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Reactive transport modeling for impact assessment of a CO_2 intrusion on trace elements mobility within fresh groundwater and its natural attenuation for potential remediation

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Abstract

A leakage of CO_2 from a geological storage site into an aquifer exploited for human use could raise concerns about potential changes of groundwater quality. We use the reactive transport code TOUGH2-ECO2N/TOUGHREACT in order to apprehend the possible geochemical mechanisms that could affect a freshwater aquifer. Our aquifer model is based on the mineralogical and geochemical features of an existing glauconitic-sandstone aquifer, to which trace elements bearing minerals are added in average proportions found in similar mineralogies. The code computes kinetic precipitation/dissolution processes. 2D sensitivity tests on: i) intrusion position (at the ceiling and at the floor) of pure CO_2 - ii) intrusion rates - iii) natural groundwater flow, were performed, exhibiting several dynamics. Dissolution of CO_2 decreases the pH to 5.0 and leads to dissolution of trace elements bearing minerals, enriching the waters in trace elements including Cd, Pb, Zn. Their concentrations may locally exceed quality parameters. Gaseous CO_2 migrates upwards and water enriched in dissolved CO_2 moves downwards due to the density gradient. The geometric impact extends and the total amounts of mobilized health-significant-elements increase with increasing intrusion rates. Groundwater flow may have an impact on these parameters too. An interruption of the CO_2 stream is immediately followed with decreasing tendencies of these parameters. A 3D test at an intrusion rate of 0.1 g/s/m^2 during 1 year shows that, at this rate, the initial shape of the plume is much more extended horizontally than vertically.
A strong limitation of the model is currently that sorption processes on clay minerals as well as on oxy-hydroxydes have not been taken into account, which most certainly means that our computations are conservative, as these mechanisms could strongly and quickly inhibit the mobilization of traces that would follow acidification and dissolution processes.

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Keywords: CO_2 storage; modeling tools; environmental impacts; freshwater aquifer

1. Introduction

In case of accidental leakage of CO_2 from its reservoir, contamination of upper fresh groundwater aquifers may become an environmental concern for Carbon Capture and Storage (CCS) [1]. Recent publications ([2], [3], [4])

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have highlighted and studied the possibility of release of trace elements and health significant elements through acidification and dissolution of minerals, which could alter water quality, and consequently water use if trace elements concentrations were found exceeding quality parameters relevant for consumption purposes. We study here with the multiphase reactive transport code TOUGH2-ECO2N/TOUGHREACT [5] the consequences of an intrusion of pure CO_2 into a glauconitic-sandstone aquifer, as well as the consequences of the natural attenuation following an interruption of the intruding stream (through the deployment of upstream corrective actions, for instance [6]), as a possible restoration action.

This work is the counterpart of [7] which studies the geochemical impact of CO_2 and its impurities (e.g. SO_x, NO_x from oxycombustion capture). Here, only the geochemical consequences of a pure CO_2 stream are considered.

2. Model set-up

2.1. Modeling code and conceptualization

All computations were performed using the TOUGH2-ECO2N/TOUGHREACT v1.0 reactive transport code with the THERMODDEM (BRGM) database [8]. The following processes were considered: multiphasic flow; aqueous species speciation; kinetic mineral precipitation/dissolution; and equilibrium redox reactions. No sorption processes are currently taken into account in this model. Two models were used for this study, both included in a 80 km long (following the direction of the groundwater flow) and 80 m thick domain:

- the 2D model (Figure 1, left) is a small (about 900 cells: 8 layers of 10 m each on Z-axis; width on X-axis refined in the center to values as small as 2 m for the finest cases; all cells are 1 m large on Y-axis) and computing time-efficient model used for sensitivity studies. The intrusions simulated in this model may represent linear intrusions (e.g. intrusion through faults perpendicular to the groundwater flow);
- the 3D model (Figure 1, right) is built to simulate punctual intrusions. It is composed of a larger number of mesh cells, hence more computationally intensive (~7000 cells using local grid refinement tools [9]; smallest cell dimensions = 2 m x 2 m x 0.1 m; Z-axis is divided in 9 layers in geometric progression).

A hydrostatic gradient of 0.7 MPa/m (6.5 MPa at the basement and 5.8 MPa at the top) is defined.

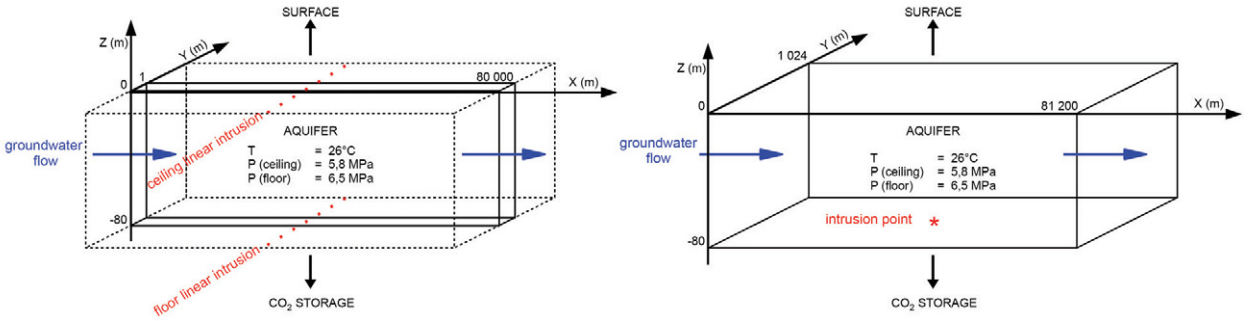


Figure 1. Conceptual models used in the study. Left: 2D model used for sensitivity studies and simulation of linear intrusions; right: 3D model for punctual intrusion simulation.

2.2. Mineralogy and aquifer water

The initial petrophysical properties of the aquifer are supposed homogeneous (porosity, intrinsic permeability, relative permeabilities, diffusion coefficient). The solid matrix is a glauconitic sandstone with some amounts of clay and carbonate minerals. The details are exposed in Table 1. Minerals reported in an existing aquifer (Albian aquifer, Paris Basin, France) are used. To study the potential release of trace elements, sphalerite, galena, greenockite and chalcocite are added in average proportions found in similar mineralogies. Otavite, cerussite, smithsonite and iron oxy-hydroxydes are considered as secondary minerals which are allowed to precipitate. Minerals precipitations and dissolutions are kinetically-constrained. The kinetic laws implemented in TOUGHREACT are exposed in [10] and one set of kinetic rates (derived from [11]) and specific surfaces have been used. They are derived from

experimental BET measurements and simplified, as it is intended to make sensitivity studies on these parameters. The thermodynamic constants of the aqueous and mineral equilibriums are taken from the THERMODDEM database (2008 release, [8]).

Table 1. Selected composition (volumic fractions) of initial mineralogy.

Minerals reported in available data for the Albian aquifer	
Quartz (SiO_2)	50
Calcite ($CaCO_3$)	8
Kaolinite ($Al_2Si_2O_5(OH)_4$)	15
Glauconite ($K_{0.75}Mg_{0.25}Fe_{1.5}Al_{0.25})(Al_{0.25}Si_{3.75})O_{10}(OH)_2$)	15
Siderite ($FeCO_3$)	3
Dolomite ($CaMg(CO_3)_2$)	2
Muscovite ($KAl_2(AlSi_3)O_{10}(OH)_2$)	5
Whitlockite ($Ca_3(PO_4)_2$)	1,9
Rhodochrosite ($MnCO_3$)	0,05
Barite (BaSO4)	0,033
Minerals added in order to study the release of trace elements	
Sphalerite (ZnS)	0,0021
[2]Galena (PbS)	0,001
Greenockite (CdS)	0,00001
Chalcocite, alpha (Cu_2S)	0,0019
Mineral added in undersaturated state in order to control dissolved sulphates	
Gypsum ($CaSO_4$. 2 H_2O)	0,0003

Table 2. Composition of initial water.

Elements	Concentrations (mol/kg water)
Al	$1{,}4.10^{-12}$
C	$3{,}0.10^{-03}$
Ca	$1{,}1.10^{-03}$
Cl	$1{,}0.10^{-04}$
Fe	$5{,}4.10^{-06}$
K	$6{,}6.10^{-05}$
Mg	$7{,}3.10^{-04}$
Mn	$2{,}6.10^{-05}$
Na	$1{,}0.10^{-04}$
P	$1{,}3.10^{-06}$
Si	$1{,}9.10^{-04}$
S	$5{,}1.10^{-04}$

The aquifer is fully saturated with a very little saline water (1.5 g/L, pH = 7.521). Its composition is indicated in the Table 2 and reflects the equilibrium with the solid matrix, as computed with TOUGHREACT, which is close to the field *in-situ* water composition. The interstitial water composition is supposed homogeneous.

3. Results and discussion

Four series of simulations (three in 2D and one in 3D) were performed in order to exhibit the main tendencies. The CO_2 stream is injected in the center cell of the ceiling or of the floor in the 2D model; a study on intrusion rates, from 0.001 to 0.1 g/s/m^2 during 10 years in the 2D model (with a 3m/yr groundwater flow speed), as well as a sensitivity study on groundwater flow (from 0 to 5 m/yr during 10 years of intrusion at 0.1 g/s/m^2) followed with attenuation (10 years) were performed; a 3D simulation of a 1 year intrusion at 0.1 g/s/m^2 was performed. Intrusion sections vary from 2 m x 1 m to 10 m x 1 m (2D domain) and 2 m x 2 m (3D domain).

3.1. Influence of the intrusion position

Figure 2 shows the spatial distributions of pH, total carbonate concentration, aqueous Pb concentration, galena

and cerussite quantity variations, after 10 years of intrusion at 1 g/s over a 10 m x 1 m section, for two intrusion points at the floor and at the ceiling. The regional groundwater flow is set at 3 m/yr.

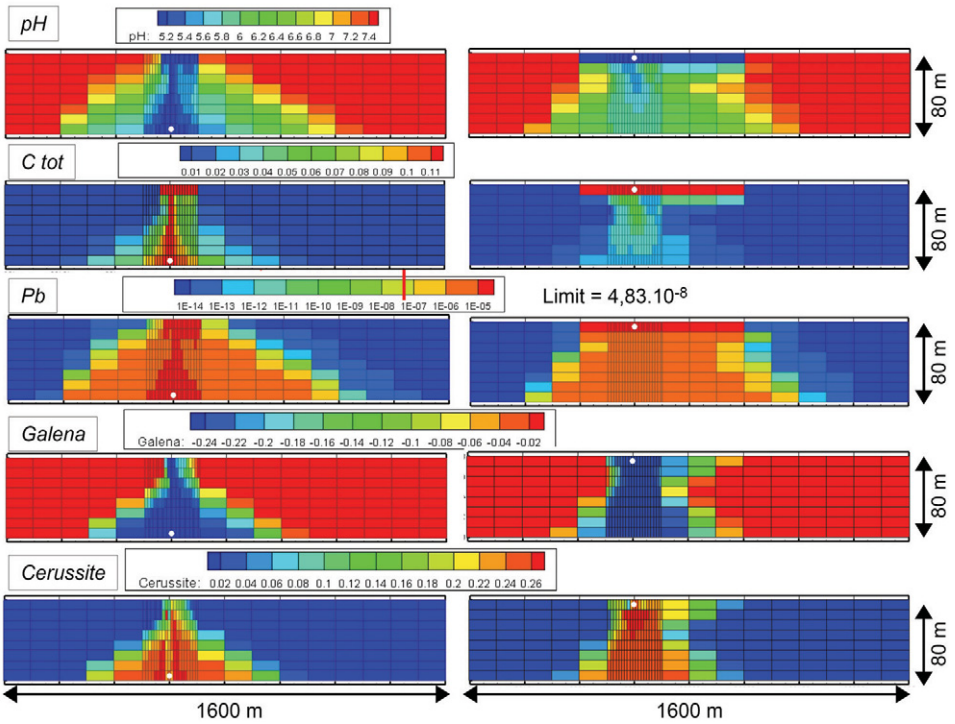


Figure 2. Spatial distributions of pH, dissolved C and Pb (mol/L) and its associated minerals (variations in mol/m^3). Left: floor intrusion; right: ceiling intrusion. White dot: intrusion cell. As an exception, this mesh is coarser than the other (center cells as large as 10 m). EU quality limit mentioned for Pb. Intrusion rate = 0.1 g/s/m^2 through 10 m x 1 m during 10 yrs; groundwater flow = 3 m/yr from left to right

These tests exhibit some dynamics that could occur during the acidification process:

- gaseous CO_2 moves upwards until it dissolves. For intrusion rates high enough, it reaches the ceiling and spreads as a gas plume in the upper zone of the aquifer, fuelled by a column of gaseous CO_2 until the flow is interrupted;
- dissolved CO_2 moves downwards due to the density gradient. The cumulating effects of this movement, the upward migration of gaseous CO_2, advection through groundwater flow and diffusion, lead to a tendency of the chemical alterations to spread in all directions.

The geometry of the impacted zone is correlated with the pH plume shape, which reaches pH = 5.0 as lowest value. Pb impact is represented on Figure 2 as it is the largest of all impact plumes observed. The impact longitudinally reaches about 900 m and vertically extends over the whole thickness of the aquifer. Considering the impact on quality, some elements are found as locally exceeding the quality parameters: Cd, Cu, Pb and Zn, up to 2 orders of magnitude for Pb. These simulations are quite conservative. If sorption processes were taken into account, according to [4] and [12], these mechanisms may strongly reduce the release of trace elements through mineral dissolution by fixing these elements into clay minerals, even possibly lowering their concentrations below the initial ones prior to acidification. In our model, if sorption processes were taken into account, at least glauconite (15 %vol) and kaolinite (15 %vol) could possibly fix important amounts of dissolved Pb, Zn and Cd. Fe and Mn are initially already slightly above the indicative quality parameters, which are not imperative thresholds according to French norms though.

3.2. Sensitivity study on intrusion rate

For studying various intrusion rates, correct simulations of the acidification process in the immediate vicinity of

the intrusion point required adapting the mesh (especially the vertical discretization) to each rate. The horizontal discretization was adapted too so that the longitudinal migration can be correctly evaluated. The pH and Pb concentration results of the simulations for 3 intrusion rates at the floor of the aquifer are represented on Figure 3. Here groundwater flow reaches 3 m/yr. Intrusion happens through a section of 2 m x 1 m at the floor.

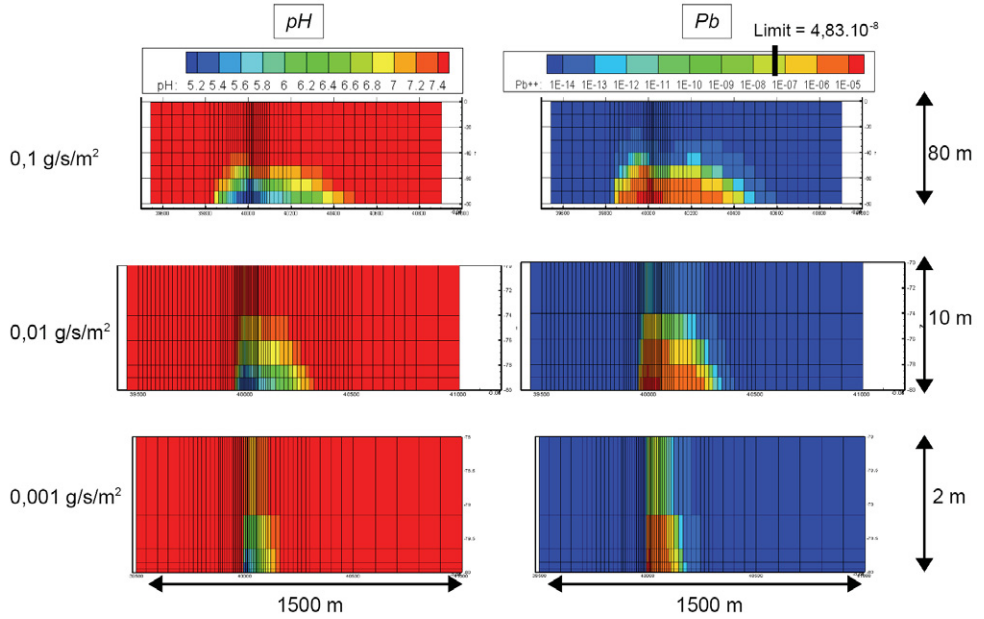


Figure 3. Impact on pH and Pb (concentration in mol/L) for intrusions at 0.1 g/s/m^2, 0.01 g/s/m^2 and 0.001 g/s/m^2 over 2 m x 1 m in the 2D model. Vertical scales are adjusted. Intrusion during 10 yrs; groundwater flow = 3 m/yr from left to right

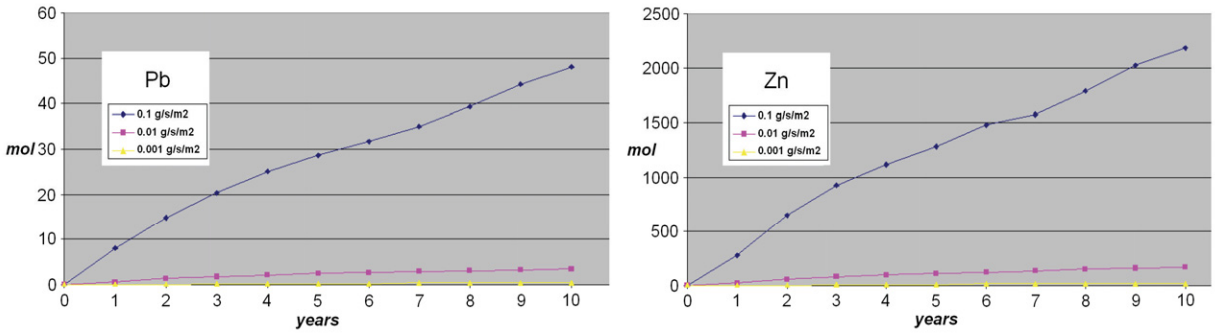


Figure 4. Evolution of the total quantities of aqueous Pb and Zn in the full 2D simulation domain (1 m thick longitudinal section of the aquifer). Intrusions at 0.1 g/s/m^2 (blue), 0.01 g/s/m^2 (pink) and 0.001 g/s/m^2 (yellow) through 2 m x 1 m during 10 yrs; groundwater flow = 3 m/yr

The intrusion rate has a direct influence on the impact and especially its vertical extent (~1 m to 30 m for Pb) and the total amounts of released elements (Figure 4), the latter being roughly correlated with the order of magnitude variations of the tested intrusion rates. The influence of the intrusion rate on the longitudinal extension is significant to a lesser extent (100 m to 500 m for Pb).

3.3. Sensitivity study on groundwater flow

Using 0.1 g/s/m^2 as intrusion rate during 10 years over the same section of 2 m x 1 m at the floor of the aquifer, we simulate three different groundwater flows including one reference case at 0 m/yr. 10 years of attenuation are simulated following the intrusion period to evaluate the possible efficiency of natural attenuation as a remediation measure.

3.3.1. Initial impact

The evolutions of pH and dissolved Pb concentration plumes after 10 years of intrusion and then after 10 years of attenuation are represented in Figure 5 (resp. left column and right column).

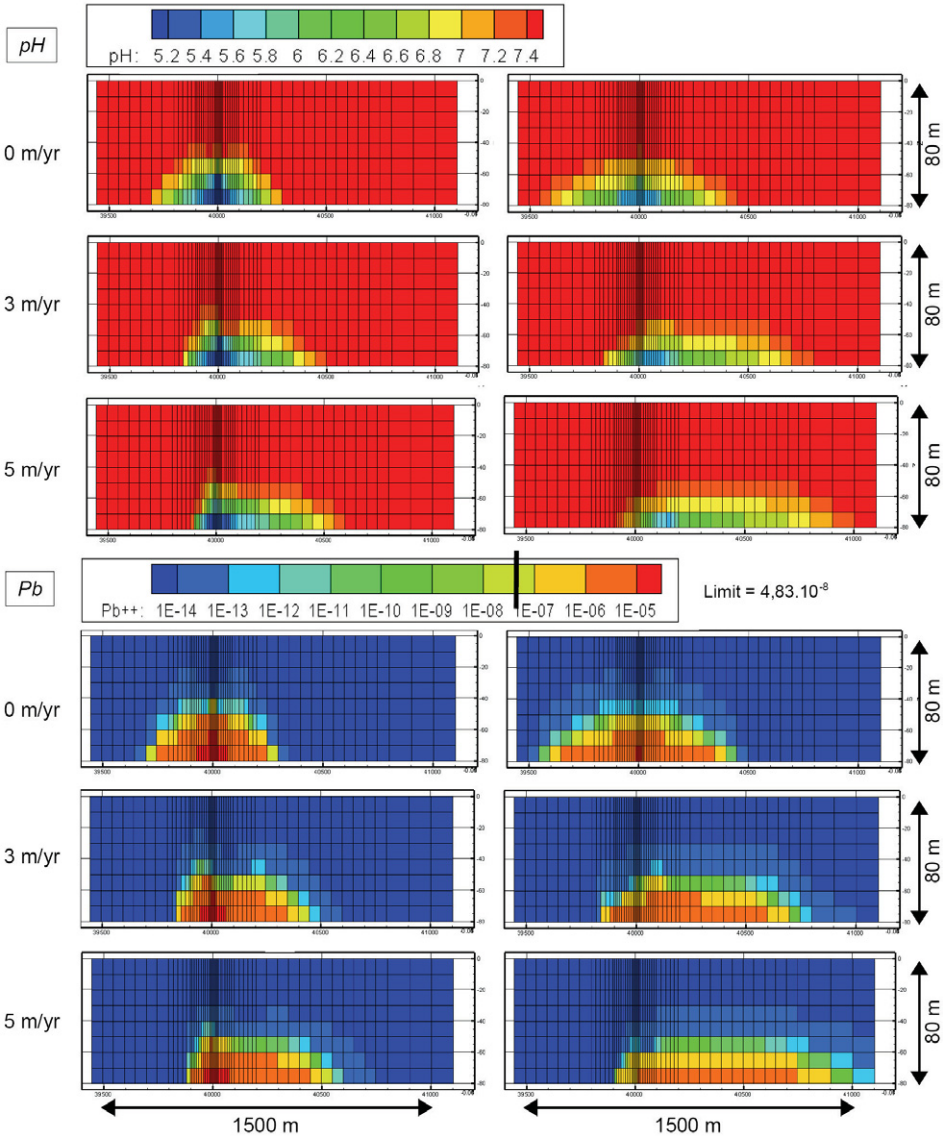


Figure 5. Spatial distributions of pH and aqueous Pb (concentration in mol/L) for three groundwater flow speed values. Left column: situation after initial impact (t = 10 yr); right column: after 10 years of stream interruption (t = 20 yrs). Intrusion at 0.1 g/s/m^2 through 2 m x 1 m in the 2D model; groundwater flow = 0 (top figure), 3 (center), and 5 m/yr (bottom) moving from left to right

The initial impact extends longitudinally over 500 m for the reference case with no flow, and slightly more (550 m) when the flow speed reaches 5 m/yr, while the vertical impact is slightly lighter. The intrusion section is smaller than the one used in 3.1 and leads to a smaller impact. As with the previous simulations, Cd, Pb and Zn exceed locally their respective quality parameters. The computations of the total quantity of released elements (Figure 6) show that during the first ten years (corresponding to the intrusion period) a stronger flow leads to fewer quantities released. These computations were only made with our unique mineralogical and geochemical sets of parameters and therefore cannot be taken as general tendencies.

3.3.2. Effect of attenuation

The intrusion is interrupted after 10 years. The right column of Figure 5 represents the effect of 10 years of attenuation. As with the impact, an increase in the groundwater flow has, in our case study, an attenuating influence on vertical impact and an amplifying impact on longitudinal impact. Figure 6 shows the evolution of the released quantities of Pb and Zn during intrusion and attenuation. The effect of attenuation on Pb and Zn is immediate and is delayed for Cd. Galena and other trace bearing minerals continue to dissolve until the remaining CO_2 fully disappears. The decrease speed is directly determined by the kinetic rates. Here, we used rather minimalist hypotheses as rather quick precipitation kinetic rates were attributed to some minerals. Therefore, even with optimistic conditions, a full recovery from the simulated impact would take at least several tens of years.

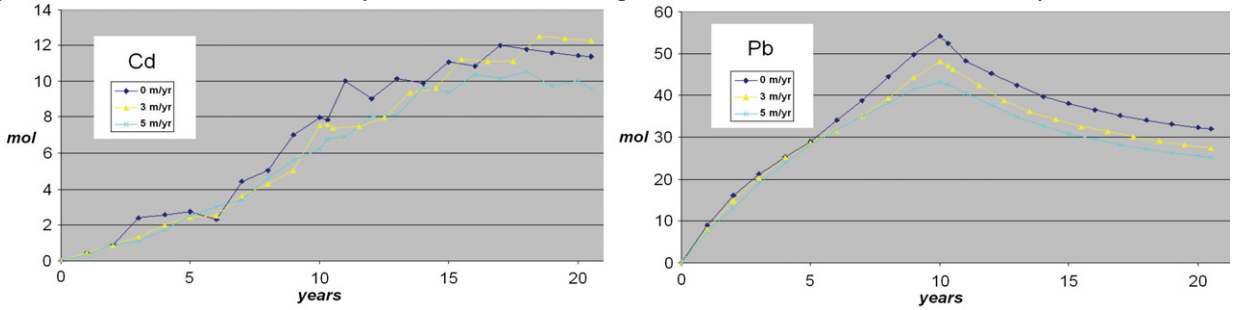


Figure 6. Evolution of the total quantities of aqueous Cd and Pb in the full 2D simulation domain (1 m thick longitudinal section of the aquifer). Intrusion at 0.1 g/s/m^2 over 2 m x 1 m in the 2D model; groundwater flow speed = 0 (navy blue), 3 (yellow), and 5 (light blue) m/yr

3.4. 3D simulation

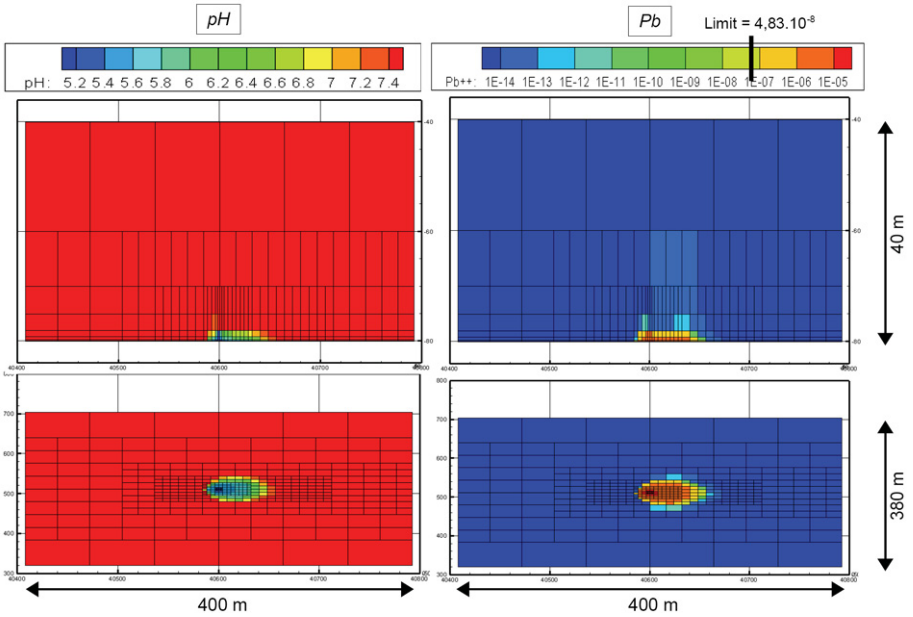


Figure 7. Distributions of pH (left) and Pb (right, mol/L) following a punctual intrusion. Above: longitudinal section; below: horizontal section at the floor level. Intrusion (1 yr) at 0.1 g/s/m^2 over 2 m x 2 m in the 3D model; groundwater flow = 3 m/yr from left to right

A 1 year long intrusion at 0.1 g/s/m^2 through a 2 m x 2 m section at the center cell of the floor of the aquifer was simulated in the 3D model with a groundwater flow of 3 m/yr. This short simulation aimed to observe the immediate impact after the beginning of an intrusion (Figure 7). After one year of continuous intrusion, total amounts of

6.9 mol of Pb, 305.2 mol of Zn, 0.3 mol of Cd were released. These elements already exceed locally the quality parameters. The shape of the impact is more horizontally extended than vertically (roughly 50 m x 40 m horizontally versus 2 m vertically).

4. Conclusion

Using the reactive transport code TOUGHREACT/ECO2N, modeling works of the potential impact of an accidental CO_2 leakage on the quality of freshwater in a glauconitic-sandstone aquifer were performed. The sensitivity studies in 2D exhibit the following dynamics:

- gaseous CO_2 moves upwards and if the stream is durably strong, a CO_2 plume could accumulate and spread at the ceiling of the aquifer;
- water enriched with dissolved CO_2 tends to migrate downwards due to density gradients;
- an interruption of the stream has an immediate decreasing effect on the total amount of released elements such as Pb or Zn, but, depending of the initial impact, the total restoration of the system to its initial state may be a long process of more than tens of years;
- a stronger groundwater flow tends to enlarge longitudinally the impact and decrease its vertical extent. In our specific case, it decreases the total amounts of released elements;
- the CO_2 intrusion rate has a direct influence on the total amount of released elements and on the vertical extent of the impact, and a lesser but nonetheless significant influence on its longitudinal dimension;
- Cd, Pb, Zn are observed as locally exceeding quality parameters. The extension of the impact depends on intrusion duration and rate.

This model evaluates the potential for precipitation and dissolution processes to impact groundwater quality. Sorption processes are not yet computed in the model. It is expected that they could strongly limit at an early stage the possible release of health significant elements by mineral dissolutions.

These computations were performed with a specific set of mineralogical, geochemical and kinetic data, hence making our computations and the tendencies described here specific to a determined situation. Especially, attenuation effects depend on selected kinetic rates.

Further investigations will include sensitivity study on geochemical parameters as well as refining the processes taken into account, by notably adding sorption processes and surface complexations on clay minerals and oxy-hydroxydes, and also testing different intrusion conditions in the 3D model.

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