Mass balance, species, phases and charge balance

In the following, notions on equilibrium chemistry and on the hydrochemical evolution of groundwater are introduced. Equilibrium chemistry can be used to quantify thermodynamic limits for the concentration of dissolved species in a defined aqueous system. In some cases, the hydrochemical evolution of a certain groundwater type can be identified by inverse methods, yielding information on the recharge environment (lithology) and type (slow soil infiltration or quick infiltration through sinkholes).

The equilibrium concept provides a description of the final state of thermodynamic reactions after an undefined equilibration time $t_e$. At any time $t < t_e$, reaction kinetics are still relevant for the concentration of different species in the system. The relation between the residence time of a given water volume and the rate of a solution/precipitation reaction determines whether the concentrations are still controlled kinetically (flow velocity control) or by equilibrium conditions (mass balance control). Further information on mineral-water interface kinetics can be found in HOCHELLA & WHITE (1990).

The concept of equilibrium chemistry, reviewed among others by DREVER (1988), APPELO & POSTMA (1996), is based on the chemical law of mass action. This law states that for a reaction between the reactants A, B and the products C, D such as the distribution of species converges towards an equilibrium state, characterized by the equilibrium constant $K$

$$K = \frac{a^a \cdot b^b}{c^c \cdot d^d}$$

where $a$, $b$, $c$, $d$ represent the stochiometric constants of the reaction and where the respective activities are given in brackets. Equilibrium constants can be calculated thermodynamically (STUMM & MORGAN, 1995) and are listed in libraries of computer codes for equilibrium calculations in aquatic solutions such as PHREEQE (PARKHURST ET AL., 1990).

The equilibrium constant depends on the ambient temperature. In general, thermodynamic data are given for standard conditions of 25° C; corrections are made using the Van’t Hoff equation (APPELO & POSTMA, 1996: 61).

Concentrations $C$ of elements measured in the laboratory need to be converted to activities $[C]$ before being introduced into mass balance calculus. This is so, because in an aquatic solution the reactivity of ions is reduced by electrostatic interactions (i.e. shielding effects) with other ions. These effects become more important with increasing salinity. Therefore, ion concentrations need to be corrected by a dimensionless activity coefficient $\gamma$, hence $[C] = \gamma C$.

The activity coefficient $\gamma$ is a function of the ionic strength $I$ of the solution, defined as

$$\log_{gamma} = -A \cdot z_i^2 \cdot ((\sqrt{I} / 1 + \sqrt{I}) - 0.3 \cdot I)$$

with $m_i$ = molar concentration (mol/l) and $z_i$ = charge of ion. In normal hydrogeological systems (no brines) with low pressures and temperatures, the Davies equation can be used, stating that for an ion with charge $z_i$, dissolved in a solution with an ionic strength $I$, the activity coefficient is:

$$I = 0.5 \cdot \sum (m_i \cdot z_i^2)$$

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A is a temperature factor, corresponding to $A=0.5085$ for 25°C.

**Methods for the quantitative evaluation of data**

**Mass balance based methods: the Chloride method**

Chloride is deposited as dry deposition and as a dissolved constituent of rainwater. Both components form the total deposition of chloride, written as mass per m² per year. Most of the chloride deposited is of oceanic origin, deriving from sea spray and advective transport of aerosols. Oceanic chloride is dominant within 300 to 700 km from the coast. However, in areas, where significant deflation of dust from dry salt pans takes place, continental sources of chloride also become important. Most plants do not take up chloride in significant amounts. Therefore it is concentrated both by direct evaporation from the soil and selective uptake of water by plants. For a simple steady state approach it is assumed that the sum of wet and dry deposition of chloride at the top of a soil profile equals the total mean outflow of chloride from the root zone (ALLISON & HUGHES, 1983; ALLISON ET AL., 1985):

$$P \times C + D = R \times C_s$$

where $P$ is mean annual rainfall, $C$ the mean chloride concentration of rainfall, and $D$ is dry deposition. The right hand side of the equation represents the flux of chloride out of the root zone as the product of mean annual recharge $R$ and chloride concentration of the soil water $C_s$. The average products can be rewritten as:

$$\overline{P} \times \overline{C} + \overline{D} = \overline{R} \times \overline{C_s}$$

provided that the covariances between annual rainfall and annual chloride deposition, and between recharge and soil-water chloride concentrations are close to zero which simplifies the equations. Mean annual recharge can then be expressed as a function of mean annual rainfall, mean concentration of chloride in the rainfall, dry deposition, and measured chloride concentrations in the soil water:

$$\overline{R} = \overline{P} \times \frac{\overline{C}}{\overline{C_s}} + \frac{\overline{D}}{\overline{C_s}}$$

Under ideal steady state conditions, an increase of chloride concentrations in the soil water within the root zone and a constant chloride concentration profile beneath the root are to be expected. However, bulge-like profiles and other deviations from the theoretical shape have been observed. These may result from:

- preferred flow paths (see macropore flow above),
- changes in the recharge rate due to climatic or environmental changes, or
- diffusion

Only in cases where chloride concentration exceeds 8,000 g/m³ diffusion will start to play a more important role.

A simplified approach is based on the chloride concentration within the saturated zone. For this approach chloride concentration in the groundwater is used as a substitute value for $C_s$ and the recharge rate is determined accordingly. Problems will arise in cases of lateral inflow of groundwater at the sampling location, and solution of salt or mixing with deeper groundwater. This method has therefore been used for validation only. A combination of chloride concentrations in the groundwater with soil chloride profiles can be very instructive, as shown by WRABEL (1999). Macropore flow
bypassing the soil matrix may dilute the signal from direct infiltration recorded in the soil chloride profile. In such cases, the comparison of chloride profiles in the unsaturated zone and in the groundwater can be used to estimate the percentage of macropore/bypass flow.

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