Post Graduate Training Course On Groundwater Tracing Techniques

Introduction to hydrogeochemistry with respect to tracing

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"Every groundwater tells a story.“

„We listen to them here and use them to help better understand and manage our groundwater resources“

(S. Fritz, Purdue University)

Introduction

Hydrogeochemistry is the science of:

- **Determining the time and source of groundwater recharge,**
- **estimating how long water has been in an aquifer,**
- **identifying mineral make-up of aquifer materials,**
- **examining how water from different sources mix and interact**
- **and evaluating what types of (bio)geochemical processes have occurred during the water's journey through the system.**

Introduction

Hydrogeochemistry use the water's chemistry and isotopic composition as a forensic tool to find out where groundwater has been and what has happened to it along its journey.

- **This information provides a broad, more regionally extensive understanding of groundwater systems .**
- **Furthermore, this improved knowledge can be used to create more comprehensive management and conservation plans, and more equitable groundwater/surface water regulations.**

Introduction – *Some good References*

GEOCHEMISTRY

by

William M. White

Cornell University

An On-Line Textbook, Eventually to be published by: **John-Hopkins University Press**

http://www.geo.cornell.edu/geology/classes/geo455/Chapters.HTML

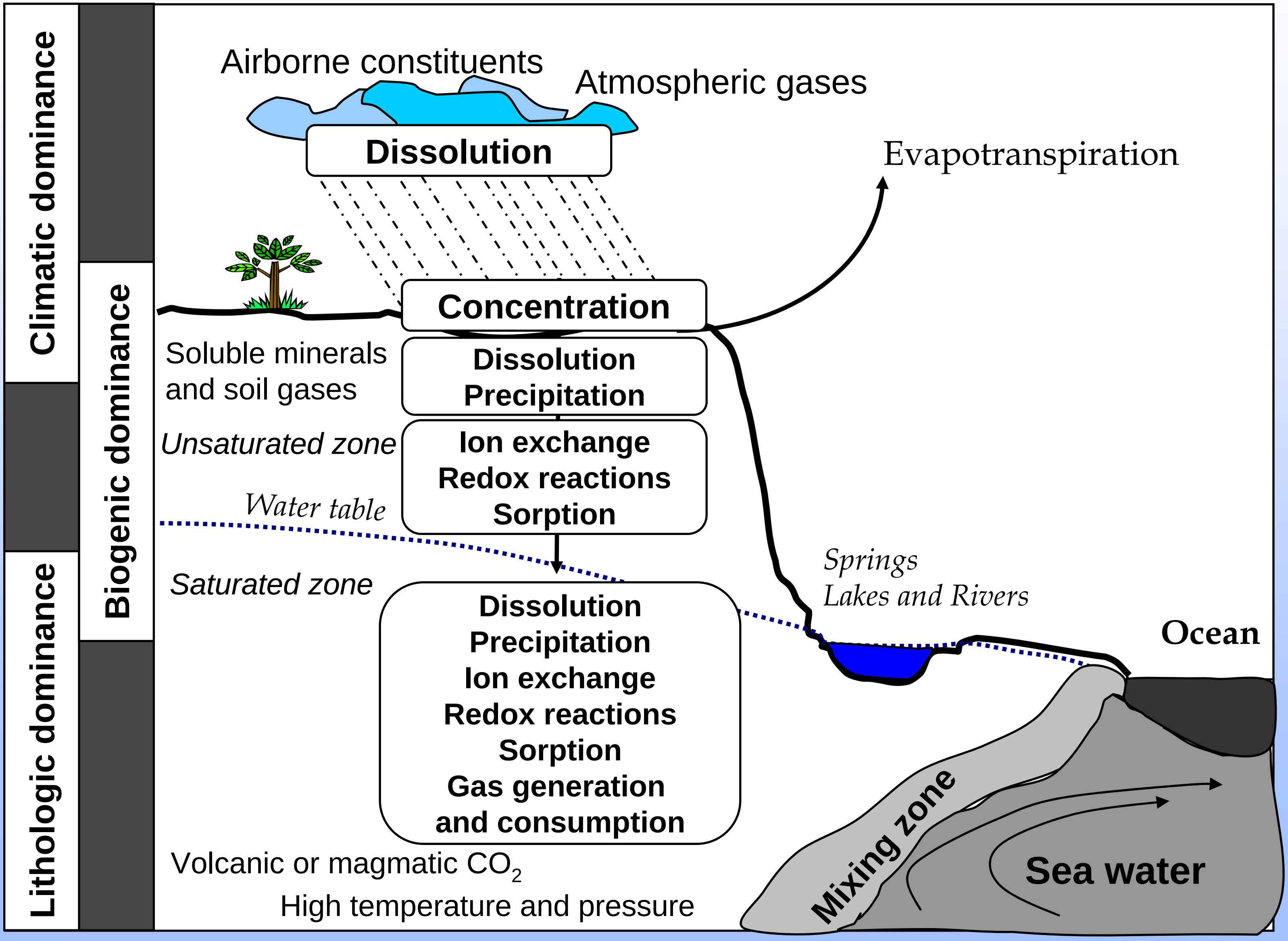
Drever, J.I.(1997): *The Geochemistry of Natural Waters.* 3rd Ed., Upper Saddle River (Prentice Hall).

Garrels, R.M. & Christ, C.L. (1965): *Solutions, Minerals and Equilibria.,* San Francisco (Freeman & Co.).

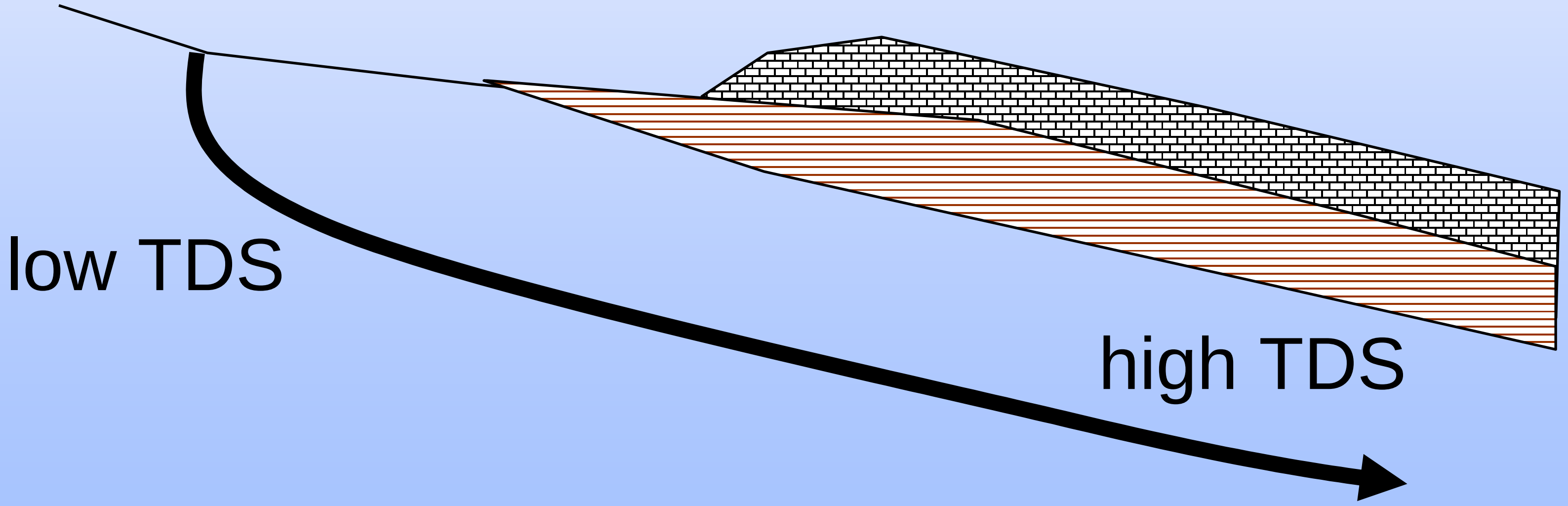
Stumm, W. & Morgan, J.J. (1996): *Aquatic Chemistry.* 3rd Ed., New York (Wiley).

Appelo, C.A.J. & Postma, D. (2005): *Geochemistry, Groundwater and Pollution*, Sec. Ed., Leiden, The Netherlands (Balkema Publishers).

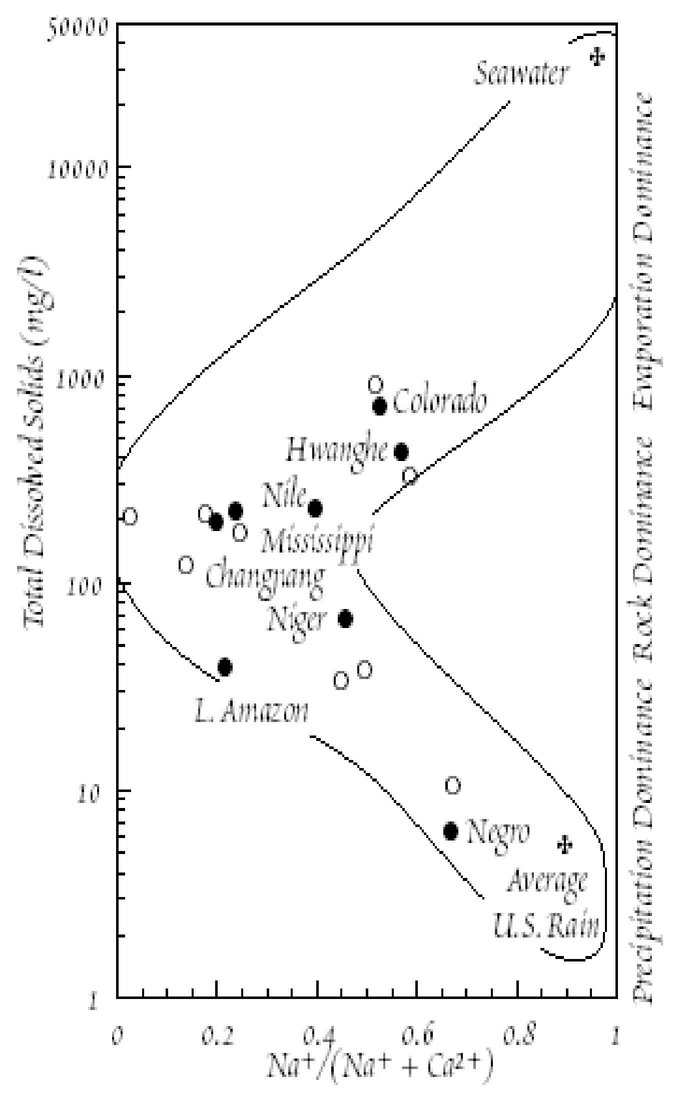
Simplified conceptual diagram of the hydrologic cycle incorporating hydrogeochemical processes



- **In general, TDS and specific conductance increase with time along flow path.**



TDS versus Na/(Ca^{2+} +Na^{+})



- Plot of total dissolved solids vs. Na+/(Na+ + Ca2+) used by Gibbs (1970) to define „precipitation-dominated“, „rock-dominated“, and „evaporation-dominated“ river compositions.

Solutes in groundwater

There are major, minor, and trace solutes in groundwater!

Major (> 5 mg/L)

Ca, Mg, Na, HCO_3, SO_4, Cl, Si,

Minor (0.01-10 mg/L)

B, Fe, NO_3, NH_4, K, Sr, Mn,

Trace (<0.01 mg/L)

The Rest!!

Major Constituents (> 5 mg/L)

- **Calcium**
- **Magnesium**
- **Sodium**

- **Bicarbonate**
- **Chloride**
- **Sulphate**

- **Silicon**
- *Carbon Dioxide*

Minor Constituents *(0.01 to 10 mg/L)*

- **Potassium**
- **Iron**
- **Ammonium**

- *Carbon Dioxide*
- *Oxygen*

- **Carbonate**
- **Fluoride**
- **Bromide**
- **Nitrate/Nitrite**

- **Boron**
- **Strontium**

Trace Constituents (< 100 μg/L)

- Li
- Be
- Al
- Sc
- Ti
- Cr
- Mn
- Co
- Ni
- Cu
- Zn
- Ga
- Ge
- As
- Se
- Rb
- Yt
- Zr
- Nb
- Mo
- Ru
- Ag
- Cd
- In
- Sn
- Sb
- Cs
- Ba
- La
- Ce
- W
- Pt
- Au
- Tl
- Pb
- Bi
- Ra
- Th
- U

Phosphate

Iodide

Noble gases

Other trace gases (Methan, CFC`s

Organic Constituents

- **Humic acid**
- **Fulvic Acid**
- **Carbohydrates**
- **Amino Acids**
- **Tannins**
- **Lignins**
- **Hydrocarbons**
- **Acetate**
- **Propionate**

Typically concentrations are very low

***Introduction** – Drinking water standards*

For drinking water standards see:

- **WHO**
  - **Guidelines for drinking-water quality, third edition**

http://www.who.int/water_sanitation_health/dwq/gdwq3/en/

- **EPA**

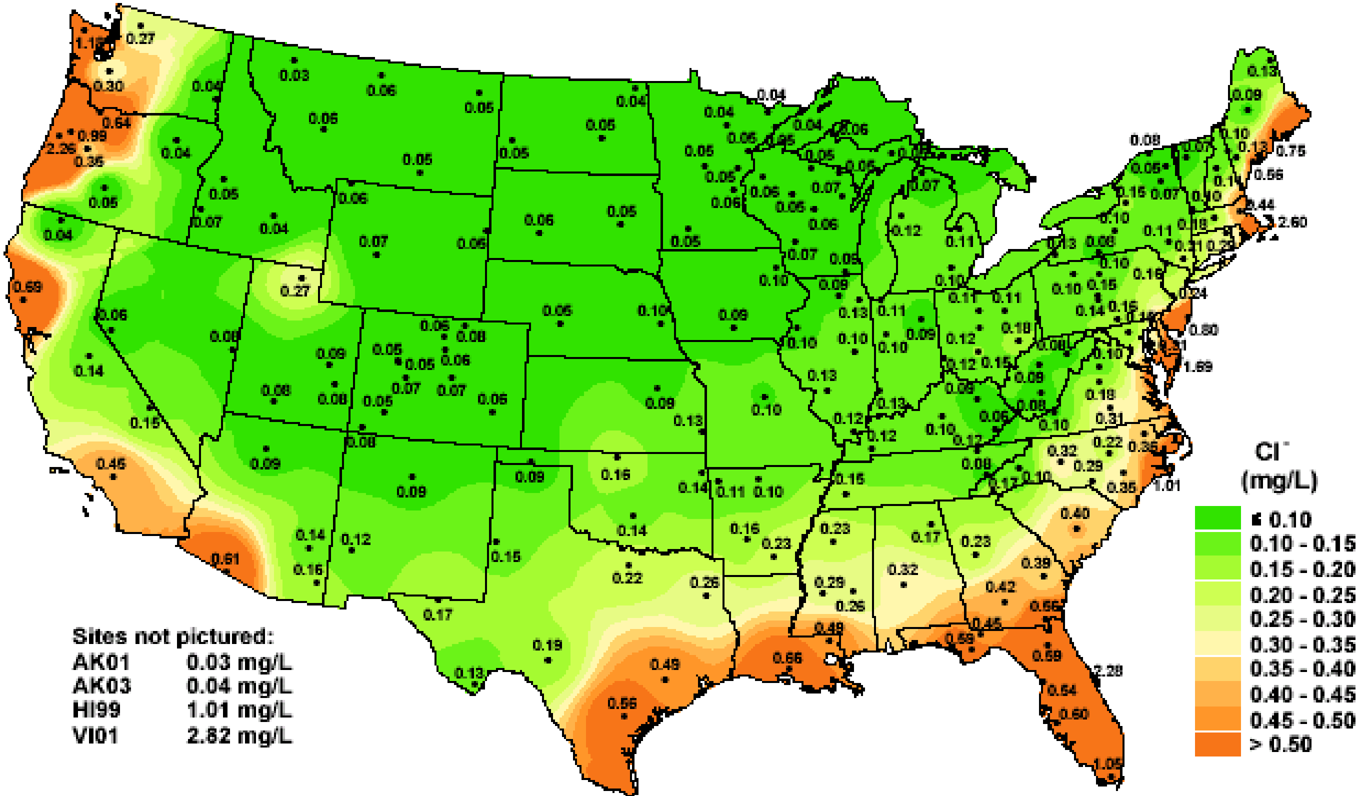
http://www.epa.gov/safewater/

Origin of solutes

- **Atmospheric deposition**
- **Rock weathering**
- **Anthropogenic sources (fertilizer, landfills, septic tanks ...)**

Distribution of Cl-Concentrations (mg/L)

Chloride ion concentration, 2001

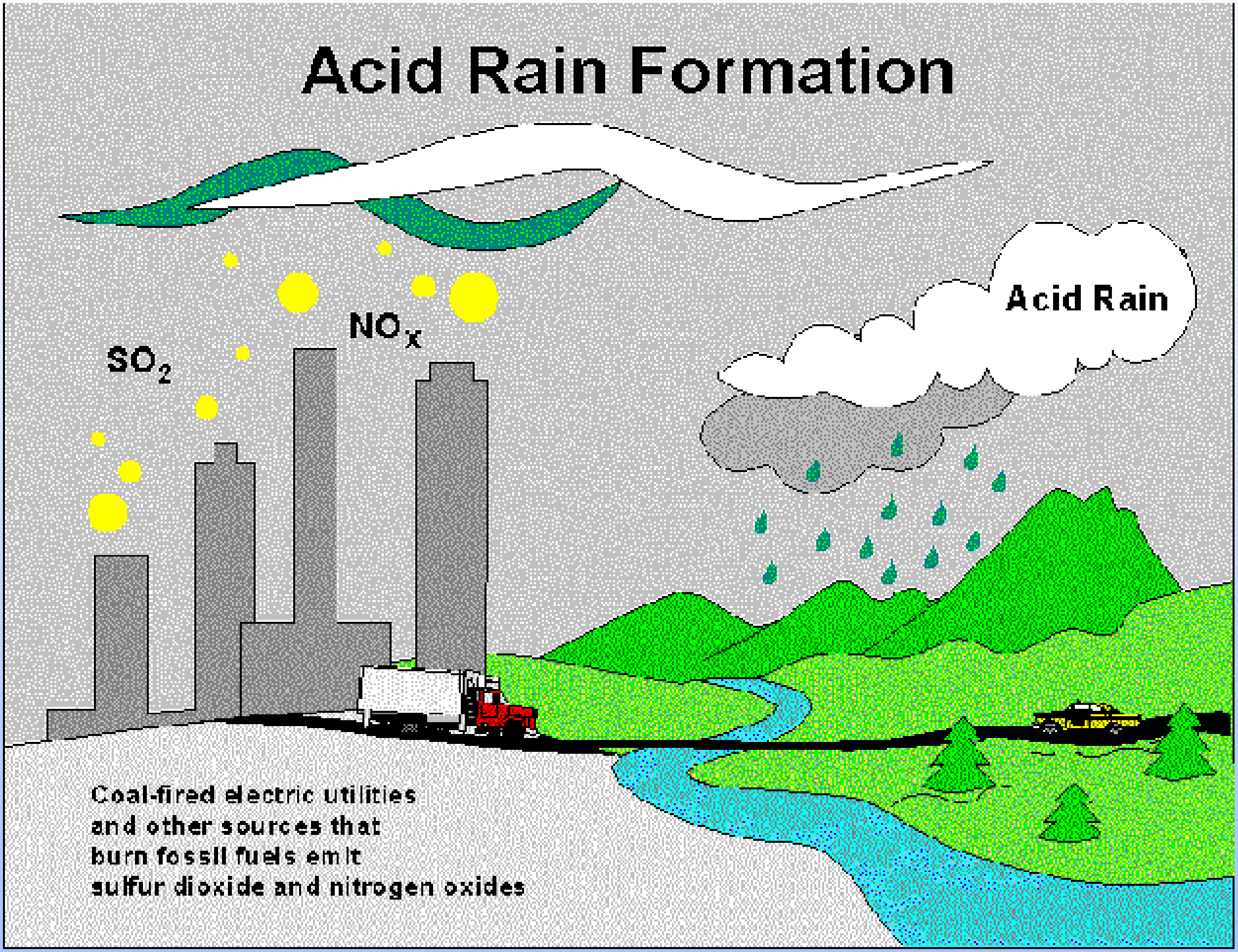


Sites not pictured:

AK01	0.03 mg/L
AK03	0.04 mg/L
HI99	1.01 mg/L
VI01	2.82 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Atmospheric deposition - Acid Rain Formation



Origin of solutes

- **Atmospheric deposition**
- **Rock weathering**
- **Anthropogenic sources (fertilizer, landfills, septic tanks ...)**

Chemical Reactions

- A wide variety of chemical reactions can take place between gases, solutes and solids in groundwater systems:
  - Some basic terms
  - Acid-base
  - Solution-precipitation
  - Adsorption
  - Complexation
  - Redox
  - Hydrolysis
  - Isotopic processes

Some basic terms?

- **Electrical Neutrality**
- **Solubility of gases**
- **Concentration and activity**
- **Law of mass action**
- **Solubility product**
- **Saturation index**
- **Chemical equilibrium**
- **Dissociation of carbon dioxide**
- **Solubility of carbonates**
- **...**

Electrical Neutrality

$$\boxed{\sum_{i} \mathbf{m_i z_i = 0}} \quad !!$$

$$\Downarrow$$

$$\boxed{\sum_{i} m_i^{+} z_i^{+} = \sum_{n} m_n^{-} z_n^{-}}$$

The sum of the positive charges in solutions must equal the sum of the negative ones!

***Solubility of gases** - Henry`s Law*

$$K_H = \frac{[A_{(aq)}]}{p_a} \, [\text{mol L}^{-1}\ \text{atm}^{-1}]$$

K_H - Henrys`s Law constant

$[A_{(aq)}]$ - concentration of the gas in the liquid

p_a - partial pressure of the component in the gas

Henry - constant 25°C

gas	**K_H [mol L^{-1} atm^{-1}] x 10^{-3}**
CO_2	33,8
CH_4	1,34
N_2	0,642
O_2	1,27

Concentration units - I

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 - II

- **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 - III

Mass concentrations (continued)

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

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

Concentration units - IV

- **Molar concentrations:**

In almost all geochemical calculations, it is necessary or easier to use molar concentrations rather than mass concentrations.

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

Molality (m) = moles of solute/1000 g 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 - V

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 - VI

Mole fraction

Another form of molar concentration, the *mole fraction (X)* is used for solid solutions, e.g., solid solutions between $KAlSi_3O_8$ and $NaAlSi_3O_8$. In such a solid solution, the mole fraction of $KAlSi_3O_8$ would be written as:

$$X_{KAlSi_3O_8} = \frac{\text{moles } KAlSi_3O_8}{\text{moles } KAlSi_3O_8 + \text{moles } NaAlSi_3O_8}$$

Concentration units - VII

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^{+}; and 0.003 mol L^{-1} La^{3+} = 0.009 eq L^{-1} La^{3+}.**

- **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 is another parameter expressed as eq L^{-1}.**

Concentration units - VIII

(Example - Determination of the equivalent weigth fraction)

Given concentration of Calcium (Ca^{2+}) = 90 ppm

Atomic weigth of Calcium: 40,08 g/mol
Charge 2

$$\textbf{Equivalent weigth} = \frac{\text{Atomic weigth}}{\text{Charge}} = \frac{40{,}08\ \text{g/mol}}{2} = 20{,}04\ \text{g/mol}$$

$$\textbf{Equivalent weigth fraction} = \frac{\text{given weigth fraction}}{\textbf{Equivalent weigth}} = \frac{90\ \text{ppm}}{20{,}04\ \text{g/mol}} = \underline{\underline{\textbf{4,49 meq/l}}}$$

Concentration and activity

- in ideal solutions :

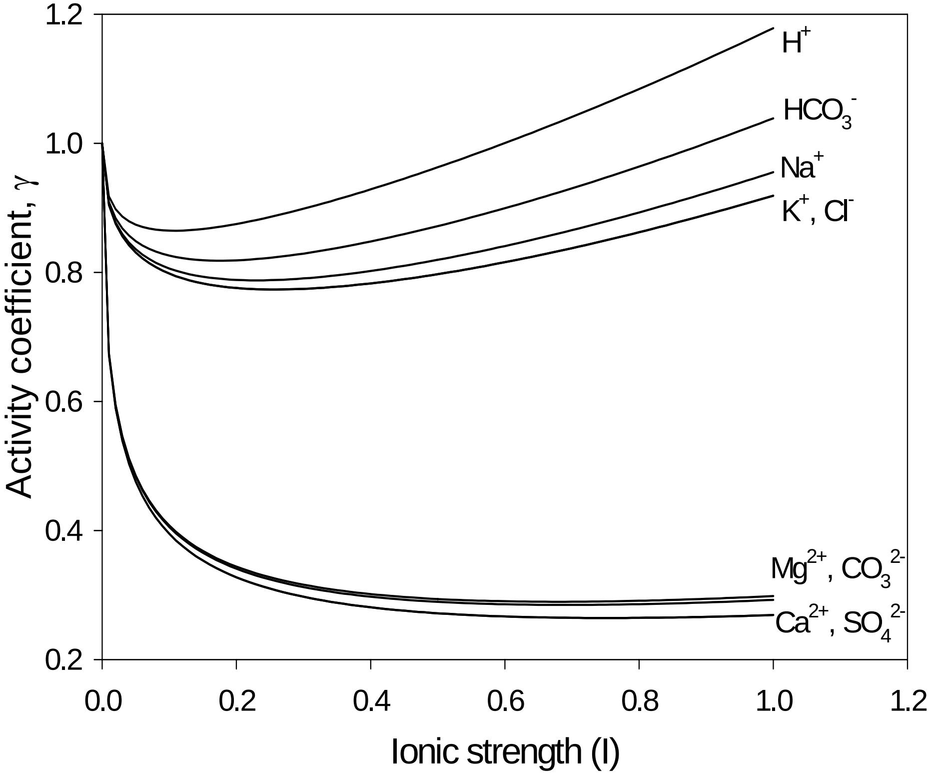
$$[A] = \{A\} \qquad\qquad f_a = 1$$

- in real solutions

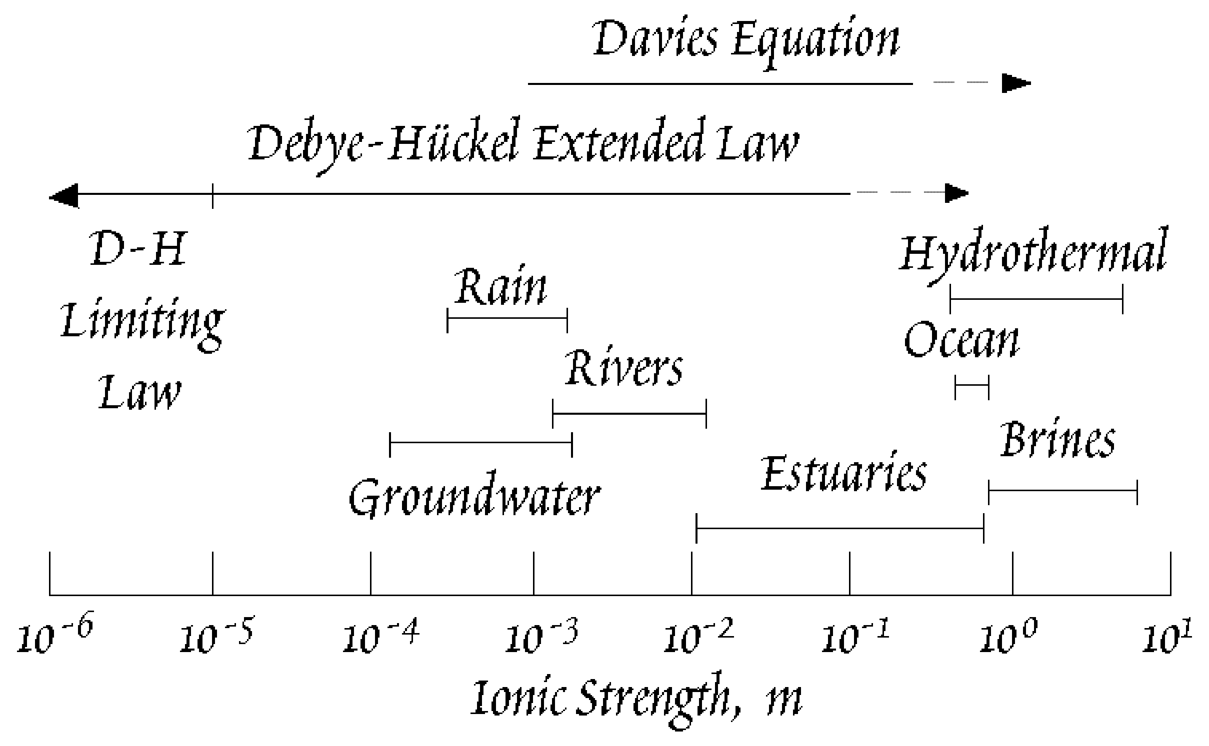
$$[A] \times \gamma_i = \{A\}$$

Activity coeffizient

Activity coefficients vs. Ionic Strength



Ionic strength of natural electrolytes



Ionic strength of natural electrolyte solutions and the applicability of the Debye-Hückel and Davies equations.

Chemical Equilibrium

Forward Rate

Reactants $\rightleftharpoons$ Products

Backward Rate

$$aA + bB \quad \leftrightarrow \quad cC + dD$$

The Law of mass action

Consider the reaction:

$$\mathbf{aA + bB \leftrightarrow cC + dD}$$

- **Where a,b, c and d are the molar amounts of compounds A, B, C and D, respectively. At equilibrium it must be true that:**

$$\boxed{K = \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b} = \text{constant}}$$

- **Thus, if we, for example, increase a_A, then to maintain equilibrium, the reaction must shift to the right so that the activities of the reactants decrease and the activities of the products increase, keeping *K* constant. This is an example of Le Chatlier's Principle.**

Solubility product

- The equilibrium constant for a reaction of the type:

$$CaSO_{4(s)} \leftrightarrow Ca^{2+} + SO_4^{2-}$$

- is called also solubility product (K_{S0}). The K_{S0} can be calculated according to:

$$\boxed{K_{S0} = \frac{a_{Ca^{2+}} a_{SO_4^{2-}}}{a_{CaSO_4(s)}} = a_{Ca^{2+}} a_{SO_4^{2-}}}$$

The ion activity product (IAP)

Consider once again the reaction:

$$\mathbf{CaSO_{4(s)} \leftrightarrow Ca^{2+} + SO_4^{2-}}$$

- **The equilibrium constant is expressed in terms of the activities of the reactants and products *at equilibrium*:**

$$K_{S0} = \left(a_{Ca^{2+}}\right)_{equil}\left(a_{SO_4^{2-}}\right)_{equil}$$

- **However, a real solution may or may not be in equilibrium. The *ion activity product* (*IAP*) or *reaction quotient* (*Q*) has the same form as the equilibrium constant, but involves the *actual* activities:**

$$IAP = Q = \left(a_{Ca^{2+}}\right)_{actual}\left(a_{SO_4^{2-}}\right)_{actual}$$

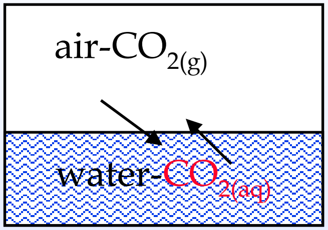
The saturation index

- **The saturation index (SI) is defined according to:**

$$SI = \log\left(\frac{IAP}{K_{S0}}\right)$$

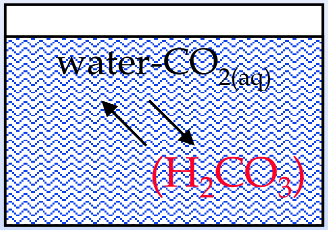
- **If $IAP = K_{S0}$, then SI = 0, and the water is saturated with respect to the mineral.**
- **If $IAP < K_{S0}$, then SI < 0, and the water is undersaturated with respect to the mineral.**
- **If $IAP > K_{S0}$, then SI > 0, and the water is supersaturated with respect to the mineral.**

Carbonate system - Dissolved carbon dioxide



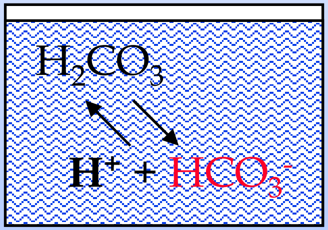
Water at the surface of the Earth inevitably contains dissolved CO2, either as a result of equilibration with the atmosphere or because of respiration by organisms.

$$CO_{2(g)} + H_2O \rightleftarrows CO_{2(aq)} \qquad [CO_{2(aq)}] = p_{CO_2} K_H$$



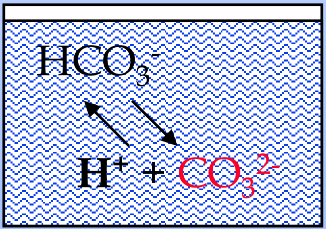
CO_2 reacts with water to form carbonic acid:

$$(CO_{2(aq)} + H_2O \rightleftarrows H_2CO_3)$$



Some of the carbonic acid dissociates to form bicarbonate and hydrogen ions:

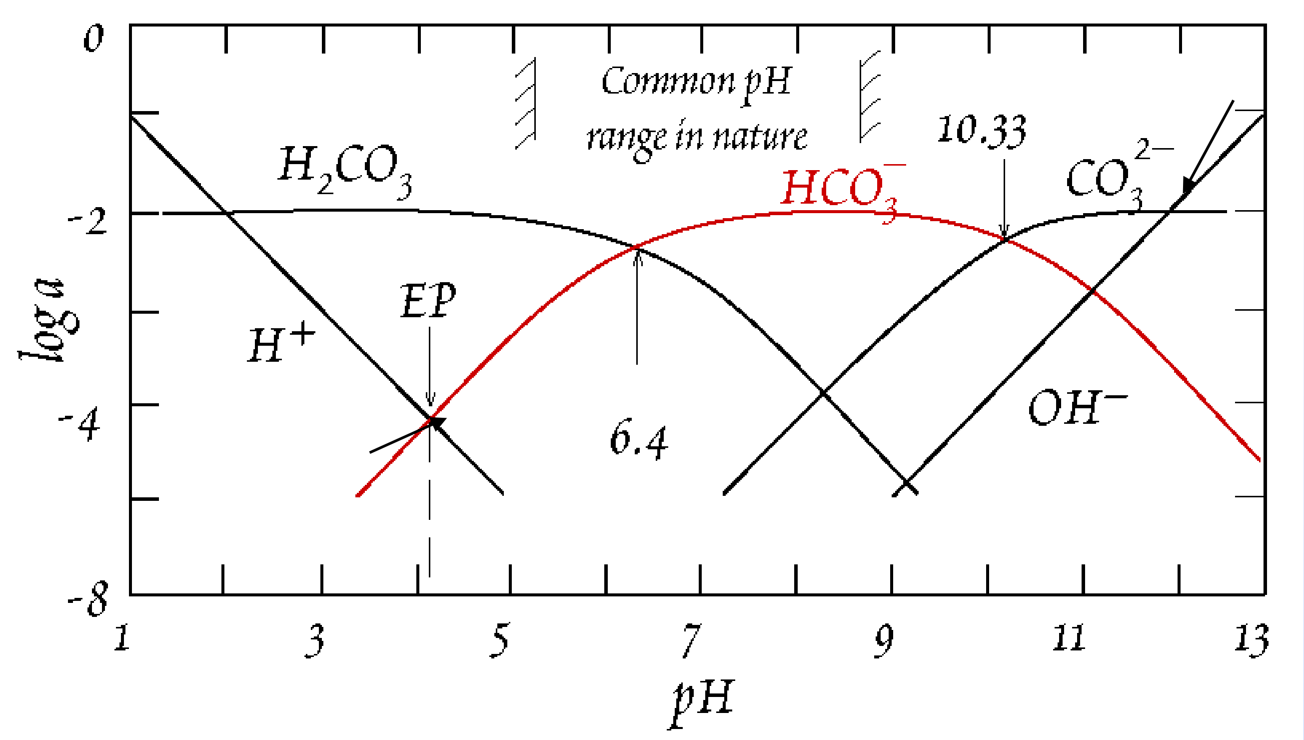
$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad [HCO_3^-] = \frac{K_1K_Hp_{CO_2}}{[H^+]}$$



Some of the bicarbonate will dissociate to an additional hydrogen ion and a carbonate ion:

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \qquad [CO_3^{2-}] = \frac{K_2K_1K_Hp_{CO_2}}{[H^+]^2}$$

Carbonate System - *Equilibrium Diagramm*



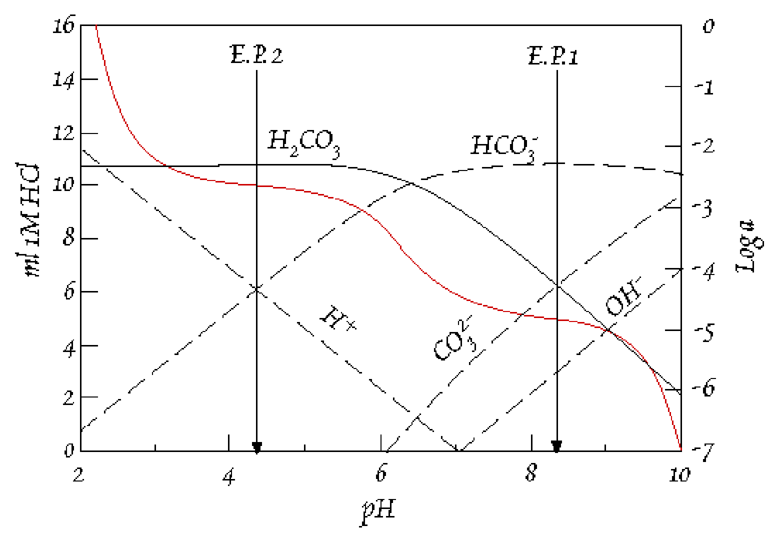
Activities of different species in the carbonate system as a function of p assuming $\Sigma CO_2 = 10^{-2}$. After Drever (1988).

Drever, J. I., 1988. The Geochemistry of Natural Waters, Prentice Hall, Englewood Cliffs, 437 p.

Carbonate System - Alkalinity and titration curve

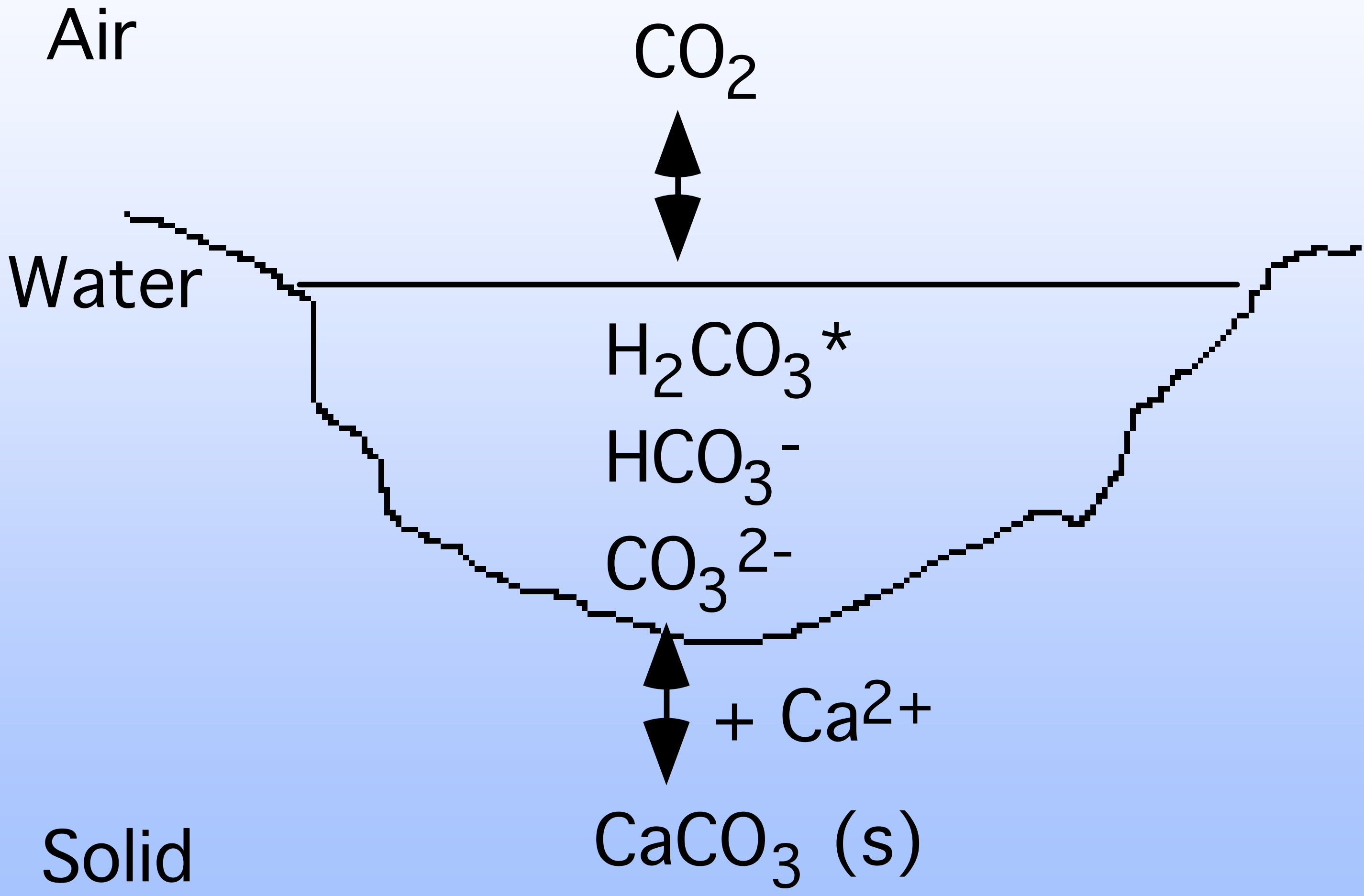
Alkalinity is a measure of acid-neutralizing capacity of a solution and is defined as the sum of the concentration (in equivalents) of bases that are titratable with strong acid.

$$[\mathrm{Alk}] = [\mathrm{HCO_3^-}] + 2\,[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] - [\mathrm{H^+}]$$



Main reaction: $\mathrm{HCO_3^-} + \mathrm{H^+} + \mathrm{Cl^-}$ ➔ $\mathrm{CO_2}\uparrow + \mathrm{H_2O} + \mathrm{Cl^-}$

Dissolution and Precipitation



Air

CO_2

Water

$H_2CO_3^*$

HCO_3^-

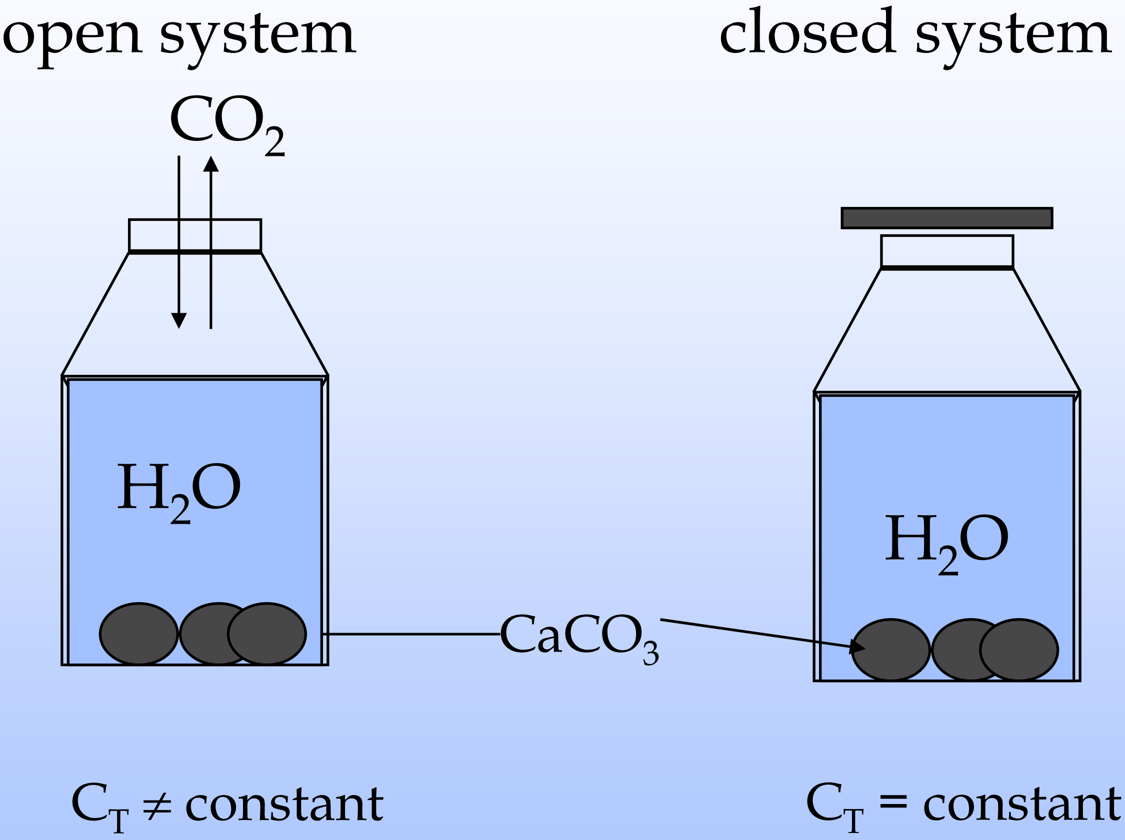
CO_3^{2-}

$+ Ca^{2+}$

Solid

$CaCO_3$ (s)

Dissolution and Precipitation - *Dissolution of Carbonates*



open system

closed system

CO_2

H_2O

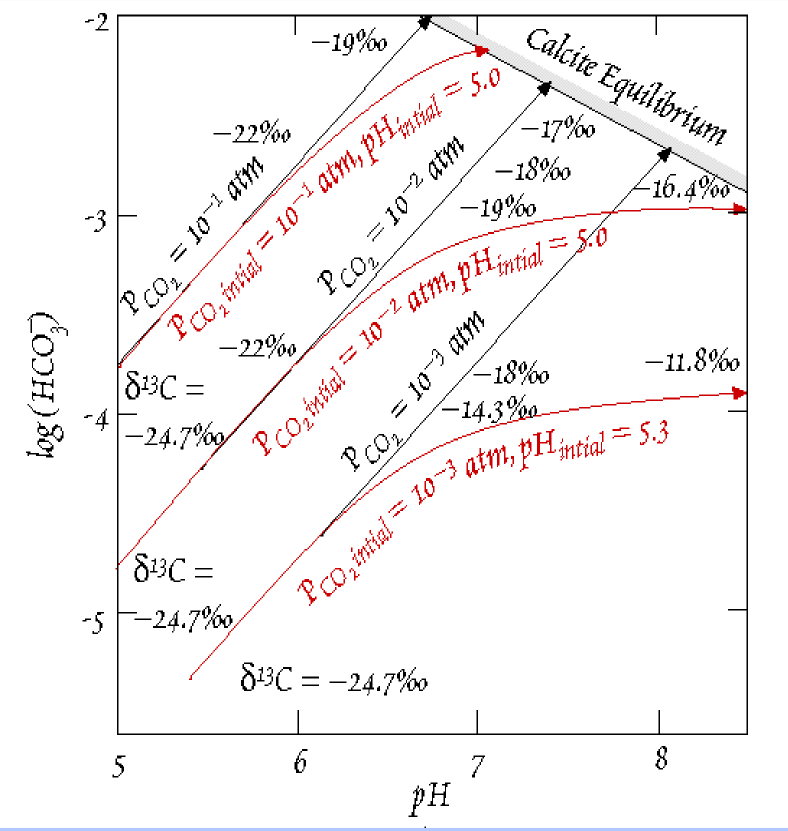
H_2O

$CaCO_3$

$C_T \neq$ constant

$C_T =$ constant

Dissolution and Precipitation *- Comparison - Open and Closed system*



Open system reach calcit saturation at higher pH and lower [HCO$_3^-$] than closed system that initally equilibrate with the same p_{CO_2}

Adsorption

- **Is solubility the only control on solute concentrations?**
  - **The answer is no! Solubility often controls the concentrations of major solutes such as Si, Ca, and Mg, and some minor or trace solutes such as Al and Fe.**
  - **However, for many trace elements, sorption processes maintain concentrations below saturation with respect to minerals.**
  - **In other words, sorption is a means to remove solutes even when the solution is undersaturated with any relevant solids.**

Adsorption

- **In general, solutes interact with mineral surfaces because the latter have acquired electrical charge.**
- **Two ways to acquire charge:**
  - **Substitution for a cation in a mineral by one of lesser positive charge. This type of charge is considered to be *fixed*.**
  - **Reactions involving functional groups on the mineral surface and ions in solution (surface complexation). This type of charge is variable and dependent on solution pH.**

Adsorption - Clays (Ion-exchange properties)

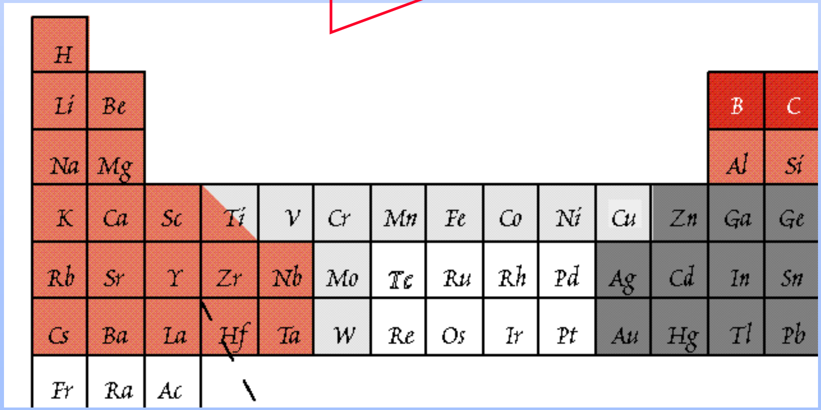
- One of the most important important properties of clays is their capacity for ion exchange.

- The ability of a substance to exchange ions is called the ion exchange capacity and is generally measured in equivalents or milliequivalents (meq).

$$X_{\text{clay}} + Y^+ \rightleftarrows Y_{\text{clay}} + X^+ \quad \Longrightarrow \quad \frac{a_{Y\text{-clay}}}{a_{X\text{-clay}}} = K\frac{a_{Y^+}}{a_{X^+}}$$

$Rb^+ > K^+ > Na^+ > Li^+$

$Na^+ < Mg^{2+} < Al^{3+}$

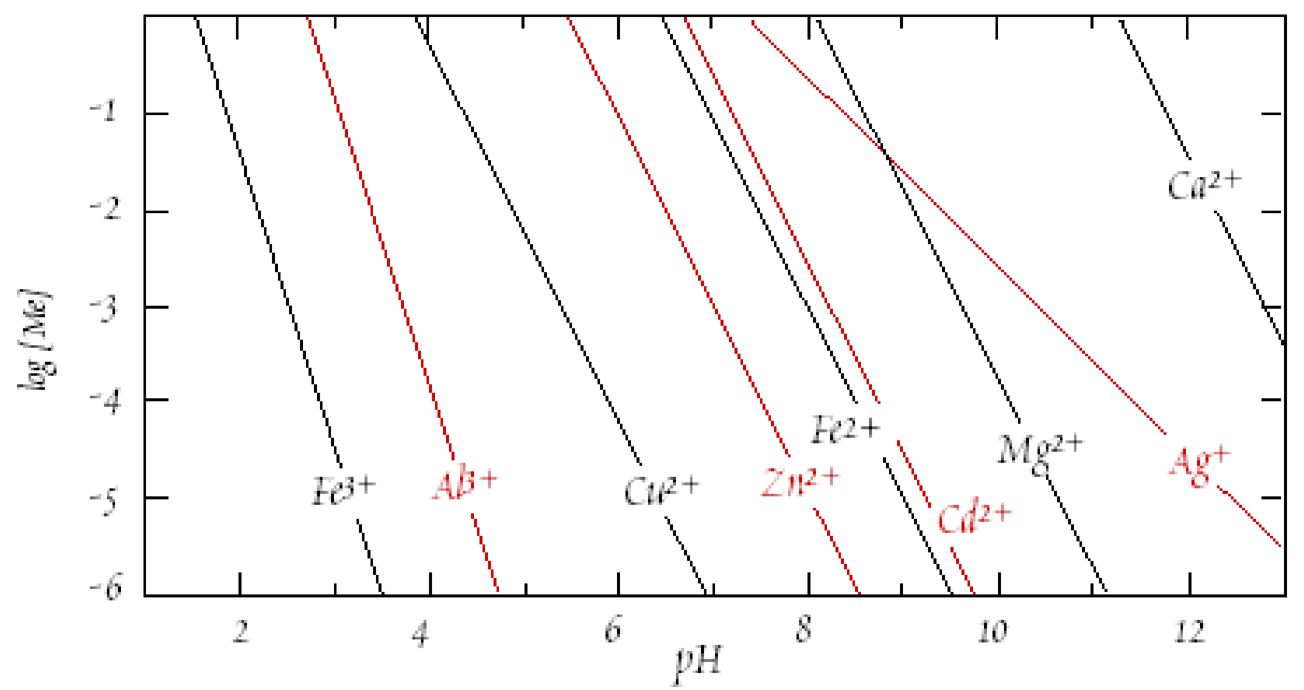


H													
Li	Be											B	C
Na	Mg											Al	Si
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb
Fr	Ra	Ac											

Metal Mobility

- **Generally, in groundwater, metals are most mobile at low pH.**
- **Ignoring surface reactions, metal concentrations begin to decline when pH increases to the point where equilibrium is reached with a solid phase.**
- **The solid phases are usually metal-hydroxides, metal-sulphides or metal-carbonates.**

Solubility of metal hydroxides



Solubility of metal hydroxides as a function of pH. After Stumm and Morgan (1981).

Redox-Reactions

*Many elements exist in nature in more than one valence state. The valence state of an element can significantly affect its geochemical behavior. Because of their abundance, **carbon, nitrogen, sulfur, iron and manganese** are the most important of these.*

$$\mathrm{Ox} + e^{-} \rightleftarrows \mathrm{Red}$$

Oxidation is the loss of electrons, reduction is the gain of electrons

Redox-Reactions - *Nernst Equation and Electron activity*

$$E_H = E_0 + \frac{2{,}3\ RT}{nF} \log K$$

E_H - Redoxpotential
n - number of electrons
F - Farady constant
R - Gas - constant

Consider the reaction:

$$Fe^{3+}_{aq} + e^{-} \rightleftarrows Fe^{2+}_{aq}$$

If we were to express the equilibrium constant for this reaction, we would write:

$$K = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}\, a_{e^{-}}}$$

Alternative Representation of Redox State: **pε**

Thus we might find it convenient to define an activity for the electron. For this reason, chemists have defined an analogous parameter to pH, called pε.

$$p\varepsilon = Eh/(2{,}3RTF\ \text{-}1) = 16.9Eh$$

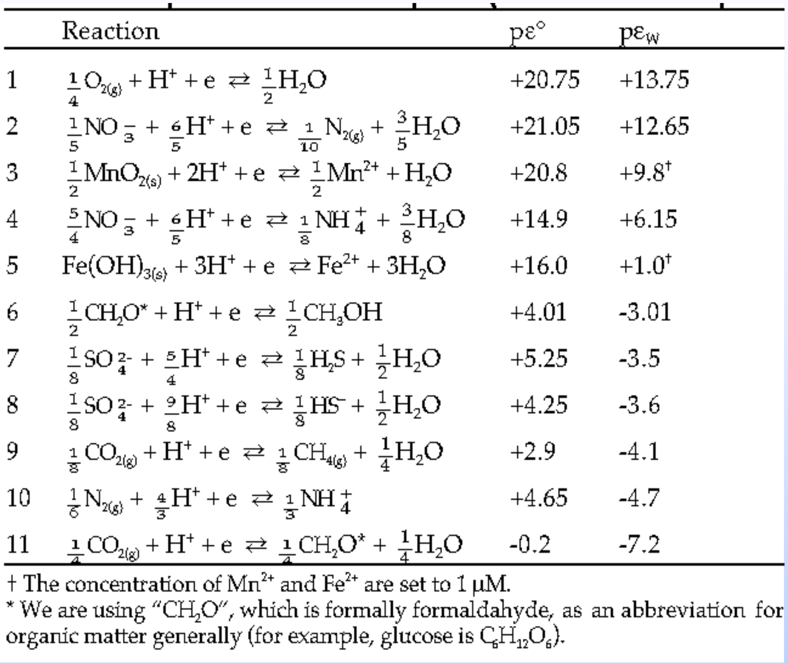
pε is the negative log of the activity of electrons in solution.

Redox-reactions - Aquatic redox couples

The table lists the pε° of the most important redox half reactions in aqueous systems. Also listed are $p\varepsilon_W$ values. $p\varepsilon_W$ is the pε° when the concentration of H^+ is set to 10^{-7} (pH = 7). The relation between pε° and $p\varepsilon_W$ is simply:

$$\mathbf{p\varepsilon_W = p\varepsilon^\circ + \log [H^+]^\nu}$$

Reactions are ordered by decreasing $p\varepsilon_W$ from strong oxidants at the top to strong reductants at the bottom. In this order, each reactant can oxidize any product below it in the list, but not above it.



	Reaction	pε°	$p\varepsilon_W$
1	$\frac{1}{4}O_{2(g)} + H^+ + e \rightleftarrows \frac{1}{2}H_2O$	+20.75	+13.75
2	$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e \rightleftarrows \frac{1}{10}N_{2(g)} + \frac{3}{5}H_2O$	+21.05	+12.65
3	$\frac{1}{2}MnO_{2(s)} + 2H^+ + e \rightleftarrows \frac{1}{2}Mn^{2+} + H_2O$	+20.8	+9.8†
4	$\frac{5}{4}NO_3^- + \frac{6}{5}H^+ + e \rightleftarrows \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+14.9	+6.15
5	$Fe(OH)_{3(s)} + 3H^+ + e \rightleftarrows Fe^{2+} + 3H_2O$	+16.0	+1.0†
6	$\frac{1}{2}CH_2O^* + H^+ + e \rightleftarrows \frac{1}{2}CH_3OH$	+4.01	-3.01
7	$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e \rightleftarrows \frac{1}{8}H_2S + \frac{1}{2}H_2O$	+5.25	-3.5
8	$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e \rightleftarrows \frac{1}{8}HS^- + \frac{1}{2}H_2O$	+4.25	-3.6
9	$\frac{1}{8}CO_{2(g)} + H^+ + e \rightleftarrows \frac{1}{8}CH_{4(g)} + \frac{1}{4}H_2O$	+2.9	-4.1
10	$\frac{1}{6}N_{2(g)} + \frac{4}{3}H^+ + e \rightleftarrows \frac{1}{3}NH_4^+$	+4.65	-4.7
11	$\frac{1}{4}CO_{2(g)} + H^+ + e \rightleftarrows \frac{1}{4}CH_2O^* + \frac{1}{4}H_2O$	-0.2	-7.2

† The concentration of Mn^{2+} and Fe^{2+} are set to 1 μM.

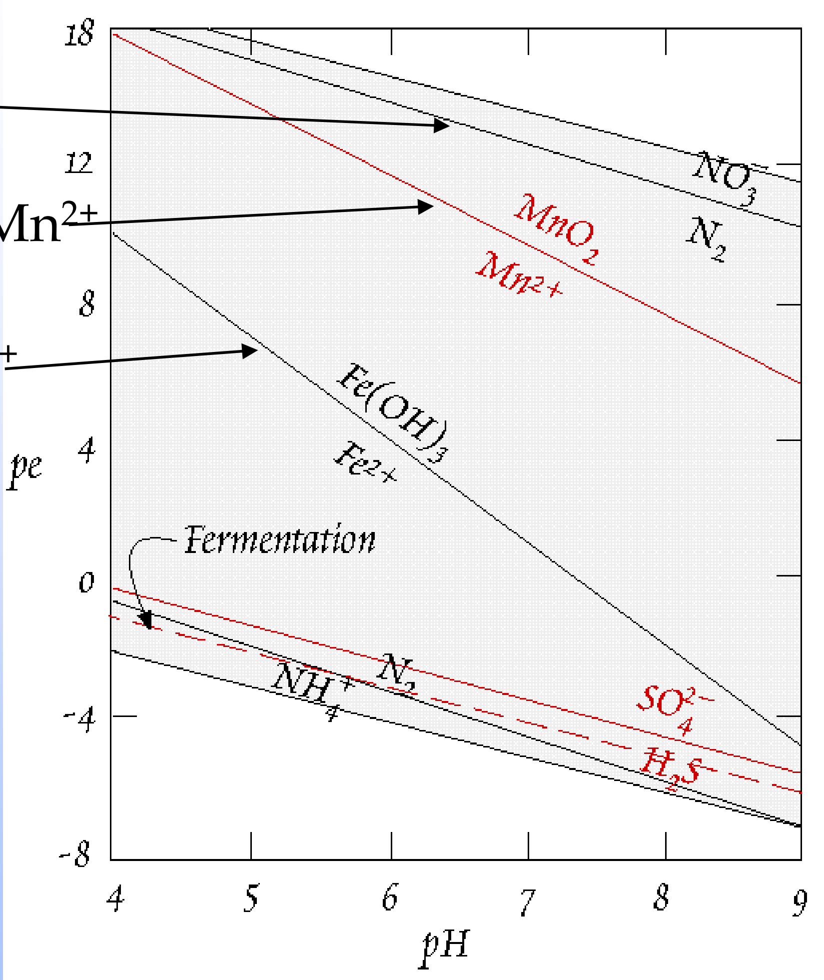
* We are using "CH_2O", which is formally formaldahyde, as an abbreviation for organic matter generally (for example, glucose is $C_6H_{12}O_6$).

Thus sulfate can oxidize methane to CO_2, but not ferrous iron to ferric iron. Redox reactions in aqueous sys-tems are often biologically mediated.

Redox-reactions- Microorganisms

- **Oxidation-reduction reactions differ from many other reactions because they are frequently mediated by microorganisms.**
- **The role of the microorganisms is usual to act as a catalyst and increase the rate of reaction.**
- **Microbial films on grains and fracture surfaces use redox reactions as a source of energy.**

Redox-reactions - *Biogeochemical redox-reactions*

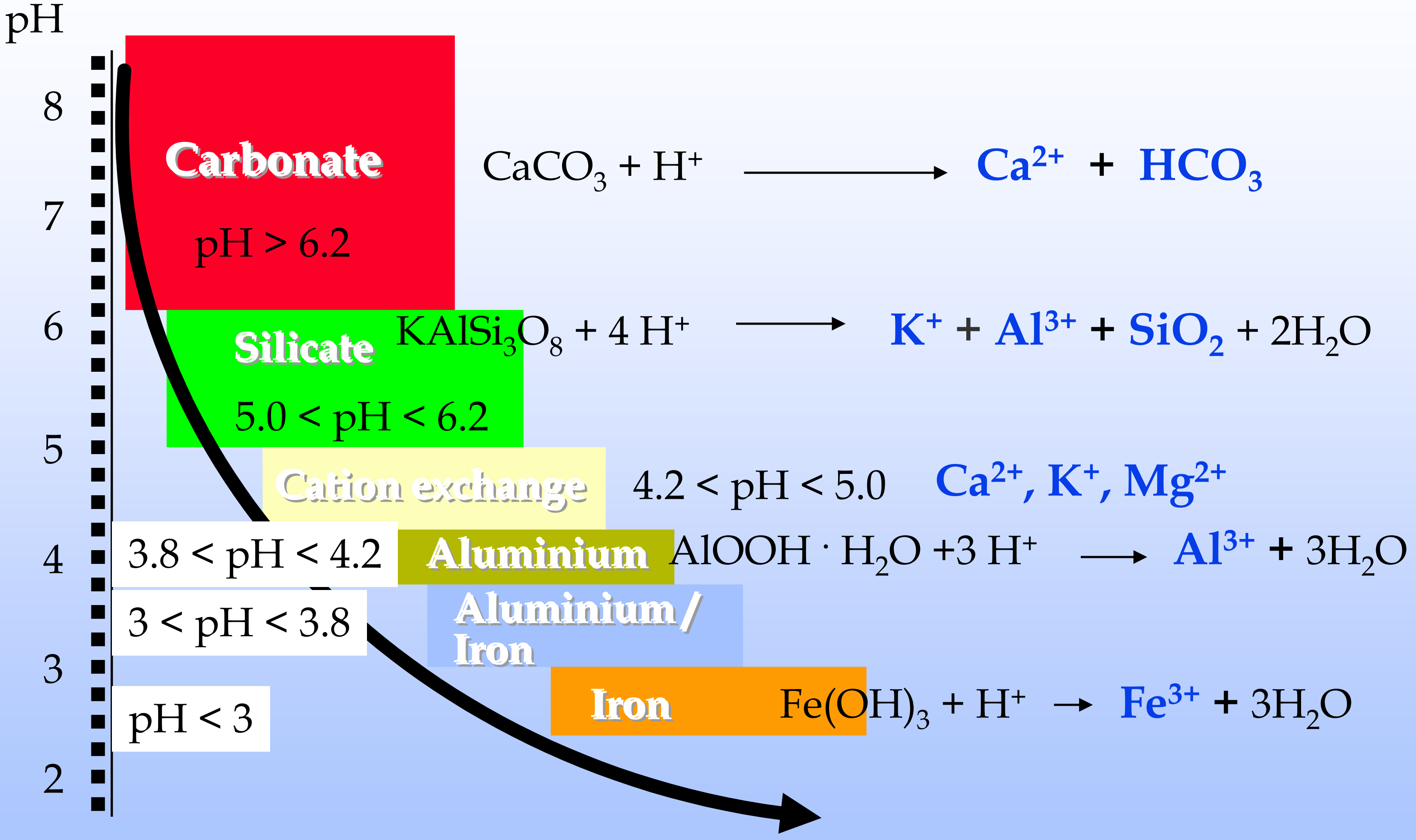


denitrification

Mn^{4+} will be reduced to Mn^{2+}

Fe^{3+} will be reduced to Fe^{2+}

Buffer-systems in soil



Carbonate

pH > 6.2

$CaCO_3 + H^+ \longrightarrow \mathbf{Ca^{2+} + HCO_3}$

Silicate

$5.0 < pH < 6.2$

$KAlSi_3O_8 + 4 H^+ \longrightarrow \mathbf{K^+ + Al^{3+} + SiO_2} + 2H_2O$

Cation exchange

$4.2 < pH < 5.0$ $\mathbf{Ca^{2+}, K^+, Mg^{2+}}$

$3.8 < pH < 4.2$ **Aluminium** $AlOOH \cdot H_2O + 3 H^+ \longrightarrow \mathbf{Al^{3+}} + 3H_2O$

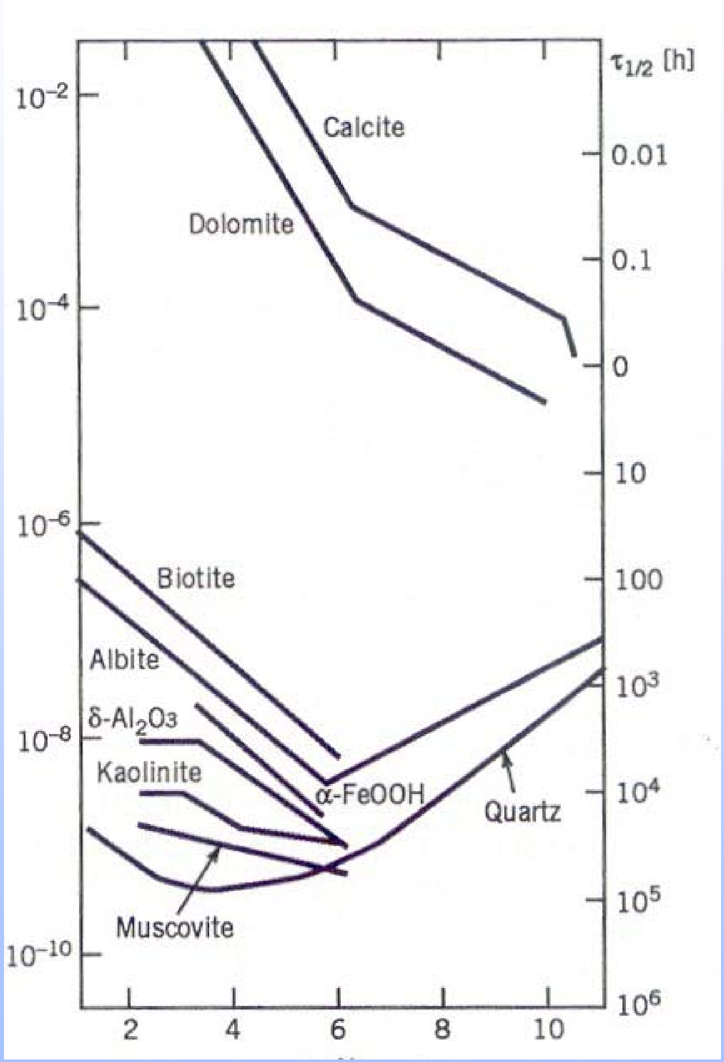
$3 < pH < 3.8$ **Aluminium / Iron**

$pH < 3$ **Iron** $Fe(OH)_3 + H^+ \rightarrow \mathbf{Fe^{3+}} + 3H_2O$

Dissolution rate of several minerals

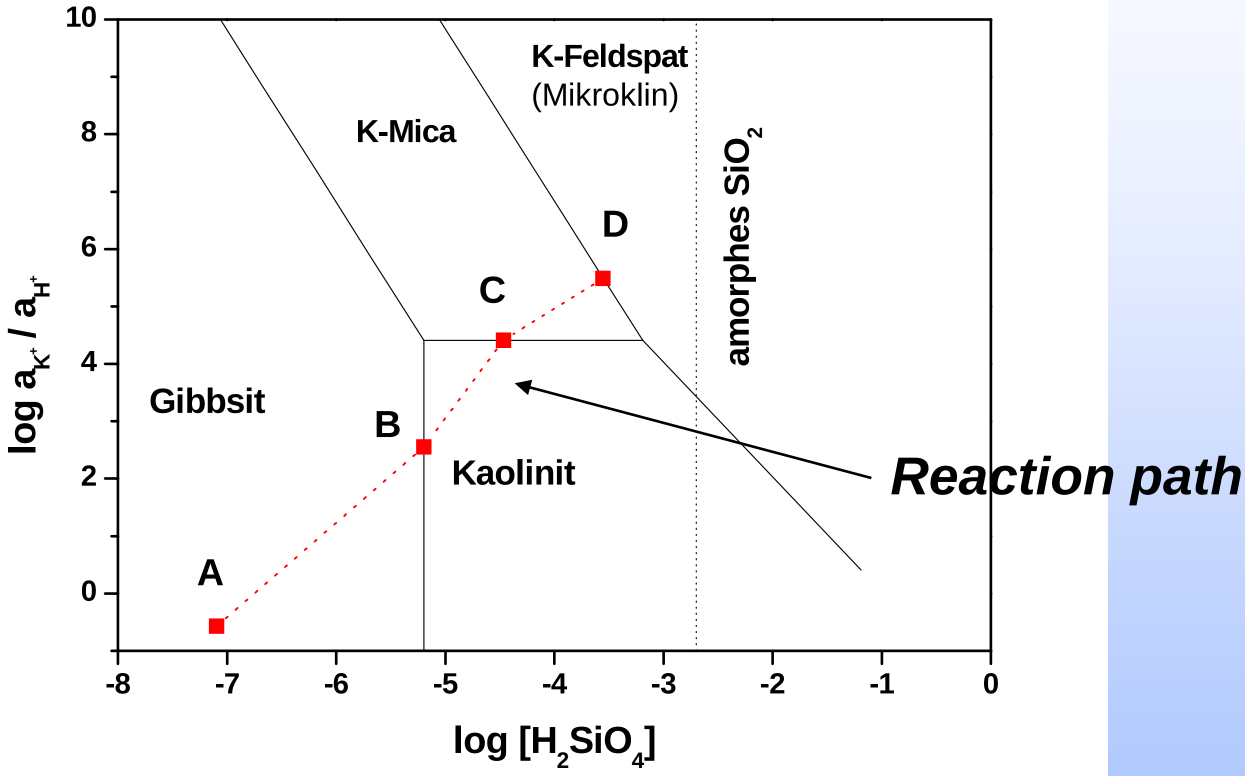
Dissolution rate

Lösungsgeschwindigkeit [Mol m^{-2} h^{-1}]



pH-Wert

Dissolution of feldspar I



Reaction path

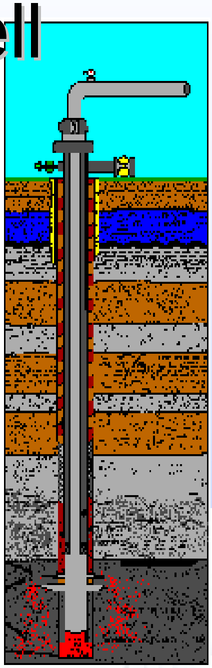
Parkhurst & Appelo, 1999

Origin of solutes

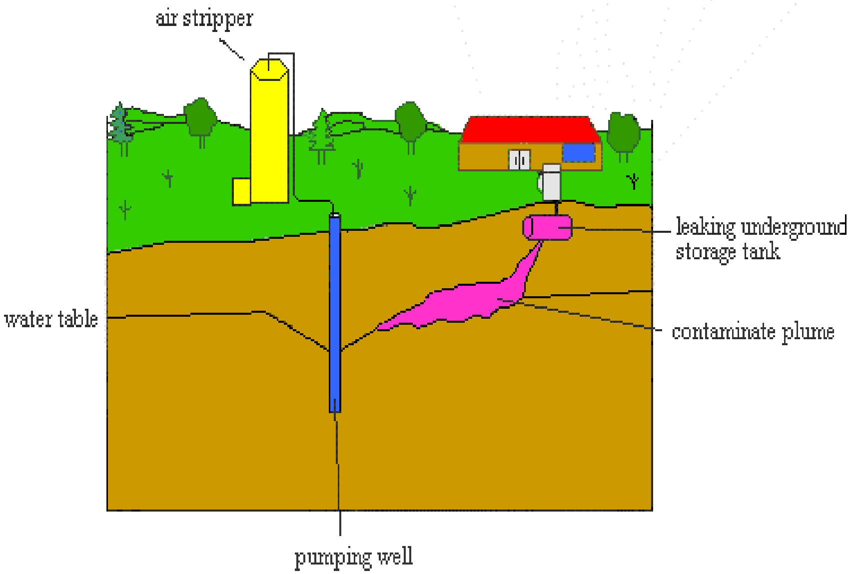
- **Atmospheric deposition**
- **Rock weathering**
- **Anthropogenic sources (fertilizer, landfills, septic tanks ...)**

Point sources - examples

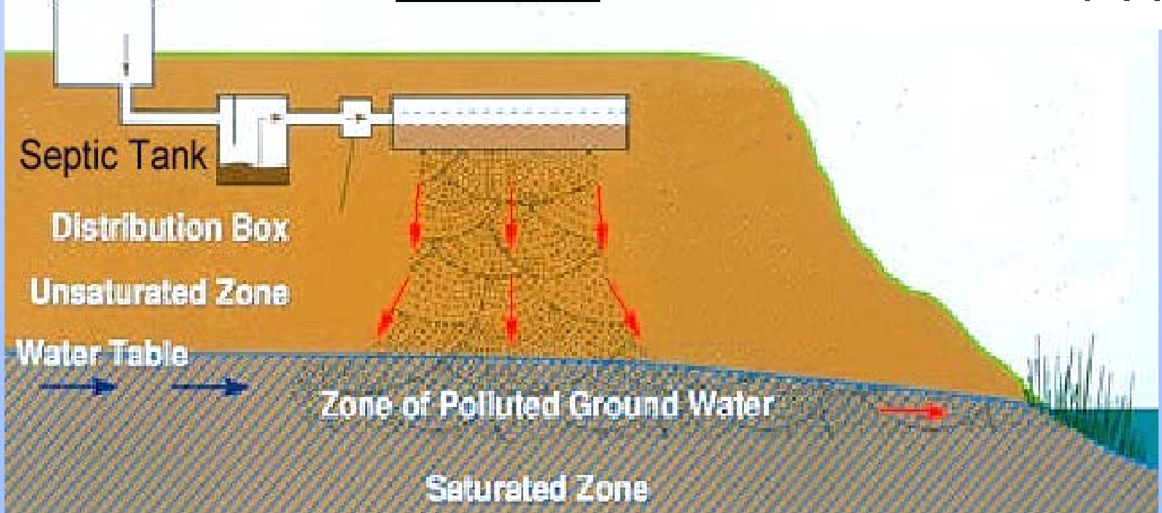
Injection well



Leaking underground storage tank



Septic tanks



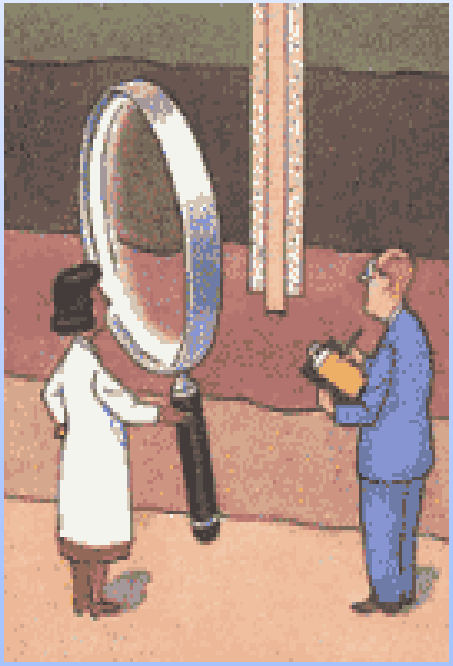
Non-point sources - examples


Pesticides


Fertilizer

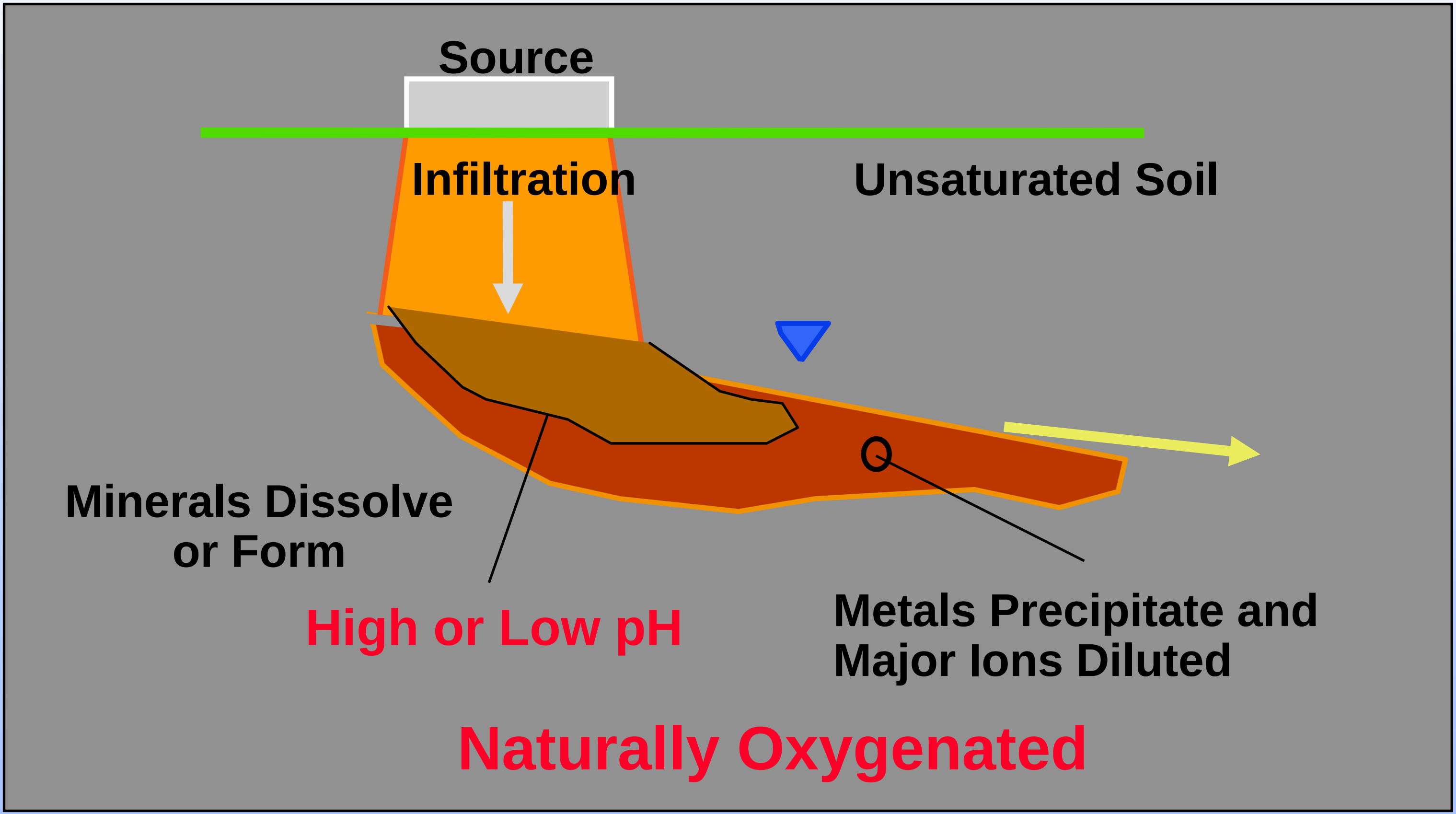
Different kinds of pollution

Basic difference between organic-rich and organic poor systems must be understood!



Anatomy of Inorganic Contamination

Examples: Coal fly ash landfills, salt storage facilities, acid/base spill, brine disposal.



Source

Infiltration

Unsaturated Soil

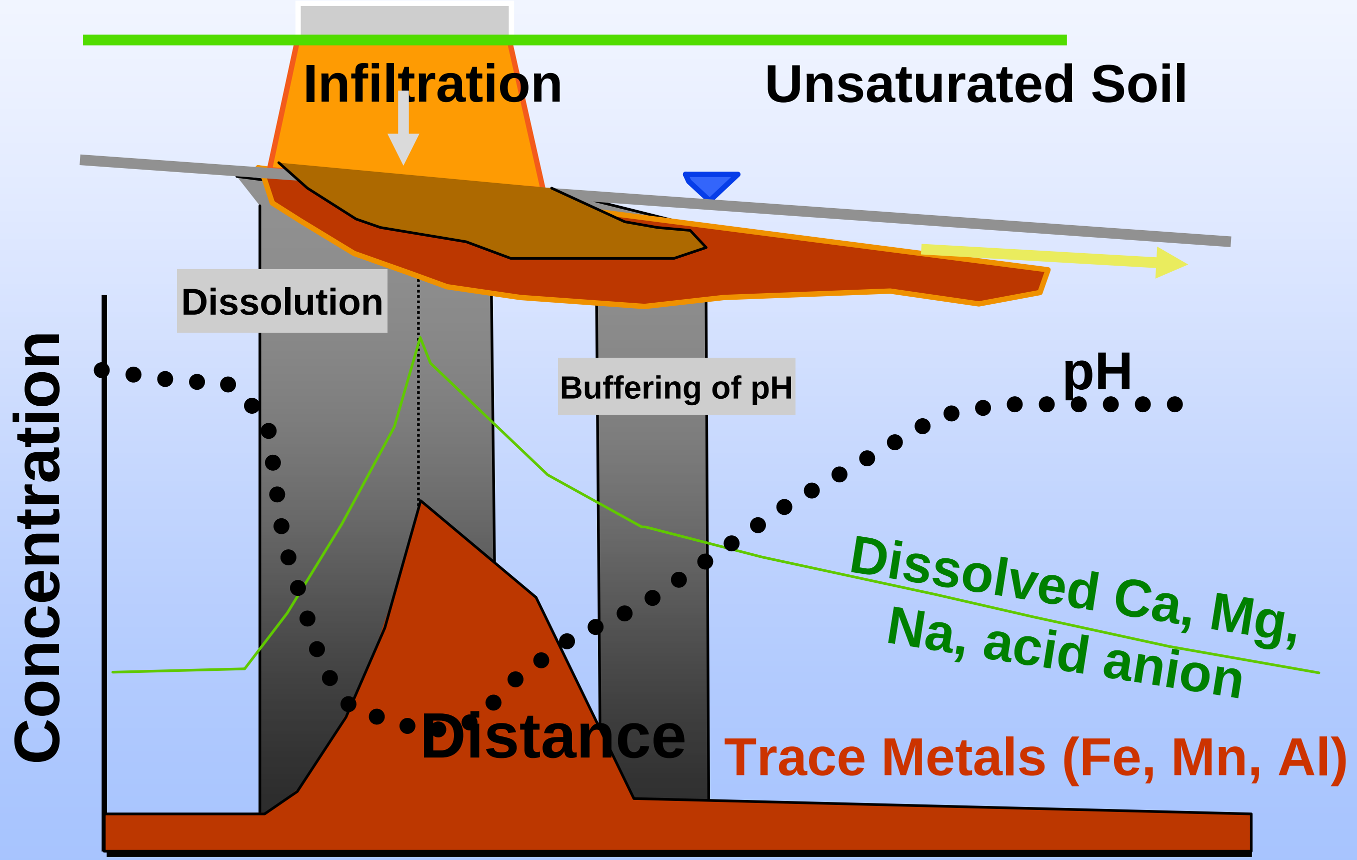
Minerals Dissolve or Form

High or Low pH

Metals Precipitate and Major Ions Diluted

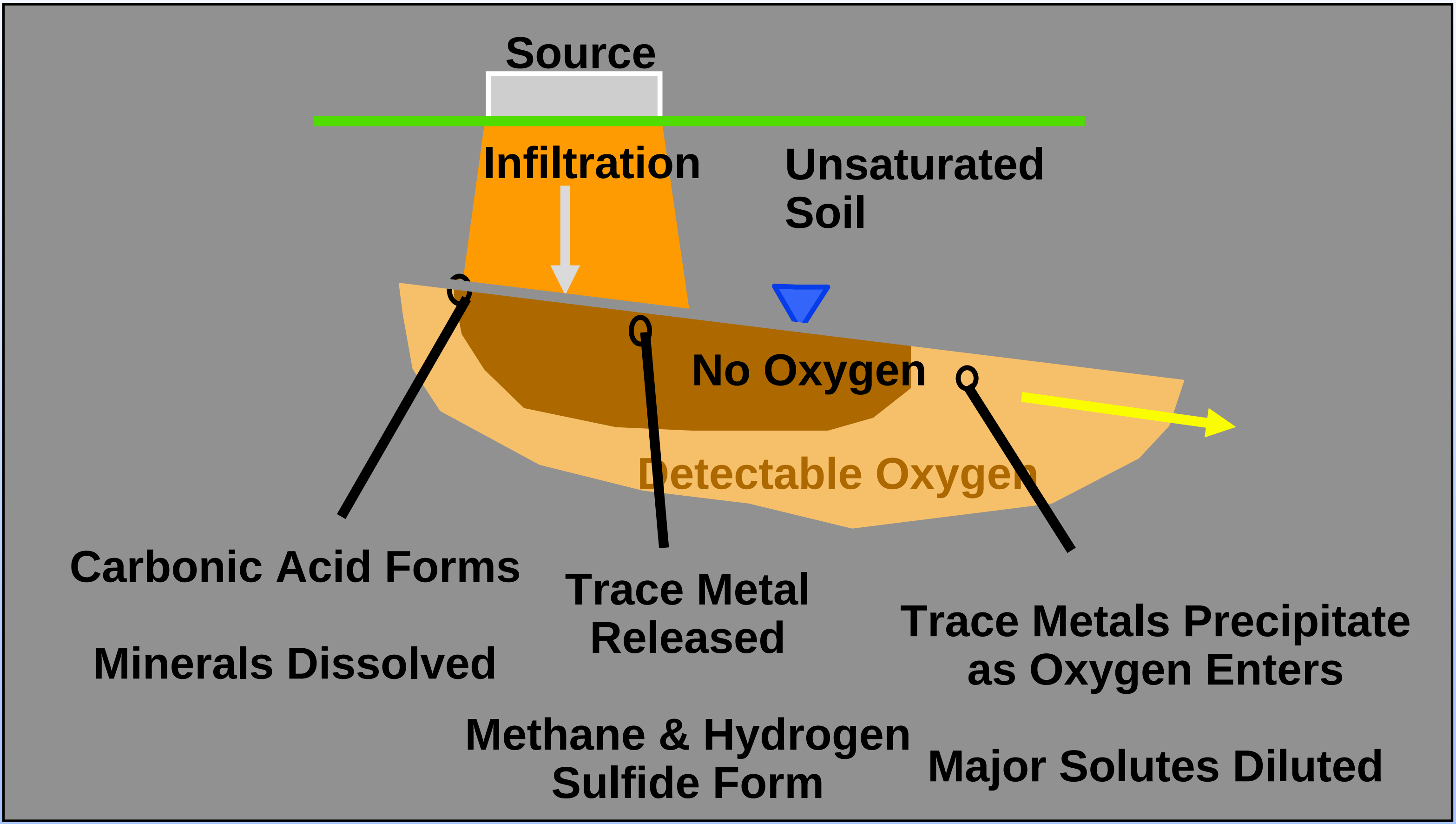
Naturally Oxygenated

Predictable Chemical Changes (Acid)

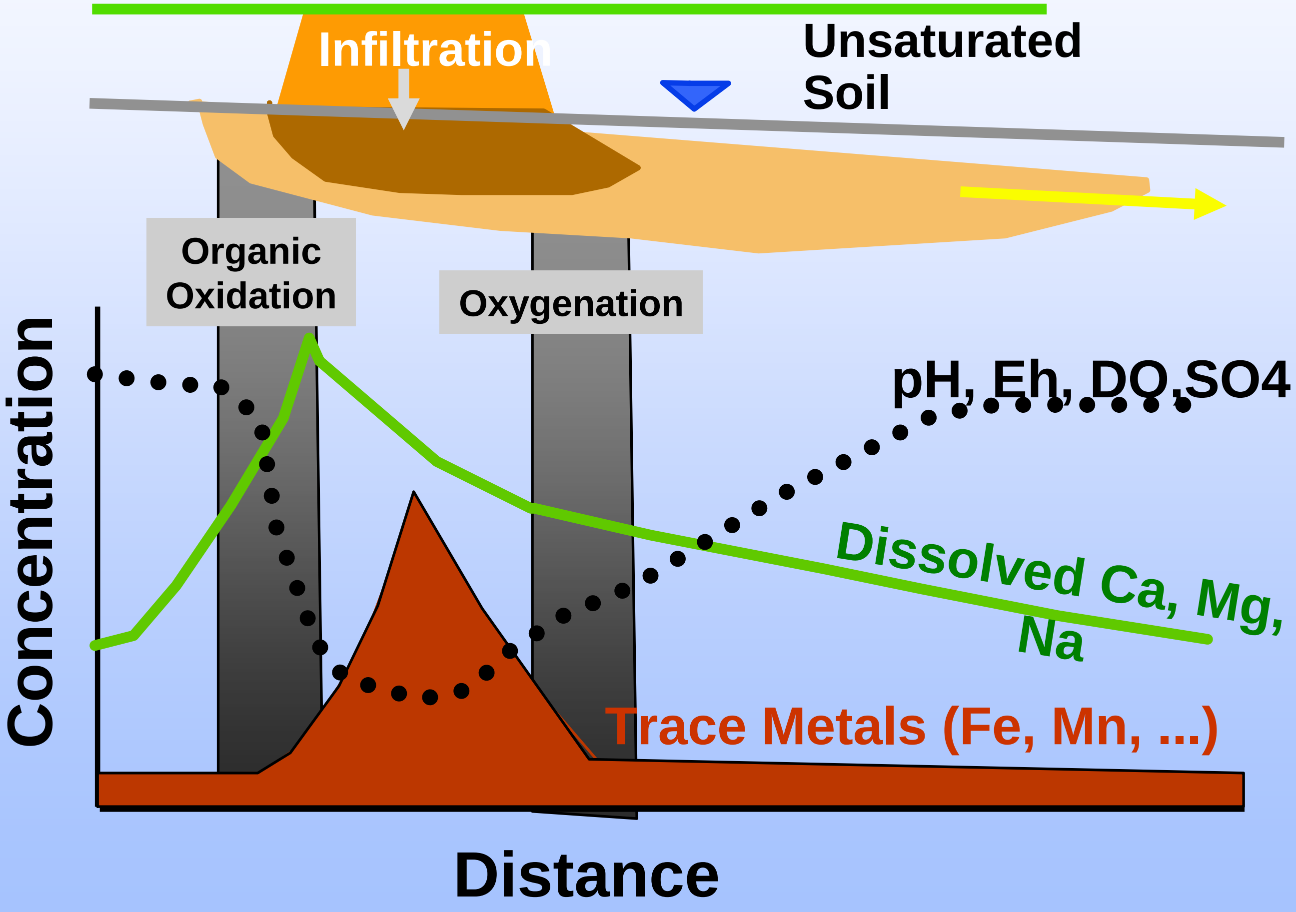


Anatomy of Organic Contamination

Examples: Landfills, gasoline and oil spills, sewage.



Predictable geochemical changes



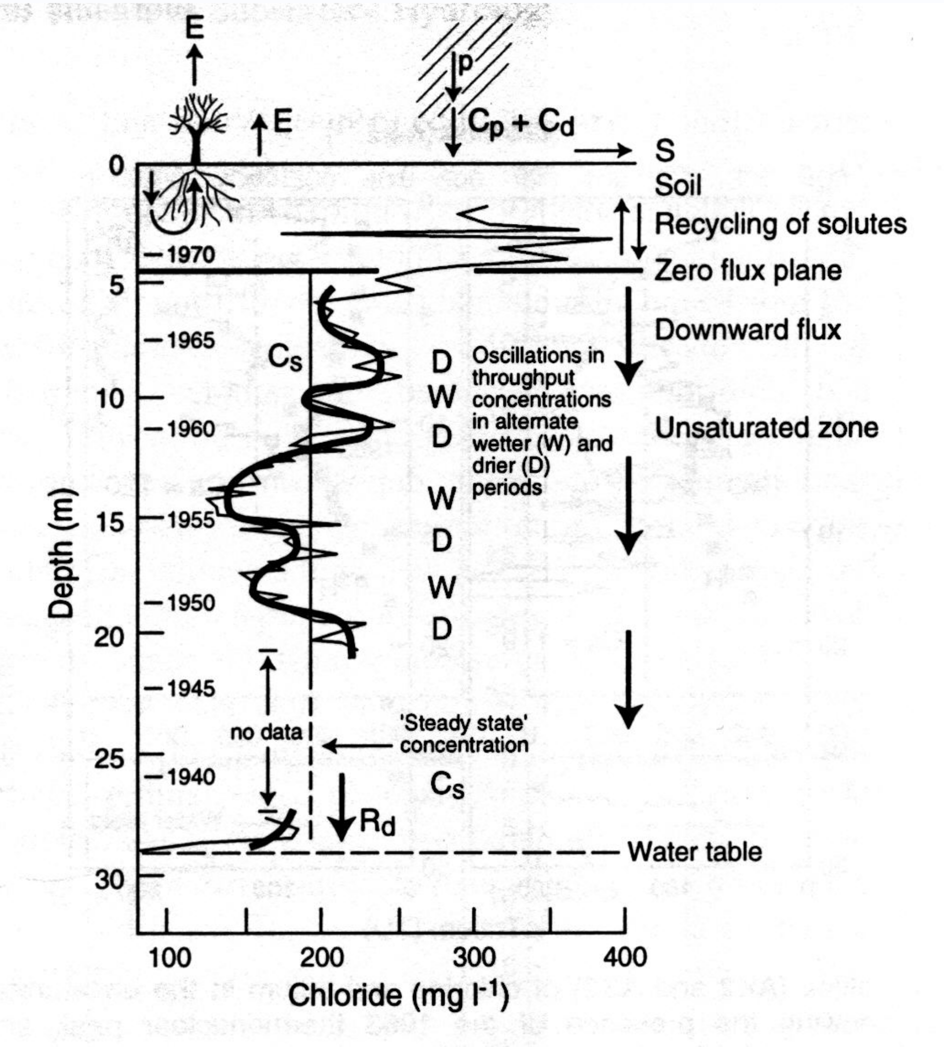
Hydrochemical applications

- **Sources of recharge**
- **Mechanism of recharge and discharge**
- **Surface groundwater interaction**
- **Mixing of different waters**
- **Salinisation of groundwater**
- **Seawater intrusion**
- **Identification of anthropogenic impact to groundwater**
- **….**

Some examples

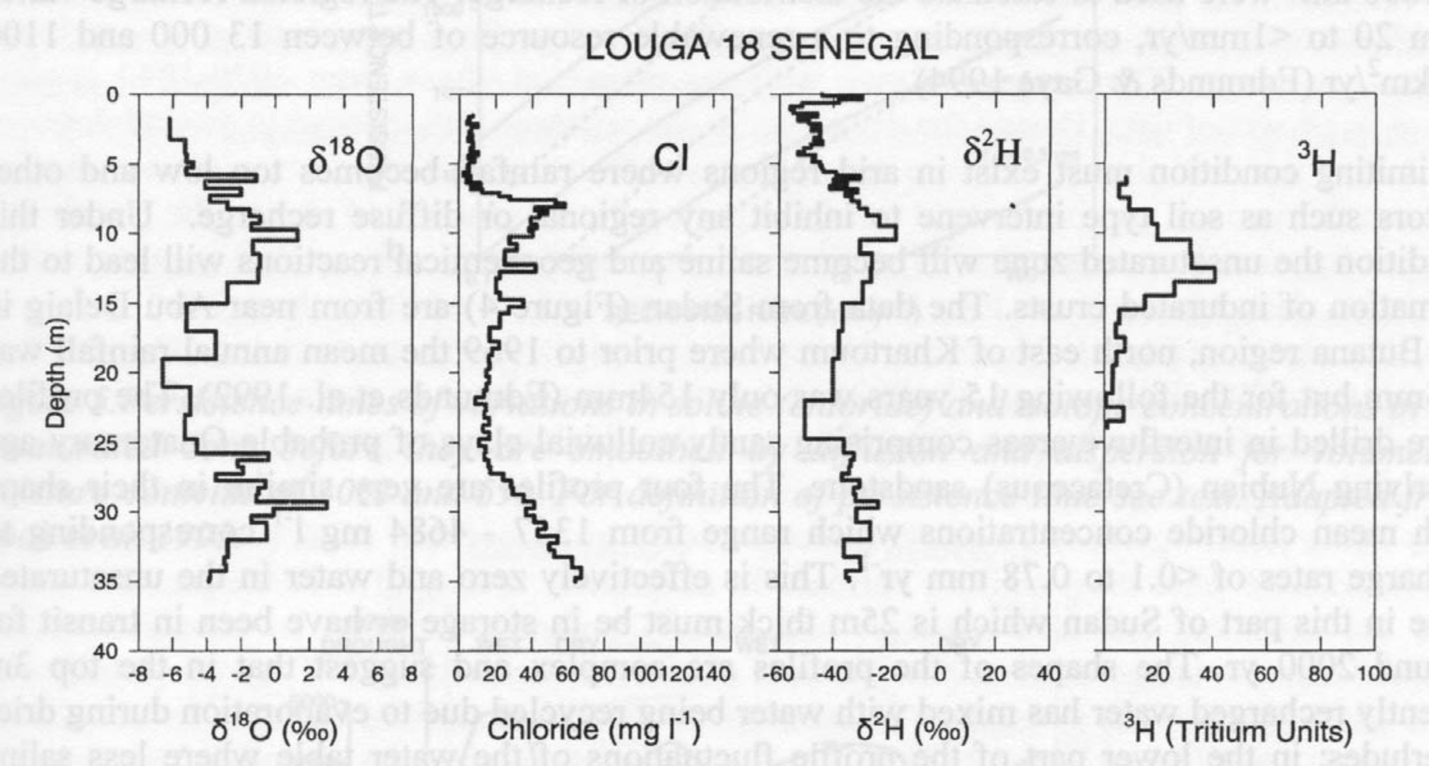
- **Conservative ions**
  - **Recharge measurement using chloride**
  - **Estimation of mixing ratios**
  - **Chloride movement in the unsaturated zone**
- **Non-conservative ions**

Recharge measurement using chloride



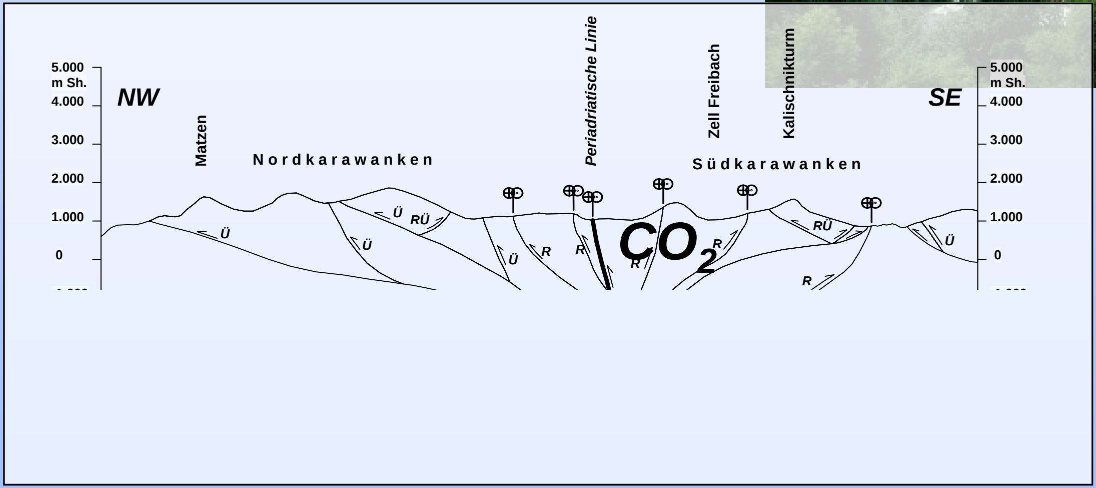
Edmunds et al. (1988)

Soil profils of chloride and environmental isotopes

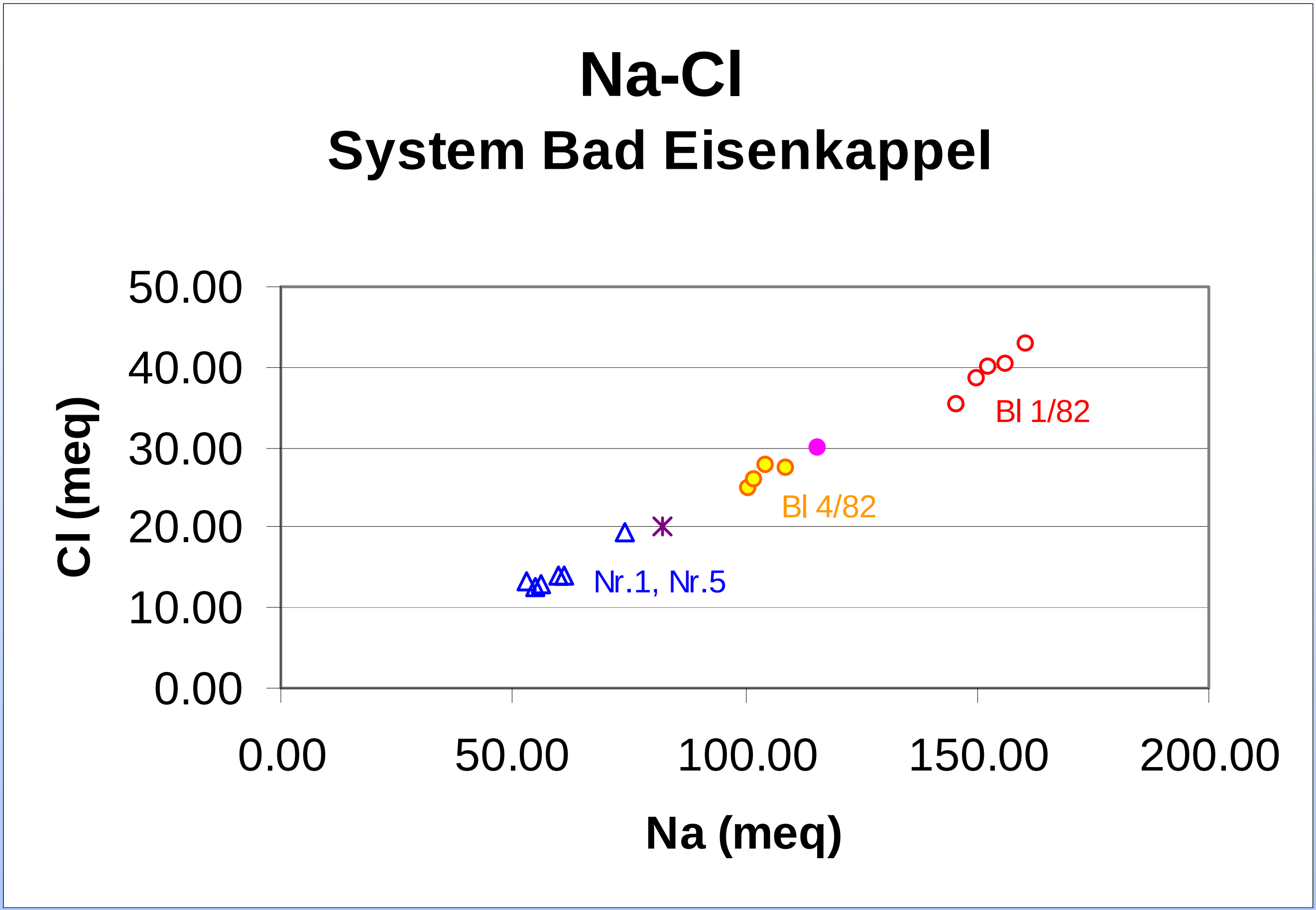


Edmunds and Gaye (1994)

Mixing of different groundwaters
Example Eisenkappel (Austria)

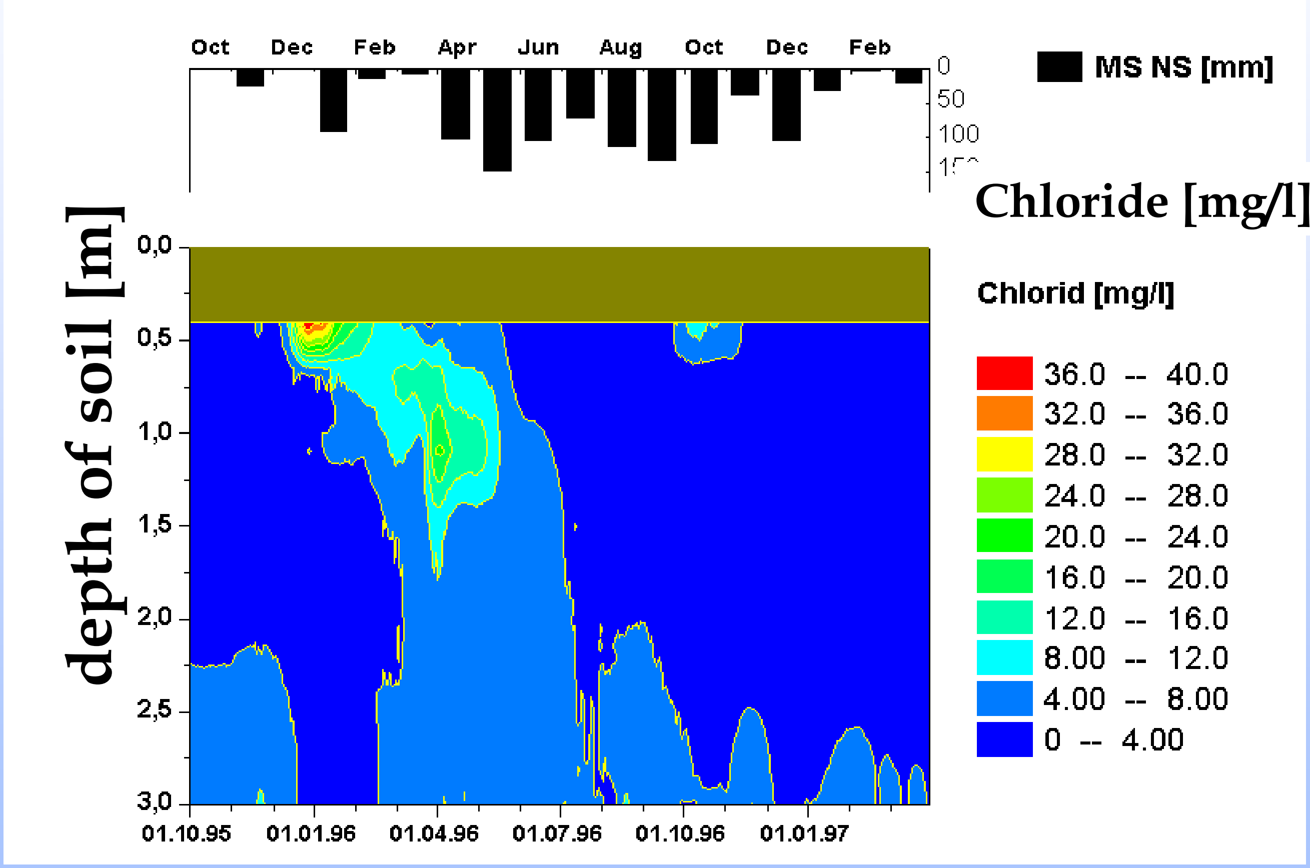


Na/Cl – ratio


Na-Cl
System Bad Eisenkappel
50.00
40.00
30.00
20.00
10.00
0.00
Cl (meq)
0.00
50.00
100.00
150.00
200.00
Na (meq)
Bl 1/82
Bl 4/82
Nr.1, Nr.5

2D-profil of chloride concentration (crop rotation 96/97)

precipitation



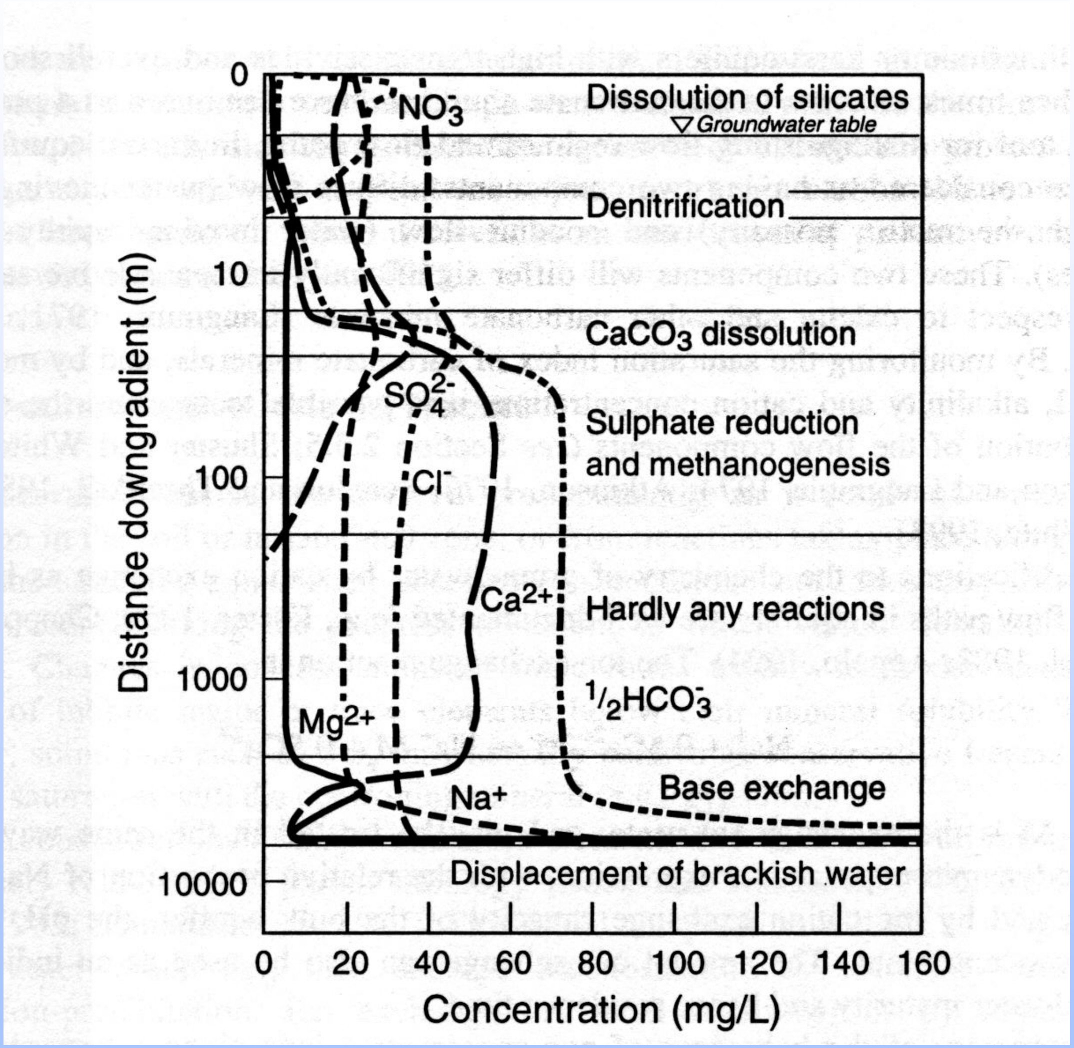
Chloride [mg/l]

depth of soil [m]

Some examples

- **Conservative ions**
  - **Recharge measurement using chloride**
  - **Estimation of mixing ratios**
  - **Chloride movement in the unsaturated zone**
- **Non-conservative ions**
  - **Behavior of non-conservative along a transect**

Distribution of major ions along a transect



Appello and Postma (1994)