

*Post Graduate Training Course On Groundwater
Tracing Techniques*

**Introduction to hydrogeochemistry
with respect to tracing**

Dr. Albrecht Leis

JOANNEUM RESEARCH

**Institute of WaterResourcesManagement
Hydrogeology and Geophysics**

email: albrecht.leis@joanneum.at

***"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>

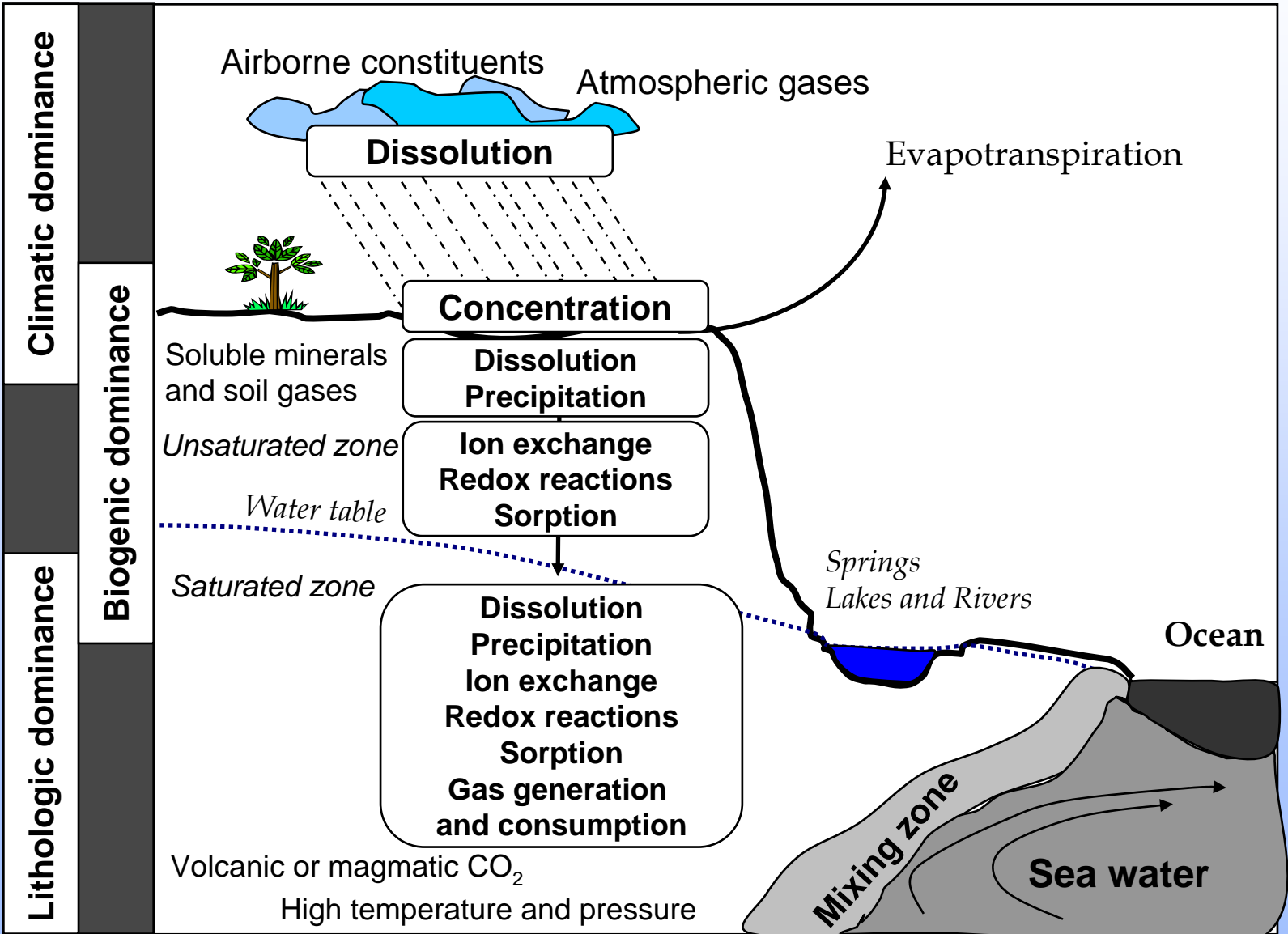
Drever, J.I.(1997): *The Geochemistry of Natural Waters*.
3rd Ed., Upper Saddle River (Prentice Hall).

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

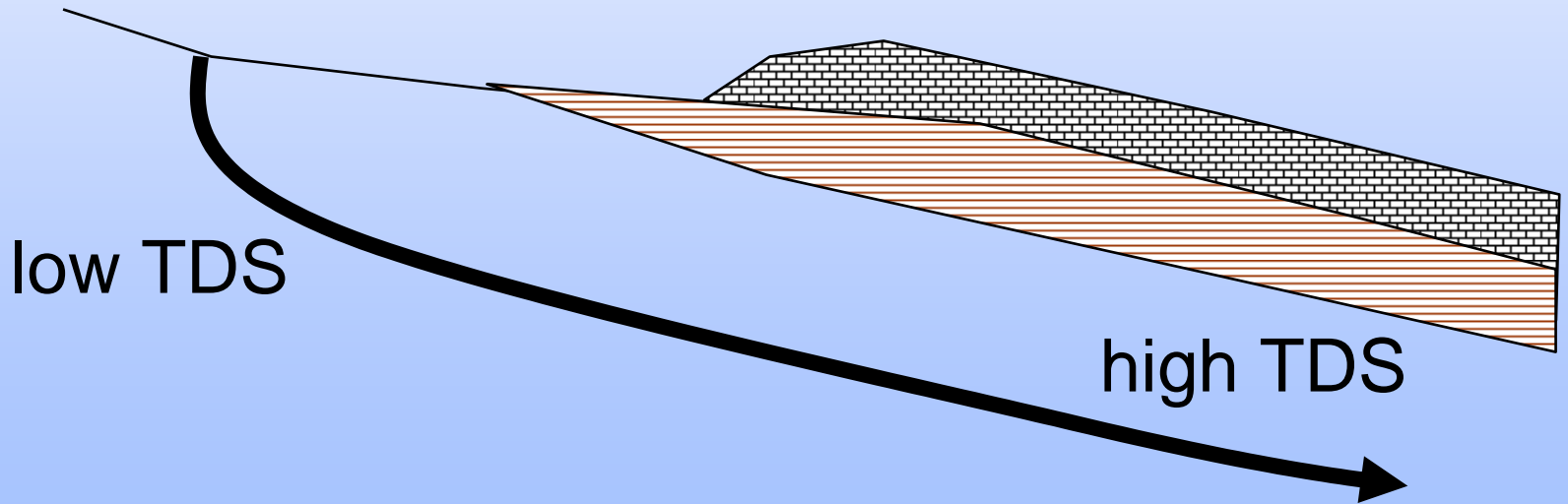
Stumm, W. & Morgan, J.J. (1996): *Aquatic Chemistry*. 3rd
Ed., New York (Wiley).

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

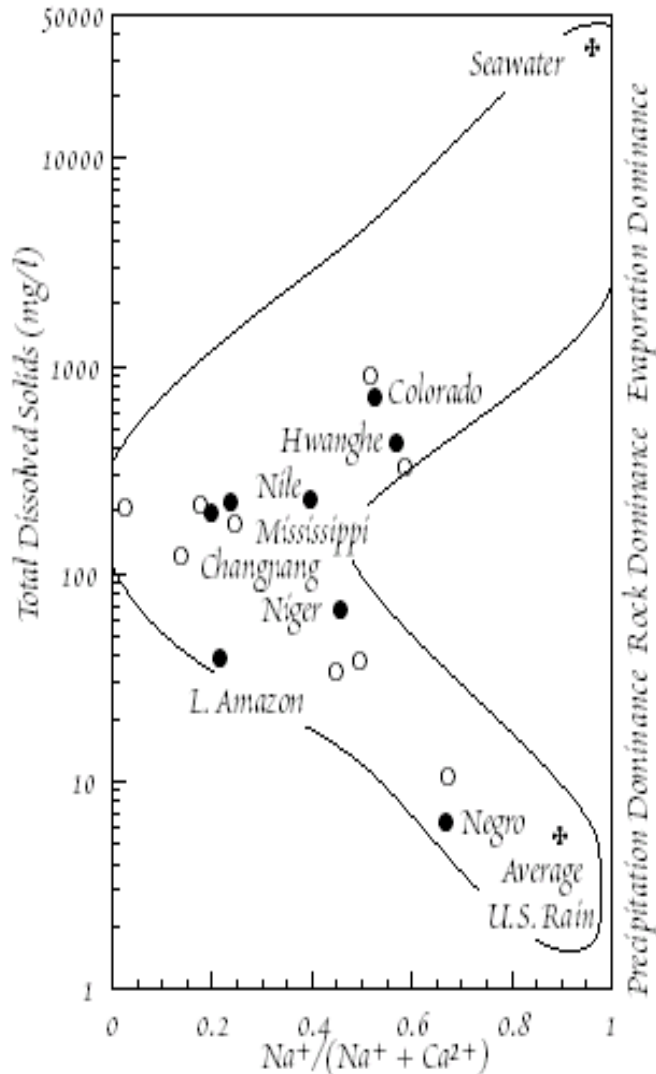
Simplified conceptual diagram of the hydrologic cycle incorporating hydrogeochemical processes



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



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



- Plot of total dissolved solids vs. $Na^+ / (Na^+ + Ca^{2+})$ 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, HCO₃, SO₄, Cl, Si,

Minor (0.01-10 mg/L)

B, Fe, NO₃, NH₄, 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
- Carbonate
- Fluoride
- Bromide
- Nitrate/Nitrite
- Carbon Dioxide
- Oxygen
- Boron
- Strontium

Trace Constituents ($< 100 \mu\text{g/L}$)

- 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/

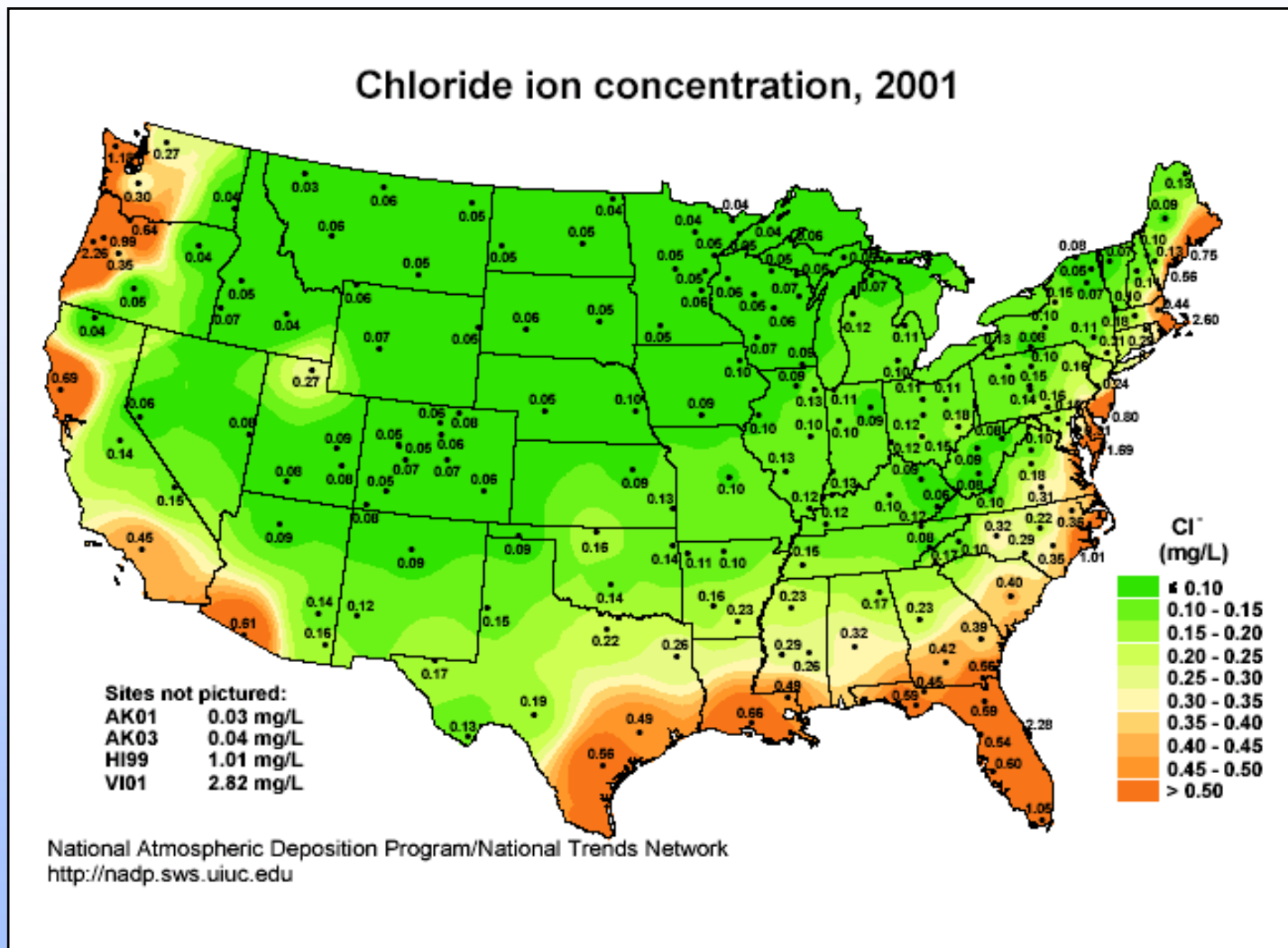
- **EPA**

- <http://www.epa.gov/safewater/>

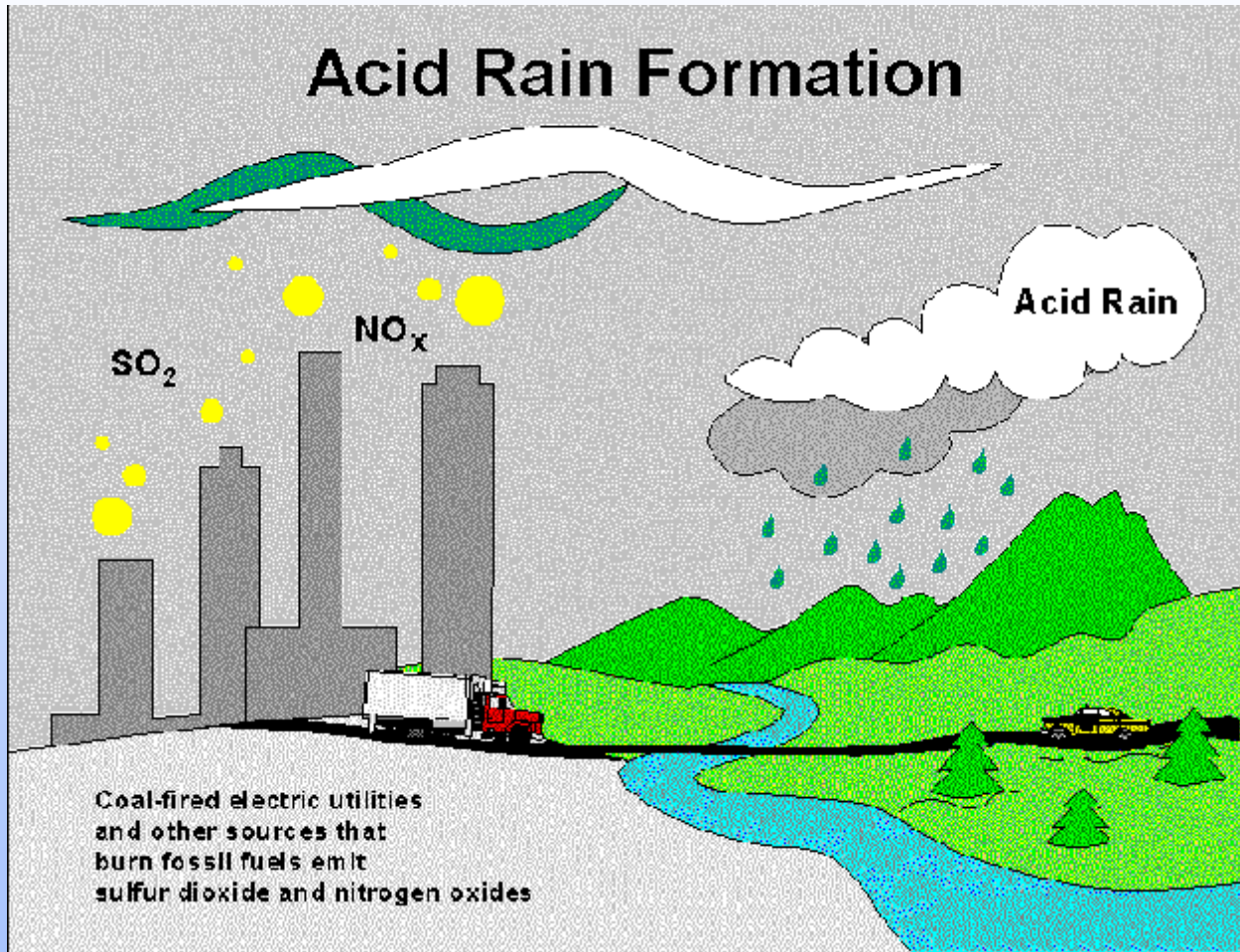
Origin of solutes

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

Distribution of Cl-Concentrations (mg/L)



Atmospheric deposition - Acid Rain Formation



Origin of solutes

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

Chemical Reactions

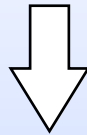
- **A wide variety of chemical reactions can take place between gases, solutes and solids in groundwater systems:**
 - **Some basic terms**
 - **Acid-base**
 - **Solution-precipitation**
 - **Adsorption**
 - **Complexation**
 - **Redox**
 - **Hydrolysis**
 - **Isotopic processes**

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

$$\sum_i m_i z_i = 0 \quad !!$$



$$\sum_i m_i^+ z_i^+ = \sum_n m_n^- z_n^-$$

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 - Henry`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

CO₂

33,8

CH₄

1,34

N₂

0,642

O₂

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 $\text{mg L}^{-1} \text{SO}_4^{2-}$ or mg L^{-1} sulfate-S.
- The relationship among these is:

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

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 $\text{NaAlSi}_3\text{O}_8$. In such a solid solution, the mole fraction of KAlSi_3O_8 would be written as:

$$X_{\text{KAlSi}_3\text{O}_8} = \frac{\text{moles KAlSi}_3\text{O}_8}{\text{moles KAlSi}_3\text{O}_8 + \text{moles NaAlSi}_3\text{O}_8}$$

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 $\text{Ca}^{2+} = 0.004 \text{ eq L}^{-1} \text{ Ca}^{2+}$; 0.001 mol L^{-1} of $\text{Na}^{+} = 0.001 \text{ eq L}^{-1} \text{ Na}^{+}$; and $0.003 \text{ mol L}^{-1} \text{ La}^{3+} = 0.009 \text{ eq L}^{-1} \text{ La}^{3+}$.**
- **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 weight fraction)

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

Atomic weight of Calcium: 40,08 g/mol

Charge 2

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

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

Concentration and activity

- in ideal solutions :

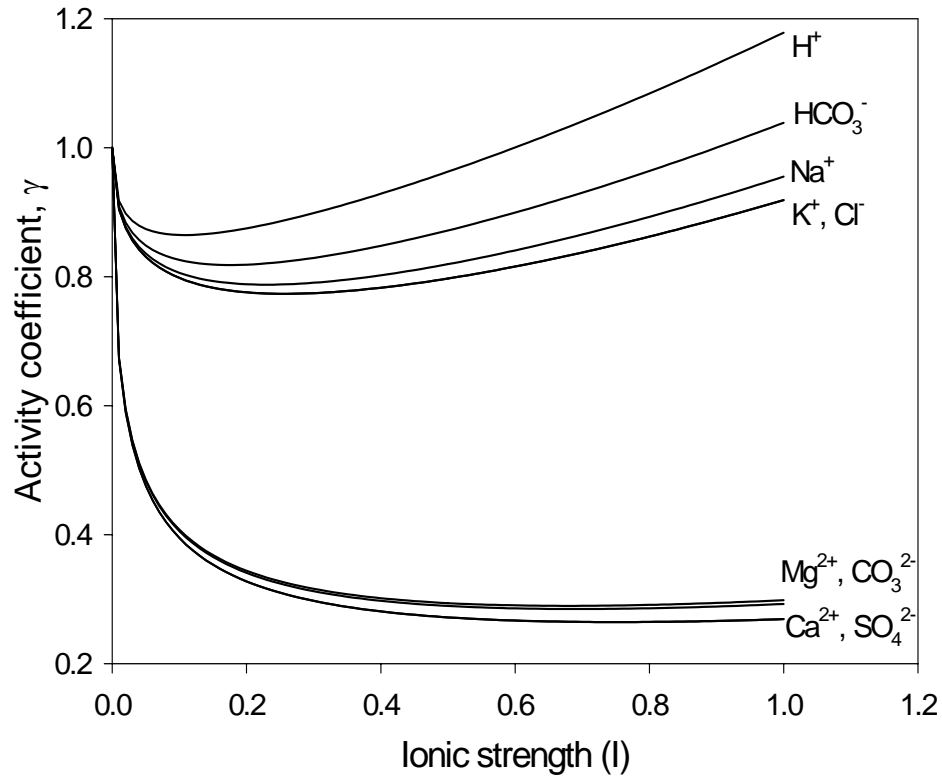
$$[A] = \{A\} \quad f_a = 1$$

- in real solutions

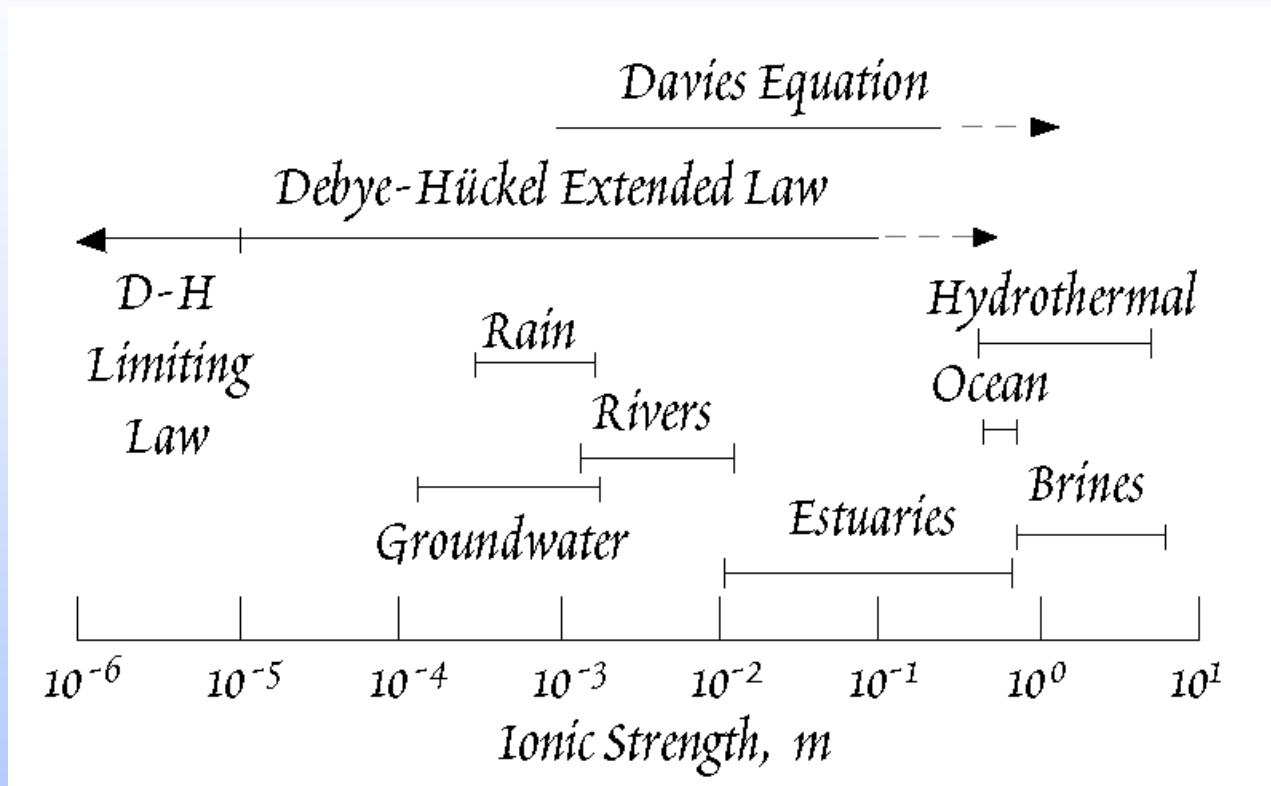
$$[A] \times \gamma_i = \{A\}$$

Activity coefficient

Activity coefficients vs. Ionic Strength



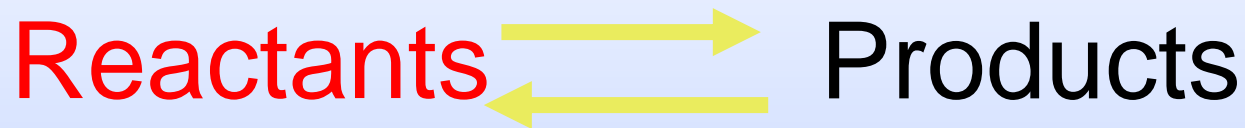
Ionic strength of natural electrolytes



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

Chemical Equilibrium

Forward Rate



Backward Rate



The Law of mass action

Consider the reaction:



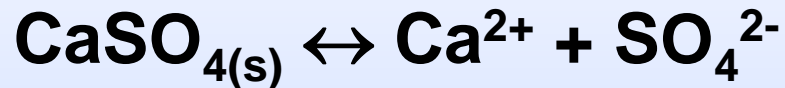
- Where a, b, c and d are the molar amounts of compounds A, B, C and D, respectively. At equilibrium it must be true that:

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

- 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 Chatelier's Principle.

Solubility product

- The equilibrium constant for a reaction of the type:

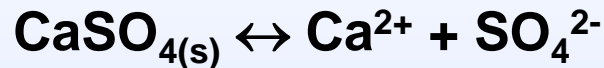


- is called also solubility product (K_{s0}). The K_{s0} can be calculated according to:

$$K_{s0} = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}{a_{\text{CaSO}_4(s)}} = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}$$

The ion activity product (IAP)

Consider once again the reaction:



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

$$K_{SO} = \left(a_{\text{Ca}^{2+}} \right)_{\text{equil}} \left(a_{\text{SO}_4^{2-}} \right)_{\text{equil}}$$

- 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:

$$IAP = Q = \left(a_{\text{Ca}^{2+}} \right)_{\text{actual}} \left(a_{\text{SO}_4^{2-}} \right)_{\text{actual}}$$

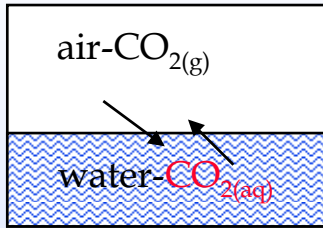
The saturation index

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

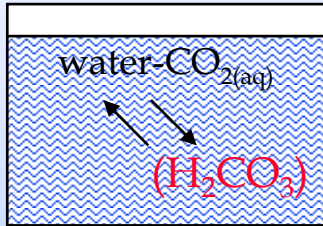
$$SI = \log\left(\frac{IAP}{K_{s0}}\right)$$

- 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.

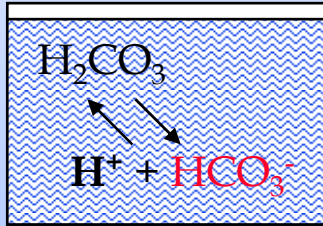
Carbonate system - Dissolved carbon dioxide



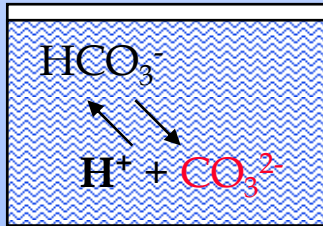
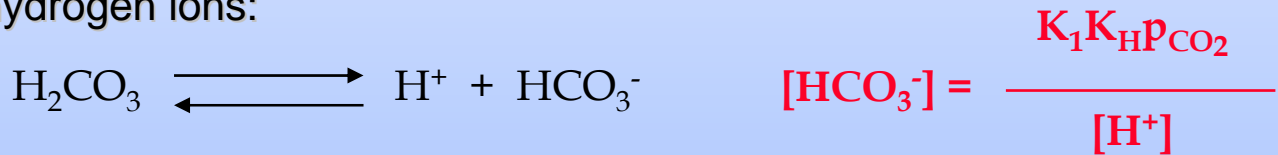
Water at the surface of the Earth inevitably contains dissolved CO₂, either as a result of equilibration with the atmosphere or because of respiration by organisms.



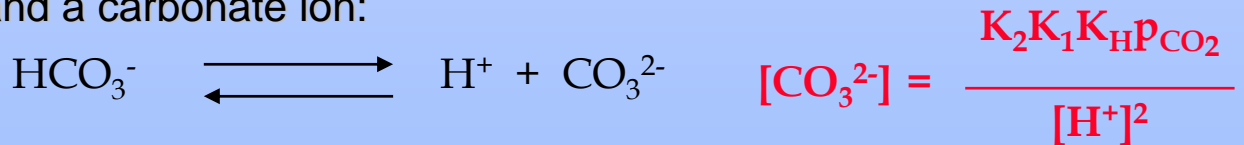
CO₂ reacts with water to form carbonic acid:



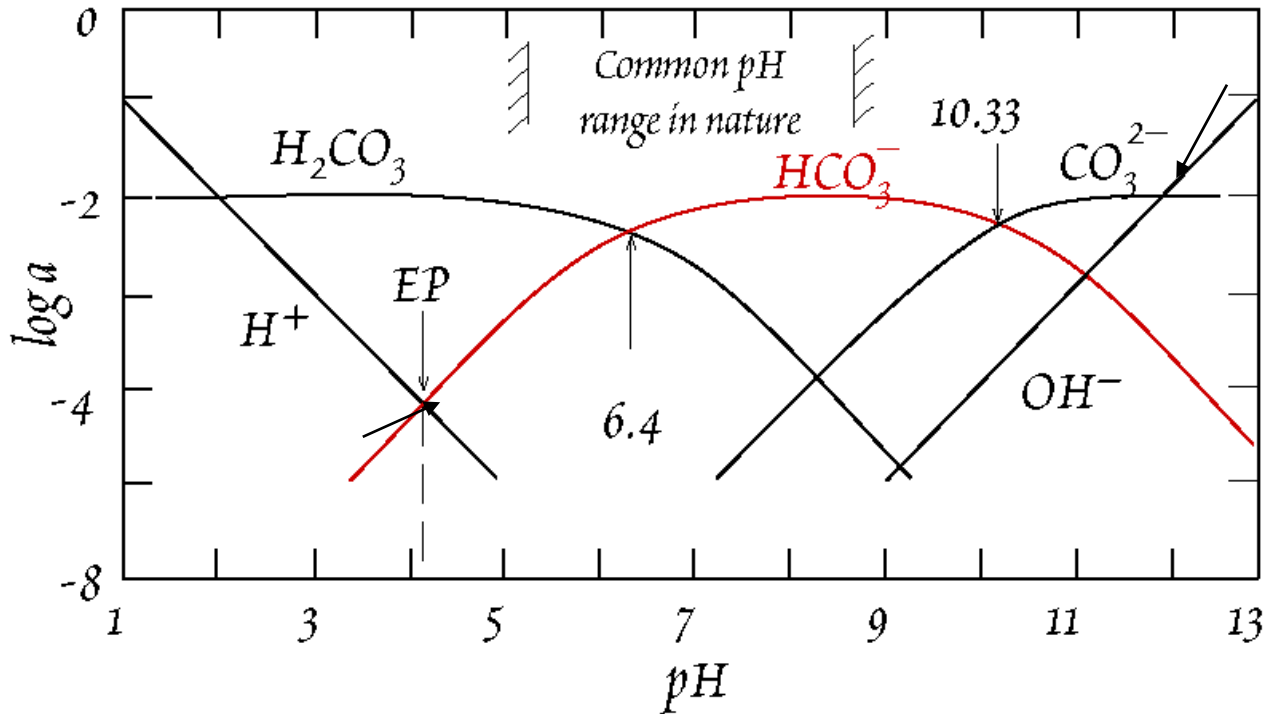
Some of the carbonic acid dissociates to form bicarbonate and hydrogen ions:



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



Carbonate System - Equilibrium Diagramm



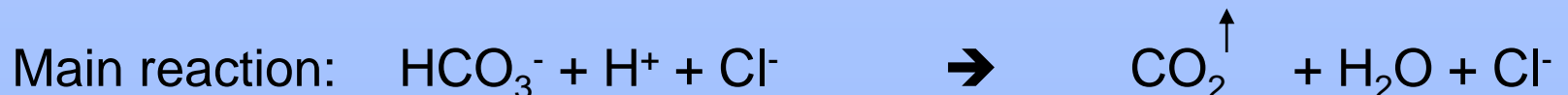
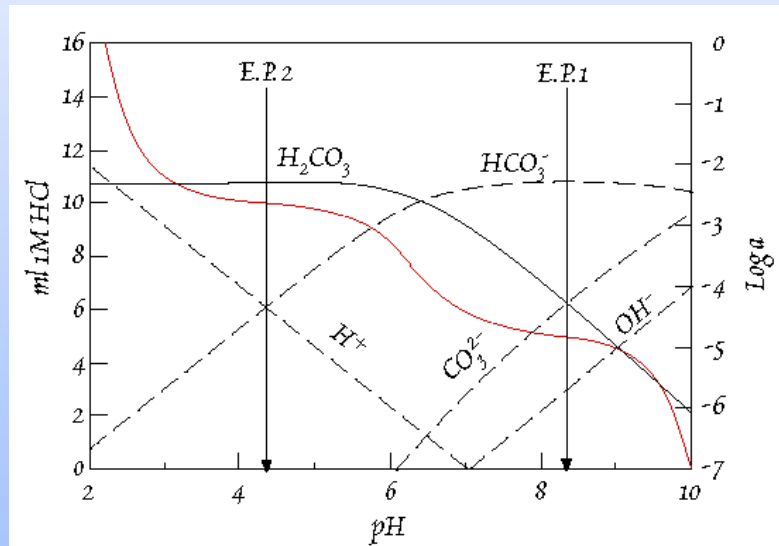
Activities of different species in the carbonate system as a function of pH, assuming $\Sigma CO_2 = 10^{-2}$. After Drever (1988).

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

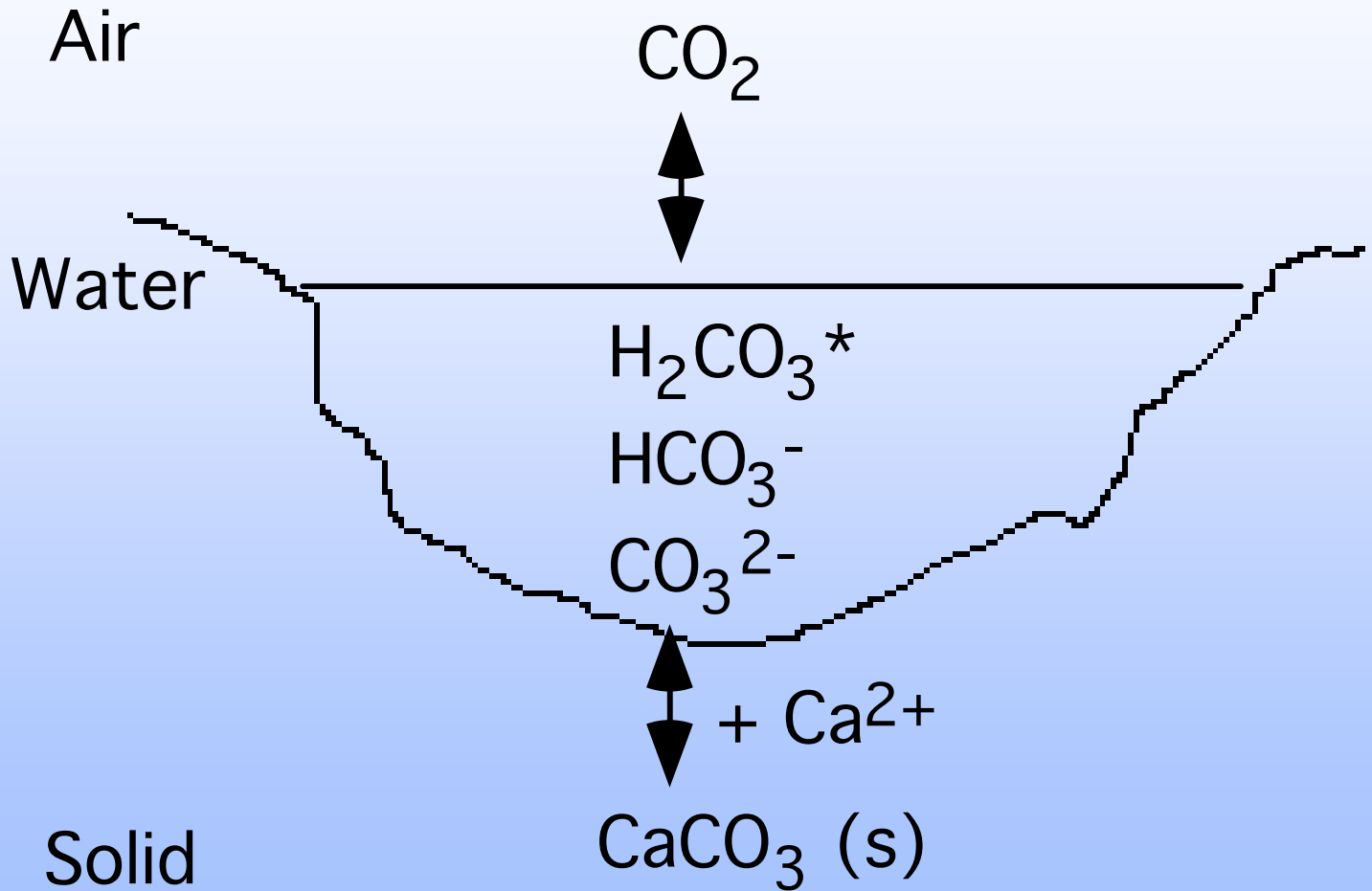
Carbonate System - Alkalinity and titration curve

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.

$$[\text{Alk}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

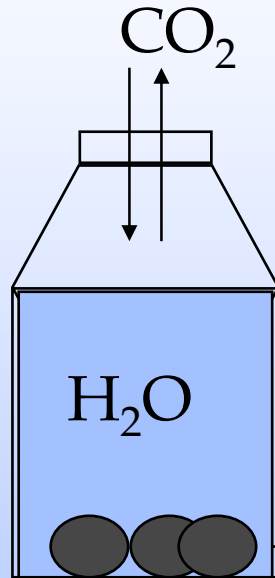


Dissolution and Precipitation



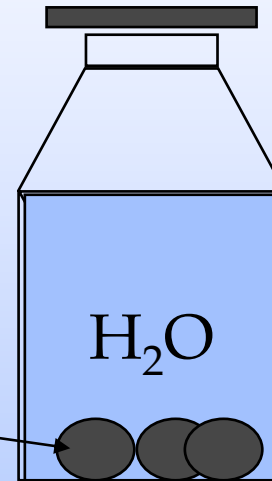
Dissolution and Precipitation - Dissolution of Carbonates

open system



$C_T \neq \text{constant}$

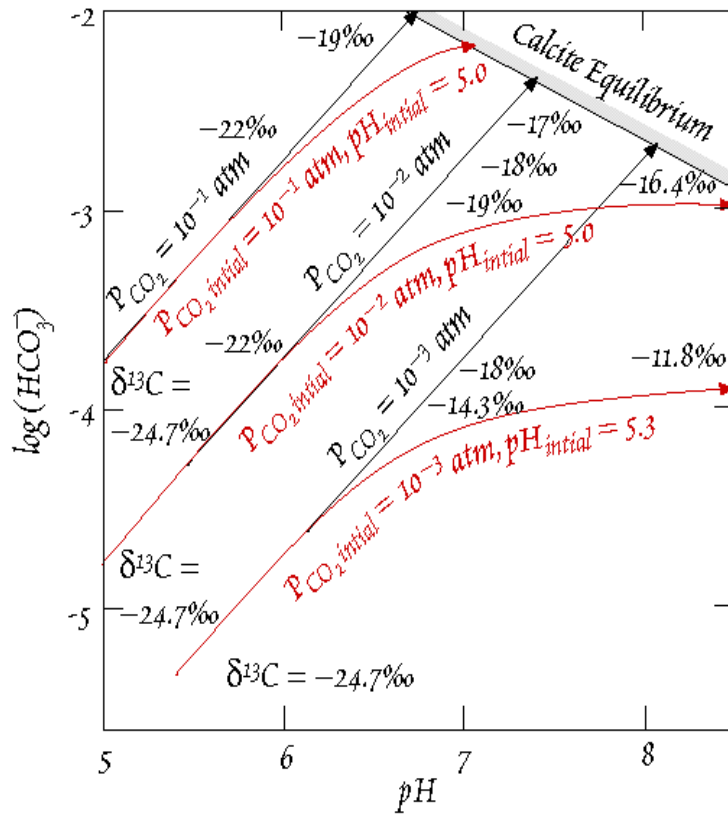
closed system



$C_T = \text{constant}$

$CaCO_3$

Dissolution and Precipitation - Comparison - Open and Closed system



Open system reach calcite saturation at higher pH and lower $[\text{HCO}_3^-]$ than closed system that initially 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.**

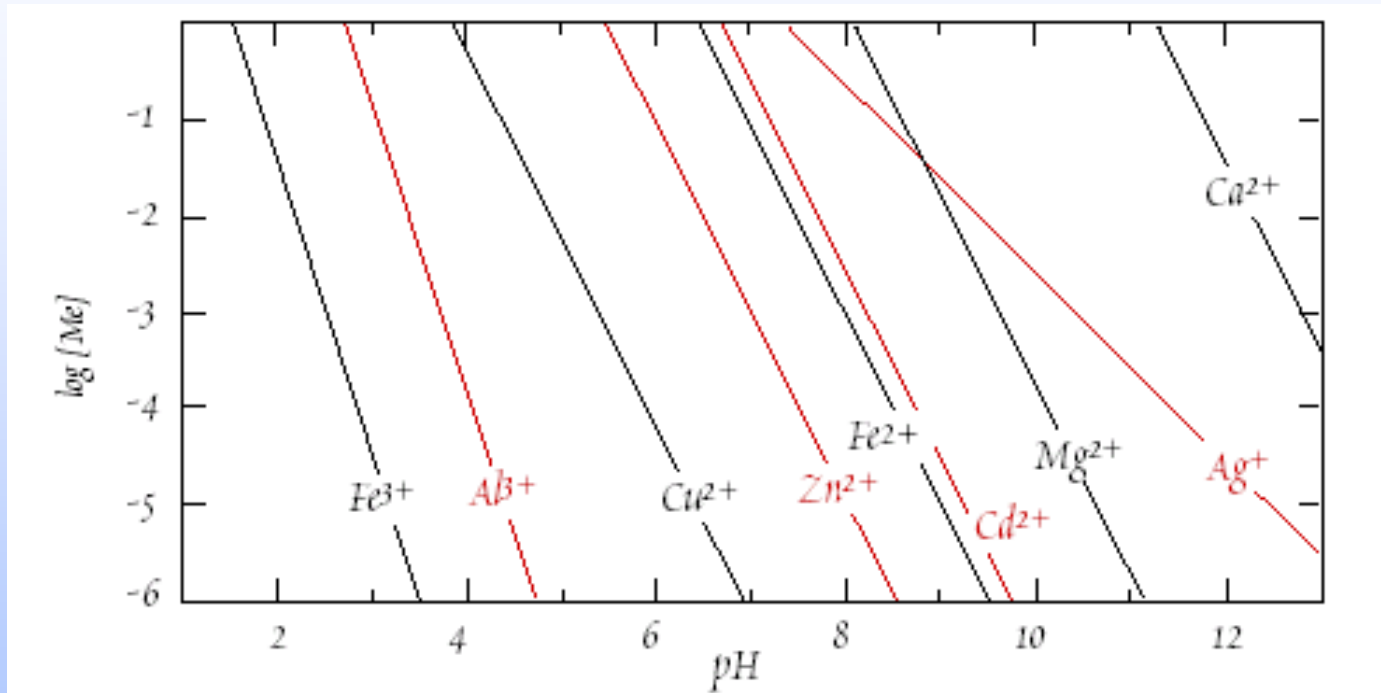
Adsorption

- **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.**

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.*



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

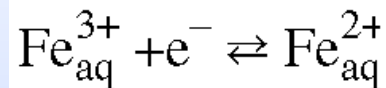
Redox-Reactions - Nernst Equation and Electron activity

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

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

Consider the reaction:

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



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

Alternative Representation of Redox State: $p\varepsilon$

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 $p\varepsilon$.

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

$p\varepsilon$ is the negative log of the activity of electrons in solution.

Redox-reactions - Aquatic redox couples

The table lists the $p\varepsilon^\circ$ of the most important redox half reactions in aqueous systems.

Also listed are $p\varepsilon_W$ values.

$p\varepsilon_W$ is the $p\varepsilon^\circ$ when the concentration of H^+ is set to 10^{-7} (pH = 7). The relation between $p\varepsilon^\circ$ and $p\varepsilon_W$ is simply:

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

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

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

* We are using "CH₂O", which is formally formaldehyde, as an abbreviation for organic matter generally (for example, glucose is C₆H₁₂O₆).

Thus sulfate can oxidize methane to CO₂, but not ferrous iron to ferric iron. Redox reactions in aqueous systems are often biologically mediated.

Redox-reactions- Microorganisms

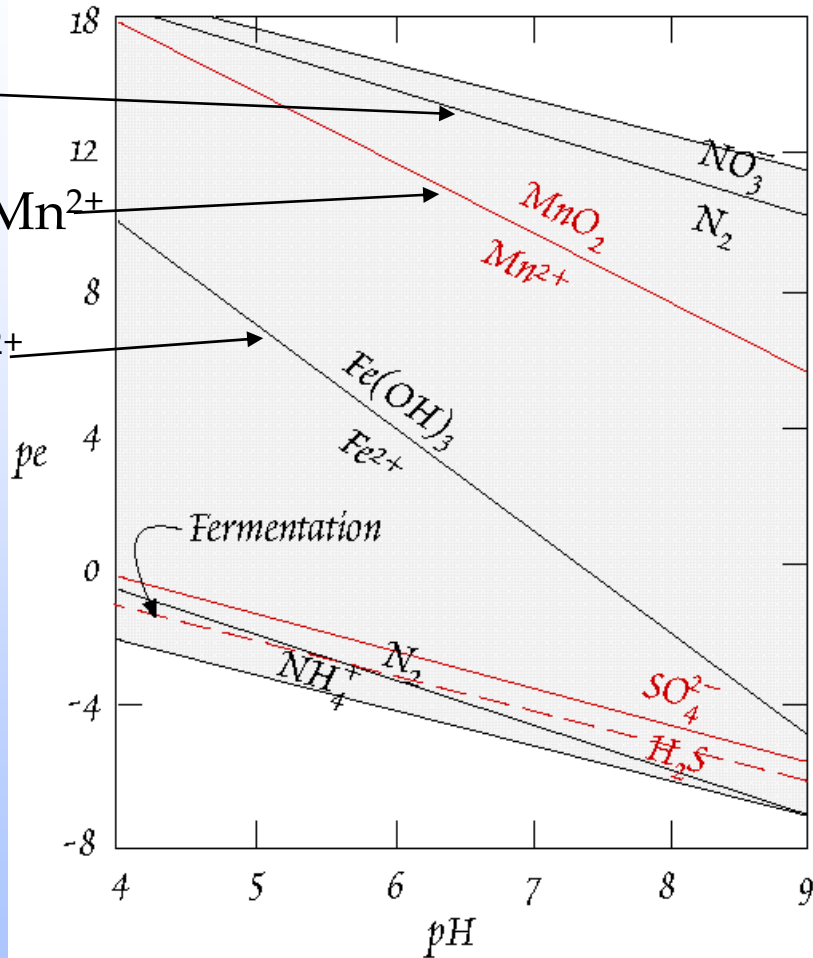
- **Oxidation-reduction reactions differ from many other reactions because they are frequently mediated by microorganisms.**
- **The role of the microorganisms is usual to act as a catalyst and increase the rate of reaction.**
- **Microbial films on grains and fracture surfaces use redox reactions as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

Redox-reactions - Biogeochemical redox-reactions

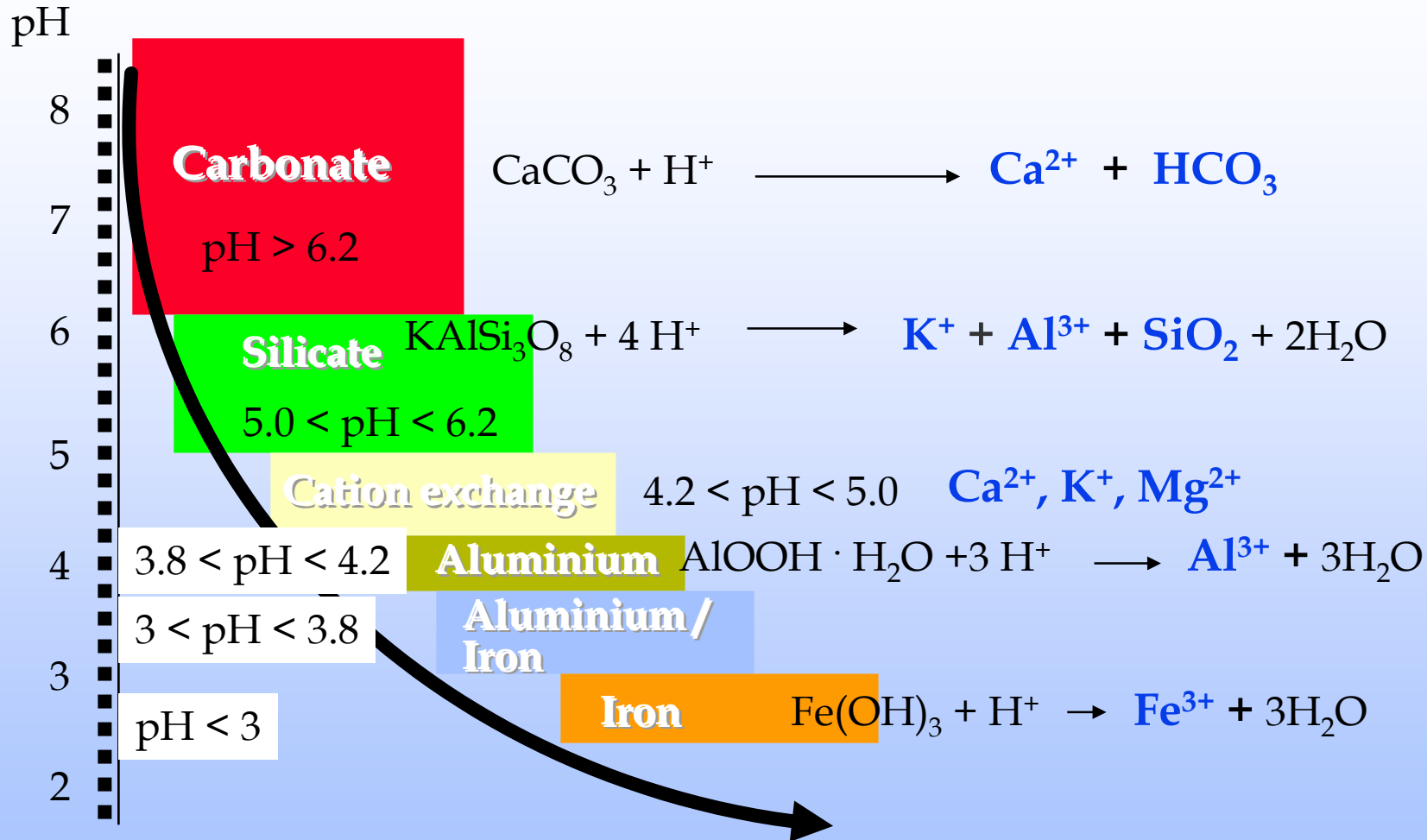
denitrification

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

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



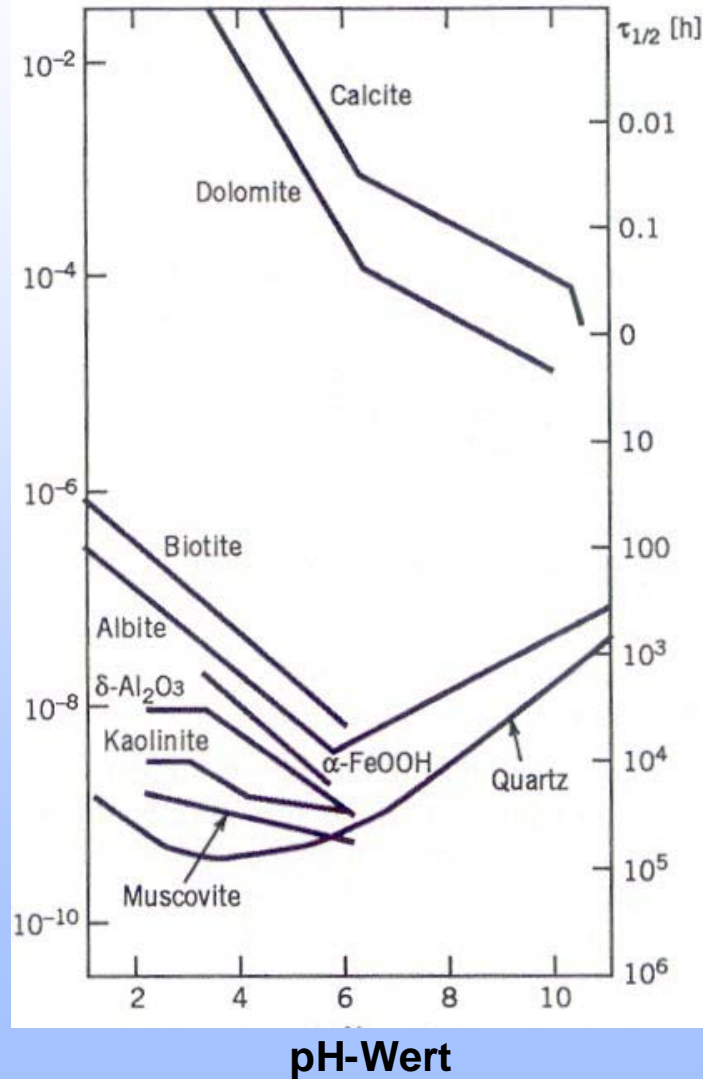
Buffer-systems in soil



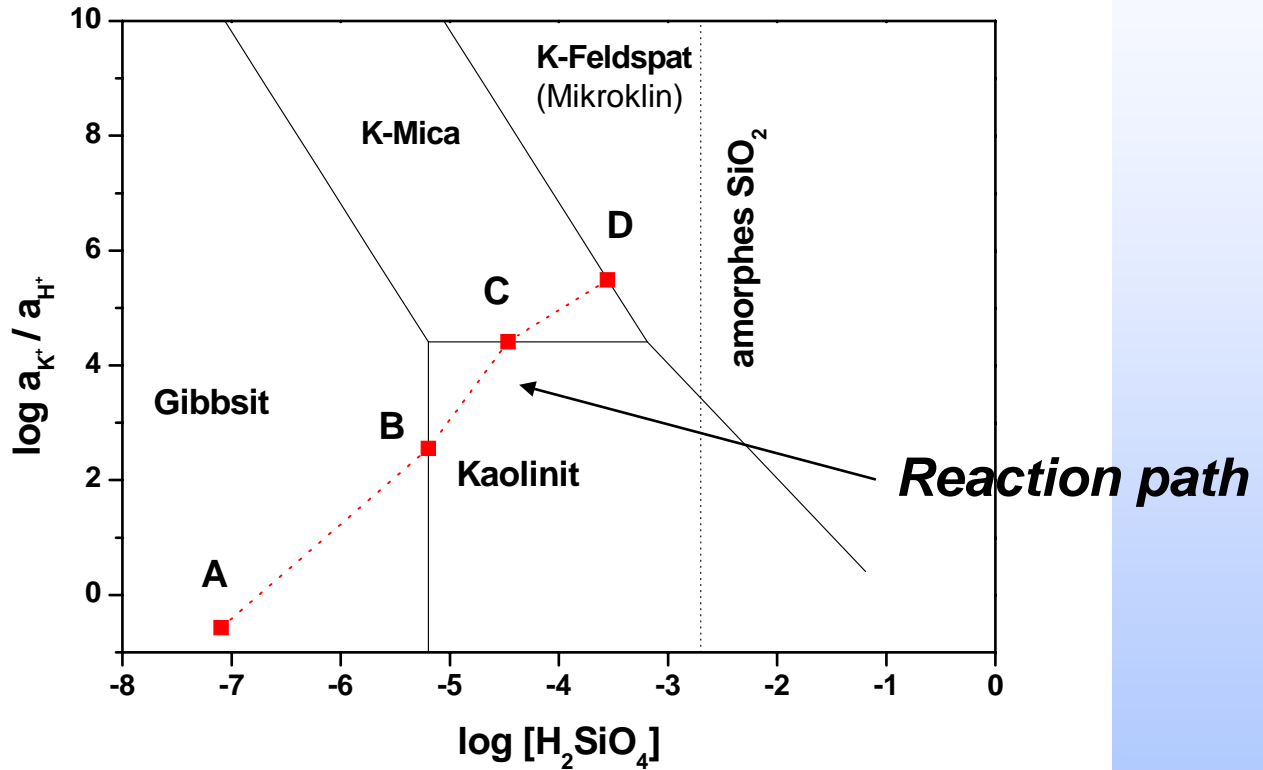
Dissolution rate of several minerals

Dissolution rate

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



Dissolution of feldspar I



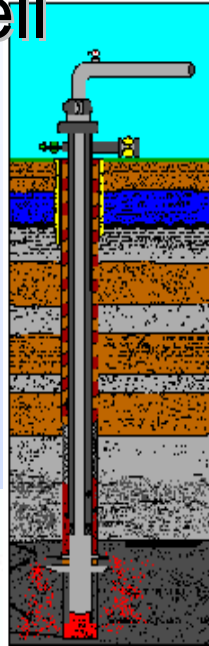
Parkhurst & Appelo, 1999

Origin of solutes

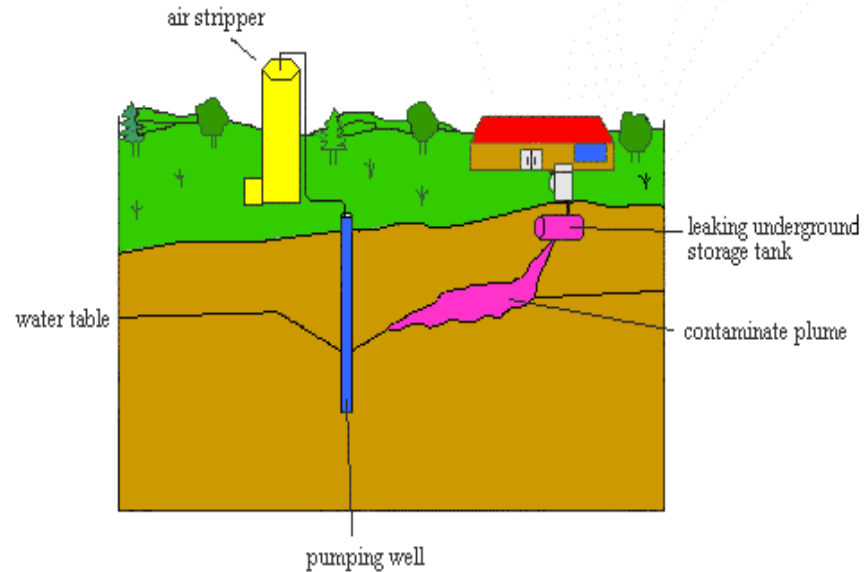
- **Atmospheric deposition**
- **Rock weathering**
- **Anthropogenic sources (fertilizer, landfills, septic tanks ...)**

Point sources - examples

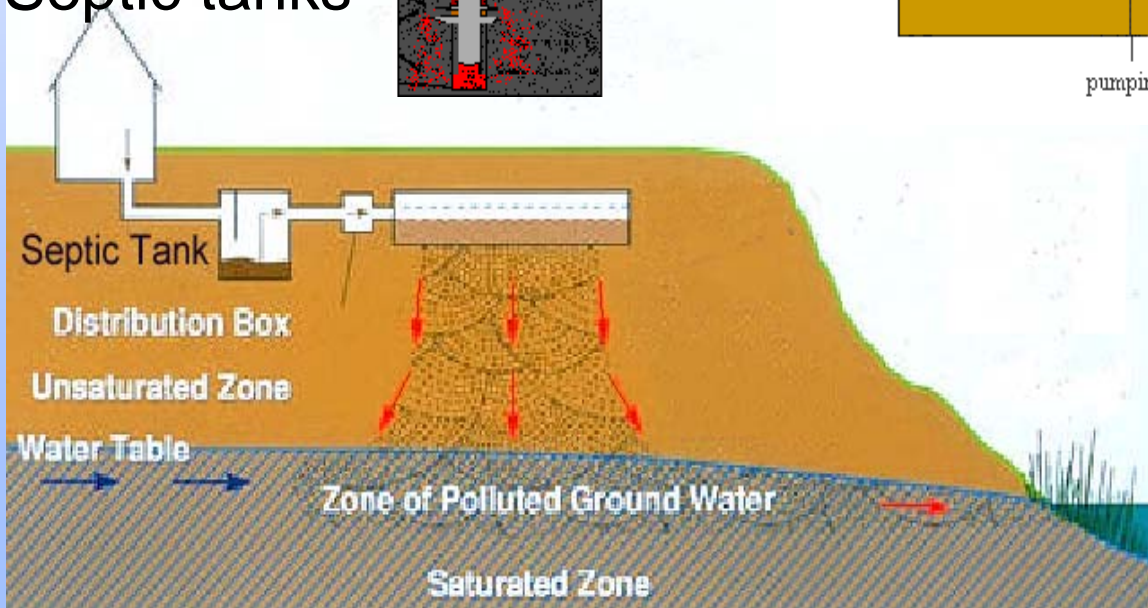
Injection well



Leaking underground storage tank



Septic tanks



Non-point sources - examples

Pesticides

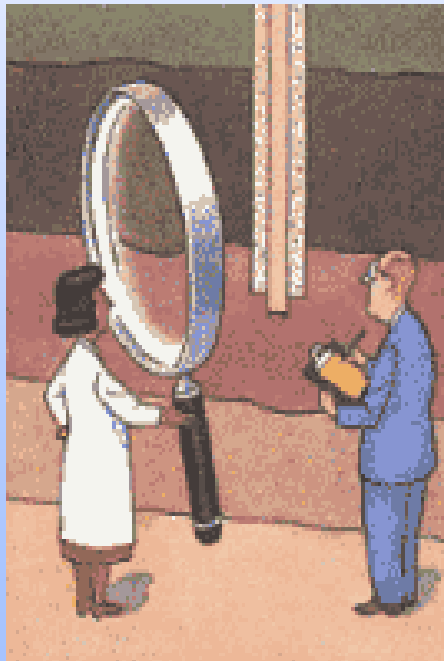


Fertilizer



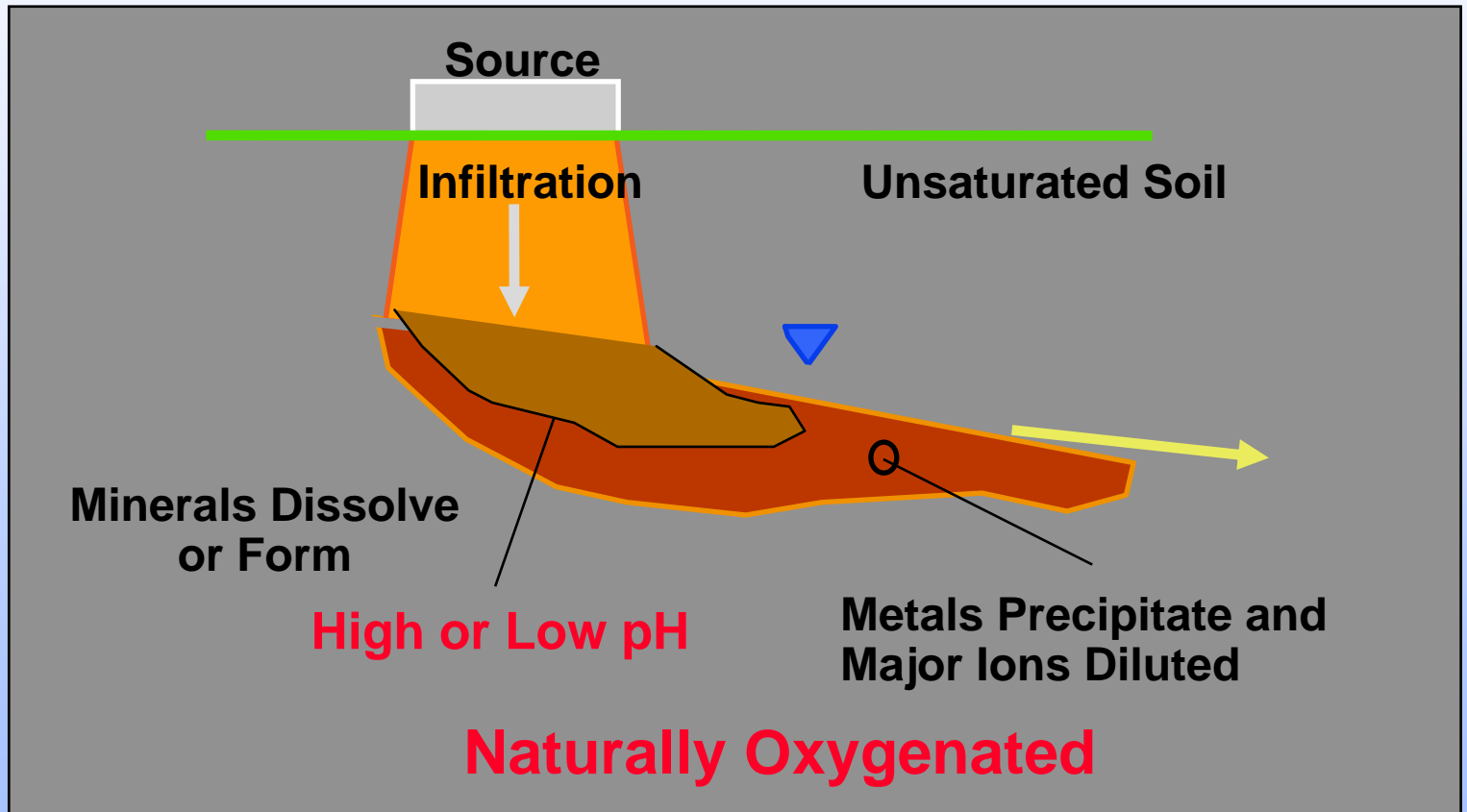
Different kinds of pollution

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

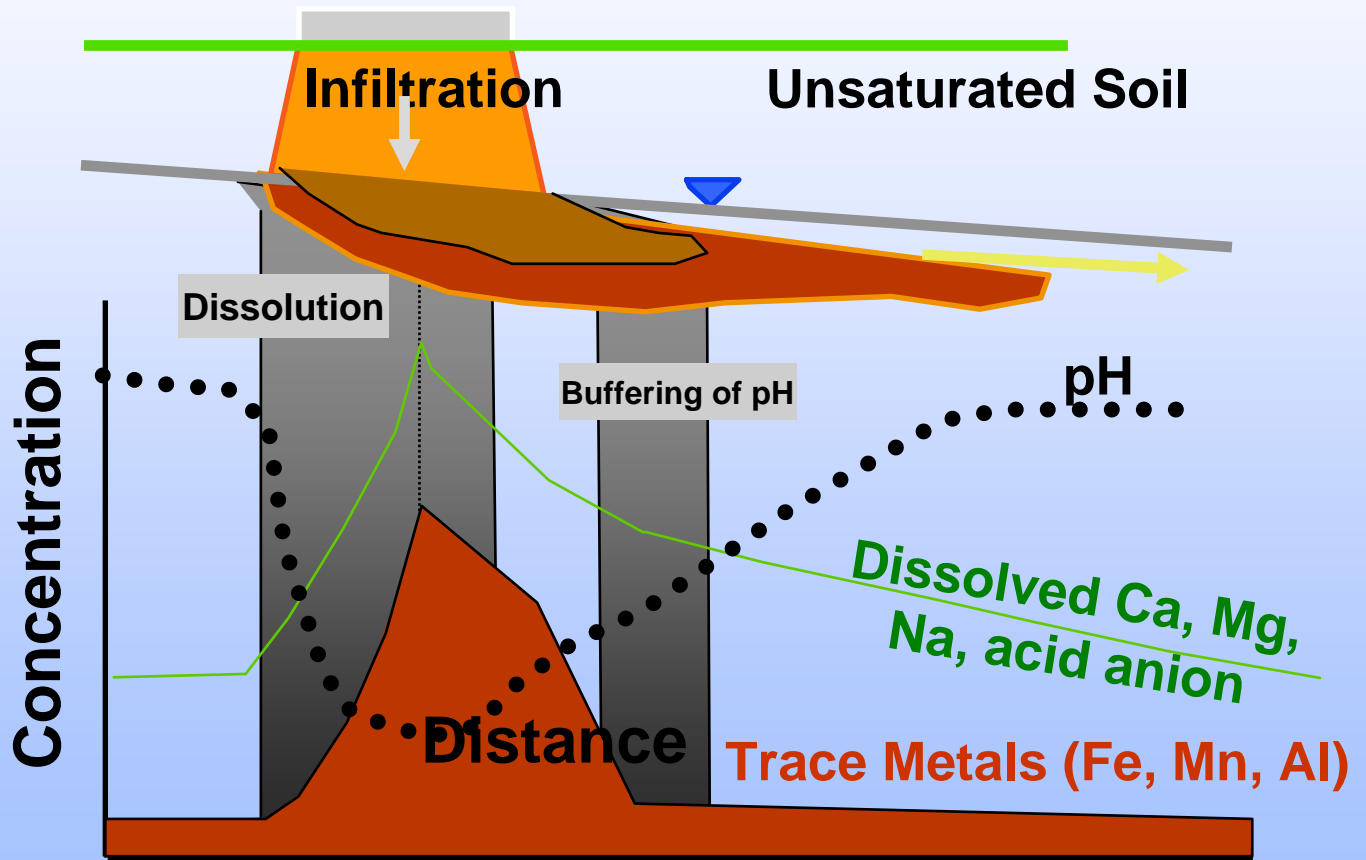


Anatomy of Inorganic Contamination

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

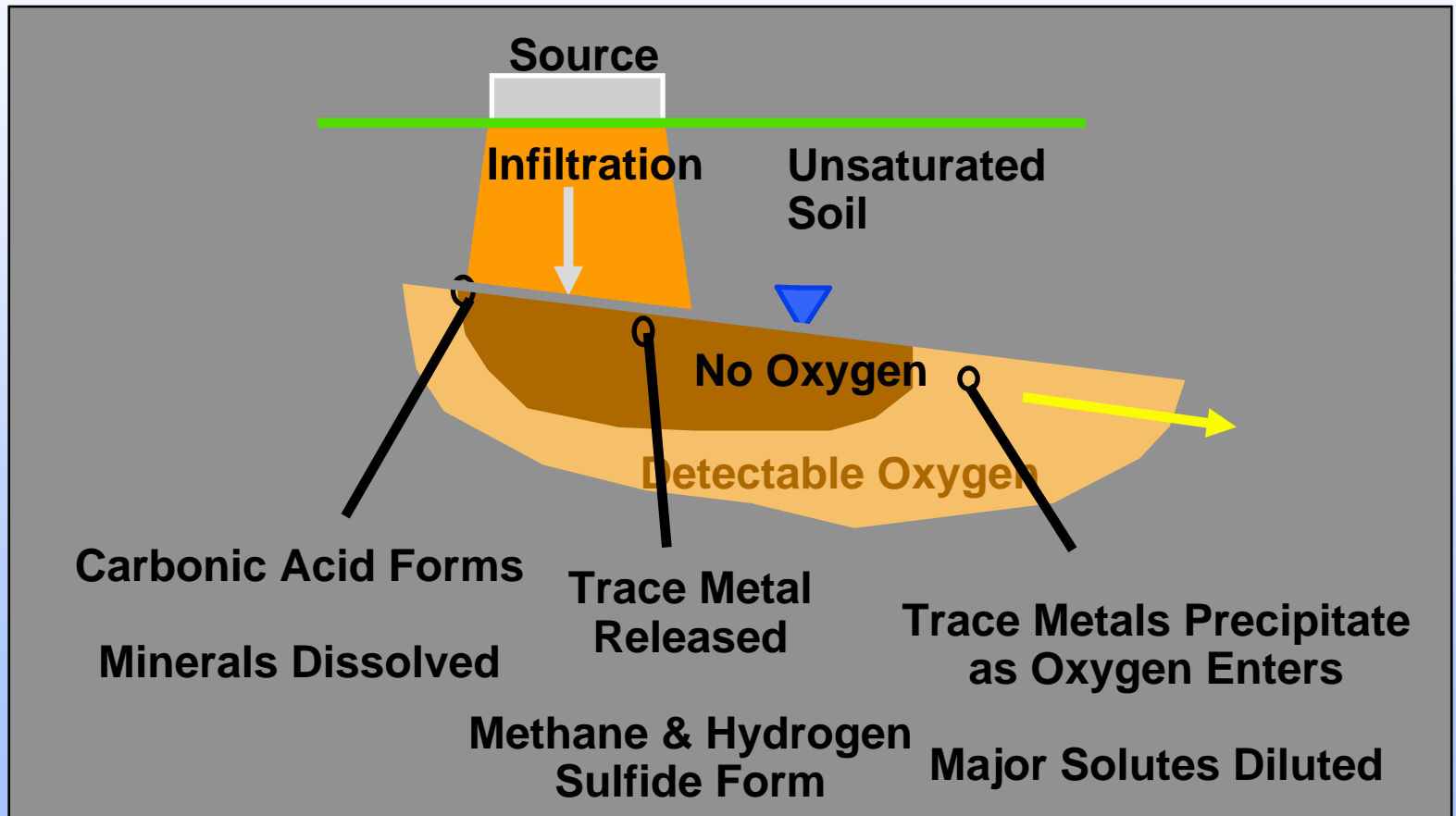


Predictable Chemical Changes (Acid)

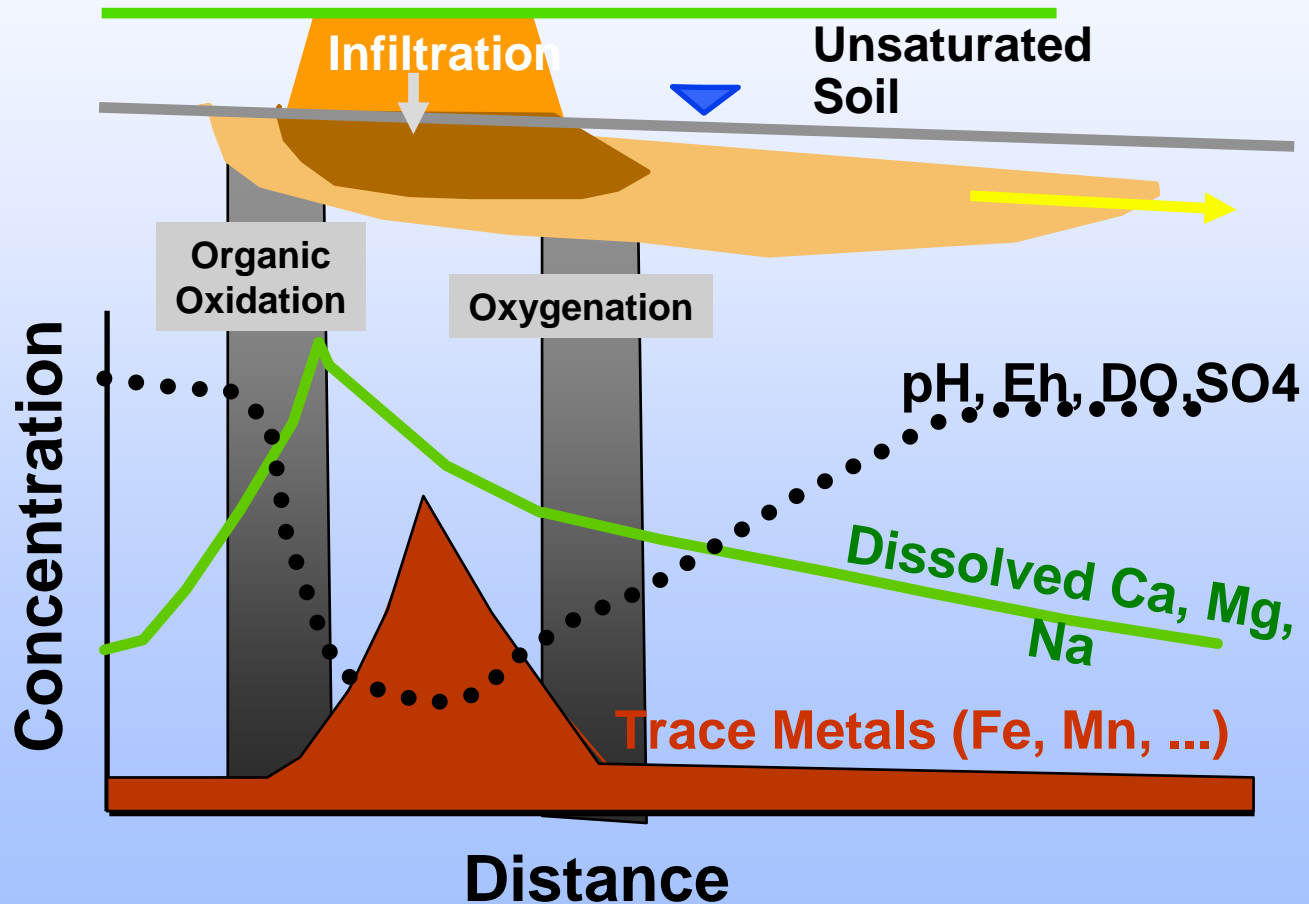


Anatomy of Organic Contamination

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**
- **....**

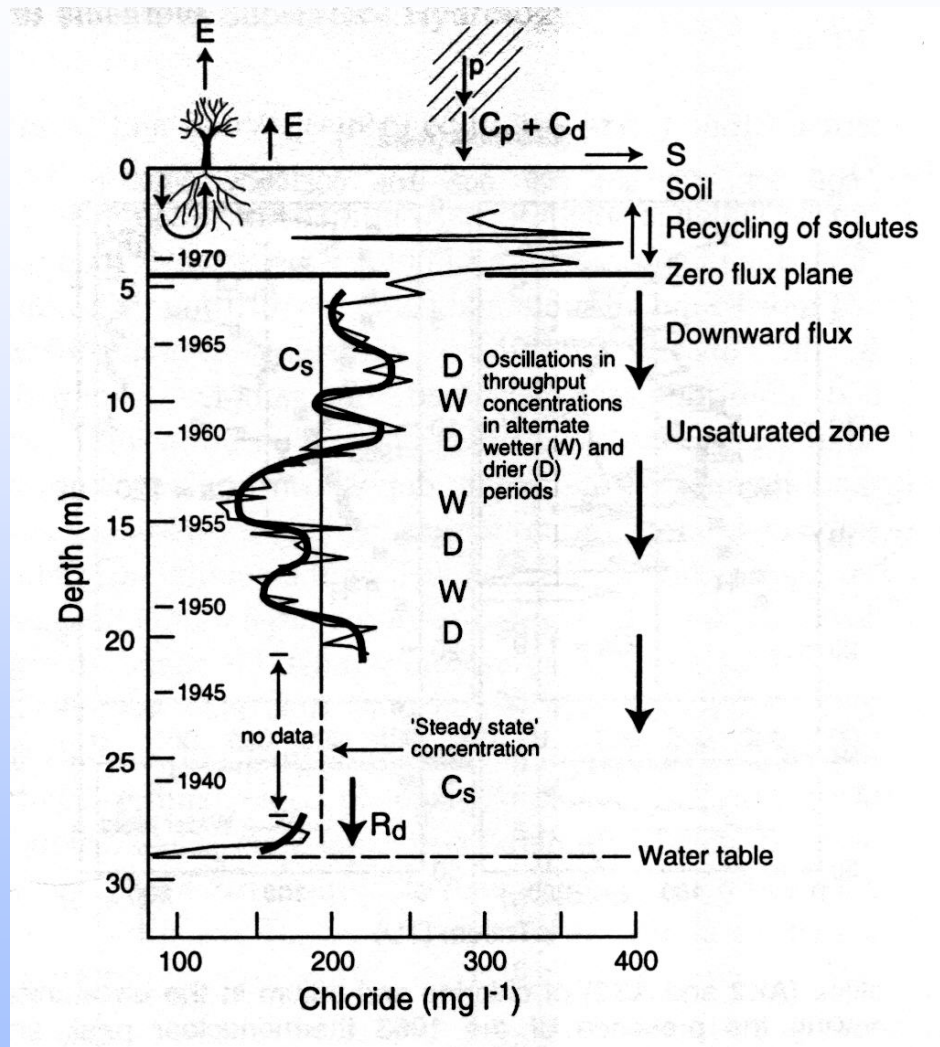
Some examples

- **Conservative ions**

- Recharge measurement using chloride
- Estimation of mixing ratios
- Chloride movement in the unsaturated zone

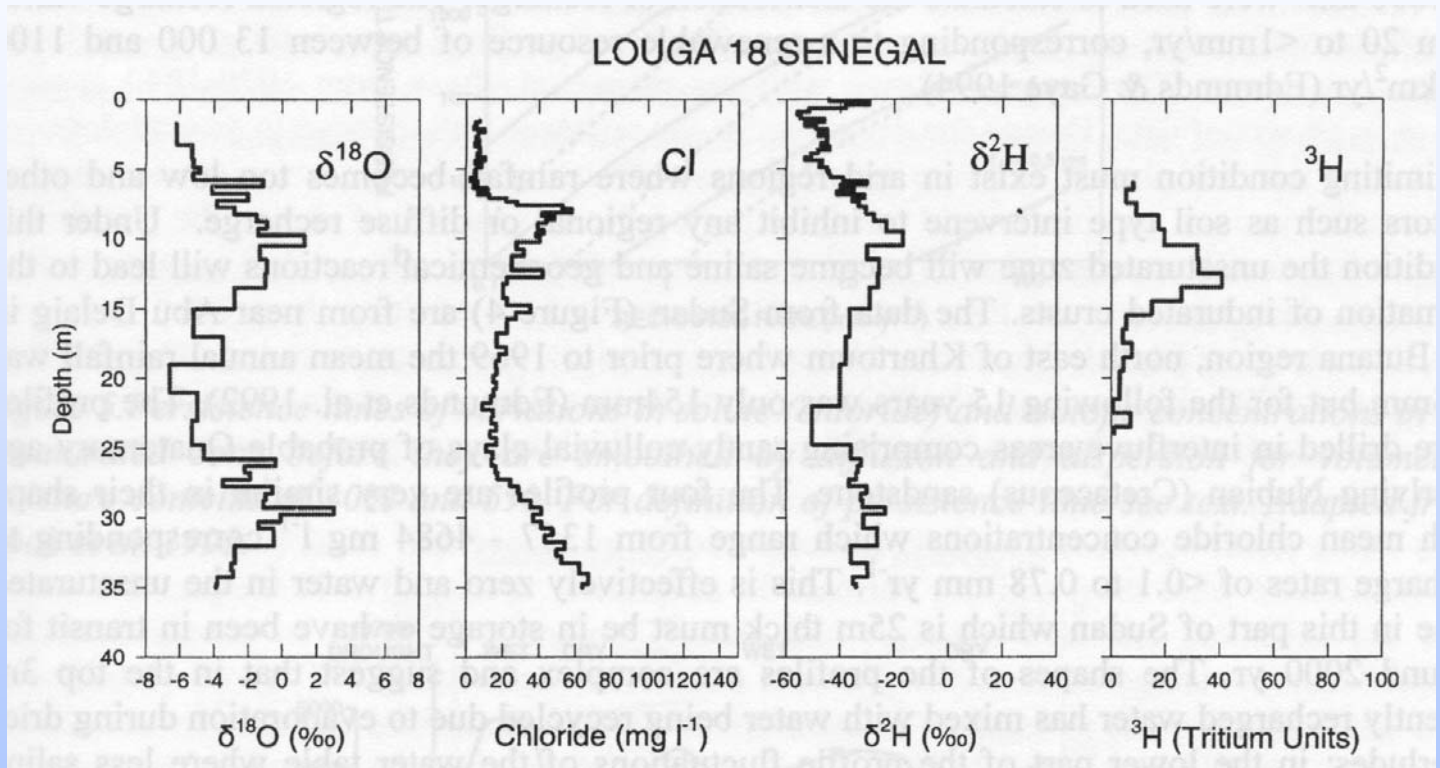
- **Non-conservative ions**

Recharge measurement using chloride



Edmunds et al. (1988)

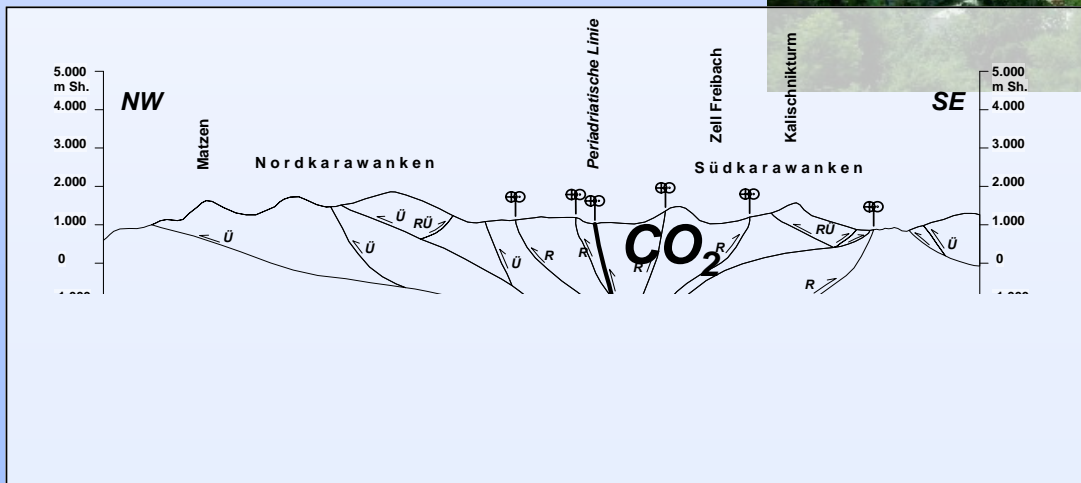
Soil profiles of chloride and environmental isotopes



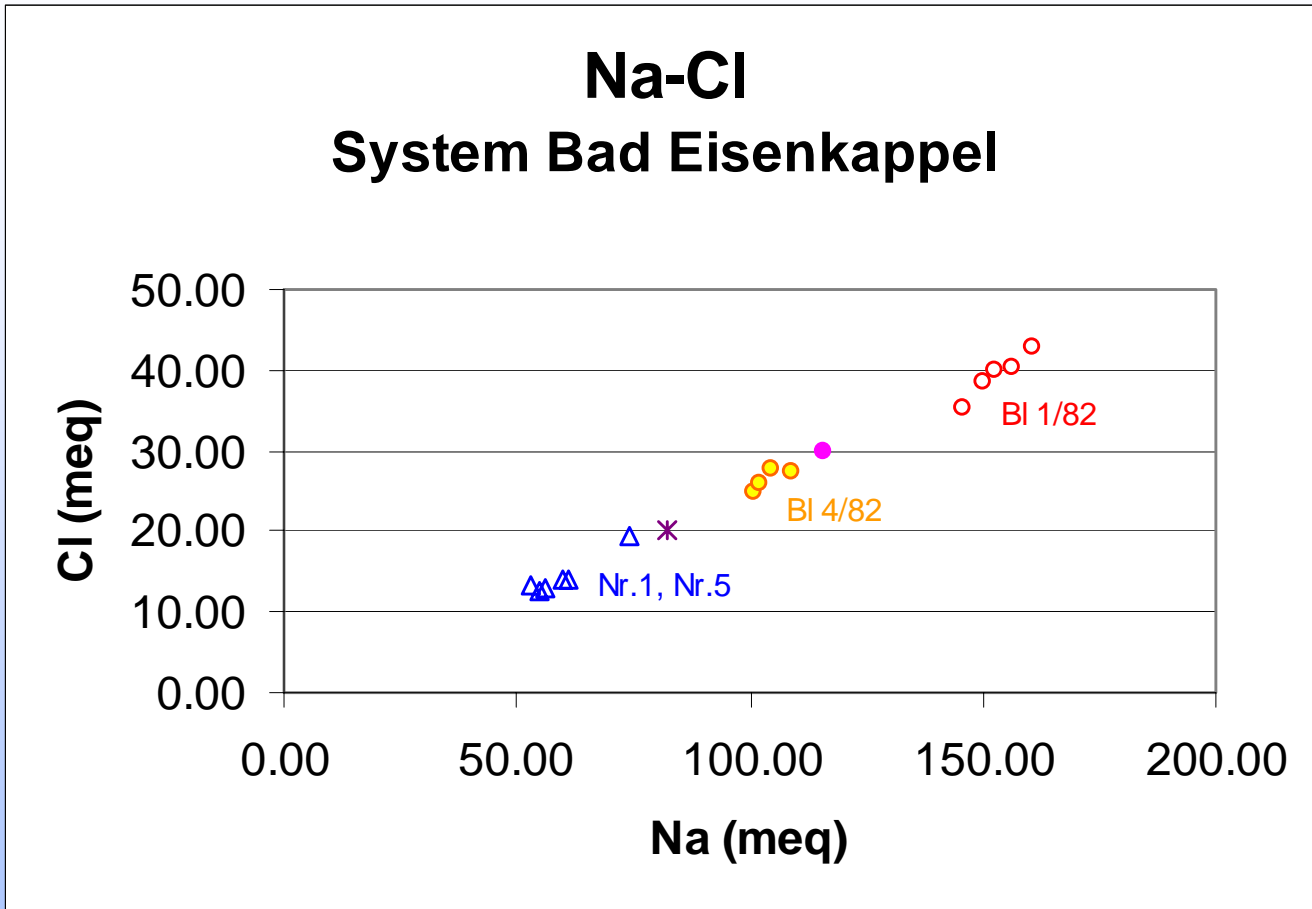
Edmunds and Gaye (1994)

Mixing of different groundwaters

Example Eisenkappel (Austria)

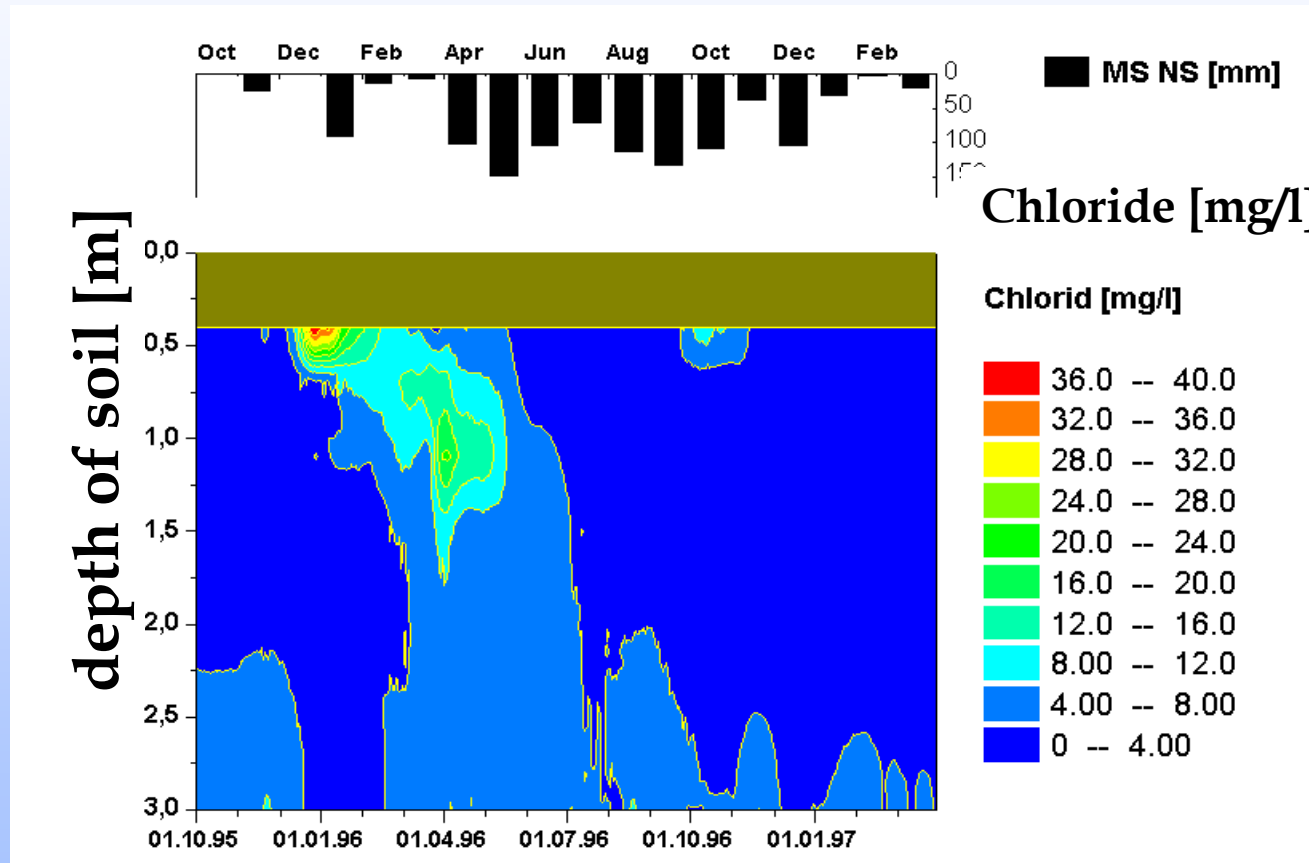


Na/Cl – ratio



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

precipitation



Some examples

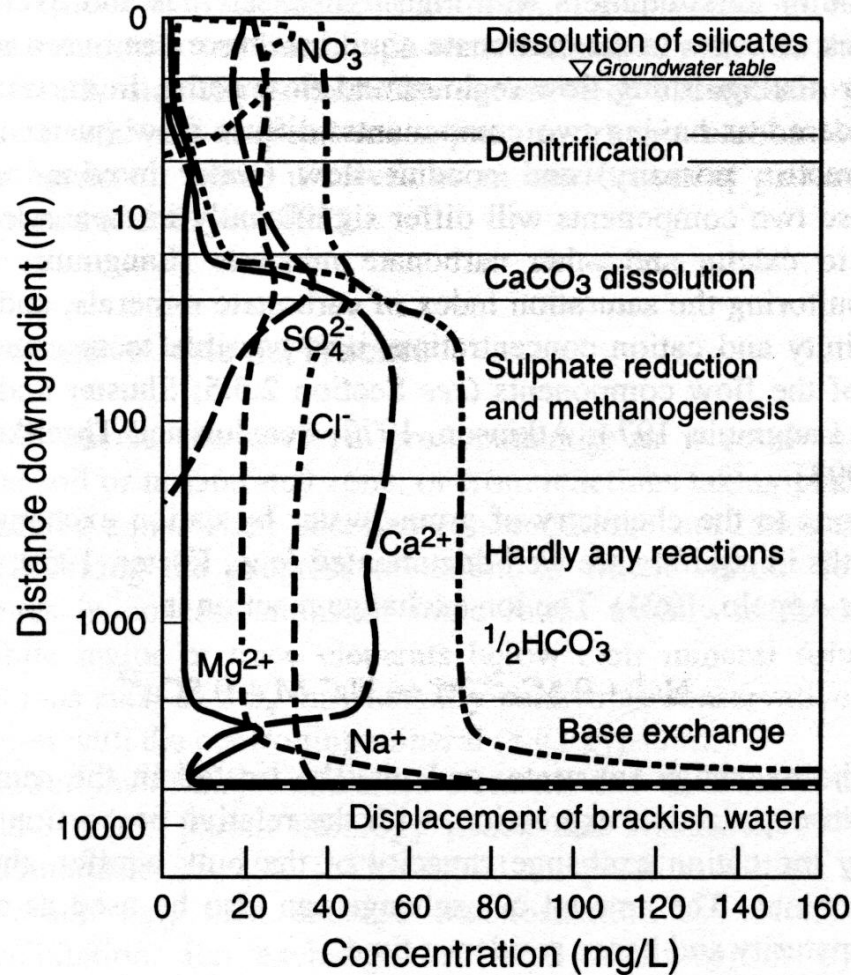
- **Conservative ions**

- 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)