

Geochemical modeling possibilities of CO₂ and brine inflow to freshwater aquifers

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In worst-case leakage scenarios of CO₂ geological storage, CO₂ or brine may contaminate shallower drinking water aquifers. This work applies an advanced geochemical modeling methodology to predict and understand the effects of the aforementioned contamination scenarios. Several possibilities, such as equilibrium batch, kinetic batch, and 1D kinetic reactive transport simulations, were tested. These have all been implemented in the widely applied PHREEQC code. The production of figures and animations has been automated by R programming. The different modeling levels provide complementary information to each other. Both scenarios (CO₂ or brine leakage) indicate the increase of ion concentrations in the freshwater, which might exceed drinking water limit values. The dissolution of CO₂ changes the pH and induces mineral dissolution and precipitation in the aquifer and therefore changes in solution composition. Brine replacement of freshwater due to the pressure increase in the geological system induces mineral reactions as well.

Keywords: CO₂ geological storage, geochemical interactions, PHREEQC, R programming

Introduction

Carbon capture and storage (CCS) is a transitional technology (EASAC 2013) for the reduction of greenhouse gas emission and the mitigation of climate change

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(IPCC 2013). Following the implementation of the 2009/31/EC Directive in the Hungarian legislation, the competent authority is required to evaluate the potentially suitable Hungarian geological structures for CCS, the geological sequestration of CO₂.

An initial assessment period ended in 2014, which included determining the geological and technical viability, estimating storage volume and evaluating the basic environmental aspects of selected structures (e.g., Falus et al. 2011; Szamosfalvi et al. 2011). A second assessment period began in 2015, including the study of the geochemical reactivity of reservoir and cap rocks, as well as evaluating disaster scenarios of CO₂ escape and brine displacement to protected shallower drinking (i.e., fresh) water aquifers of the neighboring area.

This study aims to create a variety of geochemical models representing potential CO₂ or brine-induced effects in vulnerable drinking water reservoirs above potential CCS sites in Hungary. The methodological levels are presented through a selected study area by thermodynamic and kinetic batch models, and finally a one-dimensional (1D) kinetic reactive transport simulation is also provided.

Studied area

In total, 13 potential CO₂ geological storage reservoirs, i.e., high-porosity saline water structures, were selected for the study (Fig. 1). These are primarily located in the southeast part of Hungary, in the Great Hungarian Plain, and are all overlain by thick Quaternary and Upper Pannonian (Miocene) multilayered lacustrine and fluvial aquifers (Rónai 1985). Above the brine, protected drinking water is found at shallower depths both in the Quaternary and in the upper part of the Upper Pannonian (Miocene A) layers. The worst-case CO₂ or brine-leakage modeling approach is presented through the example of the well-studied Mezőtúr area, which is characterized by regional and intermediate flow systems with a dominant upward flow, comprising a regional discharge area.

Modeling methodology

The methods applied are similar as in the work of Del Bon et al. (2015) published in this journal. All of the digital modeling work was carried out using the geochemical software, PHREEQC version 3 (Parkhurst and Appelo 2013) and its results were visualized with several programs written in R programming language (R Core Team 2017).

Model types

In this study, all available methodology levels of geochemical modeling have been applied, providing complementary information to each other and the possibility of building up the most representative reactive transport concepts of worst-case leakage

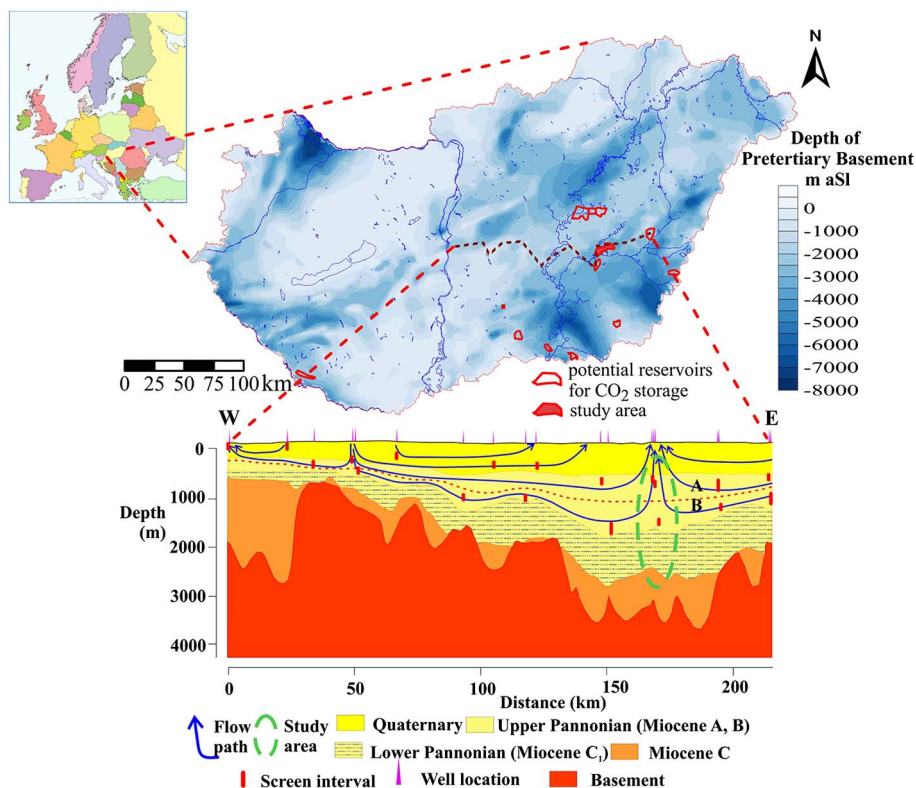


Fig. 1 Potential CO₂ storage reservoirs in the Great Hungarian Plain, with the studied area highlighted, and at the bottom, the geological cross-section presenting the location of boreholes, the geological structures, and the typical groundwater flow path in the area

scenarios. In summary, the disaster events of CO₂ or brine (saline water) inflow into freshwater aquifers have been described and compared with reference scenarios in the following concepts:

- Batch models:
 - Thermodynamic batch models representing the equilibrium state of the systems in infinite time:
 - Brine displacement of freshwater in 0%–100%,
 - CO₂ added to freshwater in 1 mmol steps up to 10 mol.
 - Kinetic batch models predicting reactions in a static concept in time, for about the first 100 years after the leakage happens the following:
 - 10% brine + 90% freshwater reacts with minerals of the aquifer in time,

- CO₂-saturated freshwater.
- 1D reactive transport models:
 - Thermodynamic reactive transport models have not been considered, because with continuous fluid flow in the cells of the model, equilibrating the system cannot provide a reasonable estimation of mineral dissolution and precipitation processes.
 - Kinetic 1D reactive transport models representing the best estimate of freshwater aquifer with continuous fluid flow and contaminating CO₂ or brine inflow:
 - reference, i.e., freshwater,
 - 10% brine + 90% freshwater flow in the aquifer,
 - CO₂-saturated freshwater.

Model input data

Thermodynamic. For all simulations, the PHREEQC.DAT thermodynamic database was used. Any missing information was taken from the LLNL.DAT database (Wolery 1979).

Kinetic. Kinetic dissolution and precipitation equations of mineral phases were defined similarly to an earlier work of Szabó et al. (2016), in which modeling methodology is primarily based on the USGS report of Palandri and Kharaka (2004). Specific surface areas of minerals are from the RES³T database (HZDR online).

Fluid and matrix properties. The solution composition of saline and freshwaters and their temperature information are accessible from the institute's (Mining and Geological Survey) geochemical database and are summarized in Table 1. The mineral composition of the freshwater aquifer formation applied in the models was determined based on XRD measurements of core samples; 10.50 albite, 1 calcite, 4.75 chlorite, 2 dolomite, 2 goethite, 10.25 illite, 1.67 kaolinite, 3.75 K-feldspar, 6.25 montmorillonite, 61 quartz, and 1% tremolite. The porosity is estimated to be 15% for the aquifer. In transport models, flow rate must be provided. It should be mentioned that hydraulic conductivity values can vary within 1–2 magnitudes in the studied Quaternary and Upper Pannonian sediments, depending on the geological settings. A previous regional 3D hydrodynamic modeling study (Tóth et al. 2012, 2016) suggests values overlapping with the hydraulic conductivity range provided by Freeze and Cherry (1979). In test models of this study, based on this hydraulic conductivity range, a realistic upper estimate of 2 m/day flow rate has been calculated and applied.

Results and discussion

Understanding reactions in a static concept – Batch models

Thermodynamic batch models. Thermodynamic models provide information on the equilibrium state of different rock–water–gas mixtures in infinite time. Mineral compositions predicted in brine and CO₂ contamination models of the freshwater

Table 1
Solution compositions of freshwater and saline water

	Freshwater	Saline water
T (°C)	17	100
pe	0.5	-4
pH	7.1	8.3
Na (mg/L)	227	10,300
K (mg/L)	1.5	1,530
Mg (mg/L)	21	51
Ca (mg/L)	38	79
Fe (mg/L)	1.38	0.23
Cl (mg/L)	18	16,900
NH ₄ (mg/L)	1.7	184
HCO ₃ (mg/L)	830	1,958
S(6) (mg/L)	10	1,592
SiO ₂ (mg/L)	10	148
Al (mg/L)	0.05	0.05

aquifer of Mezótúr area are presented in Fig. 2. These models benefit from the possibility of running several scenarios of interest simultaneously and help in the selection of the most representative ones for further modeling tasks.

Brine displacement continuously changes the equilibrium state (increasing illite, dolomite dissolution, and kaolinite, and calcite precipitation). Based on the equilibrium solution composition output, the most significant changes are linked to the first 10% saline-water inflow (because the difference in compositions then decreases). Therefore, for kinetic modeling purposes, a realistically possible 10% saline + 90% freshwater mixture has been selected. Different amounts of CO₂ inflow change the reactions in three major steps characterized by the full dissolution of albite and calcite.

Kinetic batch models. Geochemical systems are usually far from a state of equilibrium; therefore, kinetic modeling provides the necessary information for evaluating induced reactions. For this type of model, specific concepts were selected to present in Fig. 3, which were 10% brine + 90% freshwater (based on thermodynamic batch models and a realistic mixing scenario) and CO₂-saturated freshwater reaction in the aquifer simulated for 125 years. In the batch modeling approach, no significant difference was observed between the pure freshwater model and that of the

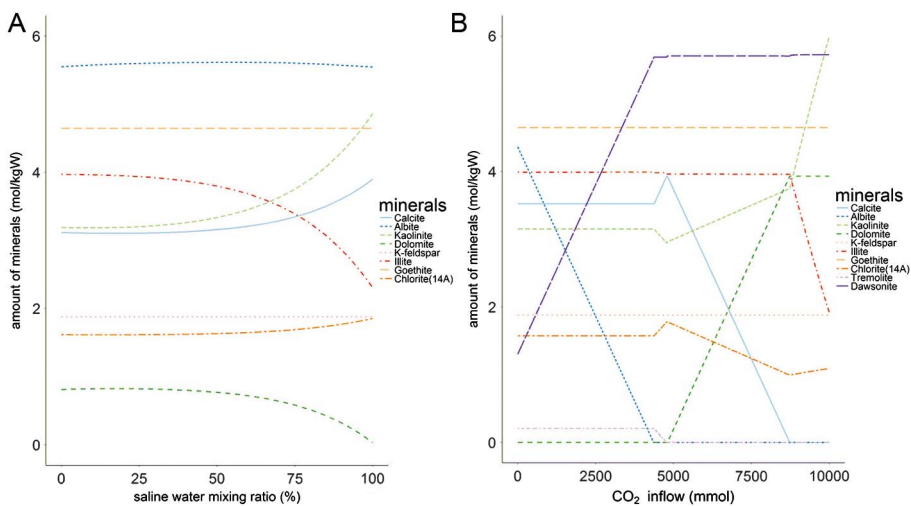


Fig. 2 Equilibrium mineral compositions predicted by thermodynamic batch models of (A) brine and (B) CO₂ inflow

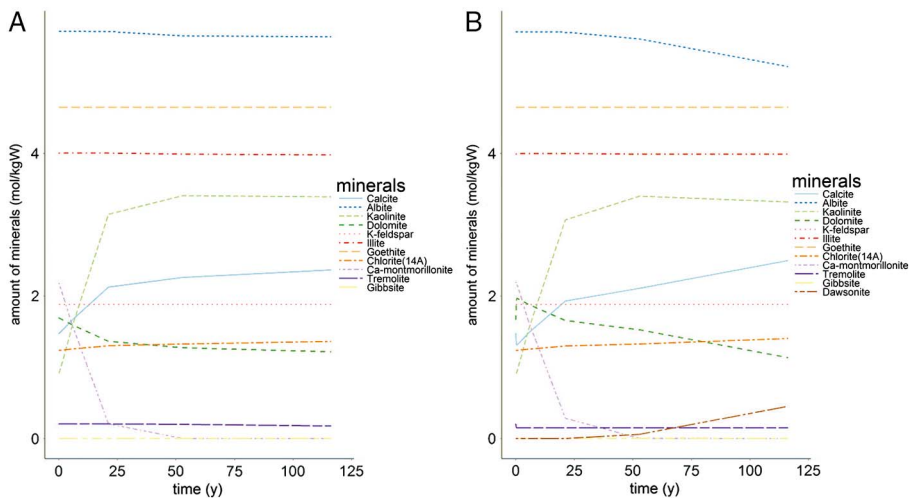


Fig. 3 Mineral compositions versus time in kinetic batch models of (A) 10% brine + 90% freshwater and (B) CO₂-saturated freshwater

brine mixture, unlike the CO₂ model. It becomes clear how the change of the flow rate in transport simulations corresponds to different parts of the presented curves (Fig. 3) and how it influences the outcome of the models are presented in the following section.

Kinetic reactive transport models

1. *Reactions in freshwater aquifer – a reference model.* Since even without any brine or CO₂ leakage, there are reactions taking place in the freshwater aquifer, it is important to provide a reference model of this continuous fluid flow in porous media. In Fig. 4, the most important observation, which can be made, is the dissolution of Ca-montmorillonite and the precipitation of kaolinite along the entire path.
2. *Effect of brine replacement of freshwater.* Brine–freshwater mixture inflow into the studied aquifer changes solution compositions corresponding to the chemistry of the brine. The front is at around 500 m for all parameters on the 150th day of the inflow (Fig. 5). Compared with the reference, only a minor illite precipitation is indicated at the entry point; therefore, the flow goes along without any disturbance by geochemical reactions.
3. *Reactions in freshwater aquifer induced by CO₂ inflow.* CO₂ dissolution in freshwater significantly reduces its pH (Fig. 6, top left). This induces much more significant and different mineral dissolution and precipitation reactions in the rock than in the above cases (Fig. 6, right). This makes it understandable why the reaction front reaches a shorter distance on the 150th day than for the transport of the brine mixture, 250 versus 500 m (Fig. 6 vs. Fig. 5). Calcite, tremolite, illite, and albite dissolve, whereas dolomite, Ca-montmorillonite, and kaolinite precipitate. At the reaction front, illite precipitation is predicted. These processes change the solution composition (Fig. 6, bottom left). K, Mg, Ca, and Si concentrations increase, among which K runs ahead of the front.

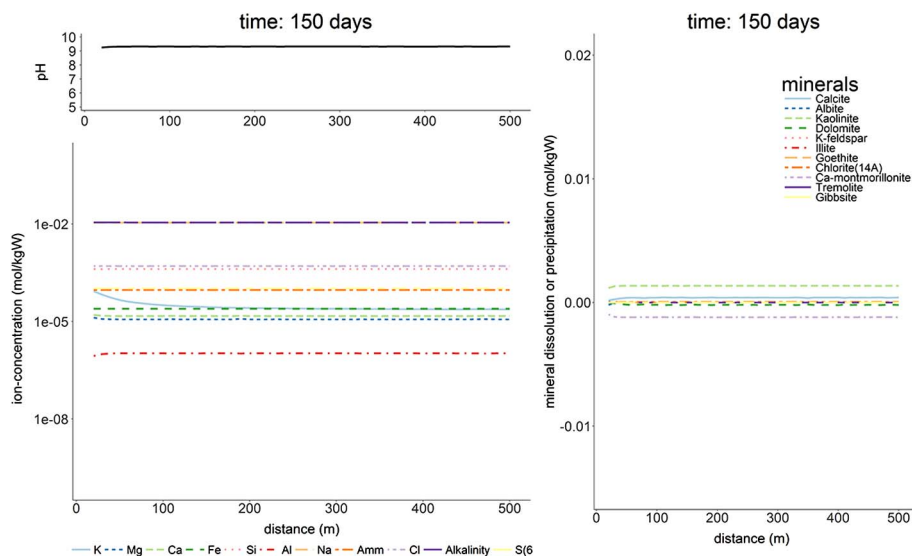


Fig. 4 Solution compositions and mineral reactions of freshwater flow

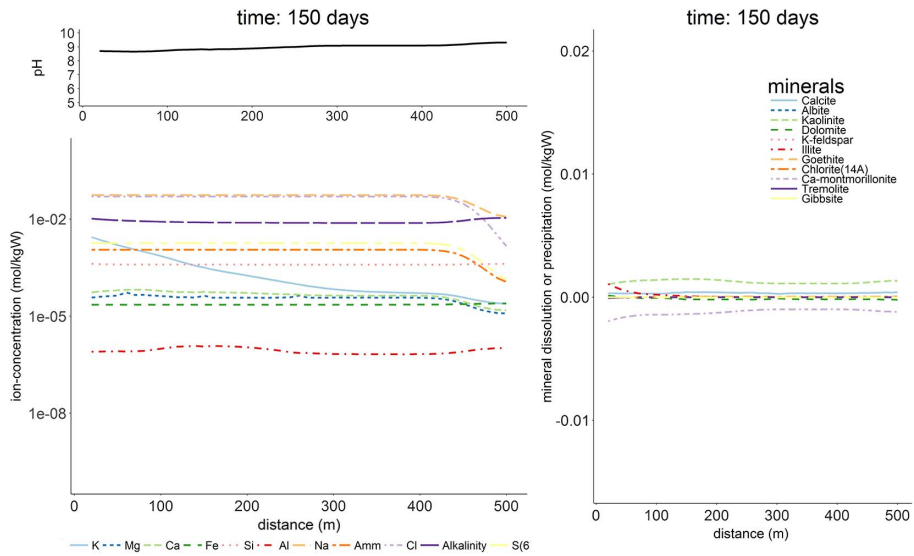


Fig. 5
Predicted consequences of 10% brine + 90% freshwater inflow

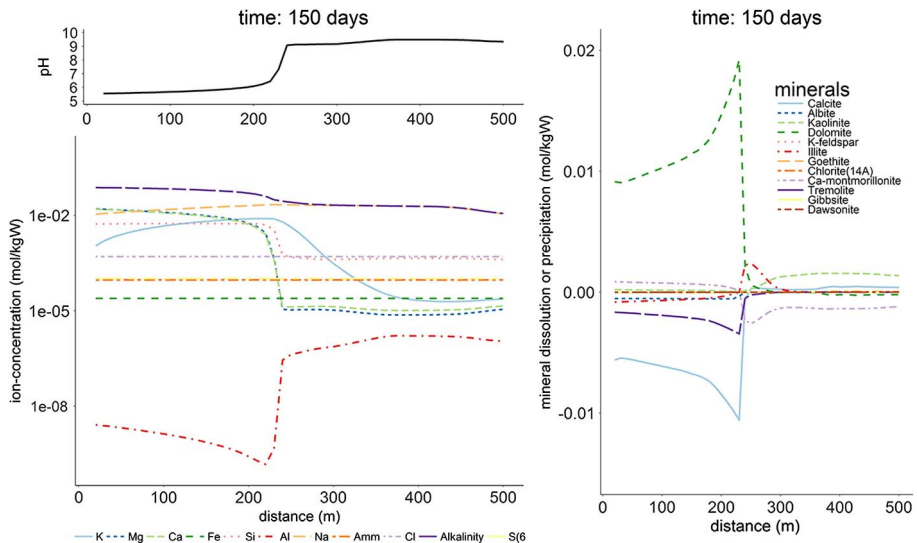


Fig. 6
Predicted consequences of CO₂-saturated freshwater inflow

Conclusions

Three main types of PHREEQC models were generated to evaluate unlikely, but potential saline water or CO₂ contamination of drinking water aquifers. These are thermodynamic and kinetic batch, as well as kinetic reactive transport models. Reactive transport modeling connected to CCS was first performed in the Pannonian Basin. The different levels of modeling results are complementary to each other and all suggest that certain ion concentrations may exceed drinking water limit or indicator values in both of the studied worst-case leakage scenarios of CCS. Based on the present state of models, it is expected that reactivity between rock and fluid slows down the reaction front in the CO₂ inflow case. Further improvement of models is planned by incorporating cation exchange capacity as modeling input, by refining applied transport parameters, and even extending the approach to 2D and 3D. Estimation of solution conductivity and rock total porosity changes are also useful and expected in later phases of the project.

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