'CHEMISTRY FOR MODELLERS' AQUEOUS GEOCHEMISTRY IN COASTAL AREAS.

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INTRODUCTION

Knowledge of the chemistry of groundwater is a requirement for a number of practical purposes. As groundwater is an important source for drinking water, one has to ascertain that its quality is sufficient for consumption. Quality requirements are equally important for other types of utilization such as irrigation or industrial purposes, as well as for the protection of vulnerable ecosystems. More recently, pollution and clean up of aquifers has become a major topic in aqueous geochemistry. Furthermore, understanding of geochemical processes is needed for safety assessment studies, e.g. for the storage of nuclear waste.

Clearly, there are numerous practical applications for aqueous geochemistry. Moreover, geochemistry is an essential tool for understanding the hydrogeological systems that we study. It provides information on the provenance of groundwater, on flow directions and on groundwater ages. These are typical parameters that hydrogeologists obtain from groundwater models, so geochemical data can (and should) be used to verify model outcomes. Conversely, geochemists rely on hydrological information for a sensible interpretation of water quality patterns. This means that aqueous geochemistry and hydrogeological modelling cannot be considered as two separate disciplines but that they are complementary. The aim of this contribution is to emphasize this point. Examples will be shown of the interdependence of geochemistry and hydrogeological modelling. In order to establish the necessary framework, first an overview of the chemistry of coastal aquifers will be given followed by some basic chemical theory.

THE GEOCHEMISTRY OF COASTAL AREAS

Water quality patterns in coastal aquifers are notoriously complex. The main reason for this is that they receive input of many different sources of water. These include precipitation, rivers, lakes (possibly polluted or saline due to strong evaporation), seawater, ascending deep groundwater and anthropogenic sources such as wastewater or irrigation return flow. Understanding the spatial variations of the groundwater's chemical composition that result from the different types of input is extremely difficult especially if concentrations have varied over time or if boundary conditions have changed, for example when dealing with shifting coastlines.

To add to the complexity, geochemical processes alter the water's composition as it travels through the subsurface. Mineral dissolution and precipitation is a well-known category of chemical reactions that can have a significant impact on solute concentrations. Especially relevant to coastal areas are ion exchange (transfer of solutes between solution and solid) and redox processes (reactions that involve electrons). Cation exchange is of paramount significance when fresh water displaces more saline water and vice versa and redox processes are important because seawater constitutes a source of sulfate (an electron acceptor) and because sediments in coastal areas often contain abundant organic matter (an electron donor). Finally, mixing (which is actually more a physical than a chemical process) of different water types exerts great influence on the composition of groundwater.

As a first example why chemical processes are important to modellers, let's look at the effect cation exchange has on the permeability of soils. If sediment contains seawater, its exchange complex, such as clay minerals, is covered mainly with Na because this is the dominant cation in seawater. In fresh water Ca is usually the dominant cation. When fresh water displaces seawater an exchange of Ca for Na will occur: fresh water will donate Ca to the exchanger in return for Na. This process can be described by the following reaction in which X denotes the exchange complex:

$$\tfrac{1}{2}Ca^{2+} + Na - X \rightarrow \tfrac{1}{2}Ca - X_2 + Na^+ \tag{1}$$
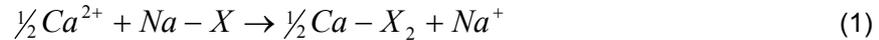
The concentration of Ca in the water will decrease whereas the concentration of Na increases. This has important consequences for the behaviour of clay particles in the sediment. These particles are surrounded by a double layer in which a negative potential extends from the particle surface into the solution. The thickness of this layer is a function of the ionic strength (see below) of the solution. When Na replaces Ca, the ionic strength will decrease (owing to the lower charge of Na compared to Ca) and the thickness of the double layer will increase. As a result, the clay particles will have the tendency to repel each other and will be mobilized. This may lead to the clogging of pores and thus reduce the permeability of the sediment (Appelo and Postma, 1994). The significance of this effect has been demonstrated in experiments, for example by Shainberg and Oster (1978; cited in Appelo and Postma, 1994), which show a marked decrease of the relative hydraulic conductivity of loam as the ratio of Na over Ca in the solution increases.
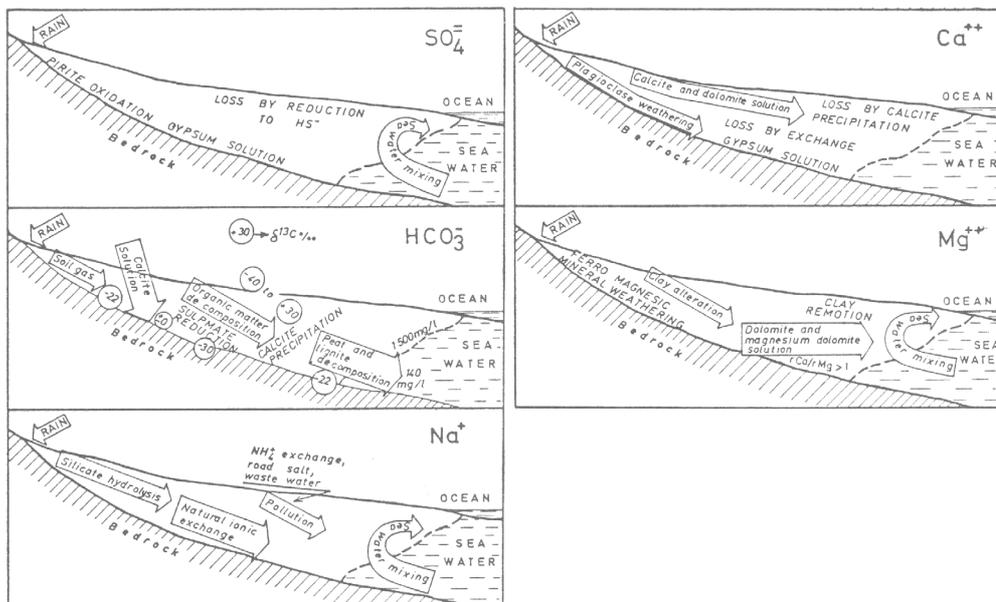

Figure 1 *Schematic representation of chemical processes that influence the concentration of major ions in coastal areas (Custodio, 1987).*

Figure 1 nicely illustrates the chemical processes that influence the concentration of the major ions of groundwater as it flows from the recharge area towards the sea. Sulfate (SO_4) derives from mineral sources such as pyrite and gypsum as well as from seawater and may be lost by conversion to HS-, e.g. by oxidation of organic matter. Bicarbonate (HCO_3) is formed in the recharge area when CO_2 is produced by aerobic respiration and decay of organic matter in the soil zone. Its concentration is further influenced by mineral equilibria (e.g. calcite, dolomite, siderite) and redox reactions that involve sources of organic carbon in the aquifer itself. Sodium (Na) is contained in some silicate minerals that may dissolve but mainly originates from seawater. Cation exchange is the most important chemical process that affects its concentration. Calcite is abundant in many geological settings and constitutes the most important source for calcium (Ca) in groundwater. Ca also derives from other minerals such as dolomite, gypsum and feldspars and also takes part in cation exchange reactions. Magnesium (Mg) finally, has a high concentration in seawater and is contained in some minerals, the most important being dolomite. Similar to Na and Ca it can be adsorbed to the exchange complex.

Considering the numerous sources and processes that influence solute concentrations, investigators that try and study the chemistry of coastal aquifers are faced with an overwhelming complexity. Traditional methods that are applied to make sense of the vast pile of numbers that follow from the chemical analyses of water samples involve plotting (Fetter, 2001) and classification of samples into groups (e.g. Stuyfzand, 1993) in order to be able to discern regional trends and to identify chemical processes. No matter how useful these methods are in deriving an idea of the reaction scheme that has given the water sample its composition, they are incapable of determining whether this scheme is feasible from a chemical point of view. In order to check whether a concept obeys basic chemical theory one needs a geochemical model that is based on the firm laws of thermodynamics. Or, as Lichtner et al. (1996) put it: "Quantitative models force the investigator to validate or invalidate ideas by putting real numbers into an often vague hypothesis and thereby starting the thought process along a path that may result in acceptance, rejection, or modification of the original hypothesis."

Before continuing with the application of geochemical modelling in coastal areas, first some elementary theory of aqueous chemistry will be treated in the following section to see why geochemical models were originally developed and how they work.

BASIC CONCEPTS OF AQUEOUS CHEMISTRY

The remaining part of this paper will be dedicated to equilibrium chemistry. For simplicity, the kinetics of geochemical processes (i.e. the description of how and at what rate a system approaches equilibrium) will not be considered. The reader is referred to the standard textbooks on aqueous geochemistry for an elaborate treatment of this subject as well as for a more detailed treatment of equilibrium chemistry (e.g. Appelo and Postma, 1994; Stumm and Morgan, 1996; Drever, 1997).

Essential to the description of the equilibrium composition of a geochemical system is the *law of mass action*. According to this law, the distribution of the species in the reaction

$$aA + bB \leftrightarrow cC + dD \tag{2}$$

is given at equilibrium by

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{3}$$

where capital characters denote the species, lowercase symbols indicate the stoichiometric coefficients and *K* is the *equilibrium constant*. The quantities between the brackets denote the activity of a species. Consider for example the dissolution of gypsum:

$$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \tag{4}$$
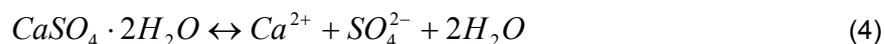
The equilibrium constant for this reaction is given by:

$$K_{gypsum} = \frac{[Ca^{2+}][SO_4^{2-}][H_2O]^2}{[CaSO_4 \cdot 2H_2O]} = 10^{-4.60} \tag{5}$$

which can be simplified to:

$$K_{gypsum} = [Ca^{2+}][SO_4^{2-}] = 10^{-4.60} \tag{6}$$

since at low ionic strength (see below) the activity of water *[H₂O]* approaches unity and the activity of a pure solid, *[CaSO₄·H₂O]* in this example, equals one by definition. This expression is referred to the *solubility product* for gypsum. Note that the equilibrium constant is temperature dependent: K_{gypsum} = $10^{-4.60}$ is valid at 25 °C. An analogue expression can be written that uses the actual activities of the species in the groundwater instead of the activities at equilibrium, which is referred to as the *ion activity product (IAP)*:

$$IAP_{gypsum} = [Ca^{2+}][SO_4^{2-}] \tag{7}$$

A comparison of *IAP* and *K* provides information on the saturation state of the groundwater for a mineral. This is commonly done by calculating the *saturation index (SI)*, for example for gypsum:

$$SI_{gypsum} = \log\left(\frac{IAP_{gypsum}}{K_{gypsum}}\right) \tag{8}$$

At equilibrium IAP_{gypsum} equals K_{gypsum}, so SI_{gypsum} = 0. Gypsum potentially dissolves in groundwater that is subsaturated (i.e. SI_{gypsum} < 0) or precipitates from groundwater that is supersaturated (i.e. SI_{gypsum} > 0).

The saturation index is an important parameter in aqueous geochemistry as it provides information on the minerals the groundwater has been in contact with and on which minerals are likely to precipitate or dissolve. The problem with its application is that the activities of the species need to be known. Generally, however, we are only provided with *concentrations*, which do not equal activities because of (1) electrostatic shielding and (2) the formation of aqueous complexes.

Electrostatic shielding

Activities reflect the tendency of ions to react and form a precipitate (Appelo and Postma, 1994). An ion in solution is surrounded by water molecules and other dissolved ions that act as a shield and reduce the reactivity of the ion. This effect can be corrected for by using a so-called activity coefficient that relates the activity of an ion to its concentration, for example Ca:

$$[Ca] = \gamma_{Ca} \cdot \frac{m_{Ca}}{m_{Ca}^0} = \gamma_{Ca} \cdot m_{Ca} \tag{9}$$

where *γ* is the activity coefficient, which is multiplied with the concentration of the ion, m_{Ca} in this example, divided by the standard state that for practical purposes conveniently equals 1 mole/kg H₂O. According to the Debije-Hückel theory, activity coefficients are a function of the *ionic strength I* of the solution:

$$I = \tfrac{1}{2} \sum m_i \cdot z_i^2 \tag{10}$$

Several empirical relationships exist to calculate the activity coefficients from the ionic strength, e.g. the Davies equation at 25 °C:

$$\log \gamma_i = -0.5085 \cdot z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I\right) \tag{11}$$

where z_i is the charge of ion *i* (i.e. 2 for Ca^{2+}).

Although these calculations can be awkward, they are straightforward and can still be done by hand, so the effect of electrostatic shielding is quite easily corrected for.

Formation of aqueous complexes

The second reason why the activity of an ion is lower than its concentration is that it forms aqueous complexes with other ions. Laboratory analyses typically report the total concentration of an ion, which may be present in many different complexes, e.g. Ca^{2+}:

$$\sum Ca^{2+} = m_{Ca^{2+}} + m_{CaOH^+} + m_{CaCO_3^0} + m_{CaSO_4^0} + m_{CaPO_4^-} + m_{CaF^+} + ... \qquad (12)$$

Note that these are dissolved species; they are not to be confused with minerals. Because Ca is tied up in these complexes, the activity of the free calcium ion is reduced. The calculation of the concentrations of all possible species is a complex task because (1) for each ion in solution a mass balances similar to 12 has to be solved and (2) at the same time the activities of all of the species have to obey the equilibrium relationships that follow from the law of mass action.

This requires an iterative procedure (figure 2#). As a first estimate it is assumed that the total concentrations of the ions equal the concentrations of the free, uncomplexed ions. It is then possible to calculate the ionic strength (step 1) and use that to find the activity coefficients and correct for electrostatic effects. From this follow the activities of the ions (step 2) that are inserted into the mass action equations to obtain the activities of the aqueous complexes (step 3). These are converted to concentrations using the already calculated activity coefficients (step 4) and finally the concentrations of the uncomplexed ions are updated from the mass balance equations (step 5). The newly found values are used to obtain a more reliable value for the ionic strength and iteration continues until the result no longer changes significantly.
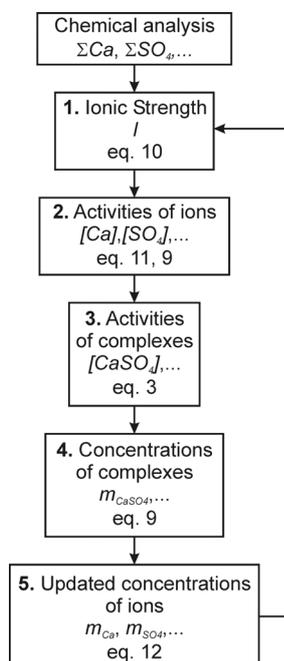

Figure 2 *Flow chart for speciation calculations (modified from Appelo and Postma, 1994).*

These calculations are ideally carried out by a computer program, which is the reason why geochemical models were initially developed in the 1960's. The original models were soon improved and extended to include chemical reactions that alter the water composition such as mineral equilibria, cation exchange and redox reactions (Plummer, 1992). By virtue of the increase in computer computational power it became possible to couple geochemical models with hydrological models to calculate how the water composition changes as it travels through the subsurface (Lichtner et al., 1996). Today's models have reached a level of sophistication that allows us to simulate real-world processes to understand and explain field observations (Van der Lee and De Windt, 2001). Elaborate treatment of the basic concepts and applications of aqueous geochemical modelling can be found in for example Bethke (1996) and Lichtner et al. (1996).

APPLICATION OF AQUEOUS GEOCHEMISTRY IN COASTAL AREAS

In the following section the application of geochemical models in coastal areas will be illustrated by some examples. The effects of mixing on the hydraulic properties of calcareous aquifers will be treated in the first example. The second example shows the strength of modern geochemical models in simulating field observations that are the result of a complicated suite of chemical processes. Finally, the third example demonstrates the need for geochemical modelling when interpreting ^{14}C ages.

Seawater speciation, calcite saturation and groundwater mixing

The basic principles of calculating water's composition at equilibrium were presented in a landmark paper by Garrels and Thompson (1963) and the theoretical framework presented therein continues to be applied in present-day geochemical models. Using a combination of equilibrium equations from the law of mass action and mass balance relations (as explained in the previous section), they calculated the distribution of dissolved species (*speciation*) in seawater at 25 °C and $1.013 \cdot 10^5$ Pa (1 atm) pressure. Their results have been summarized in figure 3#, which shows the effects of both (1) the formation of aqueous complexes and (2) electrostatic shielding. Sodium, for example, hardly forms any aqueous complex but due to electrostatic effects its activity amounts to only 75 % of its total concentration. More than 90 % of the carbonate ion (CO_3) is tied up in a complex and it can be seen that its activity amounts to a mere 2 % when the effect of electrostatic shielding is taken into account as well.
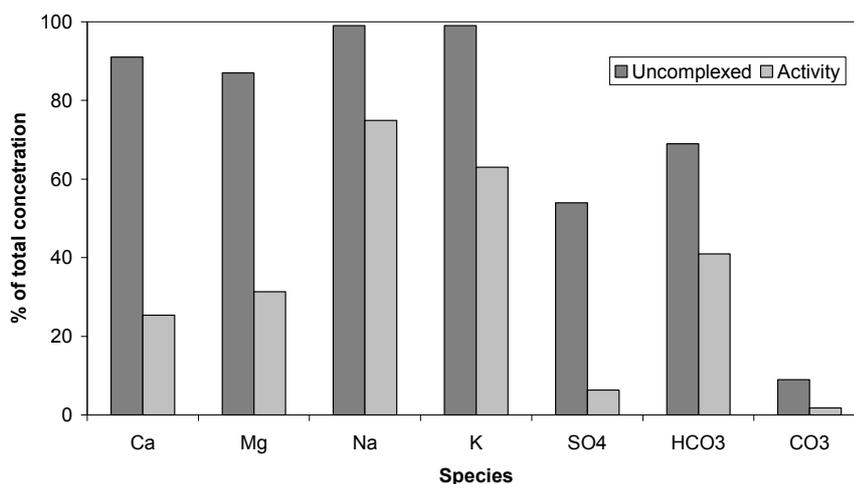

Figure 3 *Effect of complexation and electrostatic shielding expressed as percentage of total concentration. Based on calculations by Garrels and Thompson (1963).*

Clearly, neglecting the difference between total concentration and activity in the calculation of the saturation indices of seawater for minerals would result in overprediction of the values. In the case of calcite, the saturation index using total concentrations would result in:

$$SI_{cc} = \log\left(\frac{IAP_{cc}}{K_{cc}}\right) = \log\left(\frac{[Ca^{2+}][CO_3^{2-}]}{10^{-8.3}}\right) = \log\left(\frac{0.0104 \cdot 0.000269}{10^{-8.3}}\right) = 2.75 \tag{13}$$

whereas (correctly) using activities yields:

$$SI_{cc} = \log\left(\frac{2.65 \cdot 10^{-3} \cdot 4.7 \cdot 10^{-6}}{10^{-8.3}}\right) = 0.4 \tag{14}$$

The concentrations and activities in equations 13 and 14 were taken from Garrels and Thompson (1963). This result shows that seawater is slightly supersaturated with respect to calcite.

One might wonder what would happen if seawater mixes with fresh water that is in equilibrium with calcite ($SI_{cc} = 0$), which is a common phenomenon in coastal aquifers for example following seawater intrusion. Intuitively, one would say that the mixture will be somewhat supersaturated as well since the end member solutions have $SI_{cc} = 0.4$ and $SI_{cc} = 0$ and therefore, that calcite precipitation will occur. Figure 4, however, shows that according to geochemical theory, calcite will only precipitate for highest fractions of seawater (SI > 0) and that for lower fractions, calcite will dissolve (SI < 0)! This remarkable result is attributed to the redistribution of carbon species and the non-linear dependence of activity coefficients on ionic strength (Wigley and Plummer, 1976).

As calcite commonly occurs in the sediments that make up coastal aquifers, its dissolution might affect the hydraulic conductivity in the fresh- salt water-mixing zone. Sanford and Konikow (1989) coupled a geochemical model to a variable density flow and transport model to simulate the changes in porosity that occur as a result of calcite dissolution induced by mixing. Using an original porosity of 30 %, they calculated increases of up to 35 % at the toe of the mixing zone.
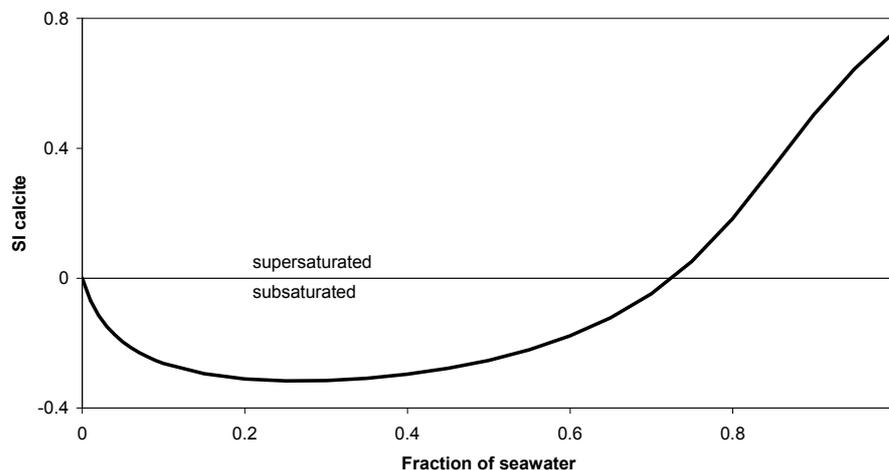

Figure 4 Saturation index of calcite plotted as a function of the fraction of seawater in the mixture.

Ion exchange and carbonate reactions in the Aquia aquifer, Maryland

Displacement of seawater by fresh groundwater following the deposition of marine sediment induces cation exchange. In seawater Na, Mg and K are present at increased levels compared to fresh water, which generally contains Ca as the dominant cation. When the fresh water displaces the seawater Na, Mg and K from the sediment's exchange complex are displaced by Ca. As the affinity of the exchanger differs for each individual cation, a spatial separation of the displaced cations occurs. Going upstream of the fresh- saltwater interface a so-called chromatographic sequence of Na, K, Mg and Ca dominated water types is found (Appelo and Postma, 1994).
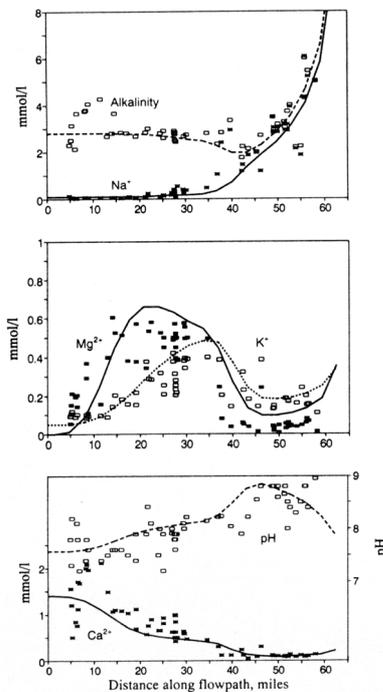

Figure 5 Concentration changes along average flow path in the Aquia aquifer (Appelo, 1994).

One of the most conspicuous examples of such a chromatographic pattern can be observed in the Aquia aquifer (Maryland, USA) that displays a distinct zonation along the flow path of elevated concentration levels of Na, K, Mg and Ca (Appelo, 1994). To test whether this pattern could be ascribed to cation exchange following freshening of the original marine sediments a reactive transport model was developed. Besides cation exchange (including proton exchange) mineral equilibria were included as well. The results and the field data are shown in figure 5#. Despite the large scatter in the field data, the ability of the model to reproduce the observed trends in water quality demonstrates the power of modern geochemical models to simulate geochemical processes on a field scale.

The recognition of displacement chromatography in the field allows for the estimation of the duration of the process, as the model calculates the number of times (a portion of) an aquifer has been flushed. In the case of the Aquia aquifer it was estimated that approximately 100 kA had elapsed since the exposure of the recharge area (Appelo, 1994). When used in this way, geochemistry provides clues on the paleohydrological development of aquifer systems.

Inverse modelling and radiocarbon dating

The geochemical modelling techniques that were described in the previous sections are referred to as 'forward geochemical modelling'. The aim of forward modelling is to predict water compositions and mass transfers that result from hypothesized reactions (Plummer, 1992). A second approach exists that is known as 'inverse geochemical modelling', which attempts to account for the chemical changes that occur as water evolves along a flow path (Plummer et al., 1994). Given the composition of two water samples A and B, where A is located upstream of B, inverse geochemical models calculate the mole transfers of gases and minerals that are needed to produce the composition of water sample B from that of water sample A (Parkhurst and Appelo, 1999).

This knowledge of the reaction scheme is a prerequisite when dating water samples with radiocarbon (^{14}C). The problem with radiocarbon dating is that chemical reactions along a flow path that involve carbon, such as carbonate-mineral dissolution/precipitation and oxidation of organic matter, alter the original ^{14}C signature of the groundwater (Plummer et al., 1994). The contribution of various carbon sources and sinks (e.g. carbonate minerals, organic matter) to the measured ^{14}C activity of the water sample needs to be corrected for in order to calculate a reliable age.

Inverse modelling was applied in a study by Van der Kemp et al. (2000) to water samples from the Ledo-Paneselian aquifer that outcrops in Belgium and extends northwards below the southern part of the Netherlands. It was shown that not taking into account chemical reactions in the aquifer overestimates calculated ages by as much as 15,000 years. A very nice aspect of this particular study is that the model also calculated the CO_2 pressure in the soil of the recharge area (P_{CO2}). A positive correlation was found between P_{CO2} and $\delta^{18}O$ of the water samples. Low (i.e. more negative) $\delta^{18}O$ values in groundwater are associated with cooler climatic conditions during recharge. Those samples with the lowest $\delta^{18}O$ have the lowest calculated P_{CO2}, which was explained Van der Kemp et al. (2000) by lower microbial activity in the soil during cooler periods. This example nicely shows that geochemical models can also provide information on former climatic conditions.

CONCLUDING REMARKS

The foregoing discussion has demonstrated the strength of aqueous geochemistry and especially geochemical modelling in increasing our understanding of hydrogeological systems in coastal areas. However, some drawbacks apply as well, including the large data-requirement of geochemical models, their computationally intensive algorithms and the sensitivity of the model outcomes to heterogeneity. Nevertheless, aqueous geochemistry has proven itself indispensable for hydrogeological research.

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