Investigating geochemical impacts of CO_2 intrusion in a groundwater aquifer

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Outlines

- Objectives
- Context & Background data
- Web-Phreeqc simulations:
  - Using Background data
  - Injecting CO_2 in the system
  - Manipulation of SO_4^{2-} concentrations
  - Mobilization of Heavy Metals (Al, Zn, Cu)
- Conclusions
- Discussions

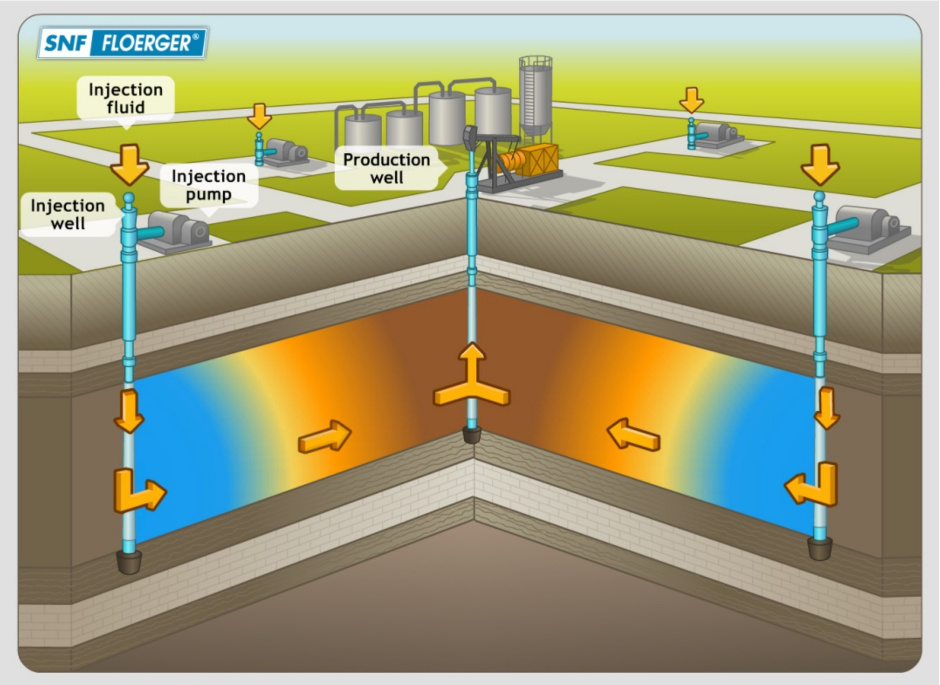
Objectives

- Predict groundwater geochemistry through Web-Phreeqc simulations
- Understand how CO_2 influences that geochemistry
- Get familiarity with using Web-Phreeqc software

Context & Background data

Enhanced Oil Recovery (EOR) technology

- CO_2 is injected around oil-pumping wells to enhance oil recovery

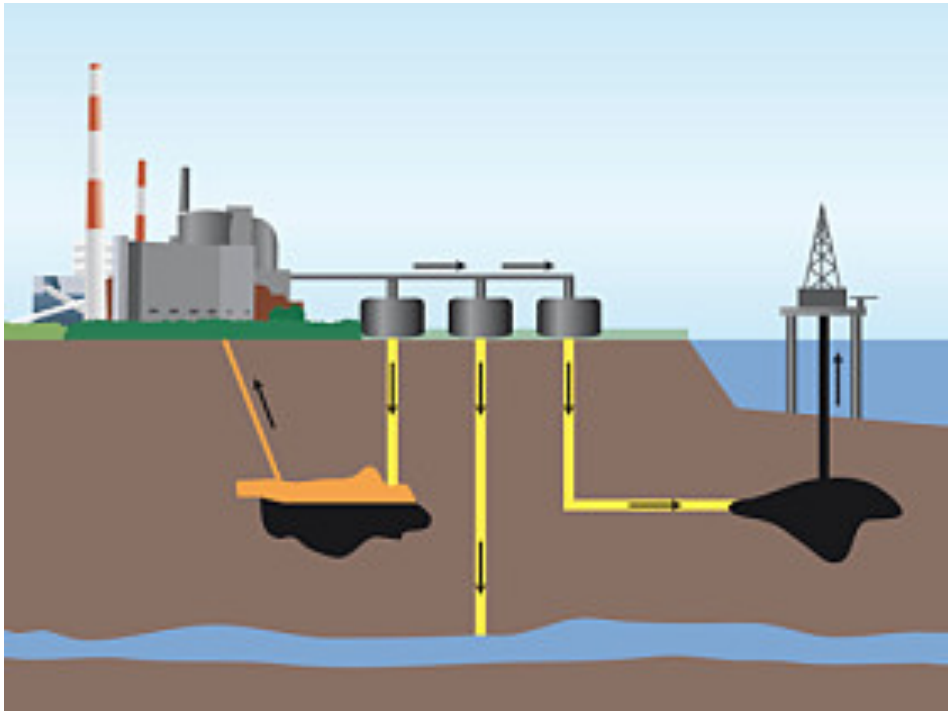


http://www.snf-oil.com/

Carbon Capture and Sequestration (CCS) technology

- Capture CO_2 from point sources (i.e. Fossil fuel power plants)

- Storage in underground geological formations



http://www.environmentallawresource.com

Principle of CCS concept

CO_2 reacts with minerals present in the formation to form stable, solid compounds like carbonates

$$\mathbf{CO_2 + H_2O \Leftrightarrow H_2CO_3}$$

$$\mathbf{Me + 2HCO_3^- \Leftrightarrow MeCO_3 + 2H^+}$$

Where Me is a mineral (mono or divalent)

Ca^{2+}, Na^+, Mg^{2+}, Fe^{2+}…

Examples of carbonate species

Calcite – $CaCO_3$

Dolomite – $CaMgCo_3$

Siderite – $FeCO_3$

Magnesite – $MgCO_3$

http://crystal-cure.com

http://commons.wikimedia.org

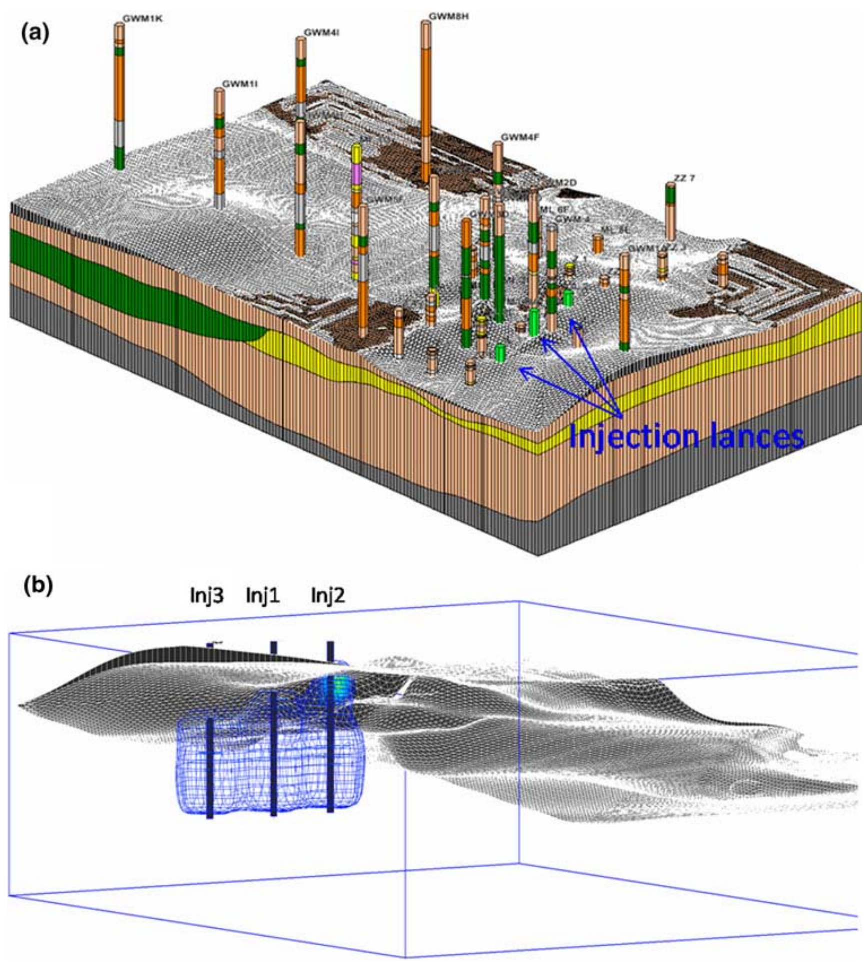
Potential Impacts of CCS

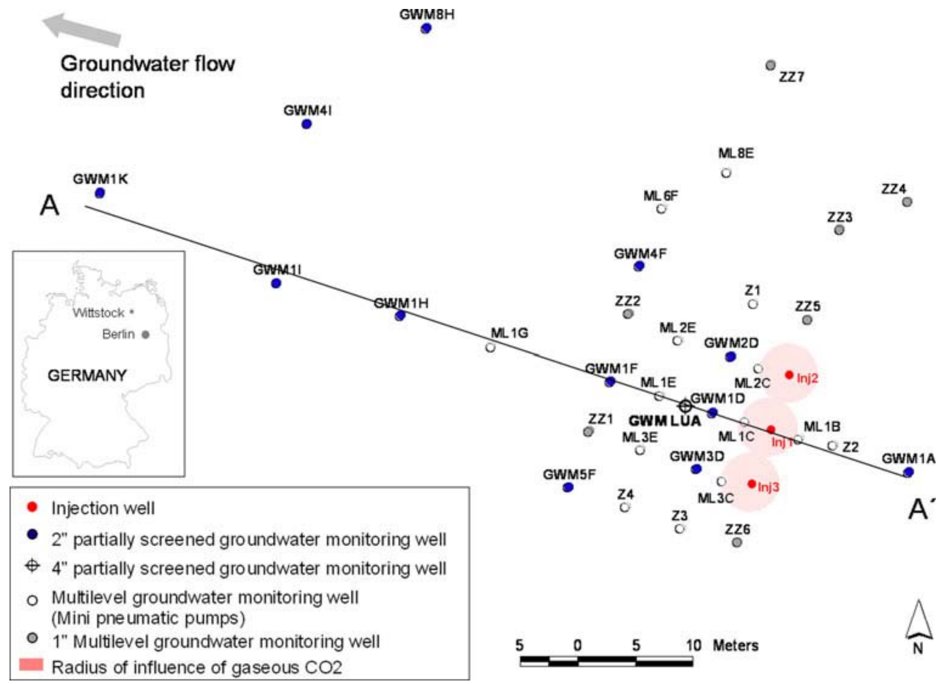
http://mineralatlas.com

- Low pH & acidification of the system
- Geochemical alteration of groundwater
- Mobilization of heavy metals such as Al, Fe, Zn,…

Investigation of the geochemical impact of CO_2 on shallow groundwater: design and implementation of a CO_2 injection test in Northeast Germany

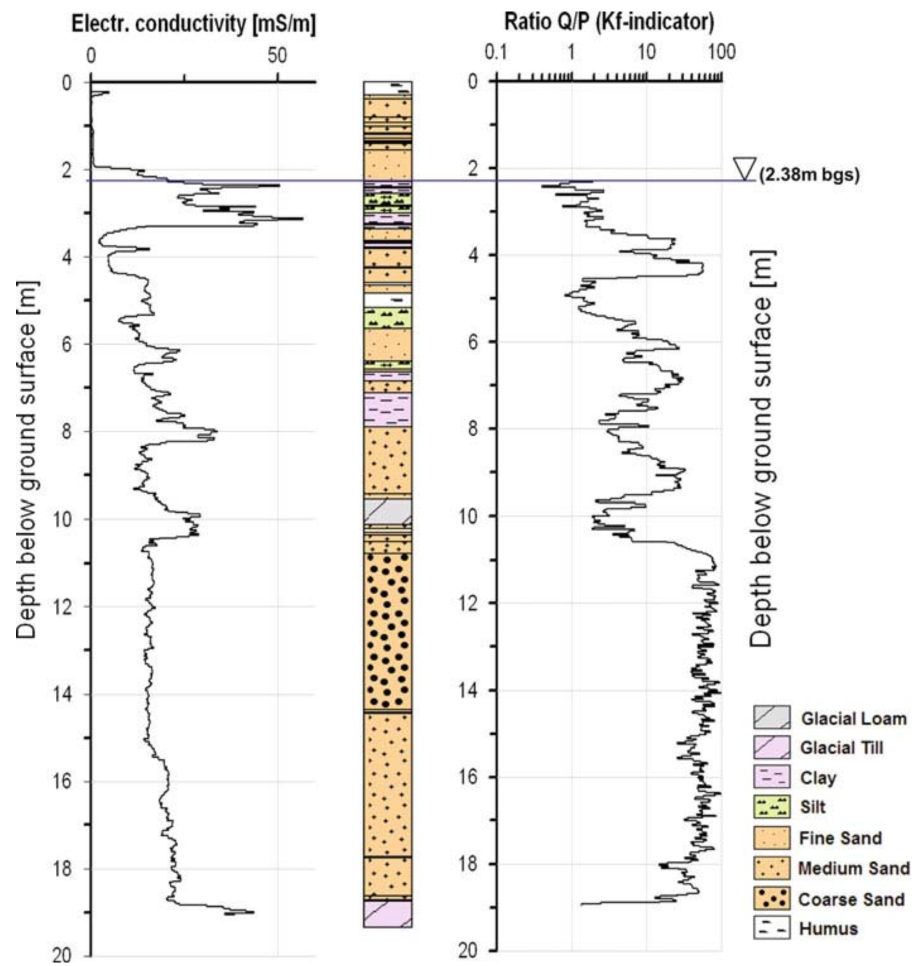
Peter et al. 2012





Soil profile of the study site

- Geology
  - Sand
  - Silt
  - Clay , &
  - Humus
- No carbonates



Peter et al. 2012

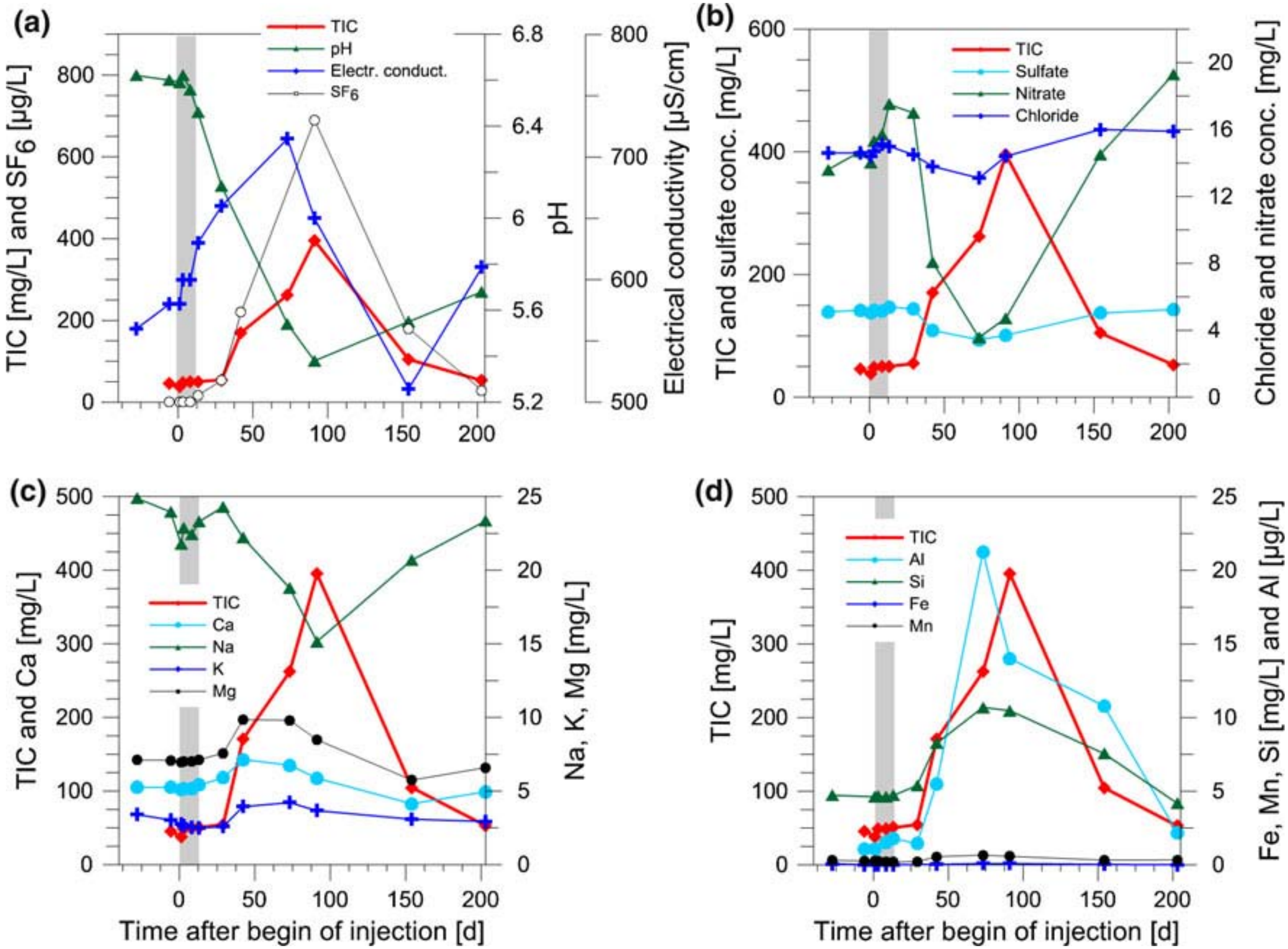
Ionic speciation (Moles)

- Ca^{2+}: 2.678×10^{-3}
- Cl^{-}: 5.671×10^{-4}
- Fe^{2+}: 3.224×10^{-6}
- Mg^{2+}: 2.880×10^{-4}
- Mn^{2+}: 3.277×10^{-6}
- NO_3^{-}: 4.678×10^{-4}
- K^{+}: 6.907×10^{-5}
- Si: 7.825×10^{-5}
- Na^{+}: 1.053×10^{-3}
- SO_4^{2-}: 1.469×10^{-3}

Preliminary Results

- Increase in the concentration of
  - Total Inorganic Carbons (TIC)
  - Bicarbonate ions (HCO_3^-)
- Decrease in pH
- Release of:
  - Cations (Ca^{2+}, Na^+, K^+, Mg^{2+})
  - Anions (SO_4^{2-}, NO_3^-, Cl^-)
  - Trace elements (Al, Si, Fe, Mn)

Peter et al. 2012



Web-Phreeqc Simulations

Case #1: No CO_2 is in the system

- Ca^{2+}: 2.678×10^{-3}
- Cl^{-}: 5.671×10^{-4}
- Fe^{2+}: 3.224×10^{-6}
- Mg^{2+}: 2.880×10^{-4}
- Mn^{2+}: 3.277×10^{-6}
- NO_3^{-}: 4.678×10^{-4}
- K^{+}: 6.907×10^{-5}
- Si: 7.825×10^{-5}
- Na^{+}: 1.053×10^{-3}
- SO_4^{2-}: 1.469×10^{-3}

pH = 6.7

$O_2 = 10^{-1.22}$

Case #1: CO_2 = 0 Atm

pH	Activity	Ionic Strength
6.572	1	1.031×10^{-2}

Total Alkalinity = 3.387×10^{-3} eq/Kg

Total CO_2 = 5.181×10^{-3} mol/Kg

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-----------------------------Description of solution----------------------------

                                       pH  =   6.700
                                       pe  =   2.440
                        Activity of water  =   1.000
                           Ionic strength  =   1.030e-02
                       Mass of water (kg)  =   1.000e+00
                     Total carbon (mol/kg) =   5.181e-03
                        Total CO2 (mol/kg) =   5.181e-03
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  -1.649e-04
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -1.27
                               Iterations  =  11
                                  Total H  = 1.110165e+02
                                  Total O  = 5.552650e+01

-----------------------------Distribution of species----------------------------
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                                                          Log       Log       Log
   Species                   Molality    Activity  Molality  Activity     Gamma

   H+                       2.187e-07   1.995e-07    -6.660    -6.700    -0.040
   OH-                      5.581e-08   5.016e-08    -7.253    -7.300    -0.046
   H2O                      5.551e+01   9.998e-01    -0.000    -0.000     0.000
C(4)                5.181e-03
   HCO3-                    3.627e-03   3.279e-03    -2.440    -2.484    -0.044
   CO2                      1.468e-03   1.471e-03    -2.833    -2.832     0.001
   CaHCO3+                  7.277e-05   6.579e-05    -4.138    -4.182    -0.044
   MgHCO3+                  7.147e-06   6.438e-06    -5.146    -5.191    -0.045
   CaCO3                    2.031e-06   2.036e-06    -5.692    -5.691     0.001
   NaHCO3                   1.737e-06   1.742e-06    -5.760    -5.759     0.001
   CO3-2                    1.154e-06   7.707e-07    -5.938    -6.113    -0.175
   FeHCO3+                  5.825e-07   5.248e-07    -6.235    -6.280    -0.045
   MnHCO3+                  5.277e-07   4.753e-07    -6.278    -6.323    -0.045
   MgCO3                    1.231e-07   1.234e-07    -6.910    -6.909     0.001
   MnCO3                    9.934e-08   9.957e-08    -7.003    -7.002     0.001
   FeCO3                    2.952e-08   2.959e-08    -7.530    -7.529     0.001
   NaCO3-                   1.505e-08   1.355e-08    -7.823    -7.868    -0.045
Ca                  2.679e-03
   Ca+2                     2.356e-03   1.573e-03    -2.628    -2.803    -0.176
   CaSO4                    2.477e-04   2.482e-04    -3.606    -3.605     0.001
   CaHCO3+                  7.277e-05   6.579e-05    -4.138    -4.182    -0.044
   CaCO3                    2.031e-06   2.036e-06    -5.692    -5.691     0.001
   CaOH+                    1.452e-09   1.308e-09    -8.838    -8.883    -0.045
   CaHSO4+                  3.221e-10   2.902e-10    -9.492    -9.537    -0.045
Cl                  5.672e-04
   Cl-                      5.672e-04   5.101e-04    -3.246    -3.292    -0.046
   MnCl+                    3.752e-09   3.380e-09    -8.426    -8.471    -0.045
   FeCl+                    1.251e-09   1.127e-09    -8.903    -8.948    -0.045
   MnCl2                    7.507e-13   7.525e-13   -12.125   -12.123     0.001
   MnCl3-                   1.173e-16   1.057e-16   -15.931   -15.976    -0.045
   FeCl+2                   9.847e-19   6.484e-19   -18.007   -18.188    -0.181
   FeCl2+                   1.640e-21   1.477e-21   -20.785   -20.831    -0.045
   FeCl3                    7.517e-26   7.535e-26   -25.124   -25.123     0.001
Fe(2)               3.221e-06
   Fe+2                     2.380e-06   1.600e-06    -5.623    -5.796    -0.172
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Carbonate ion species

SPECIES	Concentration (Molality)
HCO_3^-	3.63×10^{-3}
CO_2	1.468×10^{-3}
$CaHCO_3^+$	7.277×10^{-5}
$MgHCO_3^+$	7.147×10^{-6}
$CaCO_3$	2.031×10^{-6}
$NaHCO_3$	1.737×10^{-6}
CO_3^{-2}	1.154×10^{-6}
$FeHCO_3^+$	5.825×10^{-7}
$MnHCO_3^+$	5.277×10^{-7}
$MgCO_3$	1.231×10^{-7}
$MnCO_3$	9.934×10^{-8}
$FeCO_3$	2.952×10^{-8}
$NaCO_3$	1.505×10^{-8}

Chemical	Formula	SI
Aragonite	$CaCO_3$	-0.75
Calcite	$CaCO_3$	-0.60
Dolomite	$CaMg(CO_3)_2$	-2.05
Carbon dioxide	CO_2	-1.28
Rhodochrosite	$MnCO_3$	-0.93
Siderite	$FeCO_3$	-9.44

Case #2: $CO_2 = 10^{-3.52}$ Atm

pH	Activity	Ionic Strength
8.739	1	9.897×10^{-3}

Chemical	Formula	SI (CO_2=0)	SI ($CO_2=10^{-3.52}$)
Aragonite	$CaCO_3$	-0.75	1.32
Calcite	$CaCO_3$	-0.60	1.46
Dolomite	$CaMg(CO_3)_2$	-2.05	2.10
Carbon dioxide	CO_2	-1.28	-3.52
Rhodochrosite	$MnCO_3$	-0.93	0.61
Siderite	$FeCO_3$	-9.44	-11.36

pH increased - Ionic Strength decreased – Carbonates precipitated

	Without CO_2	With CO_2
SPECIES	**Concentration (M.)**	**Concentration (M.)**
HCO_3^-	3.63×10^{-3}	2.768×10^{-3}
CO_2	1.468×10^{-3}	9.590×10^{-5}
$CaHCO_3^+$	7.277×10^{-5}	9.590×10^{-5}
$MgHCO_3^+$	7.147×10^{-6}	5.309×10^{-6}
$CaCO_3$	2.031×10^{-6}	1.614×10^{-4}
$NaHCO_3$	1.737×10^{-6}	1.329×10^{-6}
CO_3^{-2}	1.154×10^{-6}	1.026×10^{-5}
$FeHCO_3^+$	5.825×10^{-7}	2.423×10^{-19}
$MnHCO_3^+$	5.277×10^{-7}	1.161×10^{-7}
$MgCO_3$	1.231×10^{-7}	1.002×10^{-5}
$MnCO_3$	9.934×10^{-8}	2.394×10^{-6}
$FeCO_3$	2.952×10^{-8}	1.345×10^{-18}
$NaCO_3^-$	1.505×10^{-8}	1.257×10^{-6}

MAJOR CATIONS & TRACE ELEMENTS

SPECIES	Concentration (M.) Without CO_2	With CO_2
Na^{+}	1.047×10^{-3}	1.046×10^{-3}
K^{+}	6.870×10^{-5}	6.870×10^{-5}
Ca^{2+}	2.362×10^{-3}	2.226×10^{-3}
Mg^{2+}	2.503×10^{-4}	2.417×10^{-4}
Cl^{-}	5.672×10^{-4}	5.672×10^{-4}
Al^{3+}	------	------
Mn^{2+}	2.478×10^{-6}	6.932×10^{-7} ↓
Fe^{2+}	1.324×10^{-14}	1.290×10^{-18} ↓

Case #3: Role of CO_2 in metals mobilization

Al = 6.441×10^{-4} Moles
Zn = 8.724×10^{-6} Moles
Cu = 3.889×10^{-4} Moles

	pH	Activity	Ionic Strength
Before	6.596	1	1.013×10^{-2}
After	7.686	1	9.182×10^{-3}

MAJOR CATIONS & TRACE ELEMENTS

SPECIES	Concentration (M.) Without CO_2	With CO_2
Na^+	1.049×10^{-3}	1.049×10^{-3}
K^+	6.872×10^{-5}	6.870×10^{-5}
Ca^{2+}	2.407×10^{-3}	2.412×10^{-3}
Mg^{2+}	2.548×10^{-4}	2.550×10^{-4}
Cl^-	5.672×10^{-4}	5.672×10^{-4}
Al^{3+}	1.851×10^{-7}	1.061×10^{-11}
Mn^{2+}	2.796×10^{-6}	2.871×10^{-6}
Fe^{2+}	1.230×10^{-14}	2.084×10^{-16}
Cu^{2+}	2.872×10^{-4}	1.109×10^{-5}
Zn^{2+}	7×10^{-6}	6.824×10^{-6}

Chemical	Formula	SI	
		Without CO_2	With CO_2
Calcite	$CaCO_3$	-1.04	-0.60
Dolomite	$CaMg(CO_3)_2$	-2.92	-2.05
Siderite	$FeCO_3$	-9.92	-11.25
Smithsonite	$ZnCO_3$	-2.05	-1.63
Rhodochrosite	$MnCO_3$	-1.32	-0.87

Mineral carbonates are dissolved in the system

Case #4: What if the soil has high sulfate content?

$SO_4^{2-} = 1.191 \times 10^{-3}$ Moles ➔ $SO_4^{2-} = 6.738 \times 10^{-3}$ Moles

	pH	Activity	Ionic Strength
Before	7.686	1	9.182×10^{-3}
After	7.661	1	1.899×10^{-2}

No major change in pH

MAJOR CATIONS & TRACE ELEMENTS

SPECIES	Concentration (M.) Low SO_4^{2-}	High SO_4^{2-}
Na^+	1.049×10^{-3}	1.033×10^{-3}
K^+	6.870×10^{-5}	6.726×10^{-5}
Ca^{2+}	2.412×10^{-3}	1.822×10^{-3}
Mg^{2+}	2.550×10^{-4}	1.849×10^{-4}
Cl^-	5.672×10^{-4}	5.676×10^{-4}
Al^{3+}	1.061×10^{-11}	1.644×10^{-11}
Mn^{2+}	2.871×10^{-6}	2.248×10^{-6}
Fe^{2+}	2.084×10^{-14}	2.632×10^{-16}
Cu^{2+}	1.109×10^{-5}	1.388×10^{-5}
Zn^{2+}	6.824×10^{-6}	5.137×10^{-6}

What does that mean for the carbonate species?

Chemical	Formula	SI	
		Low SO_4^{2-}	High SO_4^{2-}
Calcite	$CaCO_3$	-0.60	-0.83
Dolomite	$CaMg(CO_3)_2$	-2.05	-2.52
Siderite	$FeCO_3$	-11.25	-11.26
Smithsonite	$ZnCO_3$	-1.63	-1.87
Rhodochrosite	$MnCO_3$	-0.87	-1.09

Carbonates & most metal species are dissolved when sulfate level increases

Conclusions

- CO_2 injection leaded to a decrease in pH
- However, as CO_2 reaches saturation, pH increased
- High SO_4^{2-} soil dissolve more carbonates and metal species
- Activity of water remained constant throughout the simulation A= 1.000
- Ionic strength varied slightly

Discussions

- Throughout the simulation process, we observed that:
  - Lowest pH reached during simulation was 6.572. This pH was higher than what Peter et al. found
  - Carbonates existed prior to the injection of CO_2 probably due to alkalinity and the presence of O_2 in the system
  - SIs indicated that carbonates were unstable (super or under saturated)

- Heavy metals were dissolved with CO_2 intrusion as well as with high SO_4^{2-} which is consistent with preliminary results
- Our simulations did not confirm release of major cations and trace elements. This was not consistent with Peter's results

References

- *Peter et al. 2012. Investigation of the geochemical impact of CO2 on shallow groundwater: design and implementation of a CO2 injection test in Northeast Germany*
- *Herzog H. J., 2001 New technologies could reduce carbon dioxide emissions to the atmosphere while still allowing the use of fossil fuels*
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