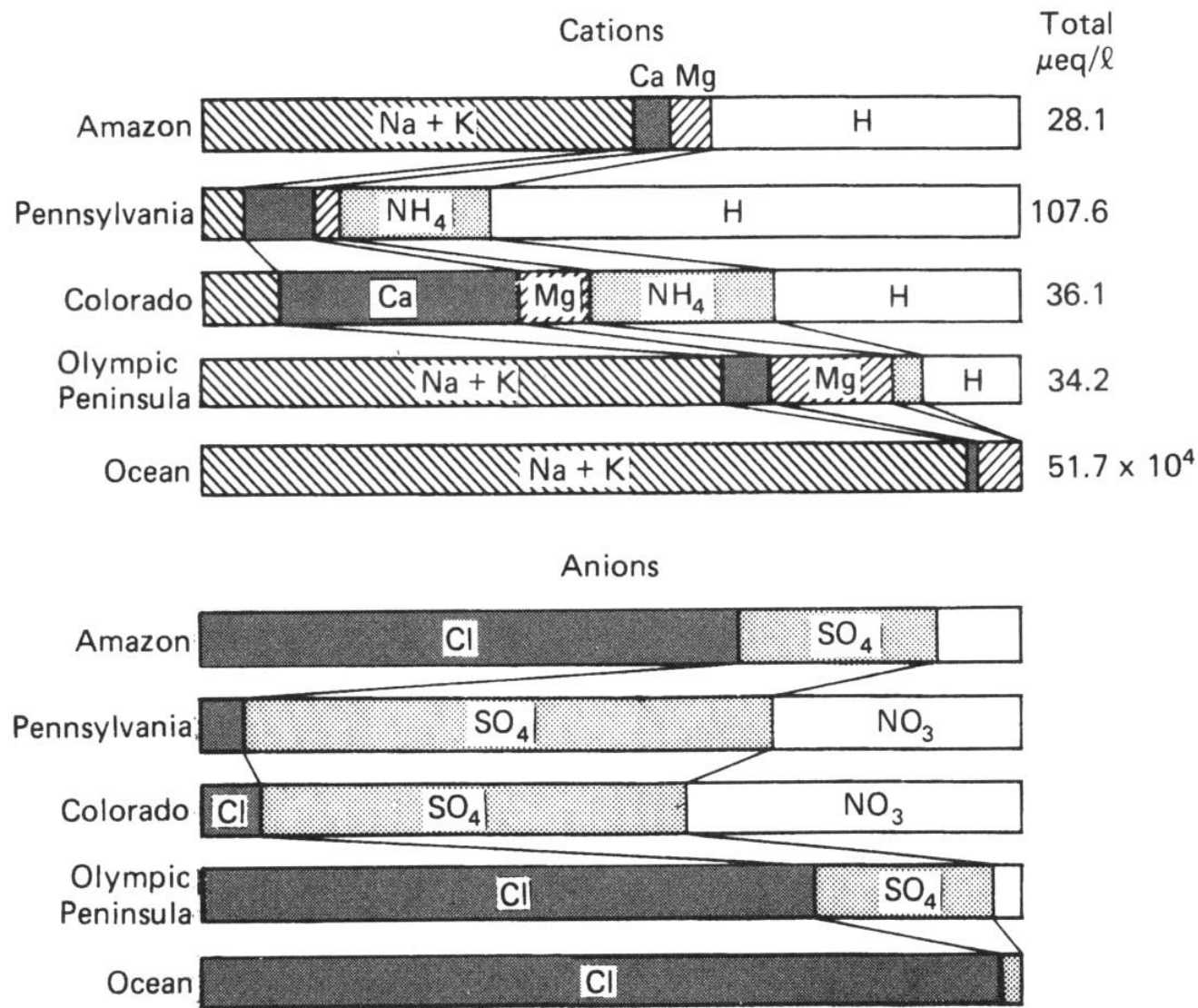# Composition of precipitation – calcium

Figure 2.5.   Average calcium concentrations (mg/L) in precipitation over the United States (Junge and Werby, 1958).

Maps

- Compare maps
- What differences do you see?
- What can be the cause?
  - You can use online maps.
- Can you deduce any laws?

Compare the relative proportions of ions in different rainfall sources
What can be the cause of deviations?
Can you deduce any rules?

FIGURE 1-5 Relative concentrations (in equivalents) of ions in the ocean and in rainfall from the Amazon basin (average from Stallard and Edmond, 1981) and from National Acid Deposition Program sites in Central Pennsylvania, Rocky Mountain National Park in Colorado, and the Olympic Peninsula in Washington State (NADP, 1985). "Total" represents the total concentration of cations in microequivalents per liter.

Drever 1997

Table 2.2. Rainwater analyses (values in μmol/L).

Period	a Kiruna Sweden '55–'57	b Hubbard Brook,US '63–'74	c De Kooy Neth. '78–'83	c Beek Neth. '78–'83	d Beek wet-only '97–'98	e Thumba India 1975	e Delhi India 1975	f Delhi wet-only 1997
pH	5.6	4.1	4.40	4.75	5.5			6.3
Na^+	13	5	302	43	26	200	30	9
K^+	5	2	9	7	3	6	7	9
Mg^{2+}	5	2	35	9	4	19	4	2
Ca^{2+}	16	4	19	47	10	23	29	13
NH_4^+	6	12	78	128	74			21
Cl^-	11	7	349	54	29	229	28	13
SO_4^{2-}	21	30	66	87	29	7	4	10
NO_3^-	5	12	63	63	35			9
HCO_3^-	21	–	–	9				25

(a) Granat, 1972; (b) Likens et al., 1995; (c) KNMI / RIV, 1985; (d) Boschloo and Stolk, 1999; (e) Sequeira and Kelkar, 1978; (f) Jain et al., 2000.

Table 2.3. Concentrations in rainwater from sources other than seawater. For the Kiruna station both the contribution from seawater and from additional sources is shown while for the other stations only the additional sources are tabulated. (Units are μmol/L, except for seawater).

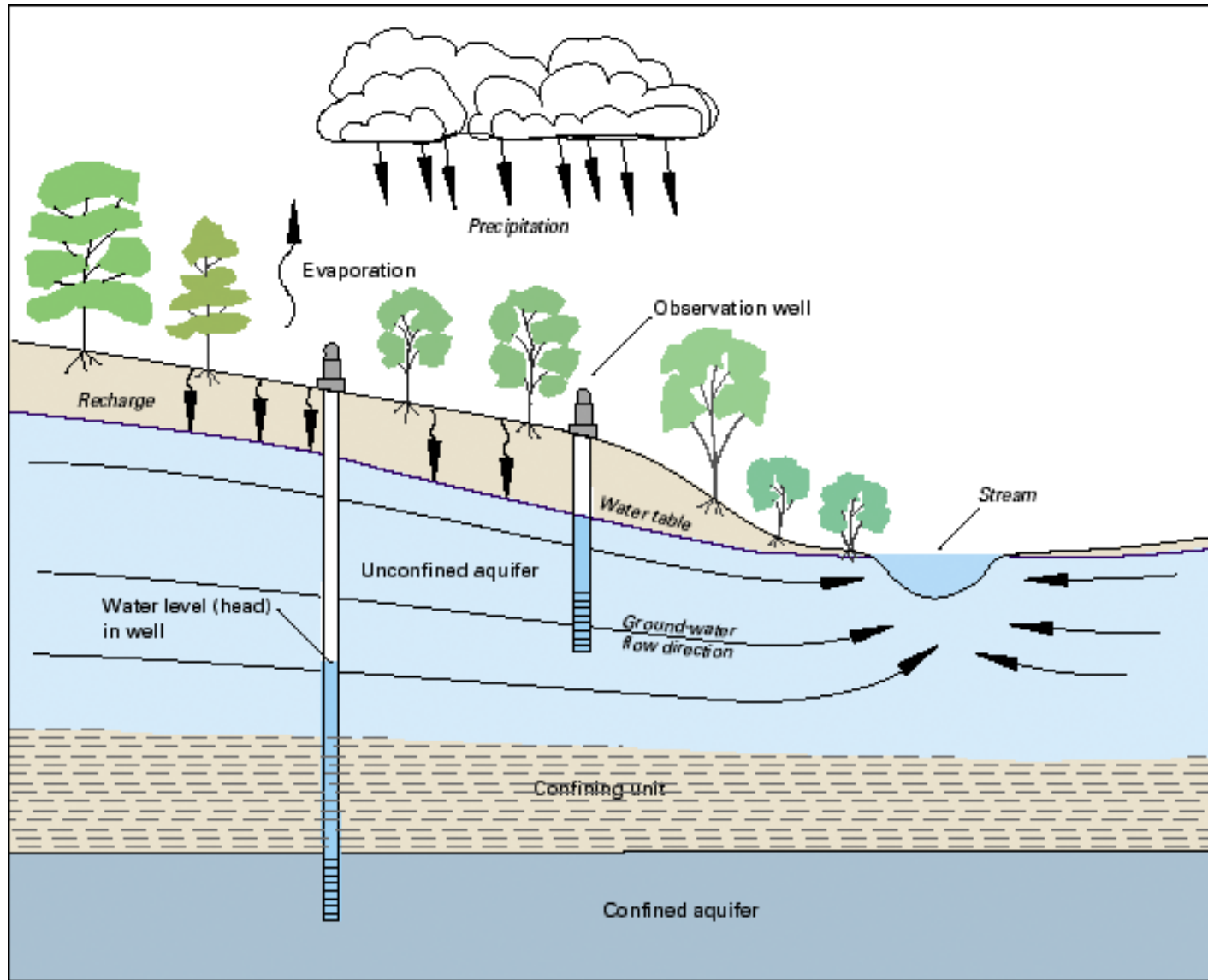|	seaw. (mmol/L)	Kiruna rain	Kiruna seaw. contr.	Kiruna other src.	Hub. Br.	De K.	Beek	Beek wet-only	Thum	Delhi	Delhi wet-only
Na^+	485	13	9.4	4	−1	3	−3	1	4	6	−2
K^+	10.6	5	0.2	5	2	3	6	2	2	6	9
Mg^{2+}	55.1	5	1	4	1	1	4	1	−3	1	0
Ca^{2+}	10.7	16	0.2	16	4	12	46	9	19	28	13
NH_4^+	2×10^{-6}	6	0	6	12	78	128	74			21
Cl^-	566	11	11	–	–	–	–	–	–	–	–
SO_4^{2-}	29.3	21	0.6	20	30	48	84	27	−5	3	9
NO_3^-	5×10^{-6}	5	0	5	12	63	63	35			9
HCO_3^-	2.4	21		21	0	−1	9				24

Water analysis

- Compare c,d and e,f analyzes
  - What is the difference?
  - What can be the cause?
  - Can you deduce any rules?
- Table 2-3 shows the enrichment / depletion of precipitation compared to seawater.
  - Where are the biggest deviations?
  - What can be the cause?
  - Can you deduce any rules?
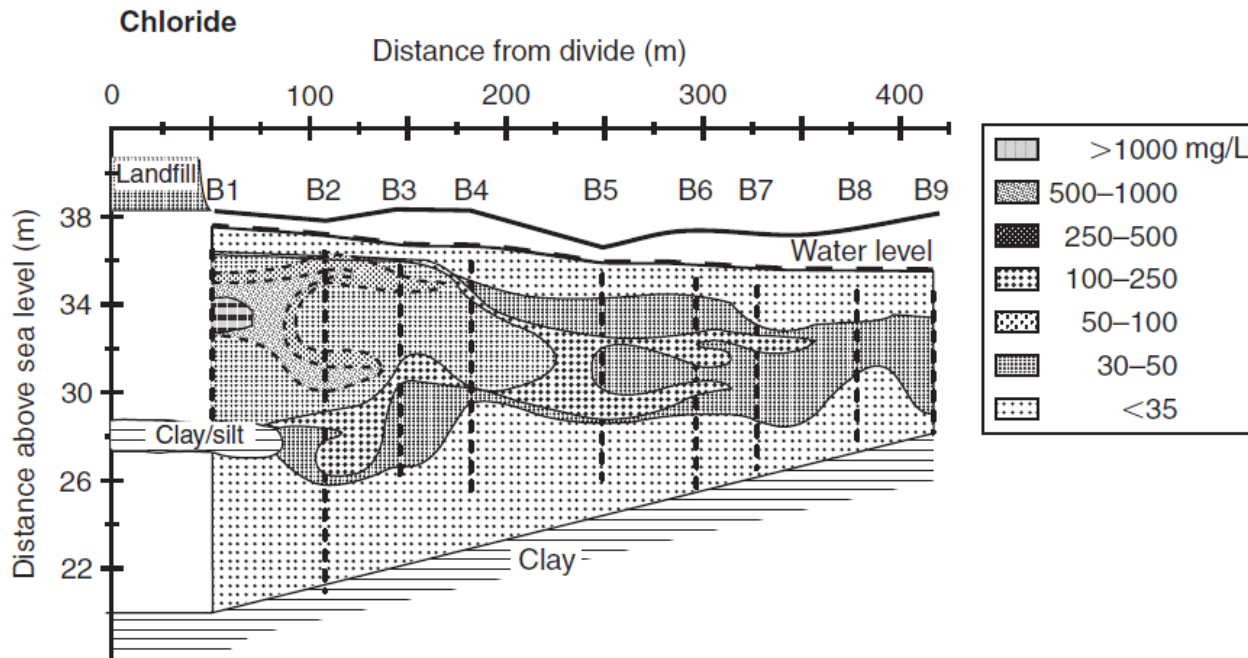
GROUNDWATER

Groundwater

Groundwater fills the spaces between soil particles and fractured rock beneath the earth's surface.
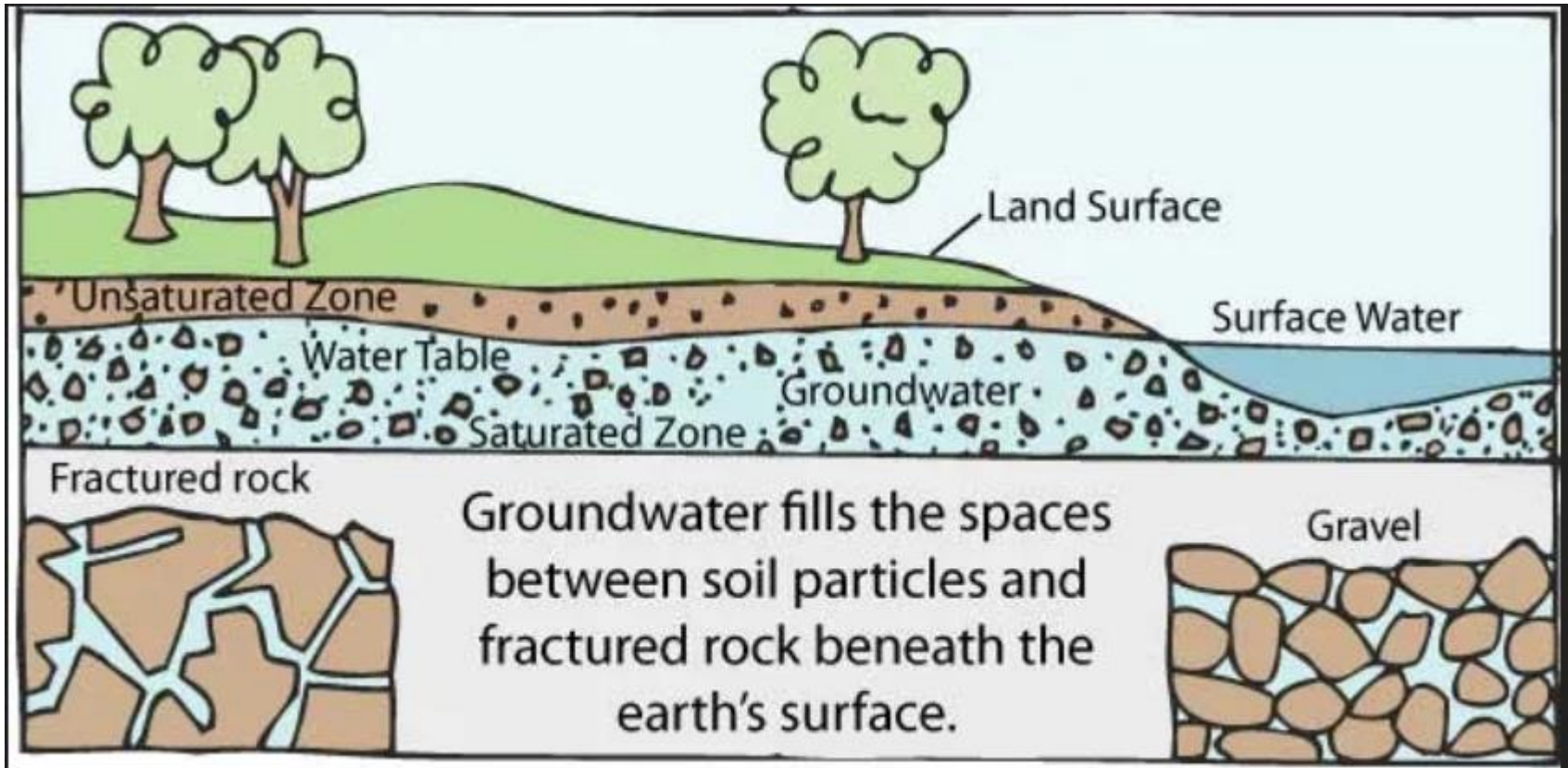
Aquifer

Groundwater

- Formed by infiltrated precipitation
- Immediate interaction with the environment
  - Soil water is different from both surface- and ground-water
- Surface flow hydrology – basal outflow + other sources
- Important medium properties
  - Porosity
  - Permeability

	A	B
Ca^{2+}	2.5	6
Mg^{2+}	0.7	1.7
Na^+	3	6.3
K^+	3	0.5
SiO_2	40	17
	A	B
HCO_3^-	<5	40
DOC^a	120	<2
Al_{total}	2	<0.005
Fe_{total}	1.5	<0.01
pH	5.2	7.5

TABLE 1–1 Chemical Composition (mg/l) of (A) Soil Water (from Antweiler and Drever, 1983) and (B) River Water (from Miller and Drever, 1977a) from Areas Underlain by Volcanic Rocks in Northwest Wyoming

^{a}DOC is dissolved organic carbon in mg carbon /l. It is a measure of the total amount of organic compounds dissolved in the water. In the soil water, organic anions are the major anionic species.

Drever 1997

Chloride

Distance from divide (m)

Legend (Chloride):
- >1000 mg/L
- 500–1000
- 250–500
- 100–250
- 50–100
- 30–50
- <35

Sodium

Distance from divide (m)

Legend (Sodium):
- >500 mg/L
- 250–500
- 100–250
- 50–100
- 20–50
- <20

Appelo & Postma 2005

- How are the pictures different?
- How does the propagation of elements differ?
- What can be the cause?
  1. Ion adsorption
  2. Dispersion
  3. Diffusion
  4. Different ion sizes
  5. Different ion charges
  6. Something else
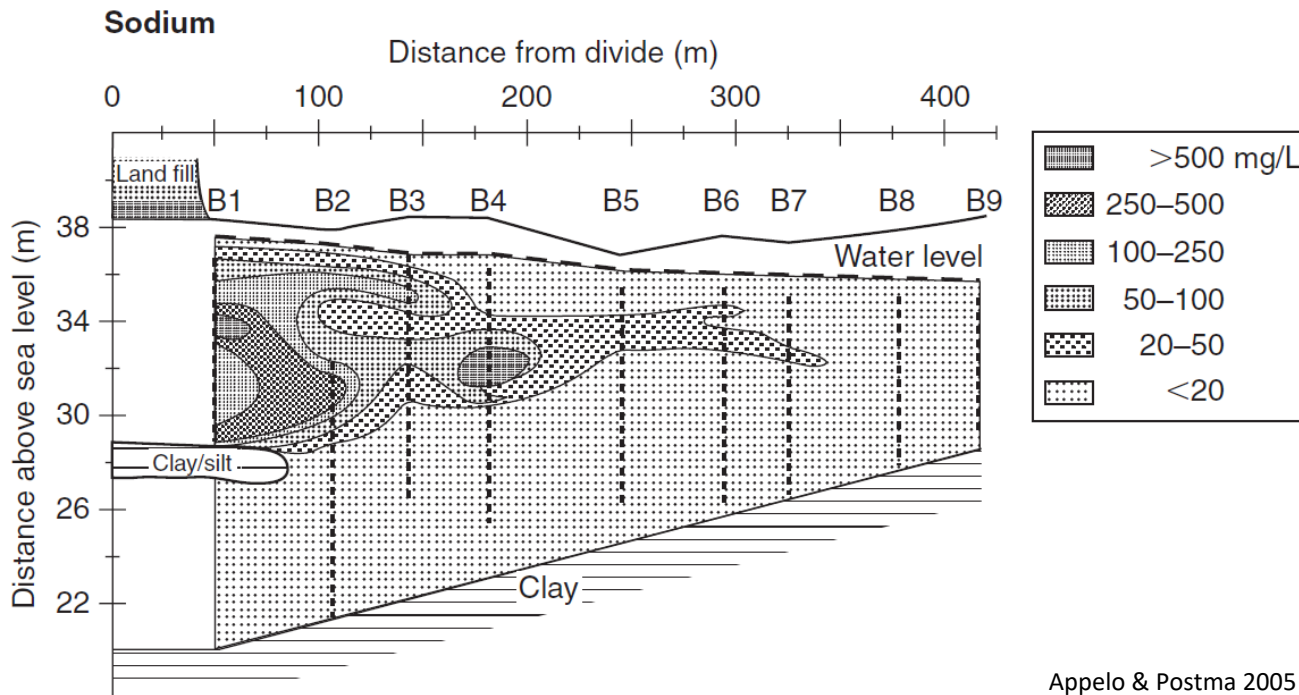
Flow in the unsaturated zone

- Under normal conditions, the water percollates vertically downward along the maximal gradient of the soil moisture
- The rate is derived from a mass balance

$$v_{H_2O} = {}^P/_{\varepsilon_{H_2O}}$$

v … velocity of water (m/year)

P… precipitation surplus (m/year)

ε… effective (water filled) porosity (m³/m³)

- Water velocity in pores
- Piston flow

Flow in the unsaturated zone
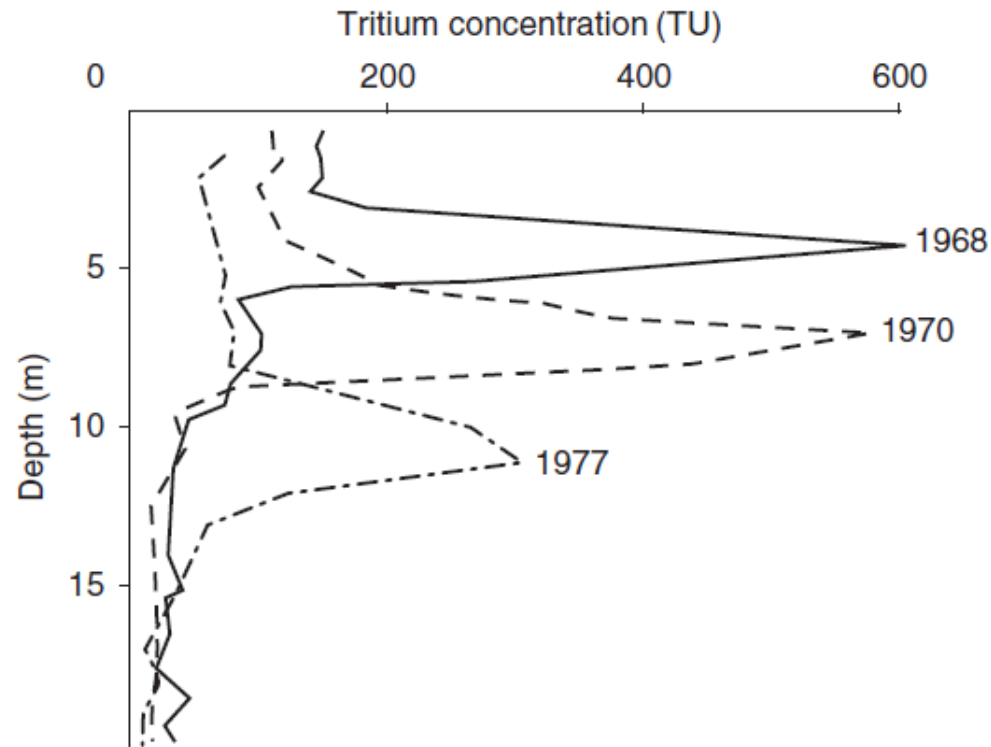
Figure 3.2.   Tritium variation in rain and piston flow displacement at three sites in the English chalk, measured in 3 different years (Foster and Smith-Carrington, 1980).

Appelo & Postma 2005

Question 1

A. What is the water velocity if $P = 0.3$ m/yr and $\varepsilon_{H2O} = 0.1$?

B. Estimate the age of water at 3 m depth if $P = 0.1$ mm/yr and $\varepsilon_{H2O} = 0.0022$?
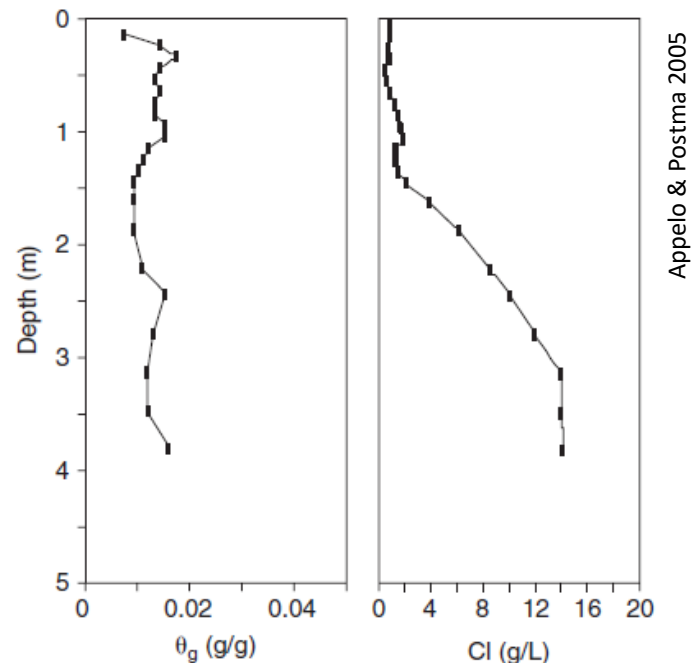
Figure 2.22. Profiles of gravimetric water content (left, grams per gram) and Cl$^-$ concentration in the soil solution below an Eucalyptus stand in a semi-arid climate, Murbko, S. Australia. Annual precipitation is 260 mm/yr, potential evaporation 1800 mm/yr and the recharge rate 0.1 mm/yr (Cook et al., 1994).
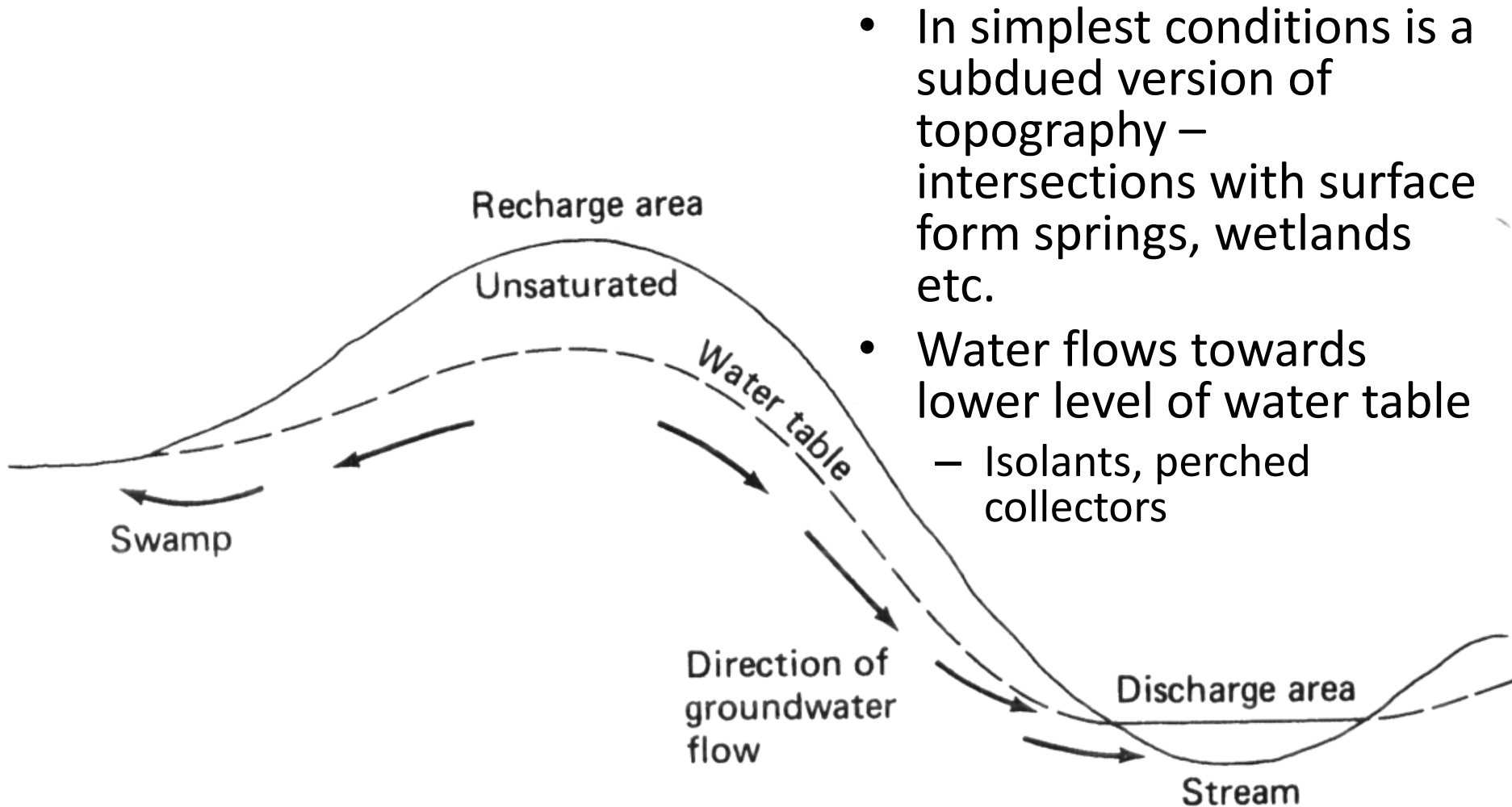
Water table

- Above – vadose zone
- Under – phreatic zone
- Capillary fringe
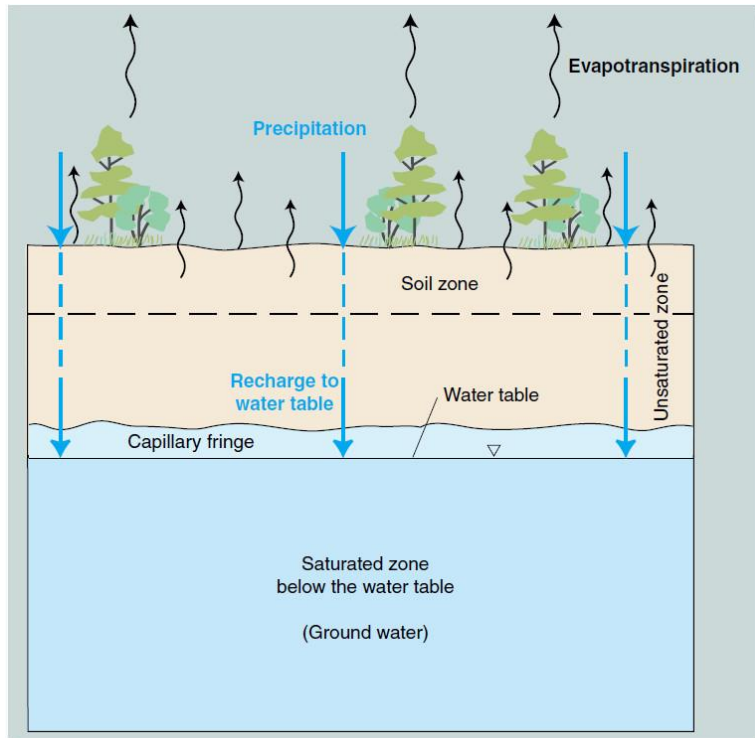
Cross-section of permable rock

Drever 1997
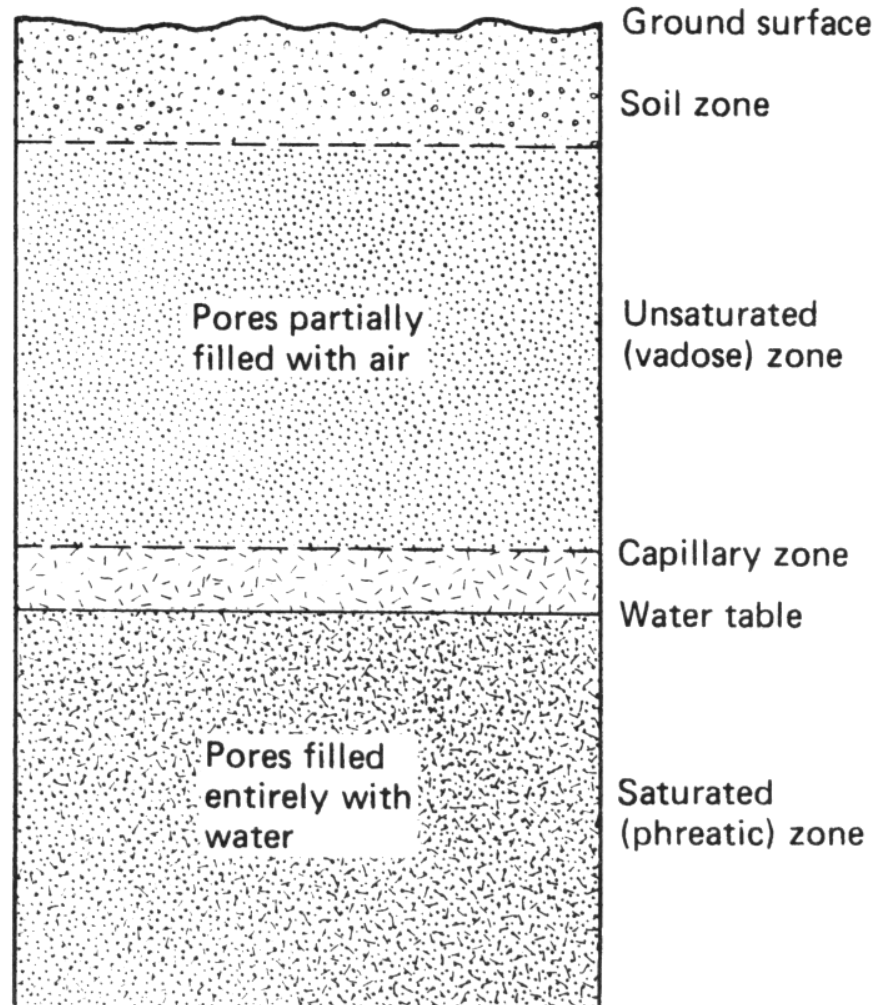
Groundwater

- In simplest conditions is a subdued version of topography – intersections with surface form springs, wetlands etc.

- Water flows towards lower level of water table
 - Isolants, perched collectors

Recharge area

Unsaturated

Water table

Swamp

Direction of groundwater flow

Discharge area

Stream

Hydraulic potential

- Water flows from place with higher water table level towards the lower water table level
  - From place with higher to place with lower hydraulic potential
- Energy state of water

$$\Phi = g\ h$$

g … gravitational acceleration
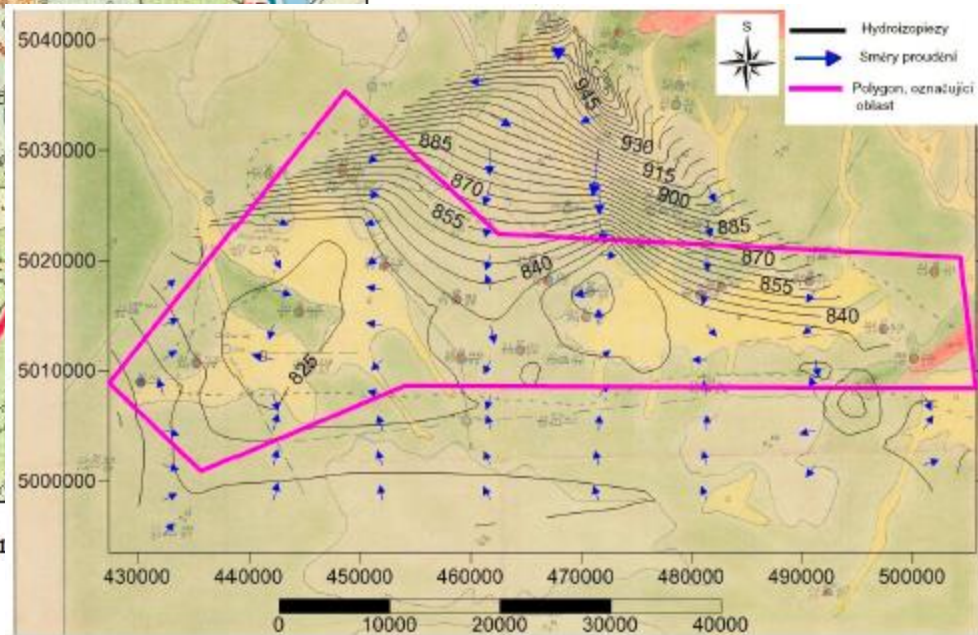
h … water table level (hydraulic height)
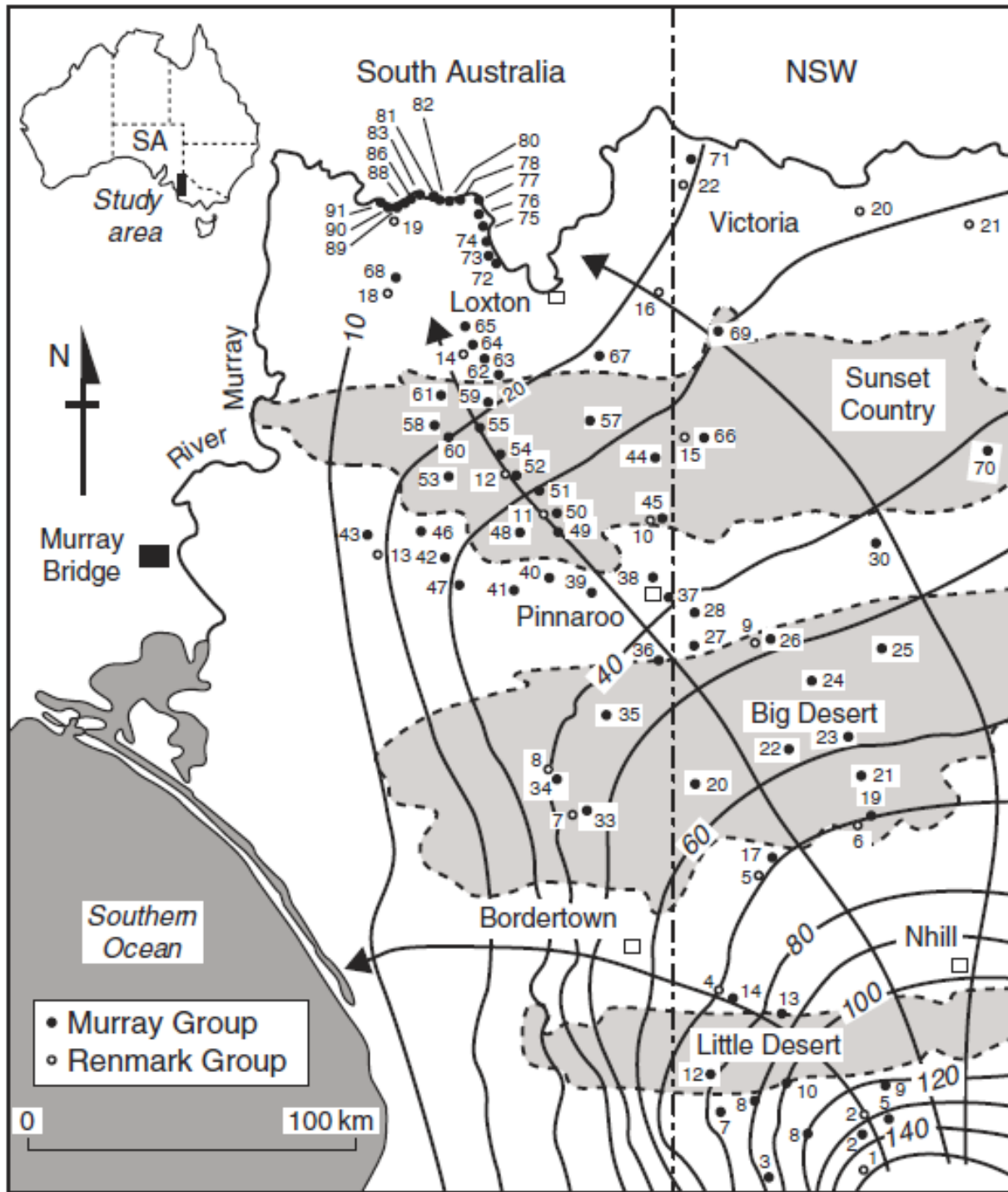
Appelo & Postma 2005
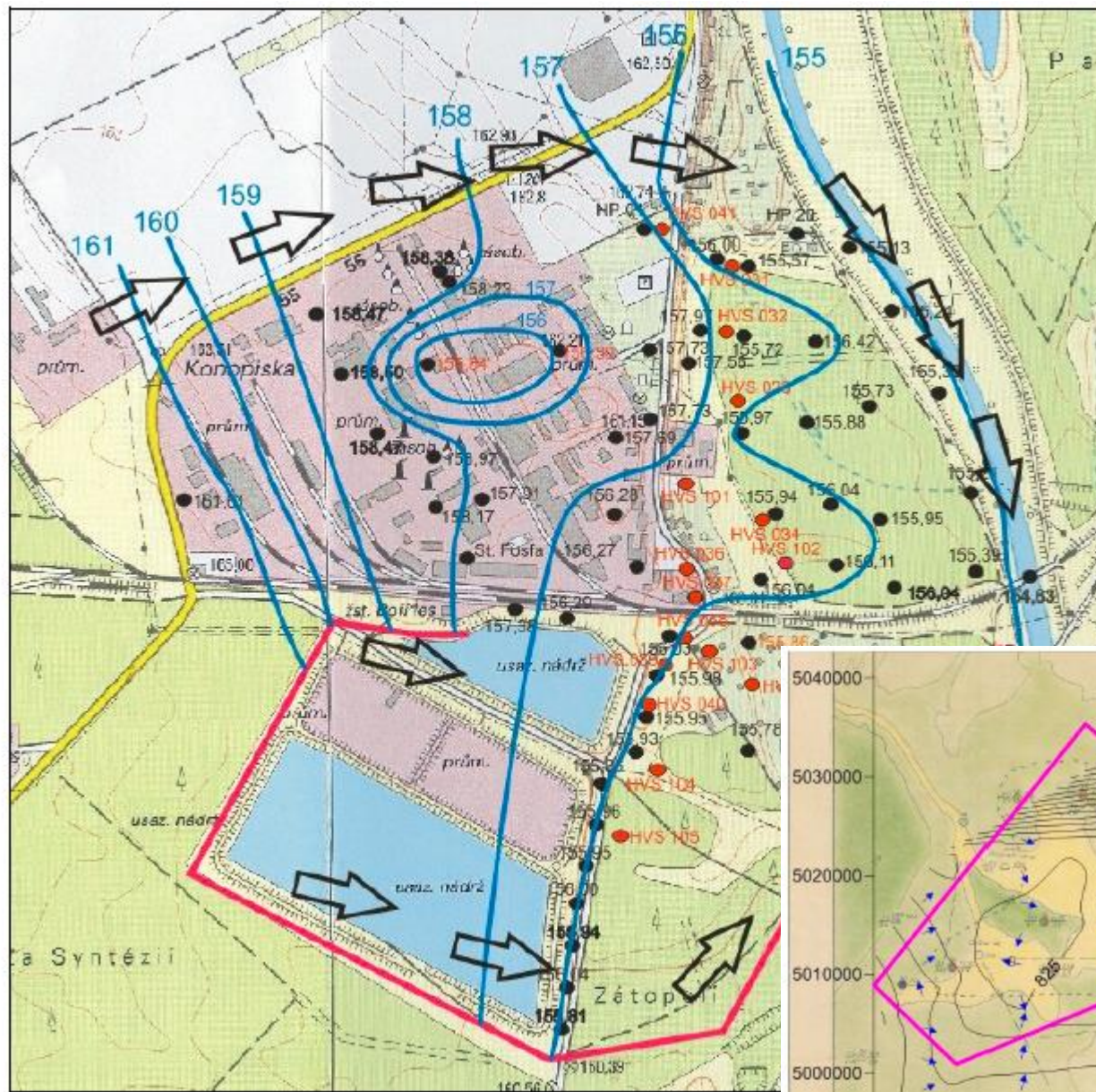
Müllerová 2015

Obrázek 6: Hydroizohypsy pro datum 24.3 2009. (upraveno podle: Mapa šir

Pilát 2013

Obrázek 8: Mapa hydroizopiez, vytvořená metodou Natural neighbor s vyznačenými směry proudění podzemní vody a podkladovou hydrogeologickou mapou na studované lokalitě. (upraveno podle: Cedenbolžir, 1988)

Darcy's Law

- Formulated in the 19th century
- Calculates **flow** (not flow **rate**)
- Homogenous porous medium (rock)

$$Q = -k\,A\,\frac{h_A - h_B}{L} = -k\,A\,\frac{dh}{dl}$$

- Specific flow

$$q = -k\,\frac{dh}{dl}$$

$\frac{dh}{dl}$ ... hydraulic gradient

k ... coefficient of permeability (hydraulic conductivity)

Darcy's Law – flow rate

- How far the water flows
- Only saturated parts of the rock should be considered

$$v_{H_2O} = q/\varepsilon_{H_2O}$$

$$v_{H_2O} = \frac{Q}{A\ \varepsilon_{H_2O}}$$

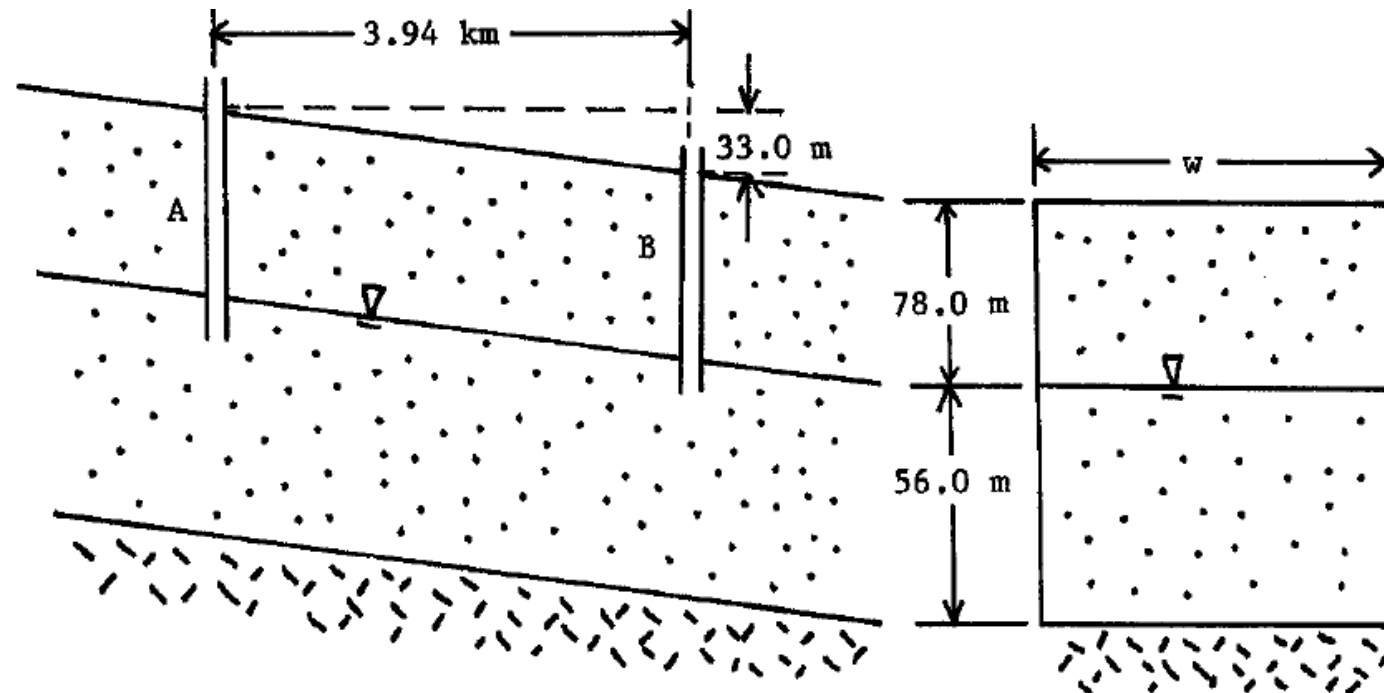# Question 2

- What is the water flow rate through sandstone?

ε_{H_2O} = 0,3

k = 5,79 × 10^{-4} m.s^{-1}

Gradient = 0,001

Question 3

- The figure shows an unconfined aquifer. Water takes 1.91 yr to move from well A to well B. The hydraulic conductivity for the aquifer rock is 135 m/d.

    A. What is the effective porosity of the aquifer?

B. 8.42×10^5 m^3 of water flows through cross section of the aquifer in 2 weeks. Find the width of the aquifer.

Flow in the saturated zone

- Homogeneous aquifer with even infiltration
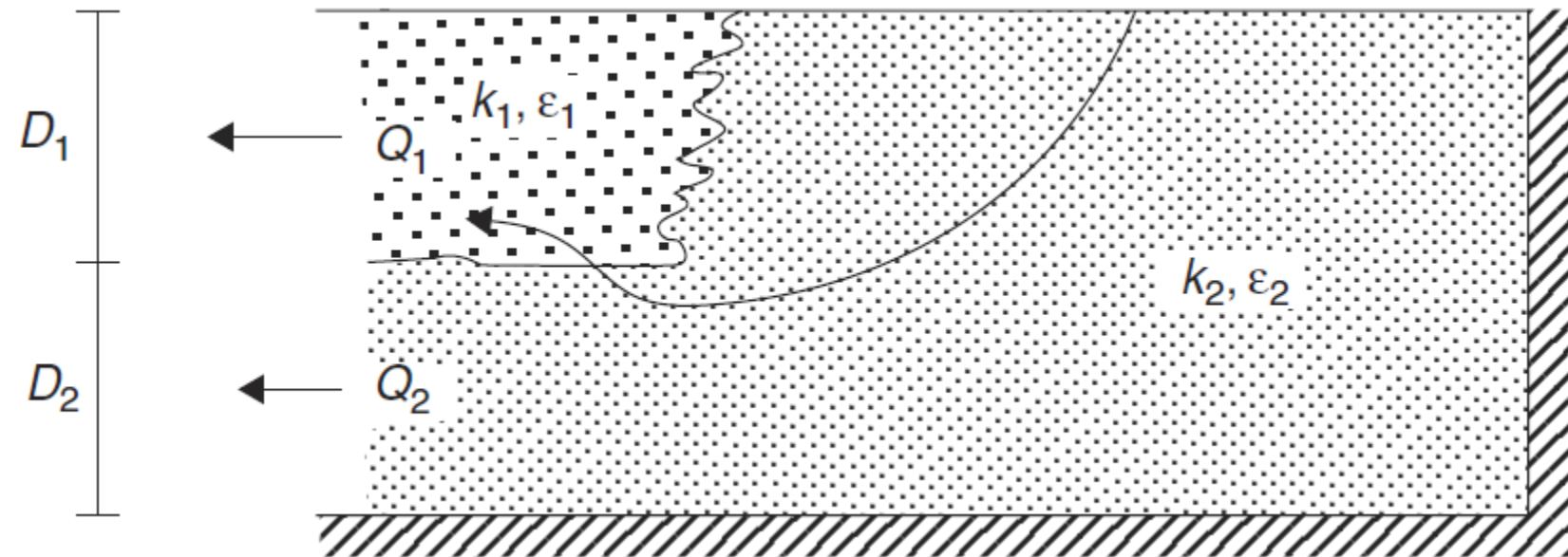 - Horizontal isochrons (ie. water at a given depth is the same age)
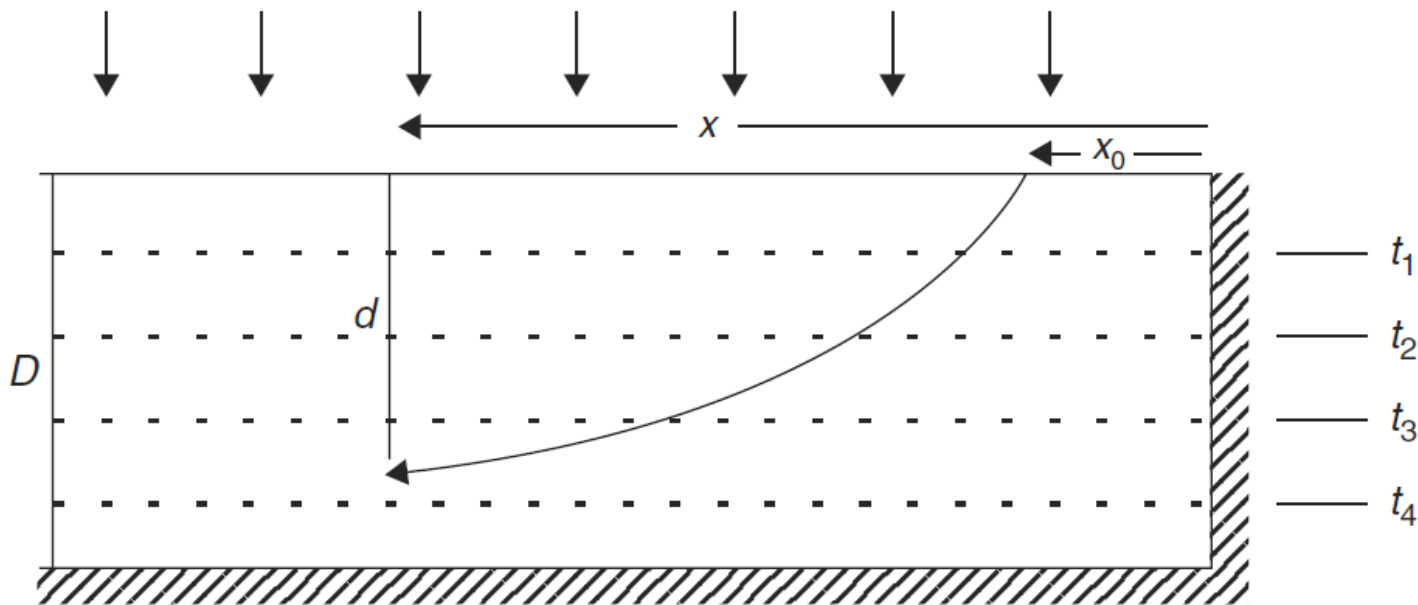
A profile through a homogeneous, phreatic aquifer.

$$d = D\left(1 - \exp\left[\frac{-Pt}{D\varepsilon_w}\right]\right)$$

Effects of inhomogeneity

- Aquifers are usually inhomogeneous – different hydraulic conductivities across the body

$$\frac{v_1}{v_2} = \frac{k_1}{k_2} \; \frac{\varepsilon_2}{\varepsilon_1}$$

Appelo & Postma 2005

Aquifer chemistry

- The well passes through all "layers" of water
- Stabilization of chemistry – exponential function
- Corresponds to a stirred reactor

$$\tau = \frac{Total\ mass}{Mass\ exchange} = \frac{M_{tot}}{dM_{in}\ /\ dt}$$

$$\tau = V\ /\ Q$$

$$c = c_0(1 - e^{-t/\tau})$$

Aquifer as a stirred reactor

- Great simplification
  - Water mixing only in the well
  - Different chemistry associated with development along stream-lines in the rock
- Suitable for the first estimate of the spread of contaminants
  - We are not interested in the interaction of water with the environment but in **dilution** of the input concentration
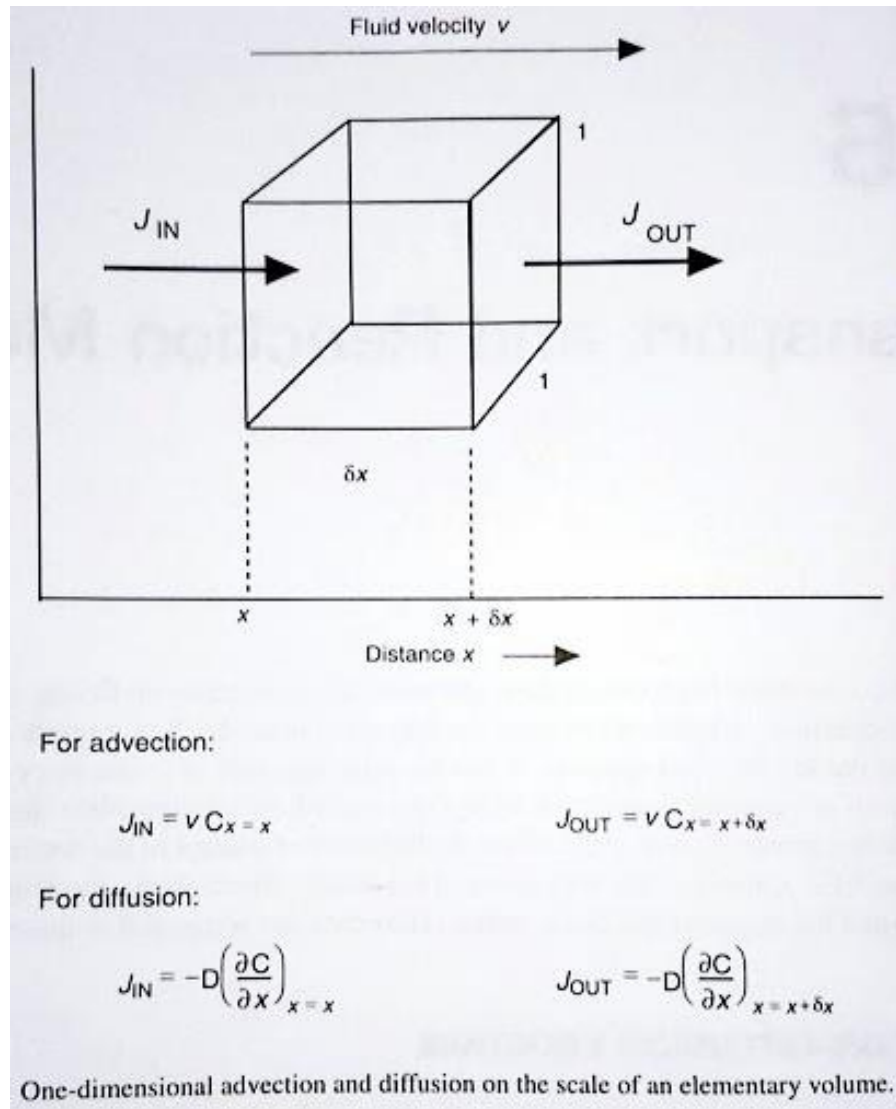
Reaction-transport modeling

- Water reacts with the environment as it percolates

- Basic description by advection-diffusion equation
  - Simple one-dimensional form

Diffusion

$$\frac{\partial C_i}{\partial t} = \boxed{D_i \frac{\partial^2 C_i}{\partial x^2}} - \boxed{v \frac{\partial C_i}{\partial x}} \pm (\text{reaction members})$$

Advection

- The sum of changes by diffusion, advection and chemical reactions

Unit volume

Fluid velocity v

J_{IN}

J_{OUT}

δx

x

$x + \delta x$

Distance x

For advection:

$$J_{IN} = v\,C_{x=x} \qquad\qquad J_{OUT} = v\,C_{x=x+\delta x}$$

For diffusion:

$$J_{IN} = -D\left(\frac{\partial C}{\partial x}\right)_{x=x} \qquad\qquad J_{OUT} = -D\left(\frac{\partial C}{\partial x}\right)_{x=x+\delta x}$$

One-dimensional advection and diffusion on the scale of an elementary volume.

Drever 1997

The overall change is a matter of mass balance in observed volume

Diffusion

- The difference in concentration between 2 points in solution balances naturally over time

- Brownian motion

- Described by Fick's 1st law (steady state)

F ... flow (Flux)

D... diffusion coefficient

*c... concentration*

x... distance

$$F = -D \frac{\delta c}{\delta x}$$

Effects on diffusion

- Influence of flow through the porous medium
  - Diffusion defined on free solution
1. Flow only via pores (porosity effect)
2. Different pore flow rate (pore edges vs. center; tortuosity ϕ)
   - $\Phi = dl/dx$
   - The ratio of distance traveled to absolute distance

Hydrodynamic dispersion

- The mixing process associated with movement through a porous medium

- Longitudinal – different water velocity in pores (large, small)

- Transverse – given by the available flow paths

- Description analogous to diffusion (derivatives of Fick's law); D = dispersion coefficient

Transverse

Longitudinal

Appelo & Postma 2005
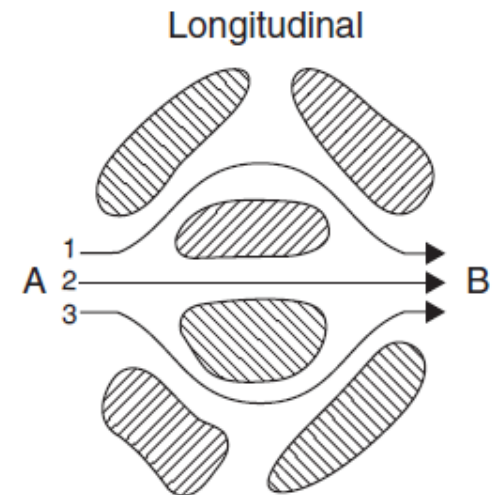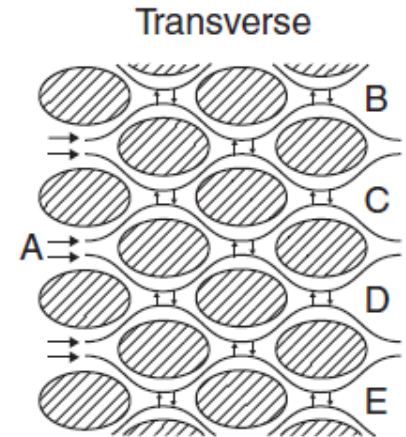
ION EXCHANGE AND ADSORPTION

Crystal surfaces

- Crystal surfaces contain numerous imperfections and defects.

- These places allow growth/dissolution because they have different energy.
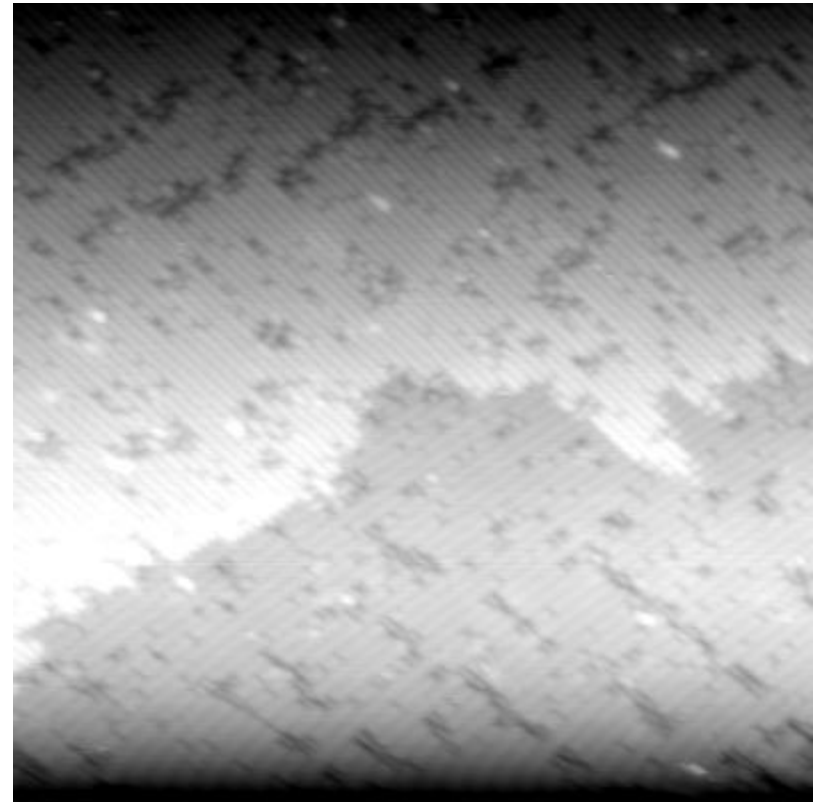
Silicon surface with visible edges, kinks and other surface defects

Mineral surfaces

The energy of all particles (and positions) on the surface is not the same – their stability differs.
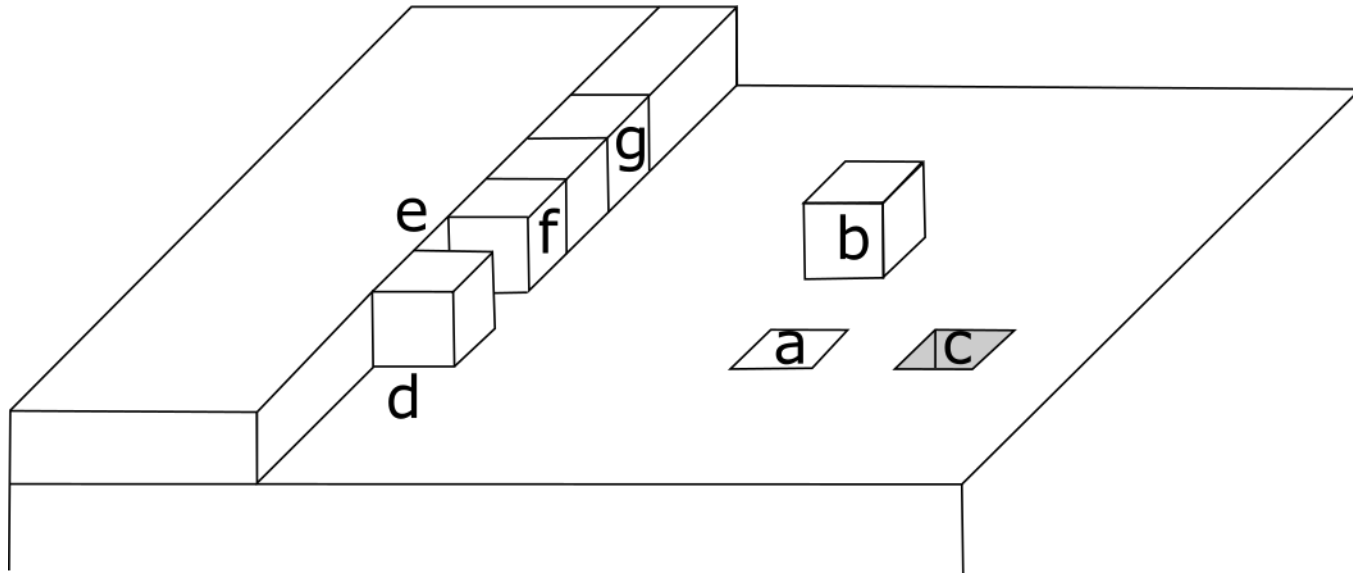
Schematic representation of the crystal surface at the level of atomic dimensions: a – atom in smooth surface area (most stable position), b – adatom (solo atom on surface – least stable), c – free space on surface, d – corner, e – niche in step, f – corner, g – atom in stairs

Ion exchange and sorption

- In terms of surface processes in aquifers:
- **Cation exchange** – change of the main cations in solution by contact with the mineral surface
- **Adsorption** – binding of trace metals and organics to mineral surfaces (contaminants)
- They are usually summarized under the term **sorption**

Sorption on mineral surfaces

- Enormous importance in environmental geology.
  - Groundwater composition, transport of contaminants, availability of nutrients for plants.
- Very fast ion bonding/releasing processes.
- Even very soluble substances can be in low concentration, thanks to sorption on surfaces:
  - The total content is then lower than the estimate based on solubility/precipitation.
  - Simple surface process – an order of magnitude faster than dissolution.
  - Reversible process – complicates measurement of rates.
- Sorption
  - Adsorption – binding to the surface.
  - Absorption – entry into the structure of the absorbent.
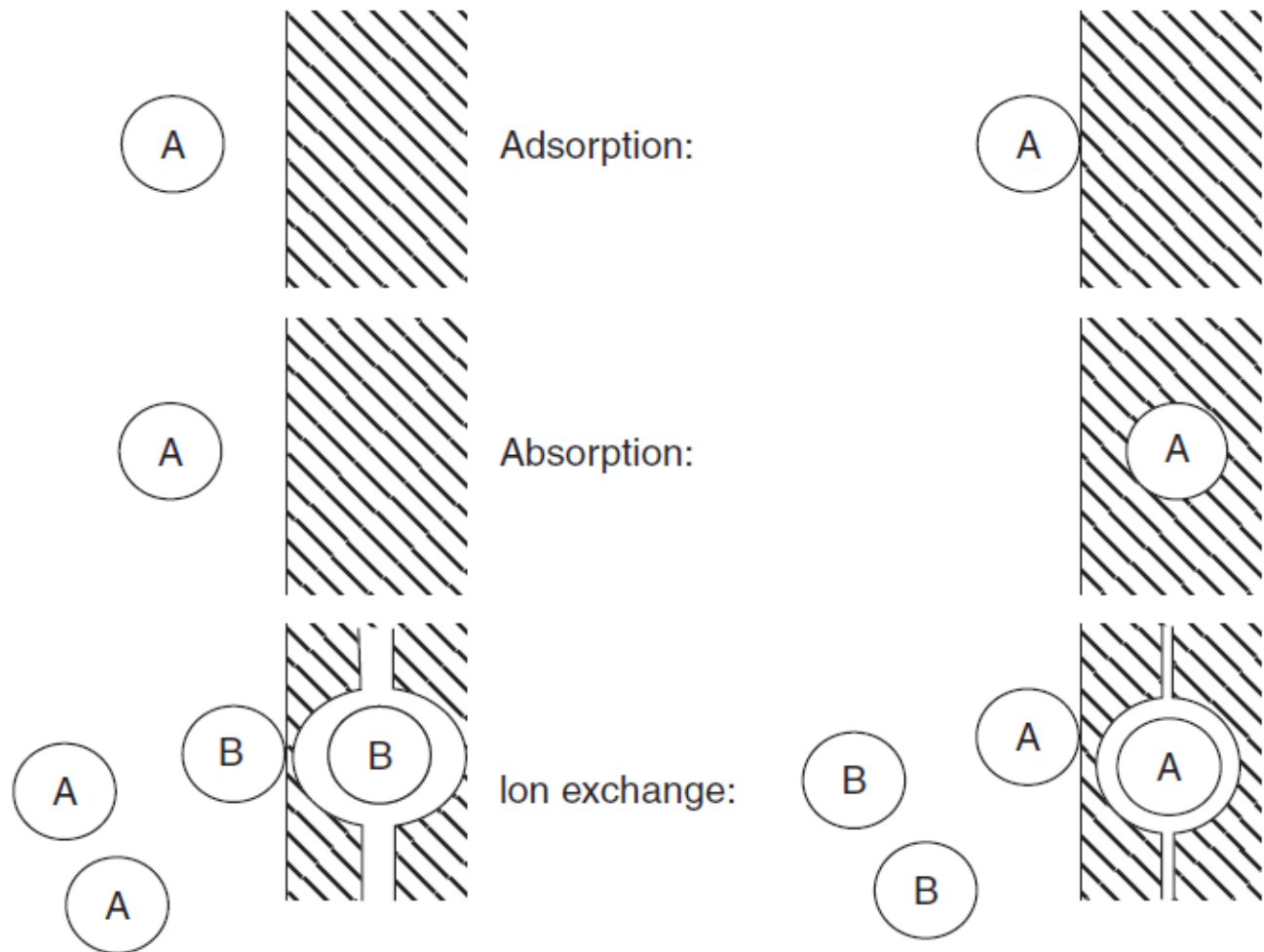
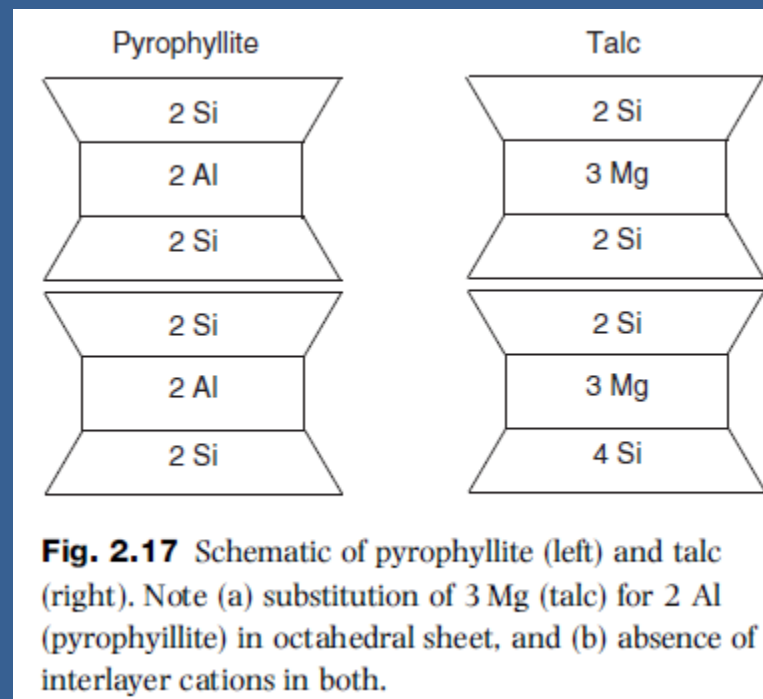Figure 6.1.   Pictorial definition of different sorption processes.

Phyllosilicates

- If all SiO_4 tetrahedra share three oxygens with another tetrahedra, a continuous planar structure is formed.
  - They form sheets (infinite planes).
- Anions can enter the „meshes" in the network.
- General formula Si_4O_{10} or Si_2O_5.
  - Al replaces up to 50% of Si in tetrahedra, although usually less than 25%.
- Different types of phyllosilicates (chlorites, clay minerals) differ in "fillers" between silicate layers.
- Silicate layers are much more cohesive than the filler - that's why they are fissile (typically mica).

Phyllosilicates

- Significant absorption capacity (especially cations).

- Relatively reactive – significantly affect the properties of water, soil and sediments.

- 2 main building elements
  - Tetrahedral layers
  - Octahedral layers

2: 1 Phyllosilicates

- "Sandwich" tetrahedral layer – octahedral – tetrahedral

- Between the "sandwiches" are cations – they fit into the hexagonal "mesh" of the tetrahedral layer

- Without an interlayer – held together by van der Waals forces

Pyrophyllite		Talc
2 Si		2 Si
2 Al		3 Mg
2 Si		2 Si
2 Si		2 Si
2 Al		3 Mg
2 Si		4 Si

Fig. 2.17 Schematic of pyrophyllite (left) and talc (right). Note (a) substitution of 3 Mg (talc) for 2 Al (pyrophyillite) in octahedral sheet, and (b) absence of interlayer cations in both.

Taken from Ryan (2014)

Trioctahedral : 3 Mg^{2+} in octahedral layer per building unit (talc)
Dioctahedral : 2 Al^{3+} in octahedral layer per building unit (pyrophyllite)
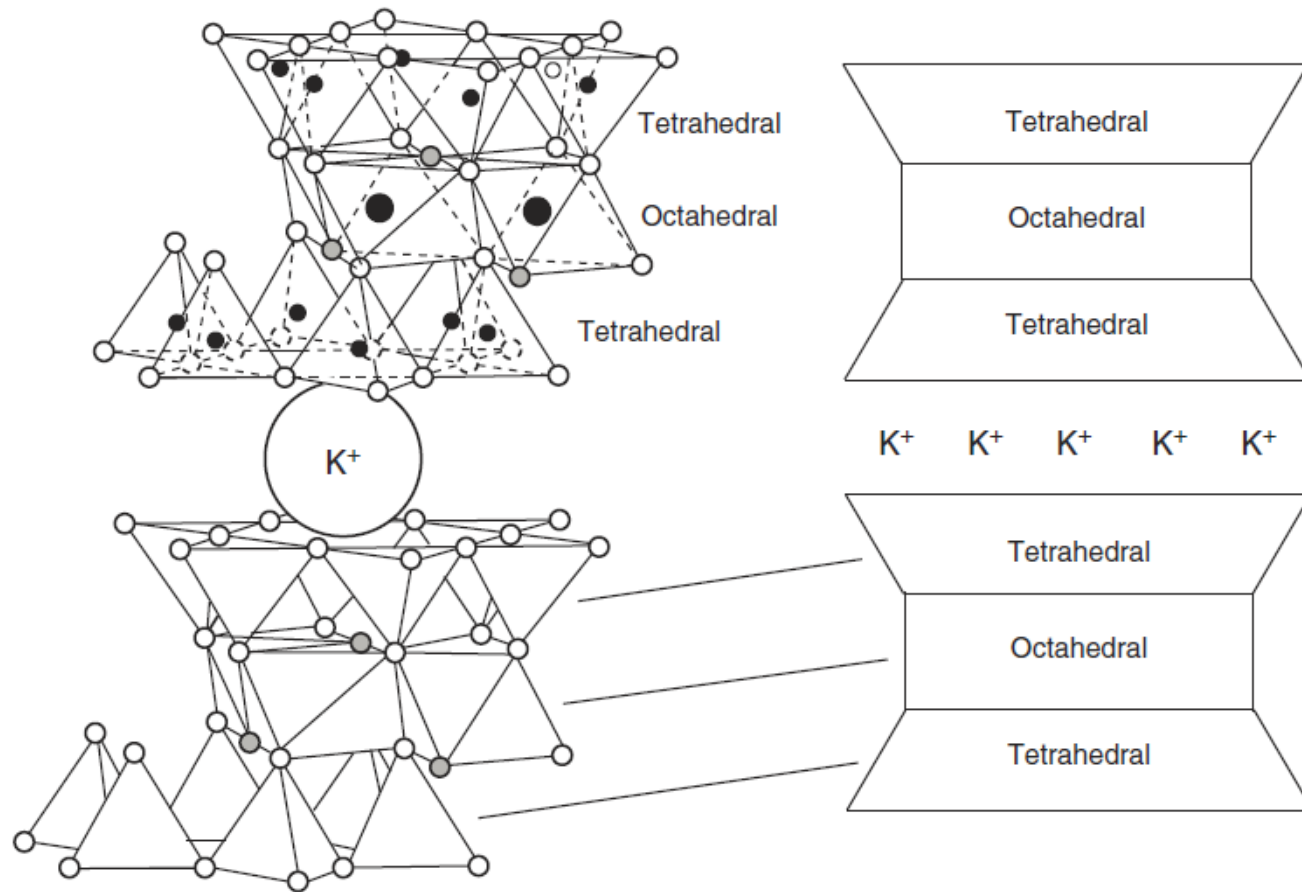
Fig. 2.16 Two representations of a mica, both showing tetrahedral and octahedral sheets as well as interlayer potassium. (Adapted from Moore and Reynolds 1997.)

1: 1 Phyllosilicates

- One octahedral and tetrahedral plate is repeated
- **Trioctahedral:** 3 Mg^{2+} in octahedral layer per building unit (serpentines)
- **Dioctahedral:** 2 Al^{3+} in octahedral layer per building unit (kaolins)

Clay minerals

- Phyllosilicates with grains below 2 μm
- Large surface area by weight – high reactivity
- The most common reactive phase in low temperature conditions
- They differ from each other by substitutions and thus by the charge on the interlayer
  - Kaolinite group – no positions in the interlayer (low CEC)
  - Smectite group – Na and Ca easily washed from the interlayer, replaced by water => swelling (+ high CEC)
  - Illite Group – tightly bound K in the interlayer (lower CEC)

Humic substances

- An important component of the soil
- Product of vegetation biodegradation
- Heterogeneous group, large molecules of COH- (N, S)
  - Three-dimensional networks of aromatic cycles lined with functional groups
  - (-COOH) and (-OH) can dissociate and form sorption binding sites
- Dark brown color of soil and water
- Humic acids soluble in pH > 2
- Humins – refractory component, strongly adsorbs on mineral surfaces

Clark 2015
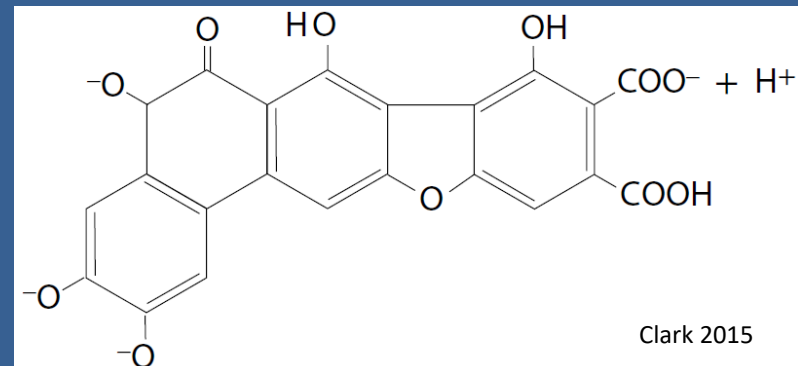
Fe (and Mn) Oxohydroxides

- Amorphous, hydrated iron oxide – coatings on grains
- Crystalline form – goethite, limonite…
- Insoluble in neutral pH and oxidizing conditions
- Oxygen has a negative surface charge

Colloids

- Small (10 μm), non-crystalline particles
- Hydroxides of Si, Fe, Mn, Al or organic comp.
- High negative surface charge
- In water with low ionic strength in suspension
- Adsorption of contaminants to the surface
  - The total content can greatly exceed the solubility (eg Pb^{2+})
  - Transport of contaminants

Zeolites

- Low temperature tectosilicates

- Open crystal structure – holds large amounts of water

- Substitution of Al^{3+} for Si^{4+} is compensated by the incorporation of cations
  - Surface charges may occur

Ions in solution
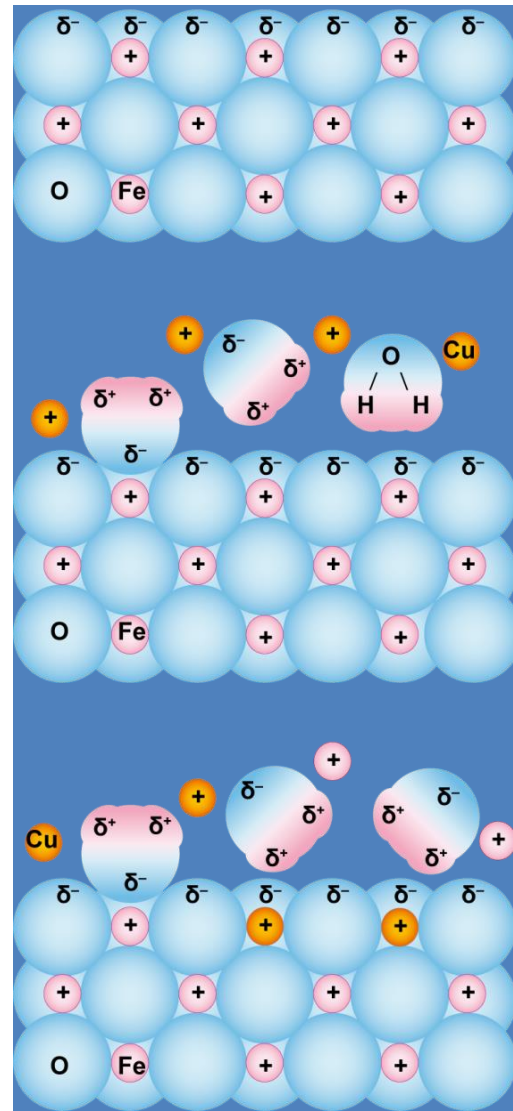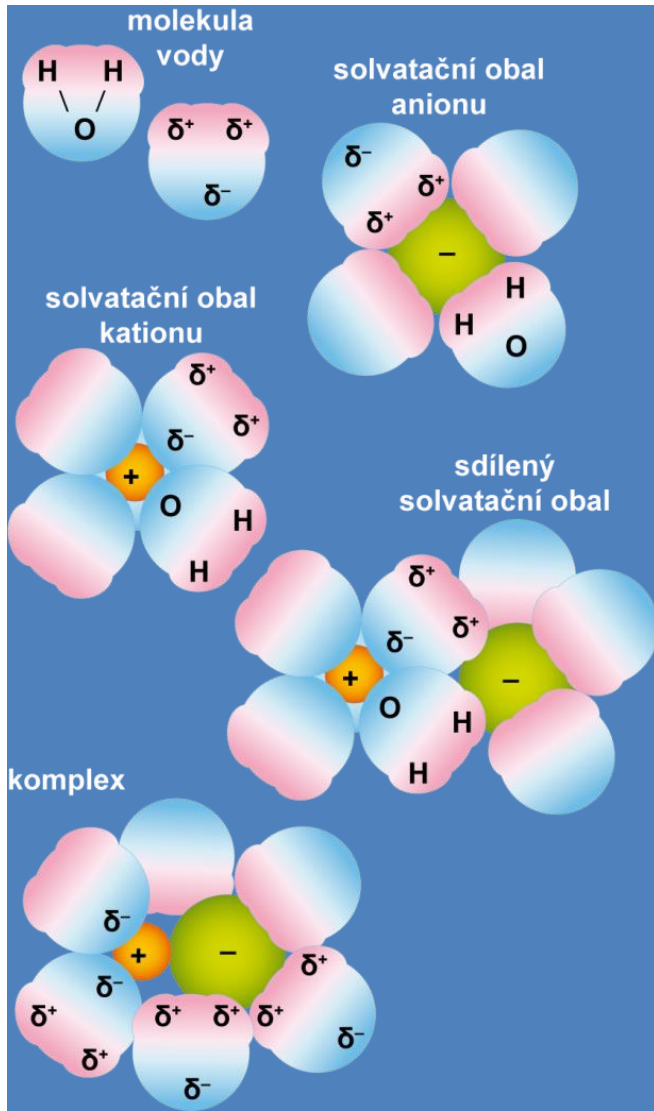
Cation exchange

- Adsorption given by the attraction of cations to mineral surfaces.
- Driven by several factors:
    1. Chemical attraction
    2. Electrostatic attraction
    3. Physical attraction (van der Waals forces)
    - All due to the properties of the mineral, sorbed substance and solution.
- Large exchange = high *exchange capacity*
- Especially clay minerals, oxohydroxides and organic matter.
- At low pH, oxohydroxides also have an anion exchange layer.

Factors affecting the attraction of cations from solution to the surface

1. Particle charge – smectite and other clay minerals have a negative charge of interlayer.

2. Particle size – large surface area to the volume of the mineral has a greater binding potential.

3. Additional binding sites – interlayers, channels in zeolites, etc.

4. Bonding sites on surface – various surface shapes (dimples and edges), suitable bonding sites because they usually contain free bonds (the metal in the octahedral position is in contact with less than 6 oxygens).

Isoelectric point

- In acidic solutions, the surfaces are coated with H^+ and attract anions.
- In alkaline solutions they attract cations (esp. oxides, hydroxides, silicates).
- *Isoelectric point* (IEP) – the pH value at which the surface charge in solution with only H^+ and OH^- ions is equal to zero.
- In natural waters with more ions: *point of zero charge* (PZC).
- pH < PZC – the surface charge is positive and attracts anions.
- pH > PZC – the surface charge is negative and attracts cations.
- Clay minerals adsorb cations even at very low pH due to the charge of the interlayer.
  – In the natural environment (soils, river sediments) the sorption of cations over anions dominates.
- PZC of iron oxides and hydroxides is in the range of pH ~ 5-9.

surface charge

záporný

Alkaline pH

nulový

Transient pH

kladný

pH acidic
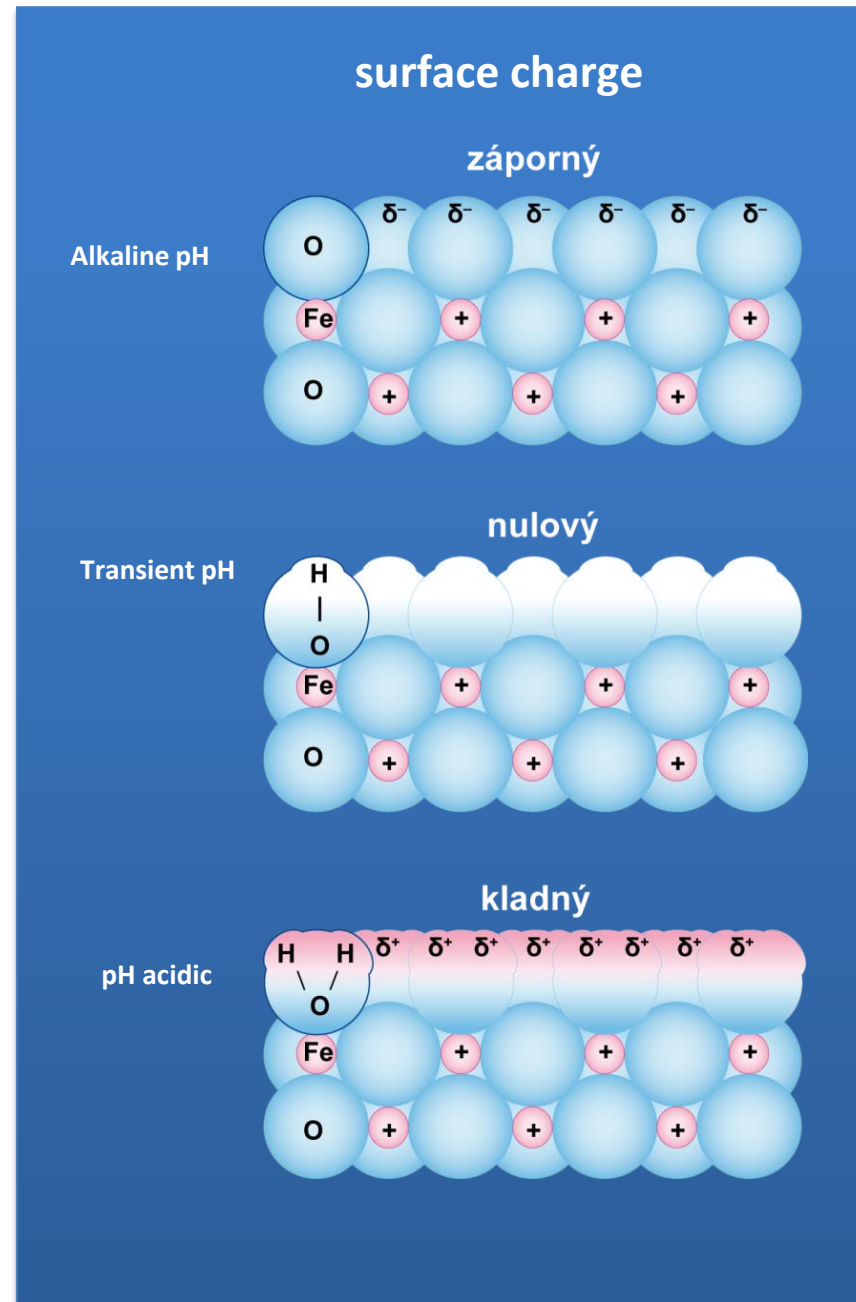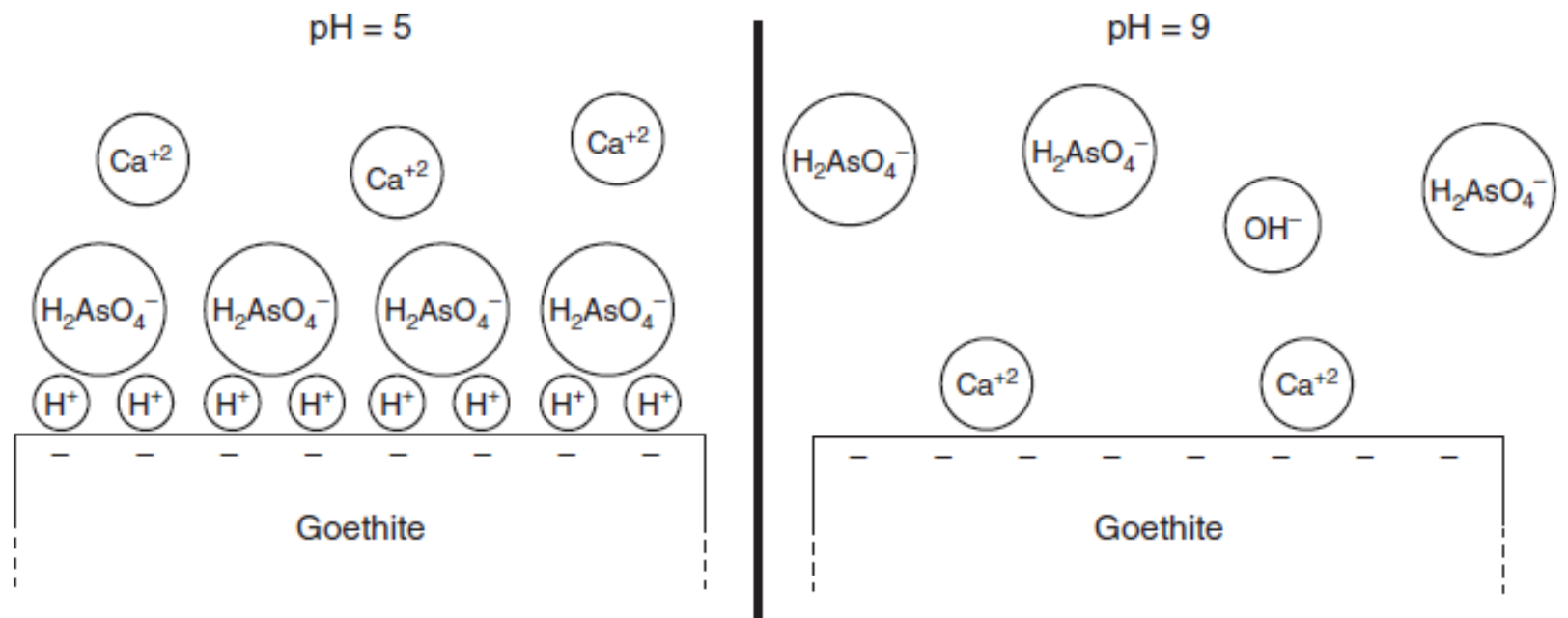
Fig. 2.26 Sketch of a goethite surface in solutions at pH = 5 (left) and pH = 9 (right), demonstrating the effect of IEP or PZC on ion-exchange capabilities of soil solids. Note the occurrence of anionic arsenate as inner sphere complex at pH = 5 (facilitated by H^+) compared to the occurrence of Ca^{+2} as an inner sphere complex at pH = 9. Negative signs near the goethite surface indicate a net negative charge at the mineral surface.
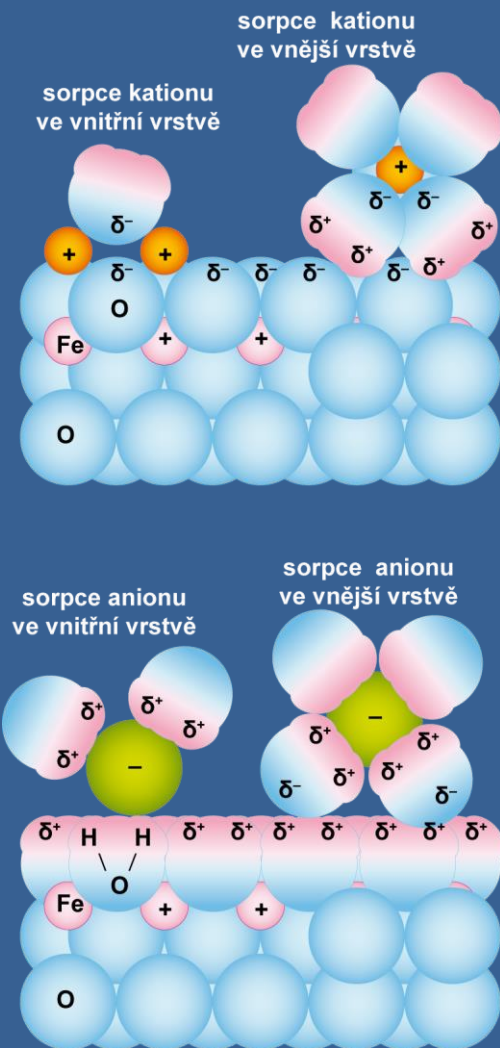
Electrical double layer

electrical double layer

povrch   kompaktní   difuzní   roztok

elektrický potenciál

ΔE

vzdálenost
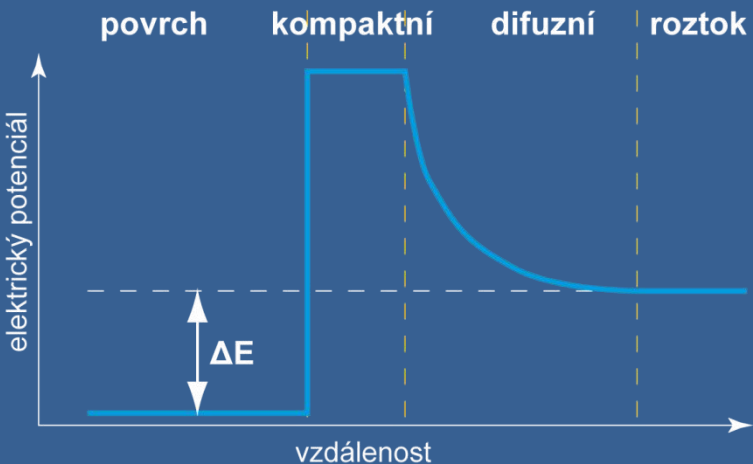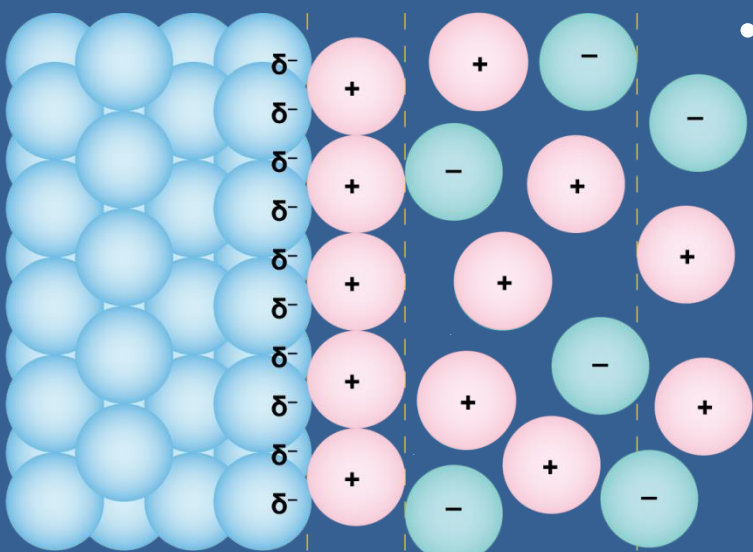
- The exchangeable ions are on the surface of the particle in the electrical double layer:
  - Complexes in the inner layer – directly on the surface, compact (fixed).
  - Complexes in the outer layer – farther from the surface, diffuse.
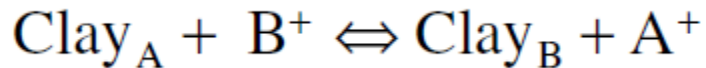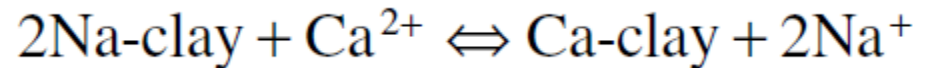 - Uneven distribution of cations and anions at the surface.

sorption

sorpce kationu ve vnější vrstvě

sorpce kationu ve vnitřní vrstvě

O   Fe   O

sorpce anionu ve vnitřní vrstvě

sorpce anionu ve vnější vrstvě

H   H   O   Fe   O

Selectivity coefficient

- The cation exchange process can be characterized by the equation:

General   **Example**

$$\text{Clay}_A + B^+ \Leftrightarrow \text{Clay}_B + A^+ \qquad 2\text{Na-clay} + Ca^{2+} \Leftrightarrow Ca\text{-clay} + 2Na^+$$

- Special type of equilibrium constant (**selectivity coefficient**):

$$K_{A-B} = \frac{[\text{Clay}_A] \times [B^+]}{[\text{Clay}_B] \times [A^+]} \qquad K_{Na-Ca} = \frac{[\text{Clay}_{Na}]^2 \times [Ca^{2+}]}{[\text{Clay}_{Ca}] \times [Na^+]^2}$$

- The activities of cations in solution are easily determined by analysis.
  - *Note that the coefficient is based on activities – it will depend on the ionic strength. Solutions with a high value of ionic strength will show a greater tendency for monovalent ions to bind.*

Selectivity coefficient

- The activities of cations on the surface of clays are best expressed as a molar fraction of the total surface:

$$[\text{Clay}_A] = \frac{\text{moles A}^+ \text{ on clay}}{\text{moles A}^+ + \text{B}^+ \text{ on clay}} \qquad [\text{Clay}_{Na}] = \frac{\text{moles Na}^+ \text{ on clay}}{\text{moles Na}^+ + \text{Ca}^{2+} \text{ on clay}}$$

- The coefficient is determinable for all cation exchange processes, yet due to complicated circumstances, it is more an empirical value rather than a constant describing a specific environment (reservoir).
- It includes surface heterogeneity, ionic strength of the solution and other phenomena affecting the final values.

Sorption nature

- Each cation has a different tendency to bind to the charged surface
- Ability of electrostatic interactions
  - Surface charge of the cation
  - Stability of the solvation envelope
- Divalent ions and smaller ions bind more
- In general:

$$more\ soluble \rightarrow$$

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$
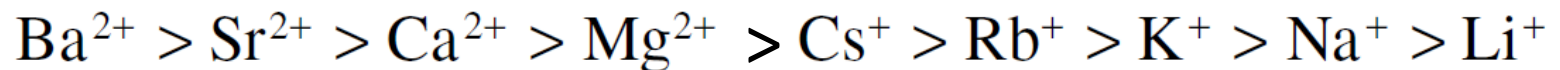
$$\leftarrow more\ sorption$$

Cation exchange capacity

- Number of absorption positions per dry weight (meq/100 g)
- Conventional inert substances (Q, crushed crystalline rocks, sand...) can have a significantly increased sorption capacity by the presence of coatings.
- Important in pedology – the nature of clays affects permeability, fertility, etc.
- Environmental geology – spread of contaminants, development of geochemical properties of waters.

Cation exchange capacity

- Determined experimentally

- Indicator of sorption and exchange potential

Clark 2015
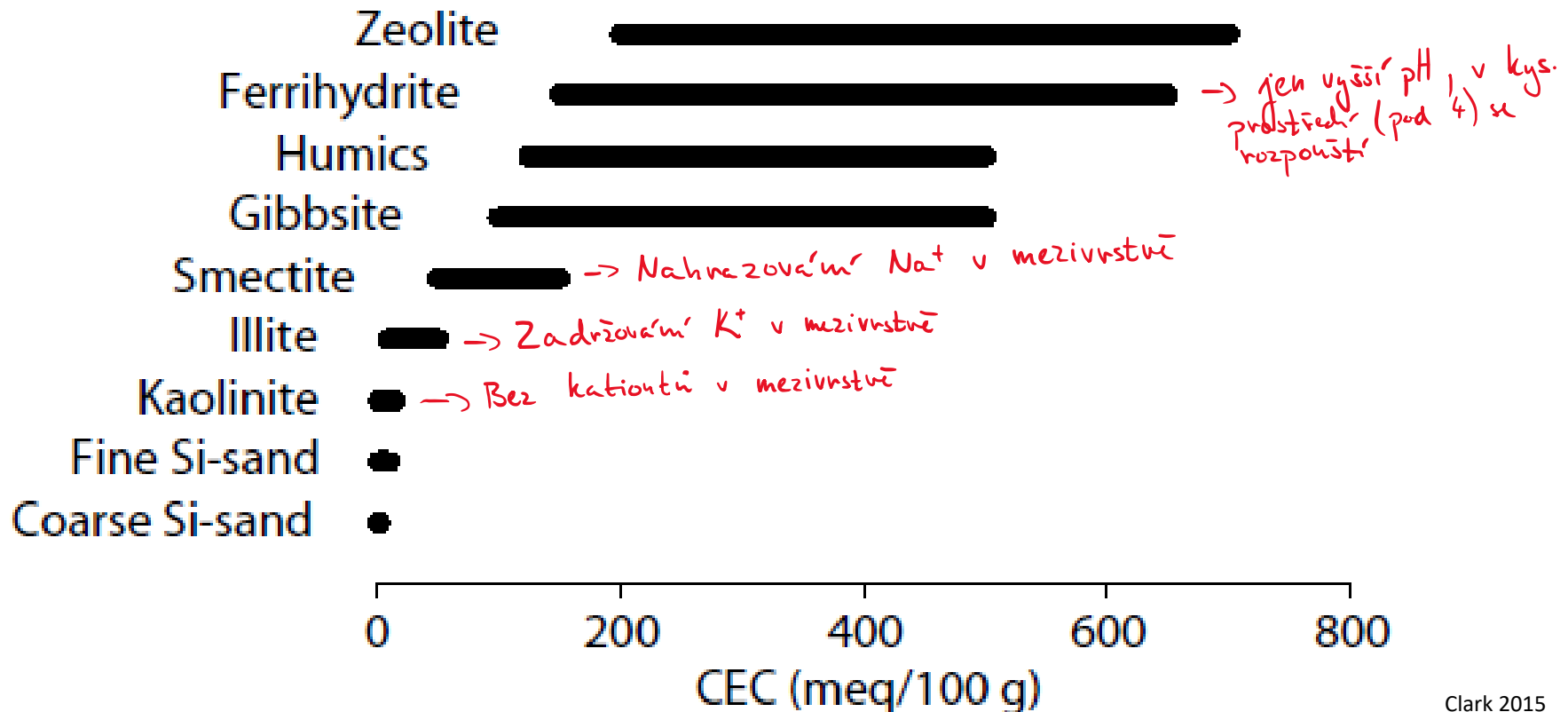
Cationic imbalance

- The evolution of the composition of water by cation exchange is a response to the disturbance of the balance between groundwater and the environment
- Anthropogenic disturbances
  - eg **winter treatment of roads**
  - Infiltrating Na-Cl type water replaces Ca^{2+} with Na^+ in clays
  - Change of water type at the outlet from Ca-HCO$_3$ to Ca-Cl
  - Replenishing Ca-HCO$_3$ type water outside the winter season, desorption of Na^+ on clays -> changing the output to Na-Cl and gradually again to Ca-HCO$_3$
- Natural disturbances
  - Flow changes, erosion, sea level movements

$$2\text{Na-clay} + \text{Ca}^{2+} \rightarrow \text{Ca-clay} + 2\text{Na}^{+}$$
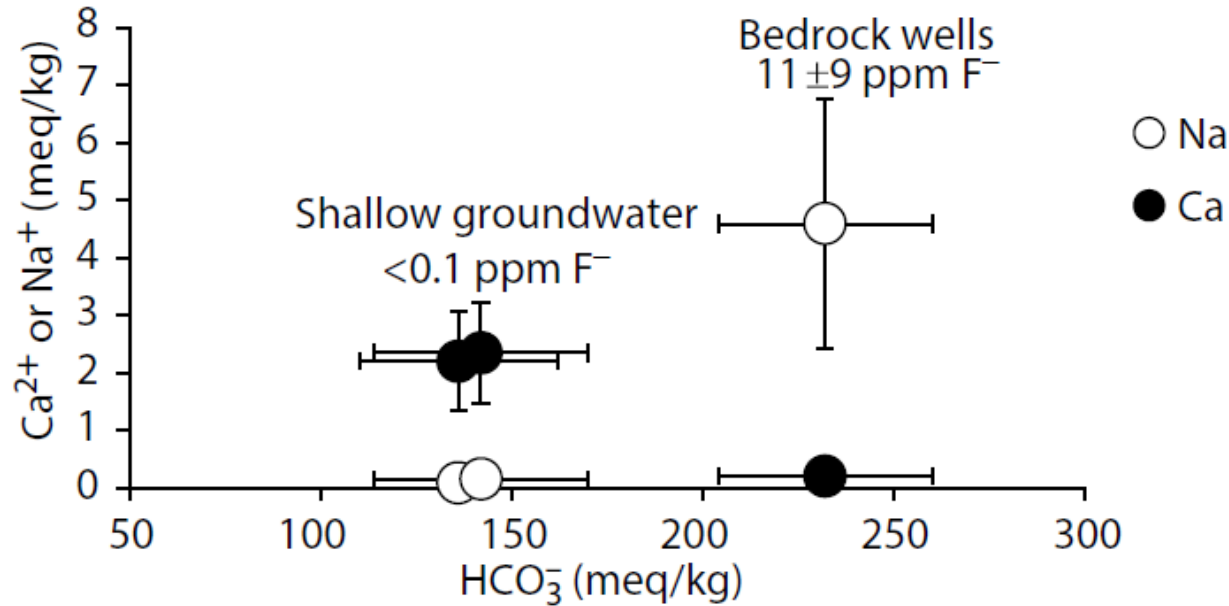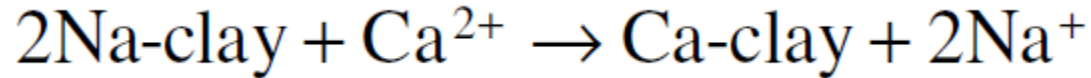
FIGURE 7.5   Natural water softening in deep groundwaters in Gaspé, Quebec (Data from Boyle and Chagnon 1995). Decreased Ca^{2+} in the deep groundwaters has allowed dissolution of fluorite, CaF_2. Consequently, the high F^- in these groundwaters has caused cases of skeletal fluorosis in the local population.

Clark 2015

Distribution coefficient

- Adsorption
- Due to lower concentrations of sorbents, we express the distribution coefficient
- The amount of sorbed substance proportional to concentration

$$K_d = \frac{\text{mass sorbed}}{\text{mass dissolved}} = \frac{\mu g/g}{\mu g/mL} = \frac{S}{C_{eq}} \quad (\text{mL/g})$$

- Depends on concentration, but also on the medium (CEC, organic, mineral composition...)
  - Empirical determination in the laboratory = non-transferable
  - Series of measurements manifests itself as a sorption isotherm of the given system

Sorption isotherm
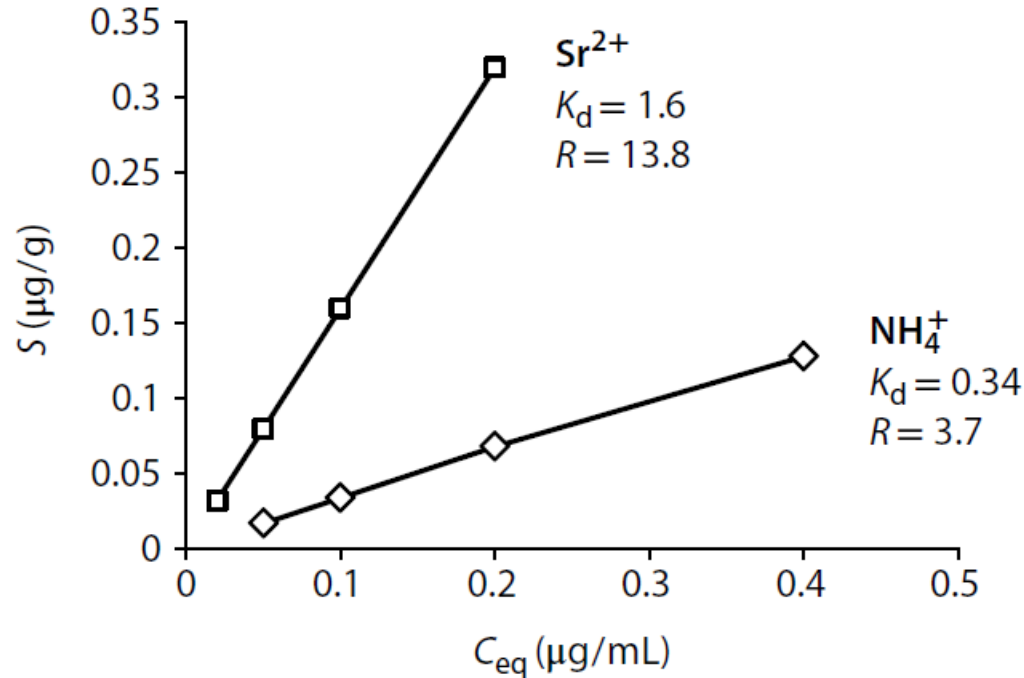
FIGURE 7.6 Sorption isotherms for two reactive solutes. Sr^{2+} sorption onto a medium-to-fine grain quartz sand aquifer was investigated by Lee et al. (1998) to remediate a ^{90}Sr plume. Böhlke et al. (2006) investigated NH_4^+ sorption onto glacial outwash sand aquifer.

$$S = K_d C_{eq}$$

The more reactive substance, the steeper the line

Slope = distribution coefficient

Nonlinear sorption isotherm

- For highly reactive substances and high concentrations, the linear isotherm is inaccurate
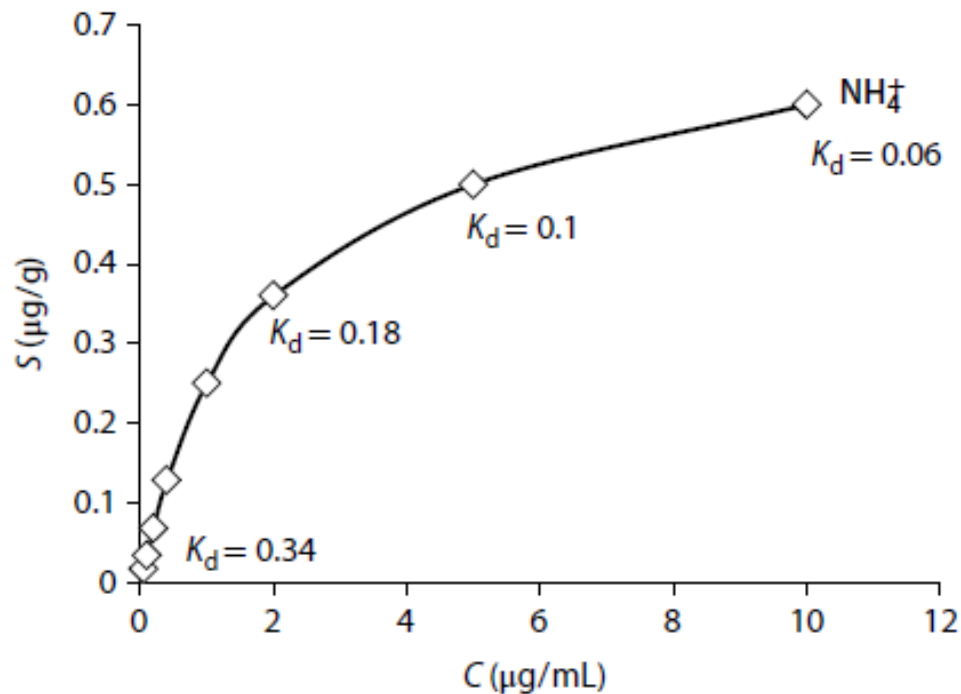
FIGURE 7.7 Sorption isotherm for ammonium at higher concentrations. Increased saturation of exchange sites leads to a reduction in the distribution coefficient, K_d, leading to reduced retardation and more conservative transport.

Clark 2015

Freundlich sorption isotherm

$$S = K_d C_{eq}^n$$

- n <1
- Less steep at higher concentrations
- Empirical or model of a gradual occupation of adsorption positions on the surface

Langmuir sorption isotherm

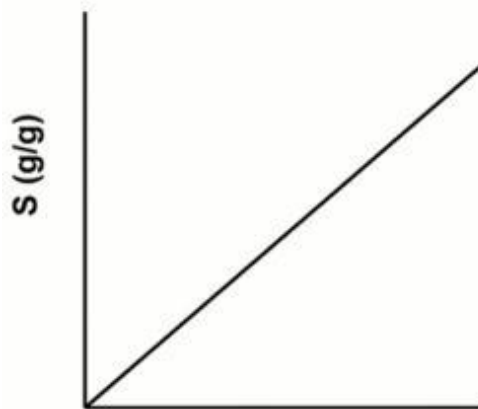$$[vacant\ site] + [A^+] = [occupied\ site]$$
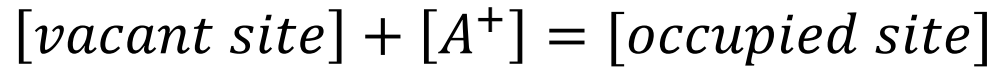
- Process equilibrium constant:

$$K_{Lang} = \frac{S}{C_{eq} \times [vacant\ sites]}$$

- Substitution $S_{max} = [vacant\ site] + S$

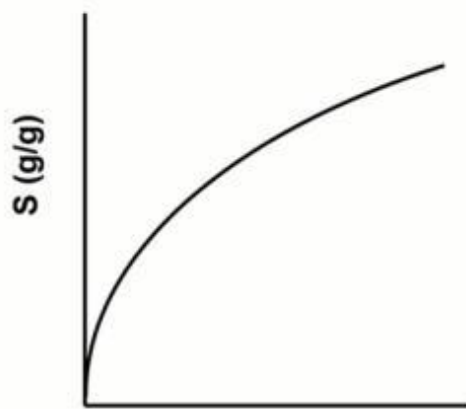$$S = S_{max} \frac{K_{Lang}[A^+]}{1 + K_{Lang}[A^+]}$$
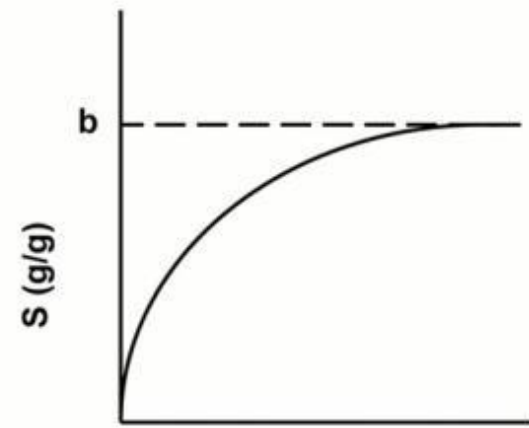

A. Distribution Coefficient

B. Freundlich Isotherm
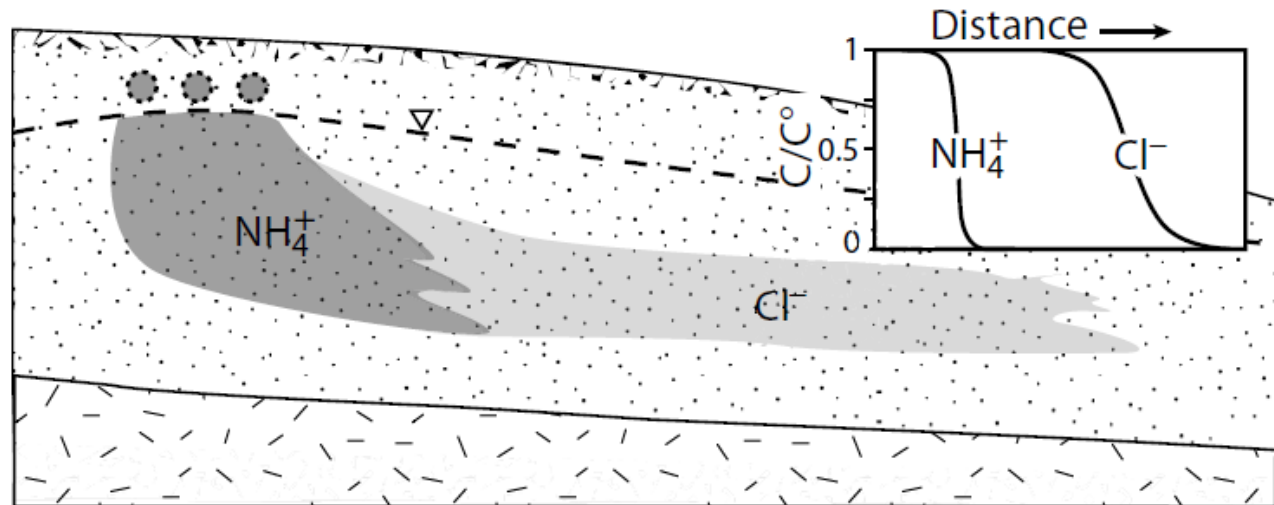
C. Langmuir Isotherm

Sorption and retardation

- Retardation given by the available surface area of the sorbent

- Retardation factor R
  - Difference between water and contaminant velocity

$$R = 1 + \frac{\rho}{\theta} \times K_d$$

$$R = \frac{v_{gw}}{v_c}$$

What will be the value of the retardation factor for conservative ions? And for the highly reactive?
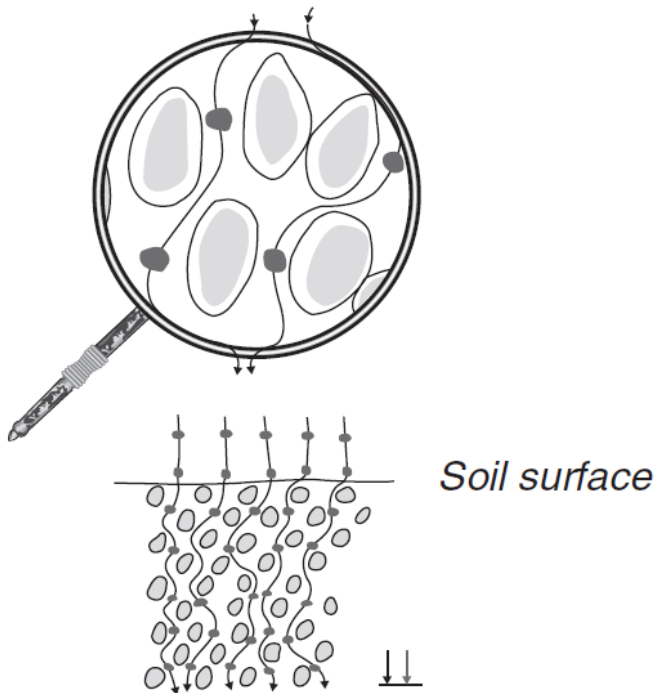
Retardation

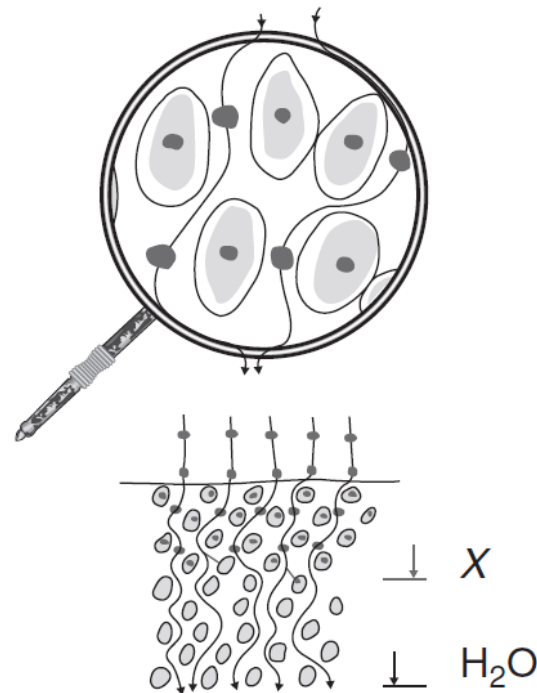**Pollutant X enters an aquifer**

Case A: no adsorption
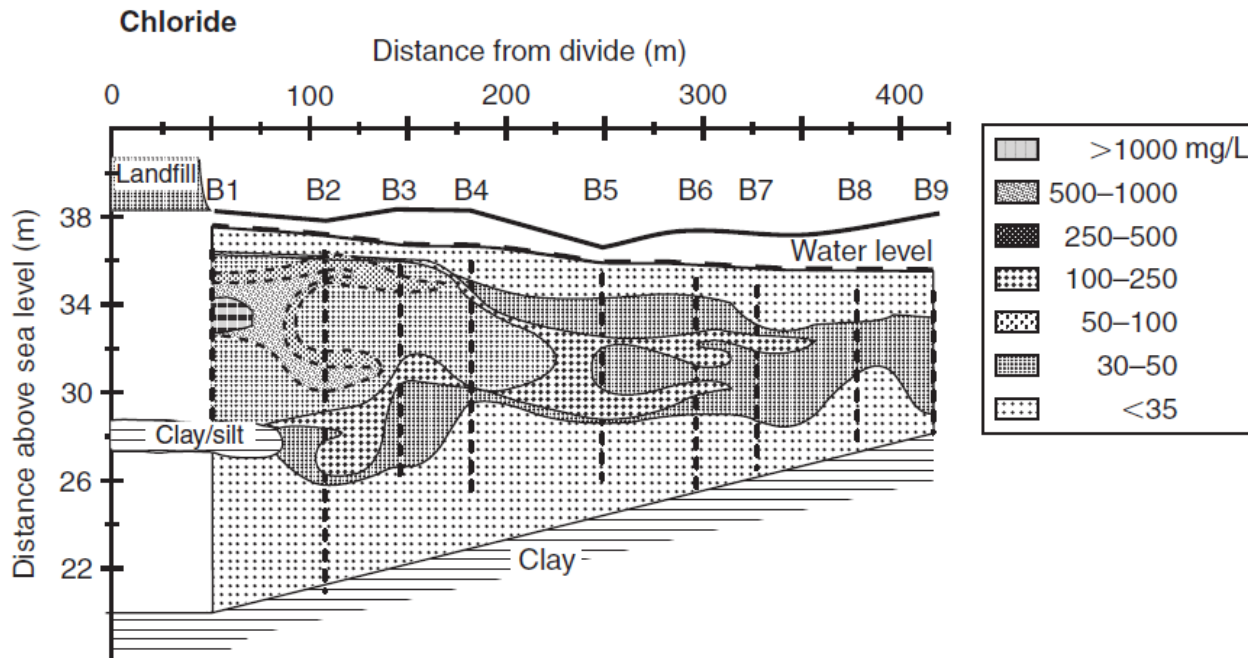
Case B: sorbed is 1 out of 2

Appelo & Postma 2005

Soil surface

X

H_2O

Ratio $\dfrac{adsorbed}{solute} = \dfrac{0}{1} = 0 = K_d$

$\dfrac{adsorbed}{solute} = \dfrac{1}{1} = 1 = K_d$

$v_X = v_{H_2O}$

$v_X = \dfrac{1}{(1+1)} v_{H_2O}$

Chloride

Distance from divide (m)

Landfill B1 B2 B3 B4 B5 B6 B7 B8 B9

Water level

Clay/silt

Clay

Legend:
- >1000 mg/L
- 500–1000
- 250–500
- 100–250
- 50–100
- 30–50
- <35

Sodium

Distance from divide (m)

Land fill B1 B2 B3 B4 B5 B6 B7 B8 B9

Water level

Clay/silt

Clay

Legend:
- >500 mg/L
- 250–500
- 100–250
- 50–100
- 20–50
- <20

- What is the difference?
- How does element transport differ?
- What is the cause?
  1. Ion adsorption
  2. Dispersion
  3. Diffusion
  4. Ion size
  5. Ion charge
  6. Something else
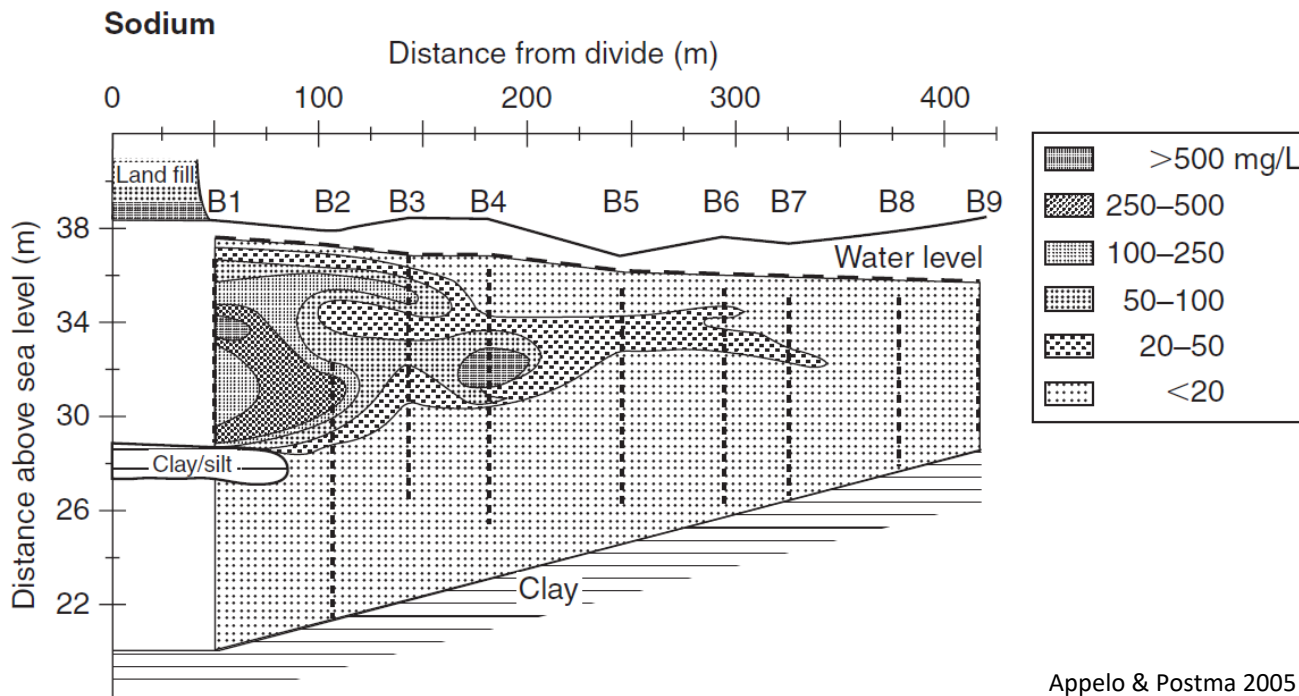
Appelo & Postma 2005

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie

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