

# Tracerhydrologie und Hydrochemie: Hydrochemische Grundlagen

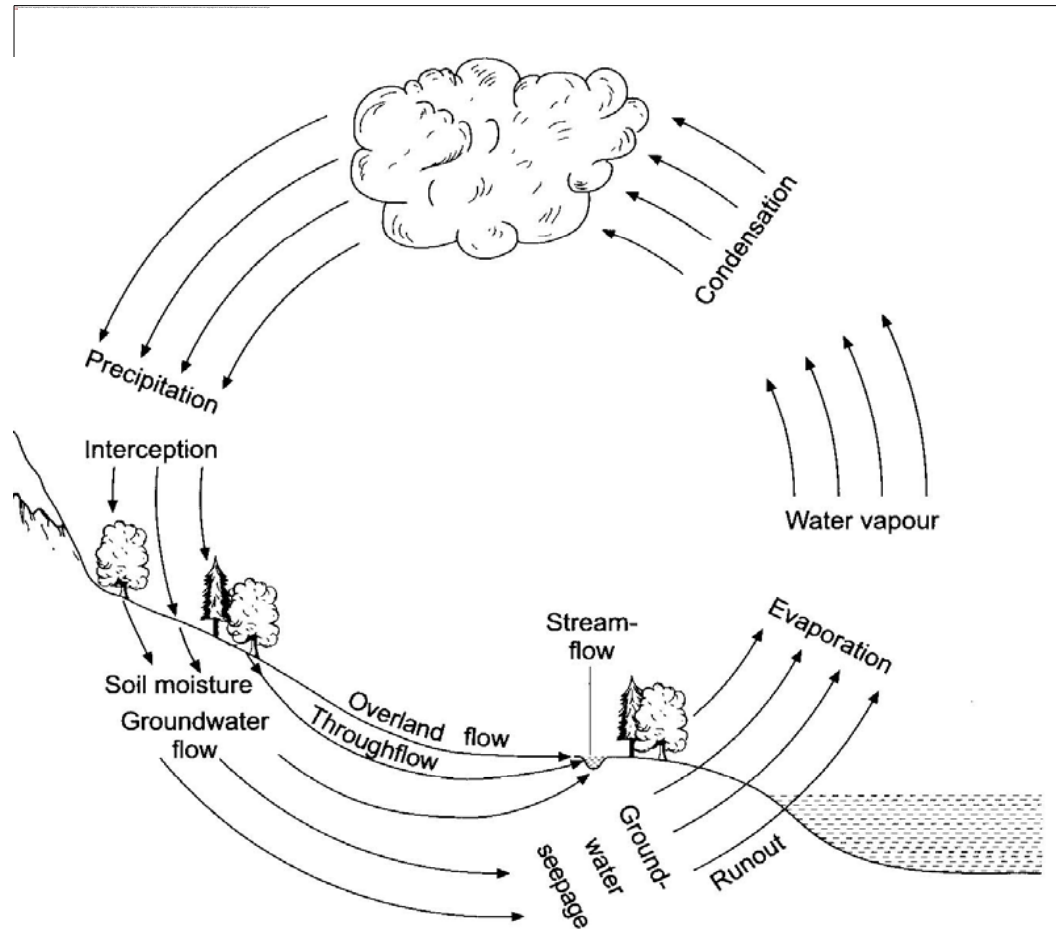
Dr. Christoph Külls,  
Institut für Hydrologie  
Albert-Ludwigs-Universität Freiburg

# Gliederung

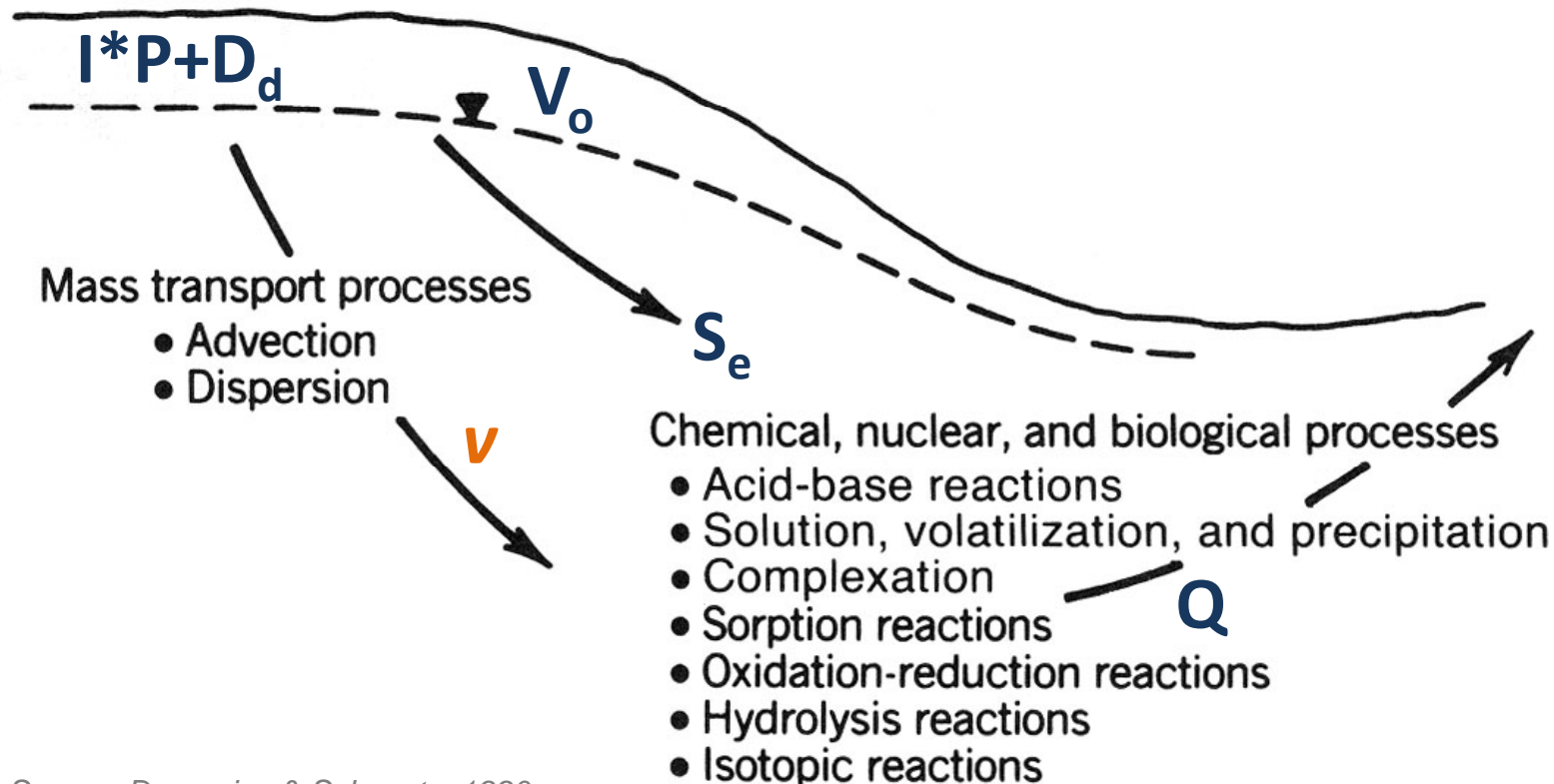
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- **Tracerkonzept**
- Grundlagen der Hydrochemie
  - Einheiten
  - Grafiken und Darstellungen
- Etwas Thermodynamik
  - Gleichgewichtsreaktionen
  - Austausch

# Vom Wasserkreislauf



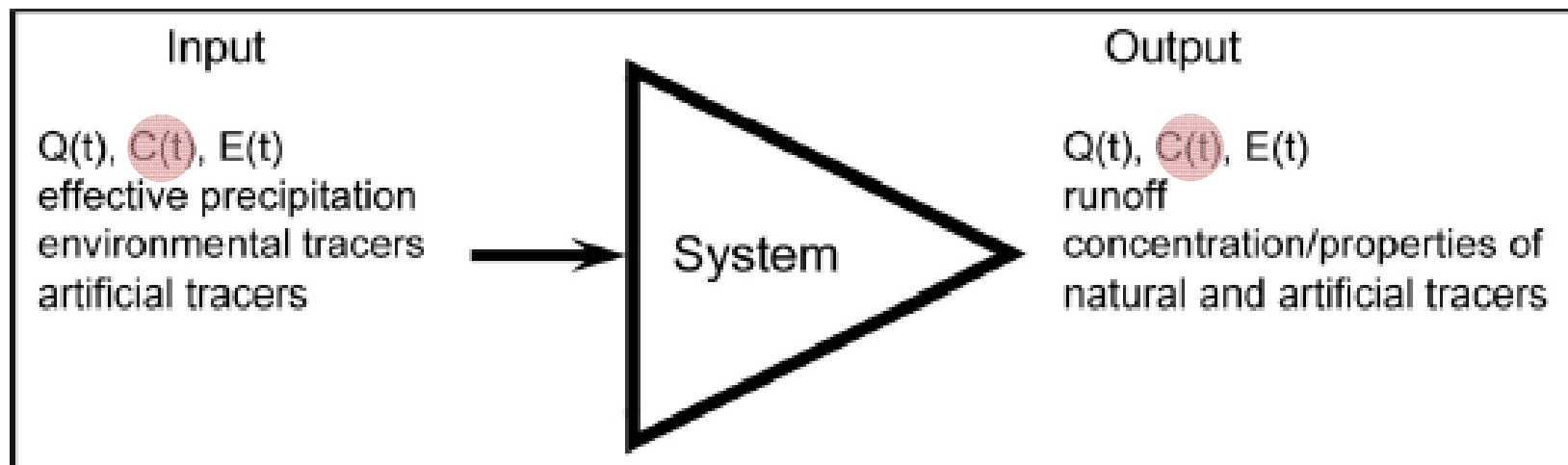
# ... zum wassergebundenen Stoffkreislauf



Source: Domenico & Schwartz, 1990

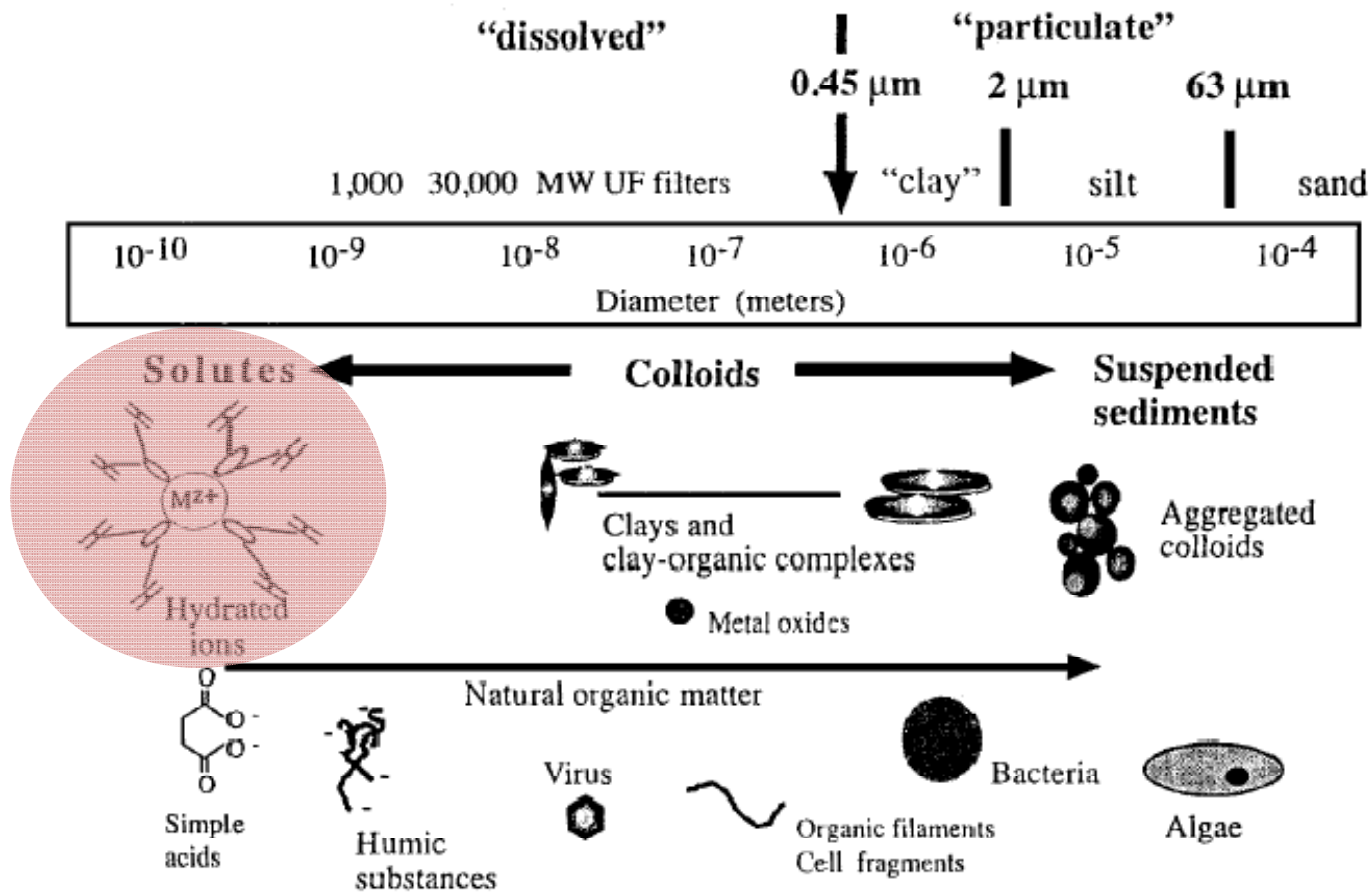
# Grundkonzept der Tracerhydrologie

*The principle idea of considering water and solute cycles is based on the application of system theory to environments.*



Source: Leibundgut et al., 2009

# Wdh: Anfang mit der Hydrochemie



# Anwendung von Tracern

*The ‘load’ of water – properties, constituents (isotopes), solutes, particles – contain and represent information. They are tracers.*

Environmental tracers	Artificial tracers
<i>Utilization</i>	<i>Application</i>
Environmental isotopes	Chemicals
Hydrochemical substances	Biological substances
Pollution tracers	Drift substances
<i>Characteristics:</i>	<i>Characteristics:</i>
Spatial input via precipitation, geogenic sources	punctual input (injection), defined by time, place, hydrological situation
	Pollution tracers (e.g. Cl <sup>-</sup> SF <sub>6</sub> CFCs)

Source: Leibundgut et al., 2009

# Hydrochemie im Rahmen aller Tracer

Environmental traces		Artificial traces	
Environmental isotopes		Solvents	
Stable		Radioactive	Salts
Deuterium	$^2\text{H}$	Tritium	$\text{Na}^+\text{Cl}^-$
Oxygen-18	$^{18}\text{O}$		$\text{K}^+\text{Cl}^-$
Carbon-13	$^{13}\text{C}$		$\text{Li}^+\text{Cl}^-$
	$^3\text{He}$		
Helium-3	$^{15}\text{N}$		$\text{HBO}_2$
Nitrogen-15			
Sulfur-34	$^{34}\text{S}$		
<i>Radioactive</i>		<i>Drifting particles</i>	<i>Fluorescence tracers</i>
Tritium	$^3\text{H}$		
Carbon-14	$^{14}\text{C}$		Uranine
Argon-39	$^{39}\text{Ar}$	Lycopodium spores	Eosine
Krypton-85	$^{85}\text{Kr}$	Fluorescent particles	Naphtionate
Silicium-32	$^{32}\text{Si}$	Bacteria	Pyranine
Chlorine-36	$^{36}\text{Cl}$	Viruses	Amidorhodamine
<i>Geochemical compounds</i>		Phages	Rhodamines
Elec. Conductivity	ec		
Sodium chloride	NaCl		
others	Si, B, DOC		

*Pollution Tracers, for example CFCs, . . . heavy metals, phosphate, radioactive compounds*

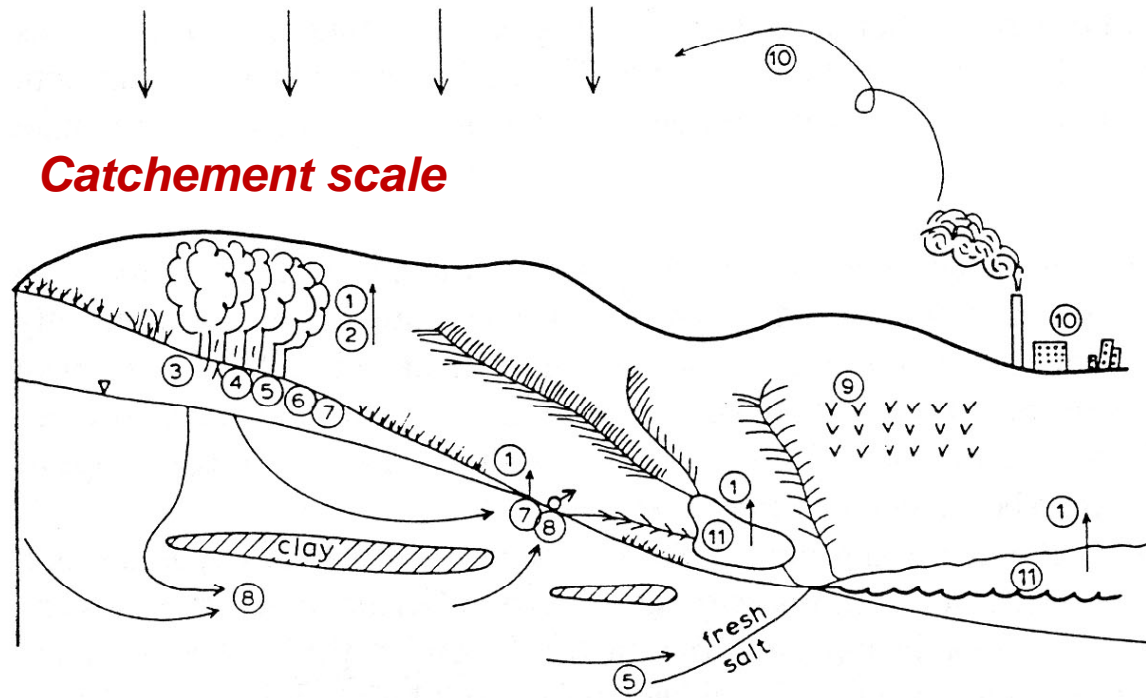


# Anwendungen

- *origin assignment of water and water constituents*: more specifically the assignment of recharge altitude or the discrimination of summer or winter recharge, detection of origin of nitrate or dissolved inorganic carbon;
- *hydrological process studies*: identification of runoff components, subsurface flow mechanisms, direct or indirect recharge mechanisms;
- *quantitative determination of flow components*: estimation of evaporation from open water surface, hydrograph separation;
- *determination of residence times*: age dating or analysis of the amplitude of the variation of stable isotopes of water.

Source: Leibundgut et al., 2009

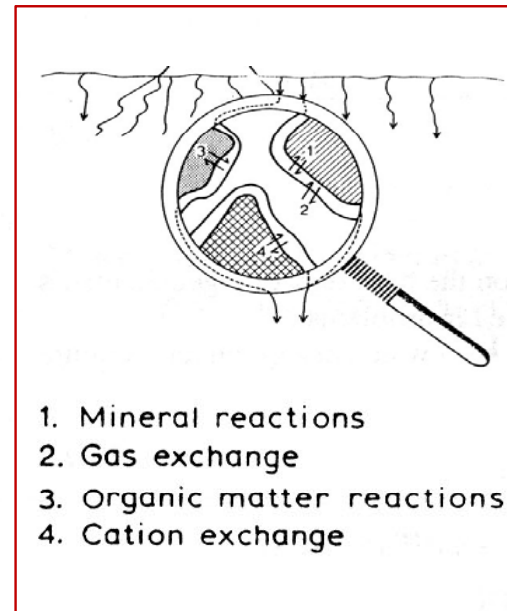
# Hydrochemische Prozesse & Einzugsgebiete



## Catchement scale

- |                                  |                                       |
|----------------------------------|---------------------------------------|
| ① evaporation                    | ⑦ precipitation of secondary minerals |
| ② transpiration                  | ⑧ mixing of water                     |
| ③ selective uptake by vegetation | ⑨ leaching of fertilisers, manure     |
| ④ oxidation/reduction            | ⑩ pollution                           |
| ⑤ cation exchange                | ⑪ lake/sea biological processes       |
| ⑥ dissolution of minerals        |                                       |

## Pore scale



1. Mineral reactions
2. Gas exchange
3. Organic matter reactions
4. Cation exchange

# Gliederung

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- Tracerkonzept
- **Grundlagen der Hydrochemie**
  - Einheiten
  - Grafiken und Darstellungen
- Etwas Thermodynamik
  - Gleichgewichtsreaktionen
  - Austausch

# Grundlagen

Elektroneutralität, Massenbilanz, Genauigkeit der Messung:

Ladungsbilanz =  $(\text{Summe Kationen} - \text{Summe Anionen})$

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$(\text{Summe Kationen} + \text{Summe Anionen})$

# Grundlagen

## Konzentrationen

mol/L      Konzentration, mit einer der Avogadro-Anzahl entsprechenden Masse des Stoffes pro Liter Wasser

meq/L      Konzentration, mit einer der Avogadro-Anzahl entsprechenden Menge von Elektronen pro Liter

Menge in g, die mit einem g Wasserstoff reagiert.

Berechnung:  $\text{mol} \cdot \text{Valenz} = \text{Eq}$

N      Normalität: Equivalent / Liter

# Grundlagen: Stoffe

## The dissolved constituents in groundwater classified according to relative abundance\*

### Major constituents (greater than 5 mg/L)

Bicarbonate	Silicon
Calcium	Sodium
Chloride	Sulfate
Magnesium	Carbonic acid

### Minor constituents (0.01–10.0 mg/L)

Boron	Nitrate
Carbonate	Potassium
Fluoride	Strontium

### Organic compounds (shallow)

Humic acid	Tannins
Fulvic acid	Lignins
Carbohydrates	Hydrocarbons
Amino acids	

### Organic compounds (deep)

Acetate
Propionate

\*Modified from Davis, S.N., and R.J.M. DeWiest, 1966, Hydrogeology. Copyright © 1966 by John Wiley and Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

### Trace constituents (less than 0.1 mg/L)

Aluminum	Molybdenum
Antimony	Nickel
Arsenic	Niobium
Barium	Phosphate
Beryllium	Platinum
Bismuth	Radium
Bromide	Rubidium
Cadmium	Ruthenium
Cerium	Scandium
Cesium	Selenium
Chromium	Silver
Cobalt	Thallium
Copper	Thorium
Gallium	Tin
Germanium	Titanium
Gold	Tungsten
Indium	Uranium
Iodide	Vanadium
Lanthanum	Ytterbium
Lead	Yttrium
Lithium	Zinc
Manganese	Zirconium

# Begriffe: Wasser & natürliche Gase

Gleichgewichtskonzentrationen in Wasser für 25°C, Atmosphärendruck und Ionenstärke von 0 (nach Alloway u. Ayres 1996, Sigg u. Stumm 1994, Umweltbundesamt 1988/89)

Gas	Volumen %	Henry Konstante $K_H$ (25°C) in mol/kg·kPa	Konzentration im Gleichgewicht	
N <sub>2</sub>	78.1	$6.40 \cdot 10^{-6}$	0.50 mmol/L	14.0 mg/L
O <sub>2</sub>	20..9	$1.26 \cdot 10^{-5}$	0.26 mmol/L	8.43 mg/L
Ar	0.943	$1.37 \cdot 10^{-5}$	12.9 µmol/L	0.515 mg/L
CO <sub>2</sub>	0.028 ... 0.035	$3.39 \cdot 10^{-4}$	Folgereaktionen	Folgereaktionen
Ne	0.0018	$4.49 \cdot 10^{-6}$	8 nmol/L	0.16 µg/L
He	$0.51 \cdot 10^{-3}$	$3.76 \cdot 10^{-6}$	19 nmol/L	76 ng/L
CH <sub>4</sub>	$1.7 \cdot 10^{-6}$	$1.29 \cdot 10^{-5}$	2.19 nmol/L	35 ng/L
N <sub>2</sub> O	$0.304 \cdot 10^{-6}$	$2.57 \cdot 10^{-4}$	0.078 nmol/L	3.4 ng/L
NO	---	$1.9 \cdot 10^{-5}$	Folgereaktionen	Folgereaktionen
NO <sub>2</sub>	10 bis $22 \cdot 10^{-9}$	$1.0 \cdot 10^{-4}$	Folgereaktionen	Folgereaktionen
NH <sub>3</sub>	$0.2 \cdot 2 \cdot 10^{-9}$	0.57	Folgereaktionen	Folgereaktionen
SO <sub>2</sub>	$10 \cdot 10^{-9}$ bis $19 \cdot 10^{-9}$	0.0125	Folgereaktionen	Folgereaktionen
O <sub>3</sub>	$10 \cdot 10^{-9}$ bis $100 \cdot 10^{-9}$	$9.4 \cdot 10^{-5}$	0.094 ... 0.94 nmol/L	4.5 ... 45 ng/L

aus Merkel B.J. & Planer-Friedrich B. (2002): Grundwasserchemie. Springer. 219 p.

# Begriffe: Wasser & natürliche Gase

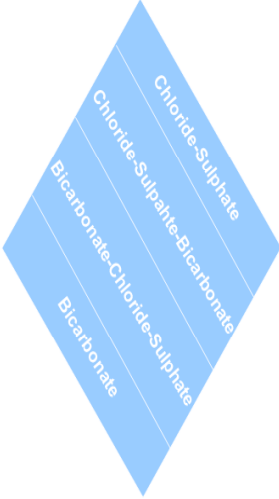
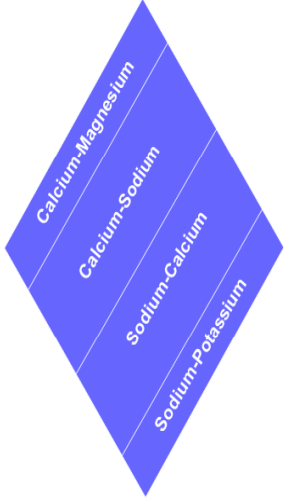
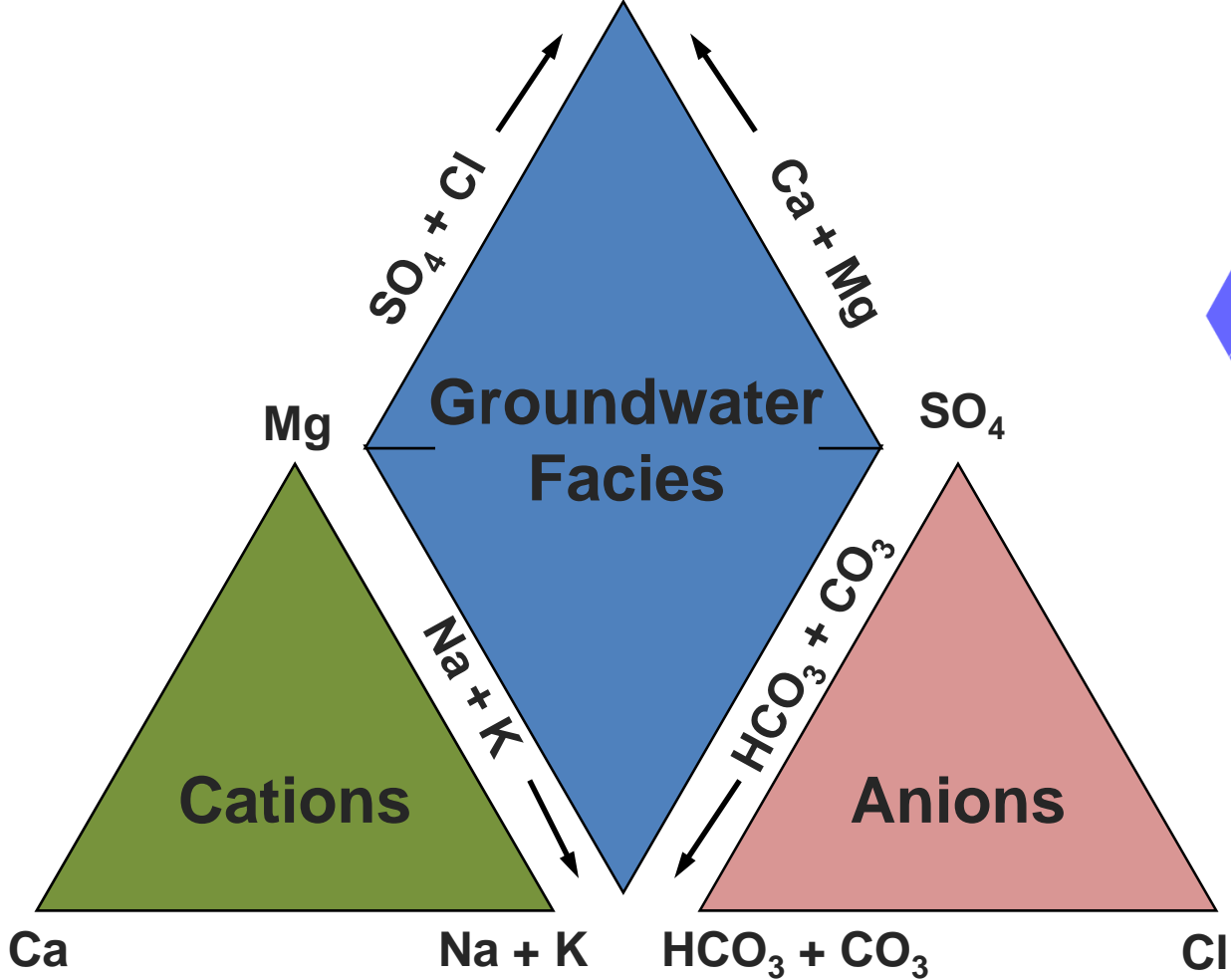
**Löslichkeit von Gasen in Wasser in mg/L unter Atmosphärendruck (Rösler u. Lange 1975)**

Temperatur	0°C	5°C	10°C	15°C	20°C	25°C
N <sub>2</sub>	22.88	20.25	18.09	16.37	15.10	14.00
O <sub>2</sub>	14.46	12.68	11.24	10.10	9.18	8.43

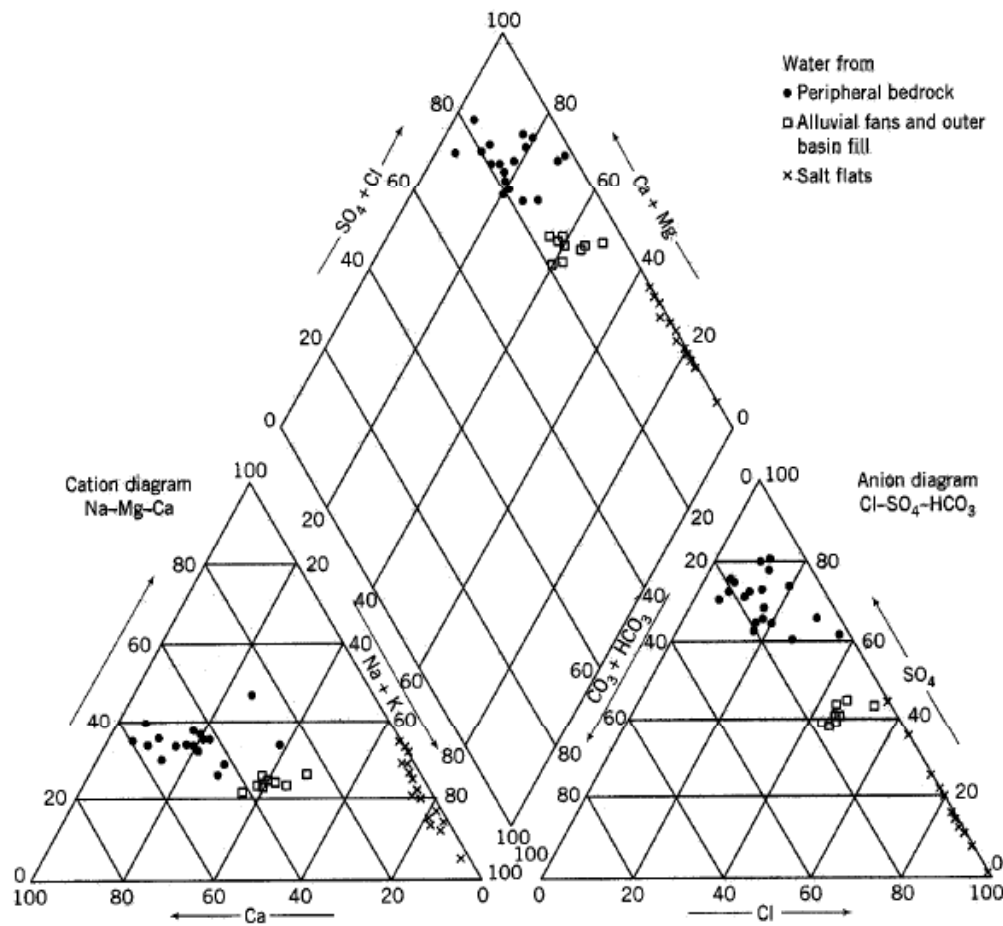
*aus Merkel B.J. & Planer-Friedrich B. (2002): Grundwasserchemie. Springer. 219 p.*



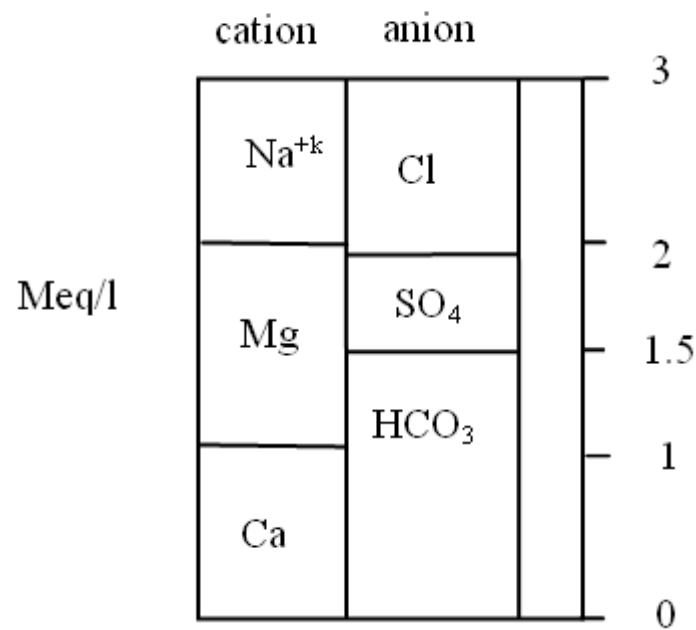
# Piperdiagramme



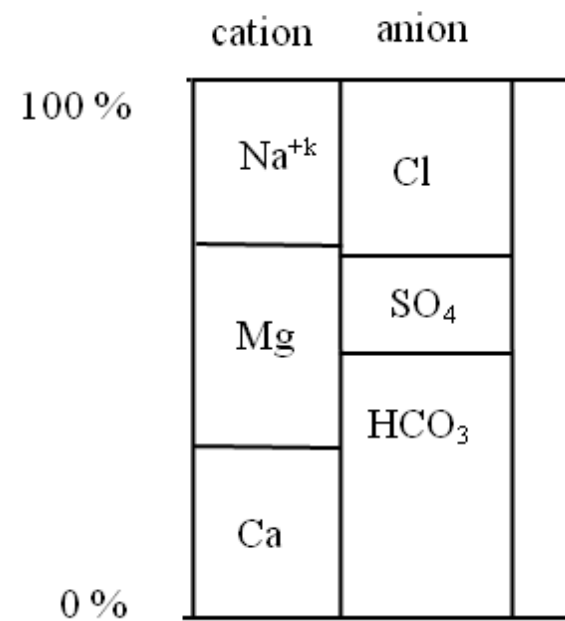
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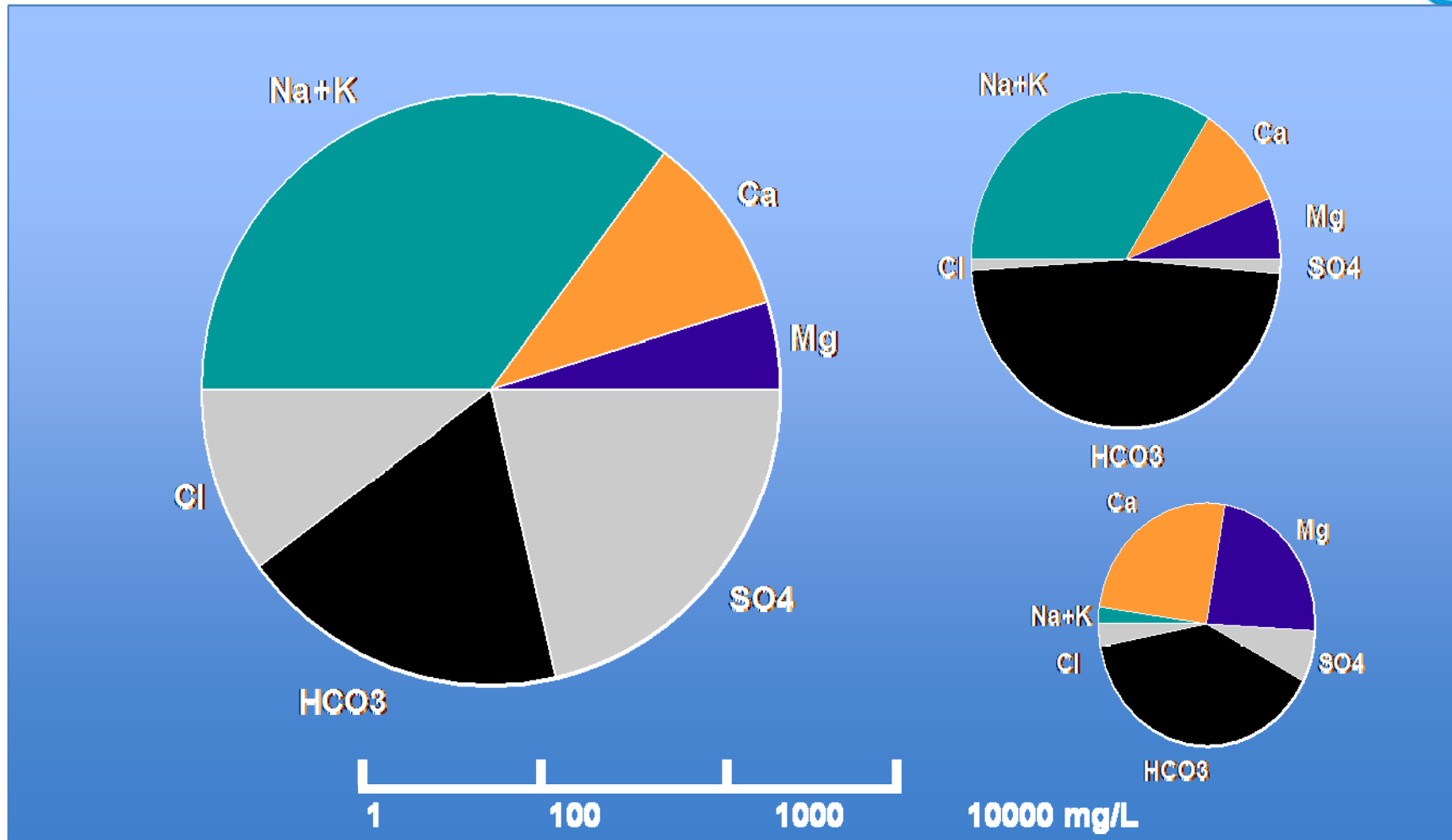
# Ladungsbilanzdiagramme



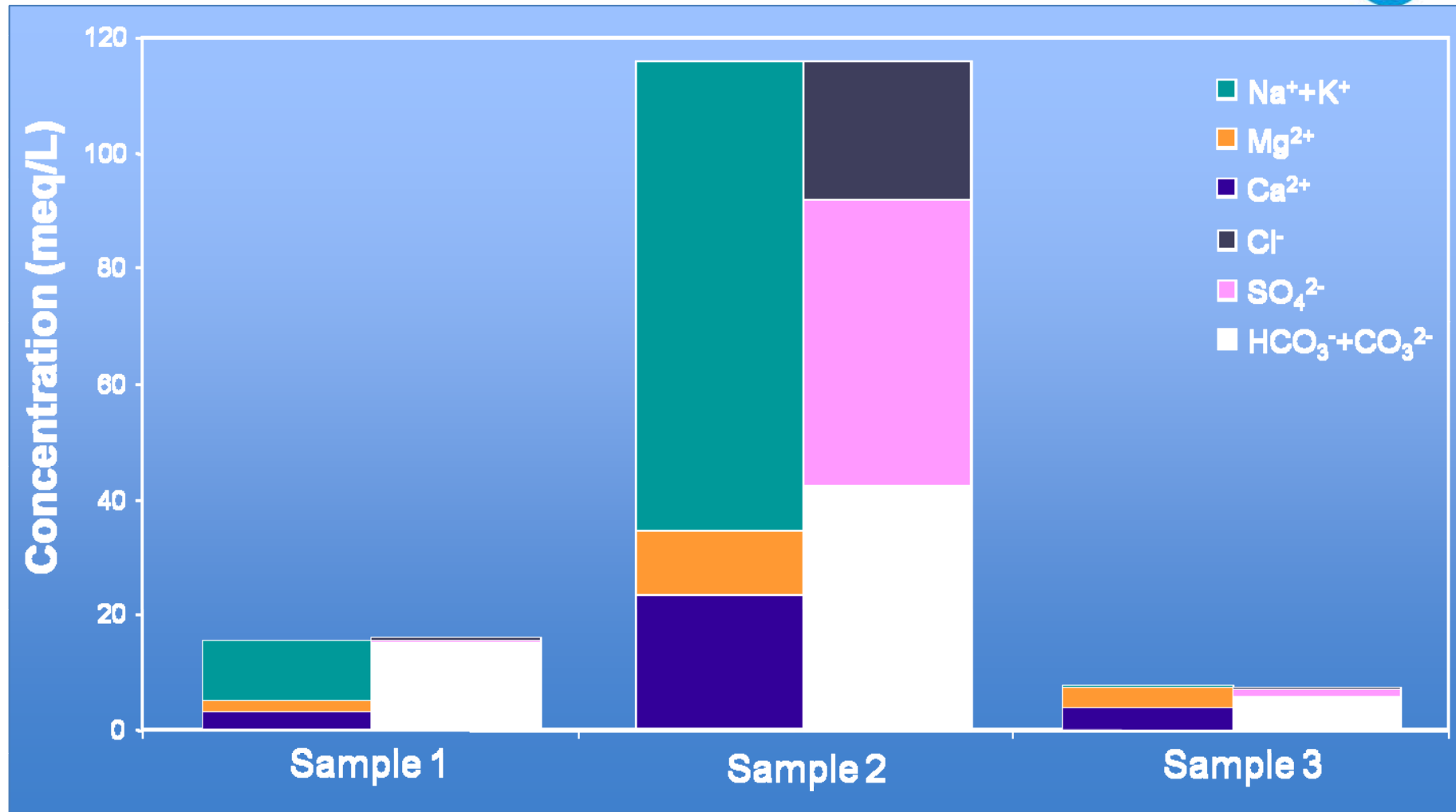
or as %



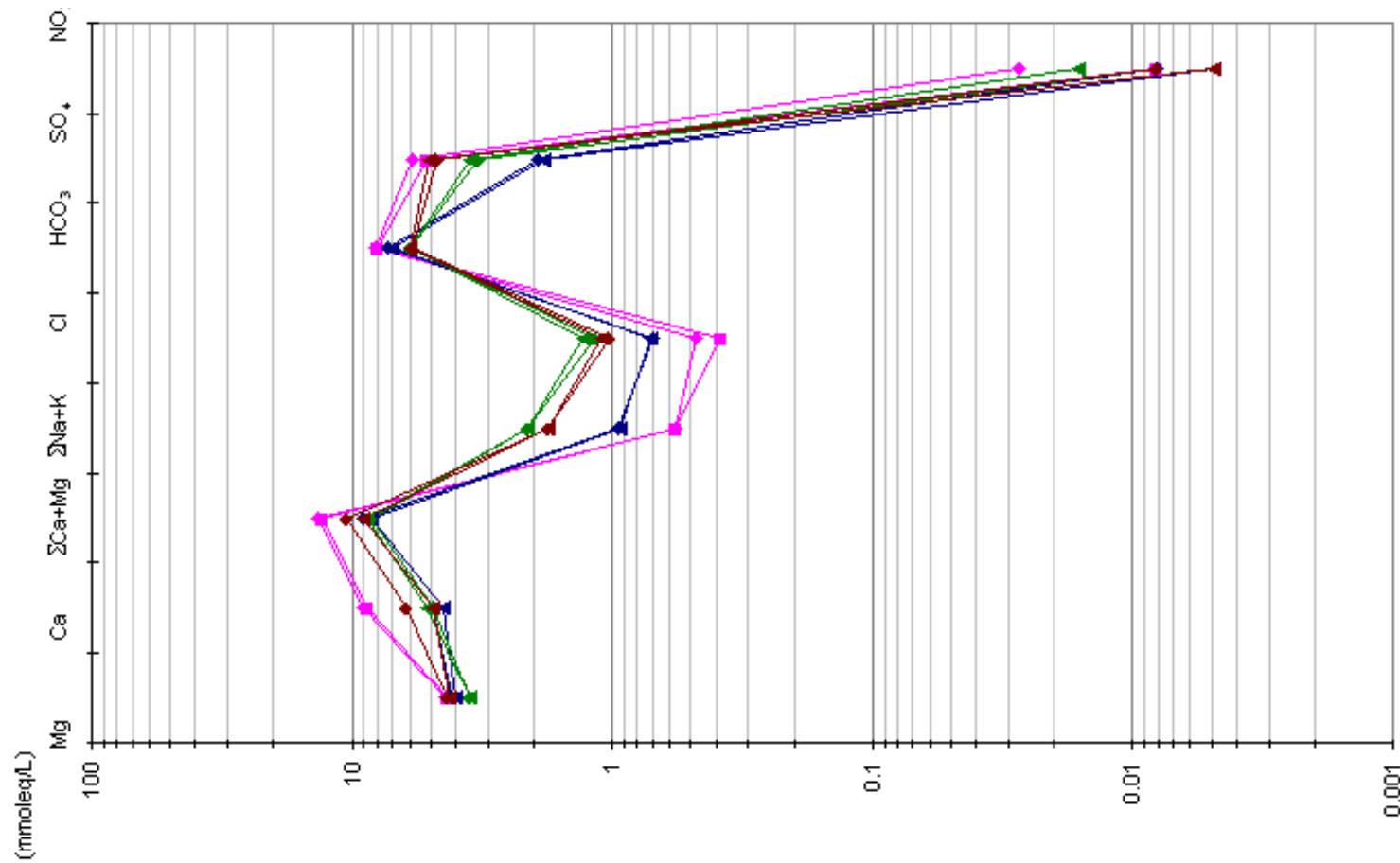
# Ladungsbilanzdiagramme



# Ladungsbilanzdiagramme



# Schoeller (Bitburg)



# Schöller-Varianten

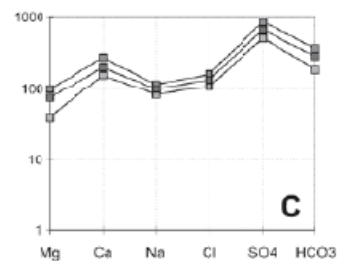
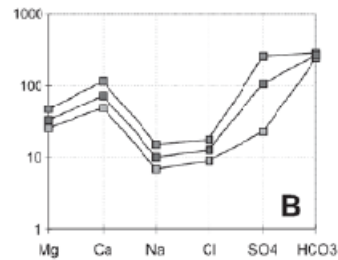
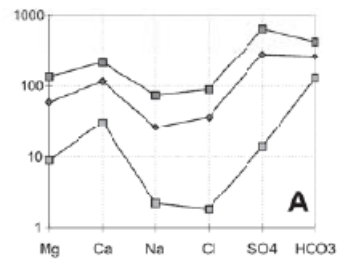
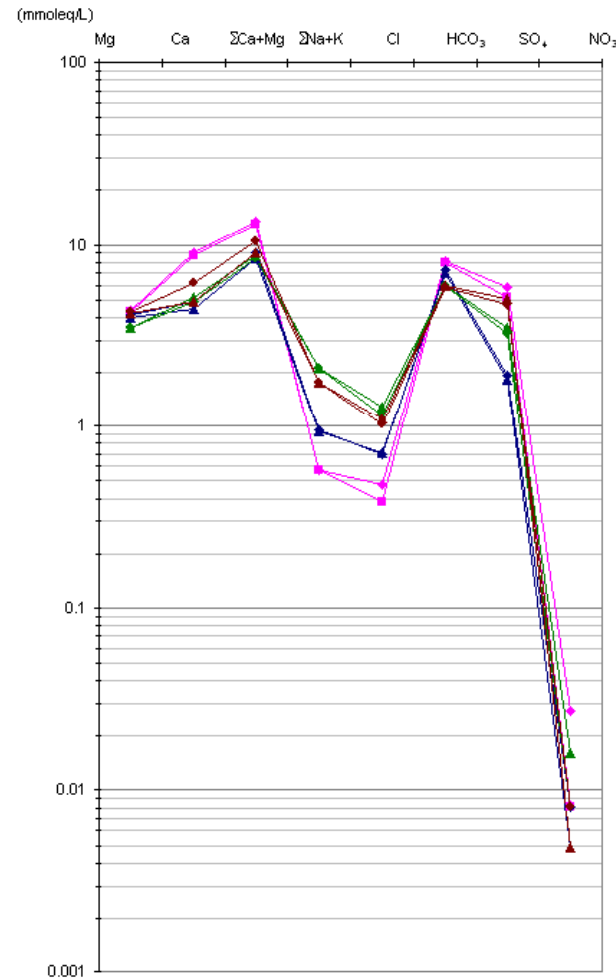
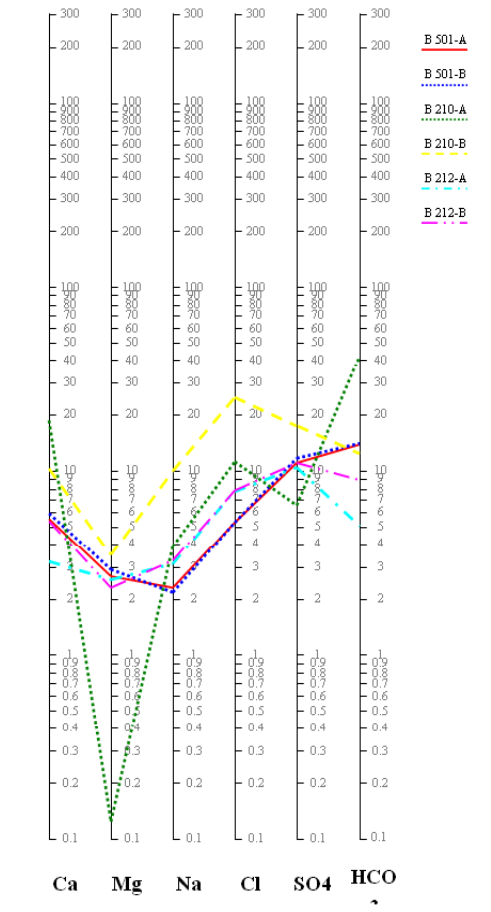


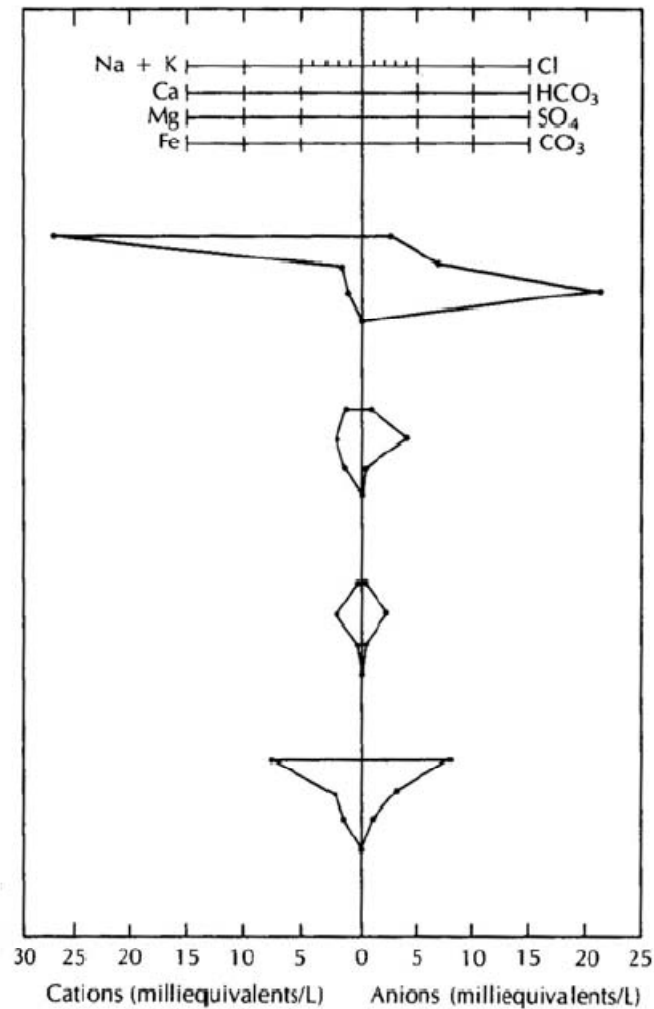
Fig. 2.- Diagrama de Schoeller-Berkaloff correspondiente a los valores máximos, medios y mínimos. (A): Aguas superficiales, (B): Acuífero Carbonatado del Alto Andarax y (C): Acuífero Detrítico en el Medio Andarax.



- ◆ Brunnen IV 17.04.01
- ◆ Brunnen IV 22.08.01
- ◆ Brunnen V 17.04.01
- ◆ Brunnen V 22.08.01
- ◆ Brunnen VI 12.06.01
- ◆ Brunnen VI 22.08.01
- ◆ Brunnen VII 22.05.01
- ◆ Brunnen VII 22.08.01



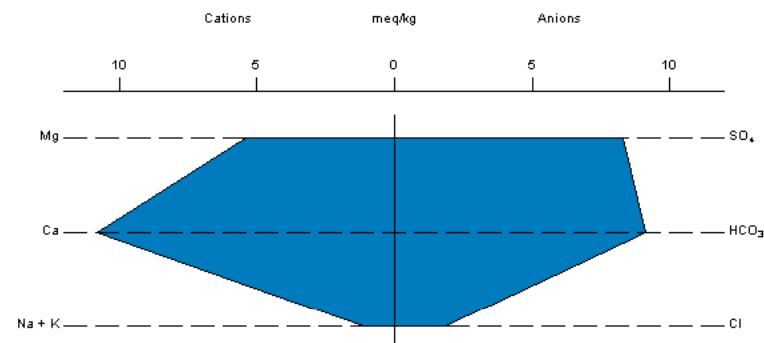
# Stiff-Diagramme



## Stiff-Diagramme

- Vorteil: Verteilung und Konzentration
- Nachteil: Interpretation umständlich

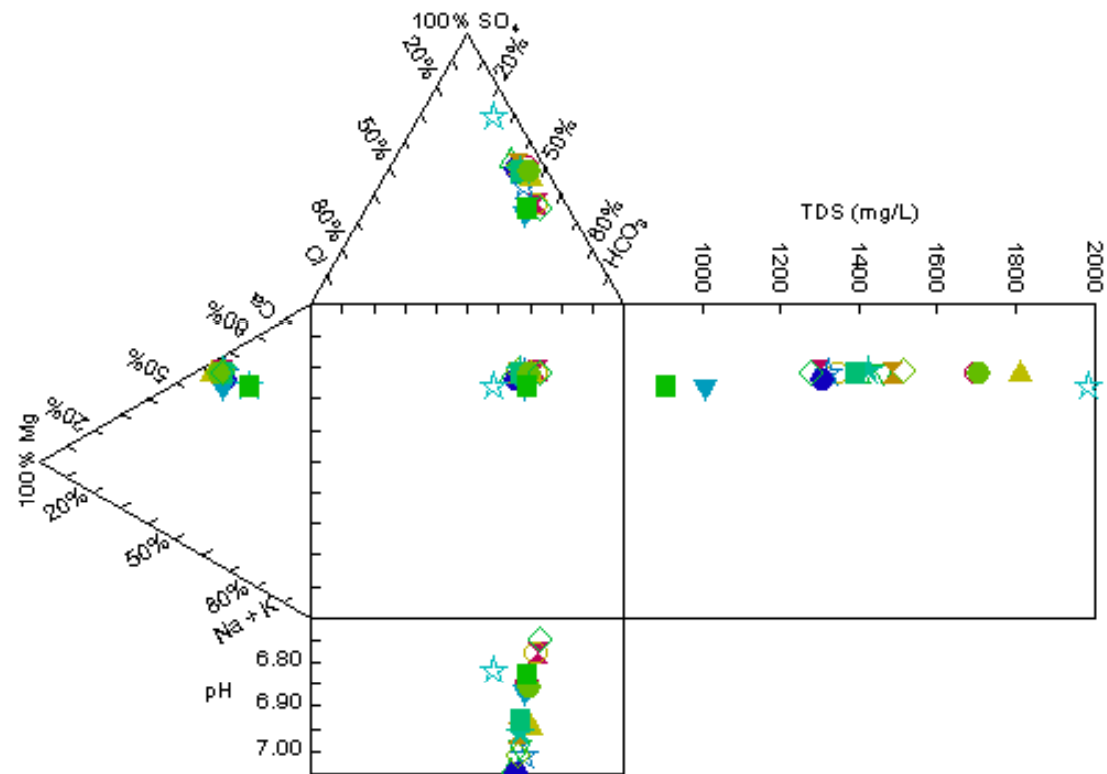
Stiff Diagram





# Durov-Diagramme

Durov Diagram



- Legend
- P3-212
  - P3-213
  - P3-214
  - P3-215
  - P3-216
  - P3-217
  - P3-218
  - P3-219
  - P3-220
  - P3-222
  - P3-227
  - P3-228
  - P3-229
  - P3-230
  - P3-232
  - P3-233
  - P3-234

# Gliederung

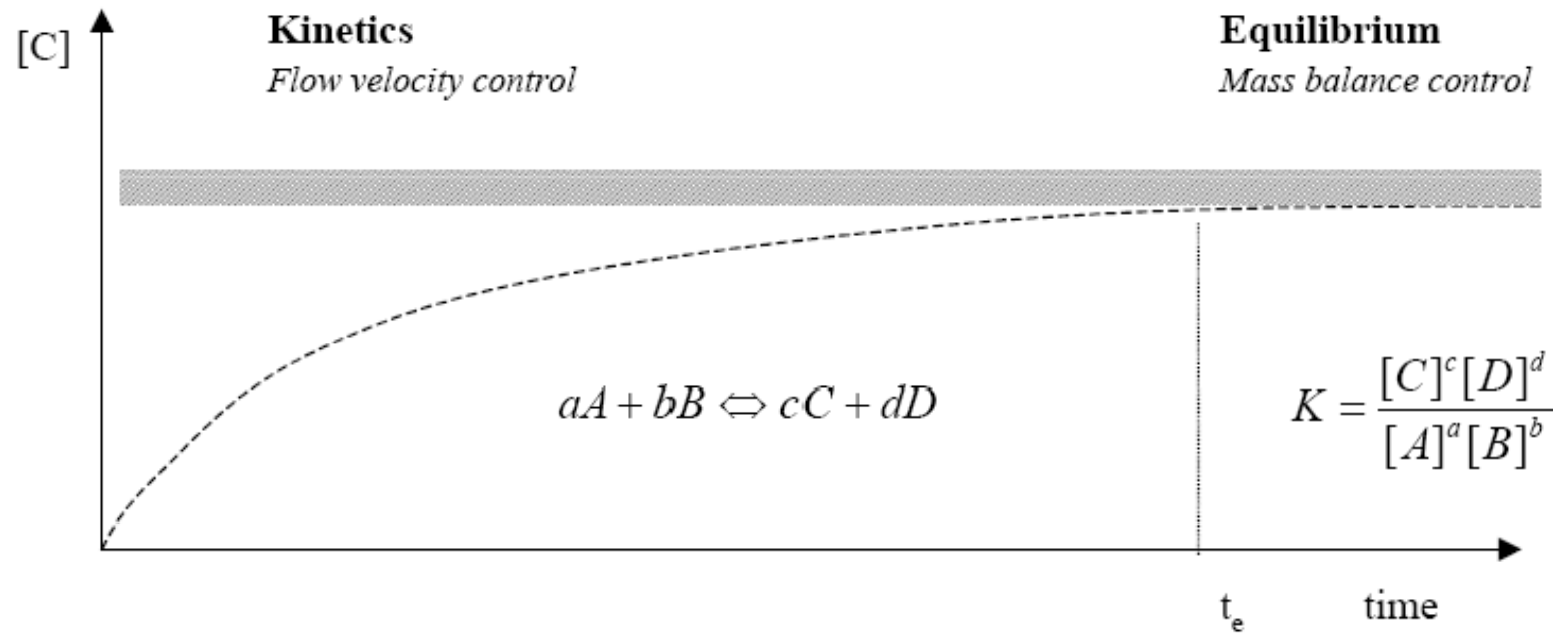
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- Tracerkonzept
- Grundlagen der Hydrochemie
  - Einheiten
  - Grafiken und Darstellungen
- **Prozesse & Thermodynamik**
  - Gleichgewichtsreaktionen
  - Austausch

# Prozesse & Thermodynamik

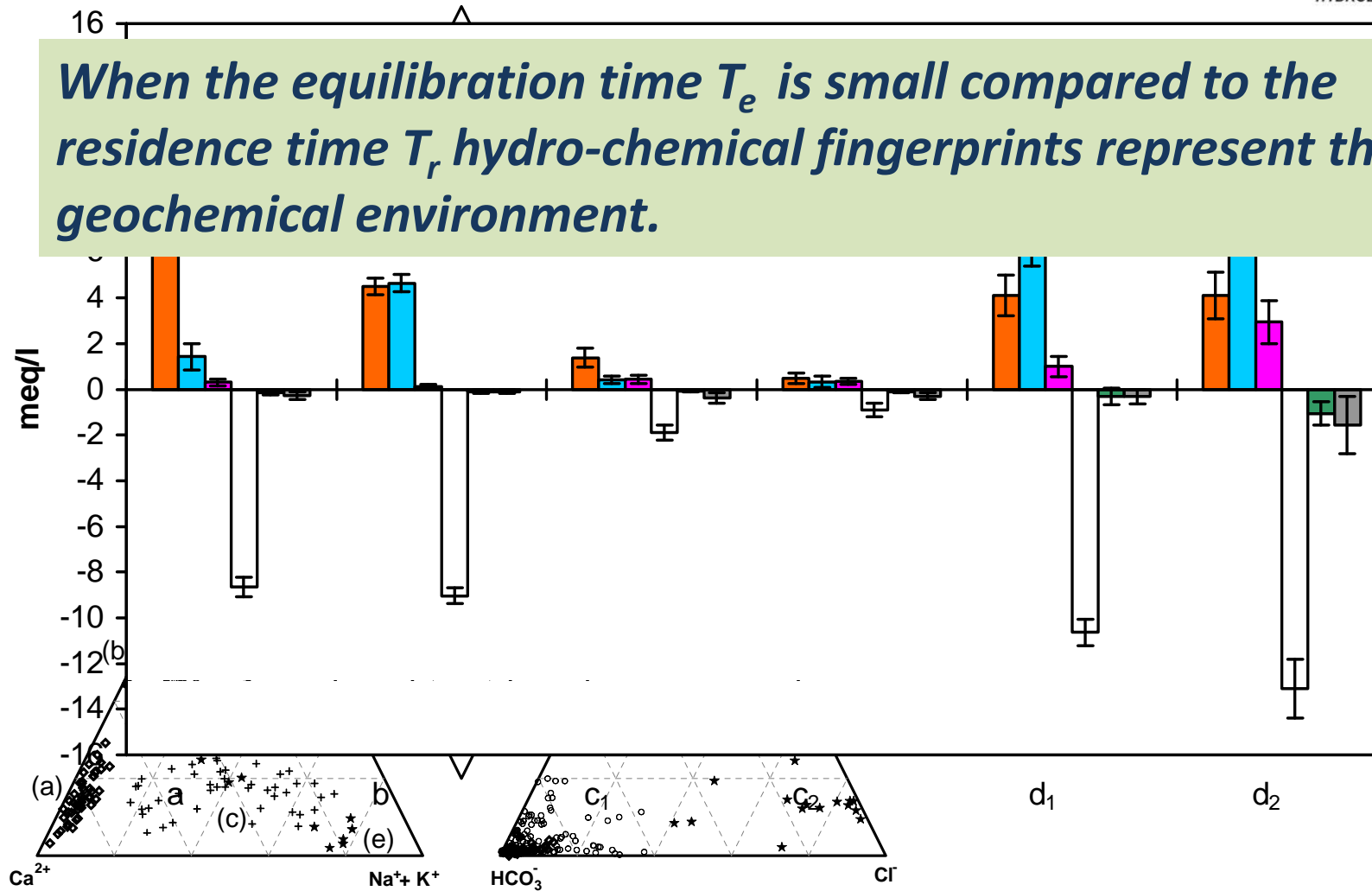
Transport- prozesse	Wechselwirkungsprozesse				Zerfalls- prozesse
	Wasser (phasen- intern)	Wasser- Gestein	Wasser- organische Substanz	Wasser- Gas	
1. konvekti- ver Trans- port ein- schließlich hydrodyna- mischer Dispersion	1. Mischpro- zesse	1. Sorption/ Desorption	1. Sorption/ Desorption	1. Lösung/ Entgasung	1. radioaktiver Zerfall
2. Diffusions- prozesse	2. Lösung/ Fällung	2. Ionenaus- tausch	2. Ionenaus- tausch	2. Redoxpro- zesse	2. Absterben der Bio- masse durch
	3. Komplex- bildung und Zer- fall	3. Protolyse	3. Minerali- sierung organischer Substanz	3. Komplex- bildung/ -zerfall	- Alterung
	4. Dissozia- tion/Re- kombi- nation	4. Lösung/ Fällung	4. Nährstoff- entzug durch Pflanzen- wurzeln		- Nahrungs- mangel
	5. Protolyse	5. Redoxpro- zesse	5. Protolyse		- Nahrungs- konkurrenz
	6. Redoxreak- tionen	6. Dissoziation/ Rekombina- tion	6. Komplexbil- dung/-zerfall		- ungünstige ökologische Bedingungen
		7. Hydratation/ Dehydra- tation	7. katalytische Redoxpro- zesse		3. Koagulation emulgierter Stoffe

# Prozesse & Thermodynamik

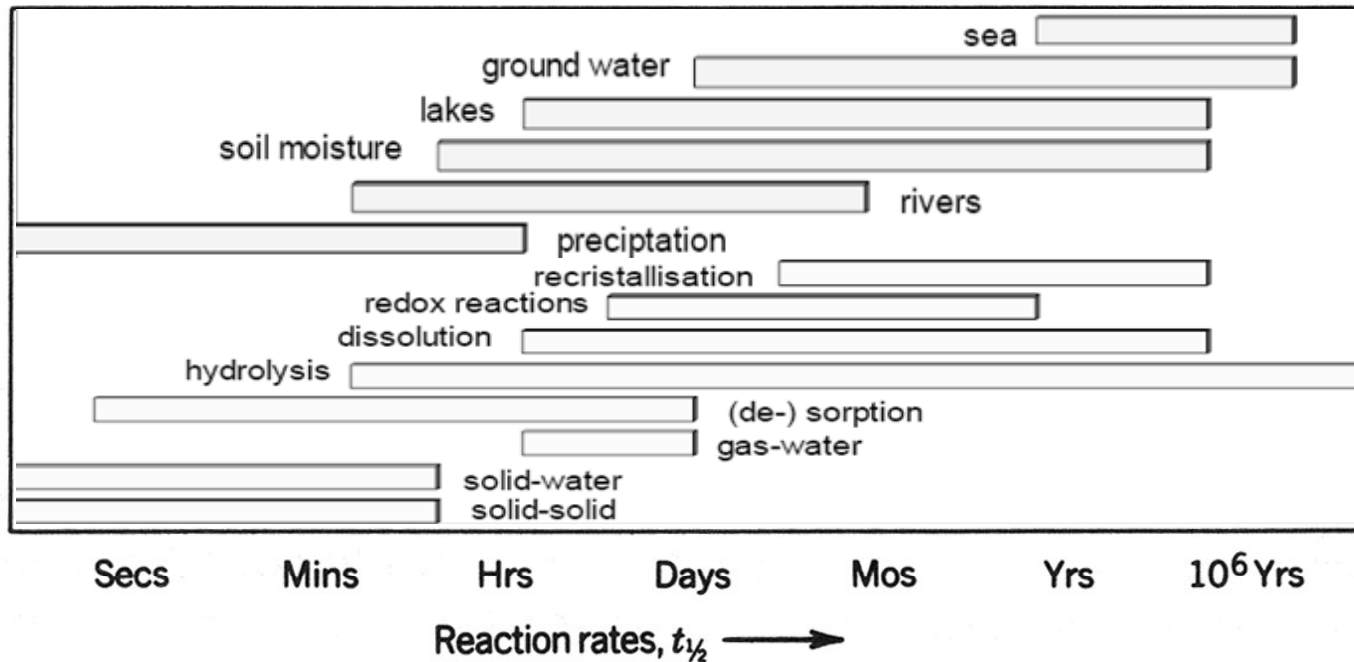


# Hydrochemical groups ( $T_e < T_r$ )

*When the equilibration time  $T_e$  is small compared to the residence time  $T_r$ , hydro-chemical fingerprints represent the geochemical environment.*



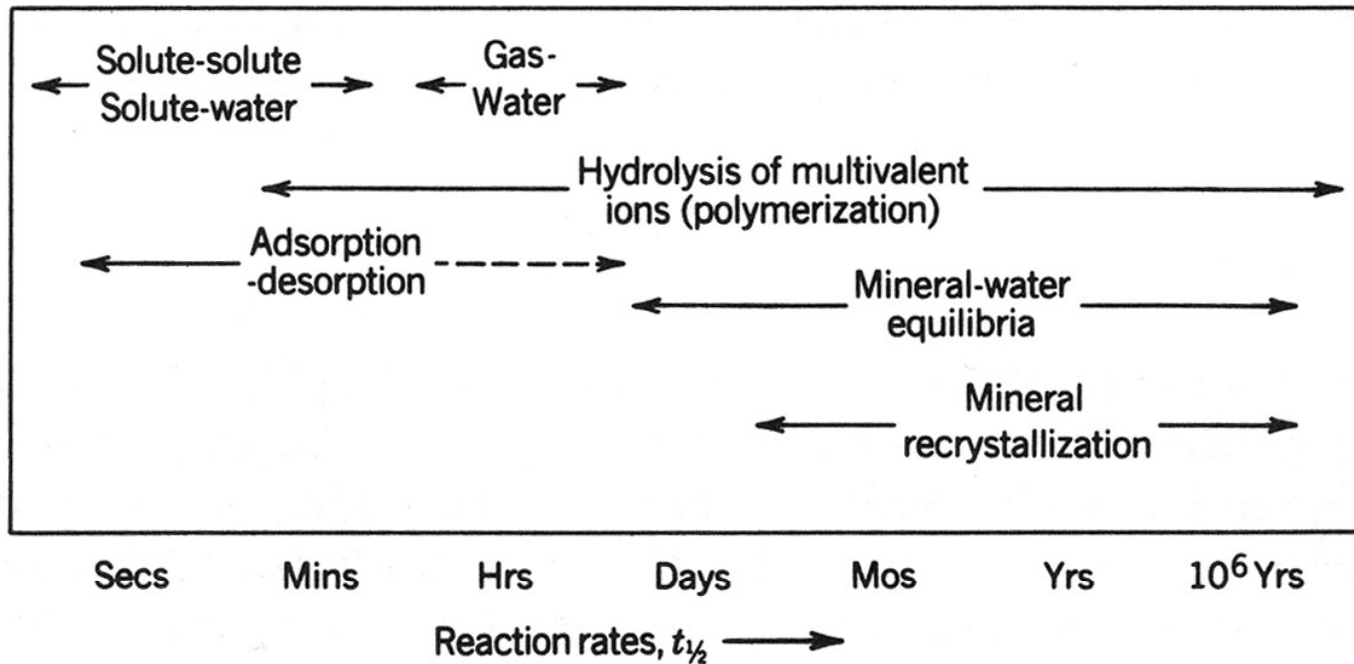
# Thermodynamik für Schnelles



A comparison of reaction half-times ( $t_{1/2}$ ) for many of the common reactions in aqueous systems (from Langmuir and Mahoney, 1984). Reprinted by permission First Canadian/American Conference on Hydrogeology. Copyright © 1984. All rights reserved.

Quelle: Stumm & Morgan, 1996

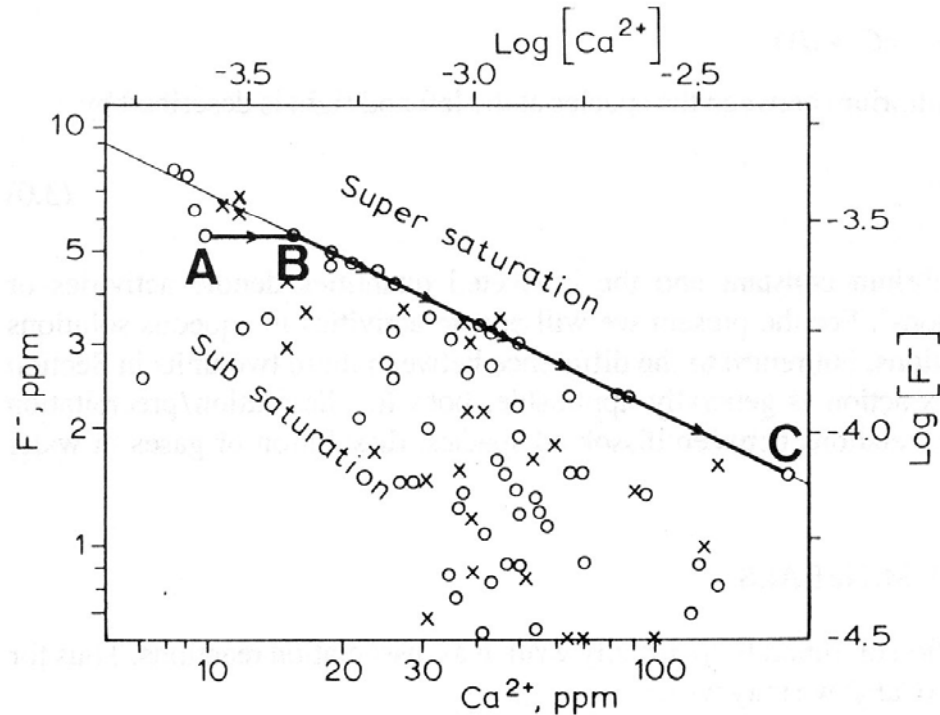
# Thermodynamik: Ionenstärke, Aktivität



A comparison of reaction half-times ( $t_{1/2}$ ) for many of the common reactions in aqueous systems (from Langmuir and Mahoney, 1984). Reprinted by permission First Canadian/American Conference on Hydrogeology. Copyright © 1984. All rights reserved.

Quelle: Stumm & Morgan, 1996

# Löslichkeitsgrenze



Grenzwerte durch  
Sättigung

Hier: Beispiel Fluorid

Figure 3.1. The stability of fluorite and the saturation of groundwaters from Sirohi, W. Rajasthan, India (modified from Handa, 1975). The evolution in water chemistry upon addition of gypsum is described by the pathway A, B to C as discussed in the text.

*Appelo C.A.J. & Postma D. (1996) Geochemistry, groundwater and pollution. Balkema, 536 p.*



# Löslichkeitsgrenze

$$\text{Ion activity product} = [A]_{\text{sample}}^a * [B]_{\text{sample}}^b$$

The ratio between the ion activity product and solubility product  $K_s$  indicates the saturation state with respect to that mineral. In general, the logarithm of the saturation state is used, called the *saturation index*

$$\text{saturation Index (SI)} = \log\left(\frac{\text{ion activity product}}{K_s}\right)$$

Quelle: Külls, 2000

# Gleichgewichtskonstanten

Equilibrium reactions and constants for mineral phases APPELO & POSTMA (1996) at 25°C.

Calcite	$\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	$K_c = 10^{-8.48}$
Magnesite	$\text{MgCO}_3 \leftrightarrow \text{Mg}^{2+} + \text{CO}_3^{2-}$	$K_m = 10^{-8.24}$
Dolomite	$\text{CaMg}(\text{CO}_3)_2 \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	$K_d = 10^{-16.54}$
(disordered)		$K_{dd} = 10^{-17.09}$
Gypsum	$\text{CaSO}_4 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$	$K_g = 10^{-4.58}$

# Thermodynamik: Ionenstärke, Aktivität

$$K = \frac{[C]^c * [D]^d}{[A]^a * [B]^b}$$

where  $a, b, c, d$  represent the stoichiometric constants of the reaction and where the respective activities are given in brackets. Equilibrium constants can be calculated thermodynamically  
The activity coefficient  $\gamma$  is a function of the ionic strength  $I$  of the solution, defined as

$$I = 0.5 \sum m_i z_i^2$$

$$\log \gamma_i = -A z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right)$$

$A$  is a temperature factor, corresponding to  $A=0.5085$  for  $25^\circ\text{C}$  (typical conditions for groundwater in Namibia).

# Thermodynamik: Ionenstärke, Aktivität

T (°C)	<i>A</i>	<i>B</i> ( $\times 10^8$ )		Ion	$a_o$ ( $\times 10^{-8}$ )
0	0.4883	0.3241		Ca <sup>2+</sup>	5.0
5	0.4921	0.3249		Mg <sup>2+</sup>	5.5
10	0.4960	0.3258		Na <sup>+</sup>	4.0
15	0.5000	0.3262		K <sup>+</sup> , Cl <sup>-</sup>	3.5
20	0.5042	0.3273		SO <sub>4</sub> <sup>2-</sup>	5.0
25	0.5085	0.3281		HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>	5.4
30	0.5130	0.3290		NH <sub>4</sub> <sup>+</sup>	2.5
40	0.5221	0.3305		Sr <sup>2+</sup> , Ba <sup>2+</sup>	5.0
50	0.5319	0.3321		Fe <sup>2+</sup> , Mn <sup>2+</sup> , Li <sup>+</sup>	6.0
60	0.5425	0.3338		H <sup>+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup>	9.0

# Lösung und Fällung bei Verdunstung

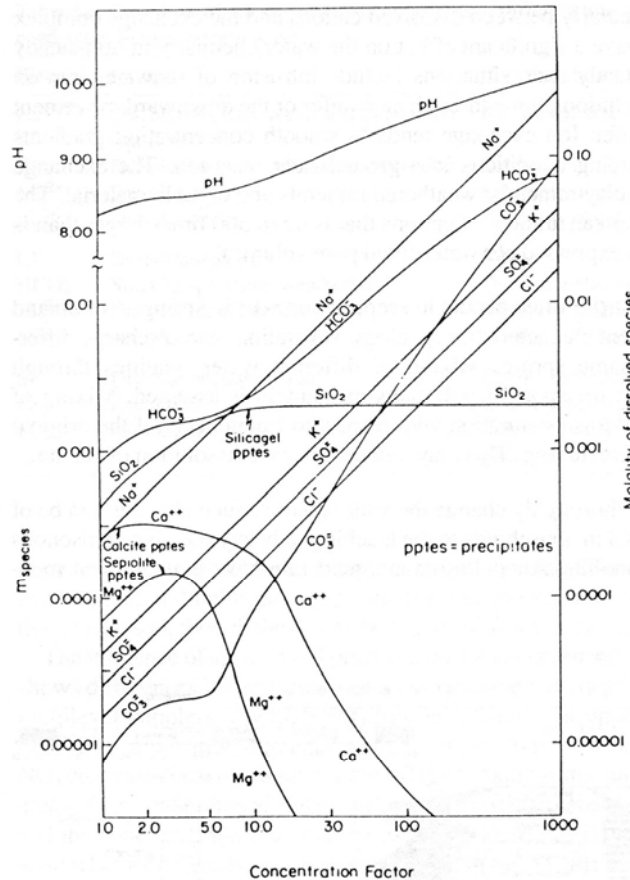


Figure 2.14. Calculated results of evaporation of typical Sierra Nevada spring water at constant temperature in equilibrium with atmospheric CO<sub>2</sub> (Reprinted with permission from Garrels and Mackenzie, Copyright 1967, American Chemical Society).

- Einfluss der Verdunstung
- persistente gelöste Stoffe:
  - Cl, SO<sub>4</sub>, NO<sub>3</sub>
- ausfallende gelöste Stoffe
  - Mg, Cl
- Plateau-Werte bei
  - Silikat
  
- Anwendung ist die inverse Berechnung der Verdunstung

Appelo C.A.J. & Postma D. (1996) *Geochemistry, groundwater and pollution*. Balkema, 536 p.

# Lösung und Fällung bei Verdunstung

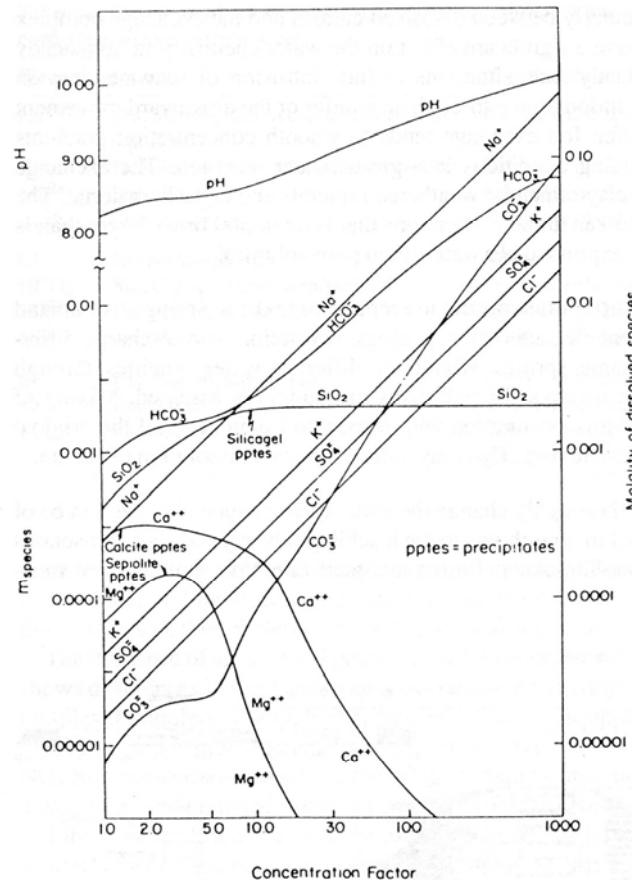


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  - $\text{Cl}$ ,  $\text{SO}_4$ ,  $\text{NO}_3$
- ausfallende gelöste Stoffe
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  - Silikat
  
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Appelo C.A.J. & Postma D. (1996) *Geochemistry, groundwater and pollution*. Balkema, 536 p.

# Theory: Henry's Law – $c(k(t),p)$

The dissolved concentration  $c_i$  (mol/l) of the gas is calculated according to Henry's law as a function of partial pressure  $p_i$  (Pa) and of the Henry constant  $k_{Hi}$  (mol/l\*Pa)

$$c_i = k_{Hi} * p_i$$

$$p_i = x_i(p - p_{H_2O})$$

where  $x_i$  is the volumetric ratio of gas in air (pptv). A correction for atmospheric moisture  $p_{H_2O}$  (Pa) is taken into account. The dissolution constant  $k_{Hi}$  depends on temperature and for saline water also on salinity  $S$  (‰ mass ratio). The water temperature  $T$  (K) can be taken into account (IAEA, 2006) according to:

$$\ln k_H = a_1 + a_2 \left( \frac{100}{T} \right) + a_3 \ln \left( \frac{T}{100} \right) + S \left[ b_1 + b_2 \left( \frac{T}{100} \right) + b_3 \left( \frac{T}{100} \right)^2 \right]$$

# Tracerhydrologie

