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Origin of the Patchy Emission Pattern at the ZERT CO₂ Release Test

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1 **Abstract**

2 A numerical experiment was carried out to test whether the patchy CO₂ emission patterns observed
3 at the ZERT release facility are caused by the presence of packers that divide the horizontal injection
4 well into six CO₂-injection zones. A three-dimensional model of the horizontal well and cobble-soil
5 system was developed and simulations using TOUGH2/EOS7CA were carried out. Simulation
6 results show patchy emissions for the seven-packer (six-injection-zone) configuration of the field
7 test. Numerical experiments were then conducted for the cases of 24 packers (23 injection zones)
8 and an effectively infinite number of packers. The time to surface breakthrough and the number of
9 patches increased as the number of packers increased suggesting that packers and associated along-
10 pipe flow are the origin of the patchy emissions. In addition, it was observed that early breakthrough
11 occurs at locations where the horizontal well pipe is shallow and installed mostly in soil rather than
12 the deeper cobble. In the cases where the pipe is installed at shallow depths and directly in the soil,
13 higher pipe gas saturations occur than where the pipe is installed slightly deeper in the cobble. It is
14 believed this is an effect mostly relevant to the model rather than the field system and arises through
15 the influence of capillarity, permeability, and pipe elevation of the soil compared to the cobble
16 adjacent to the pipe.

17

18

1 **Introduction**

2
3 The main challenge addressed by the geologic carbon sequestration near-surface monitoring
4 community is how to detect small CO₂ seepage fluxes and anomalous concentrations in the presence
5 of relatively large natural background fluxes caused by biological processes (e.g., Oldenburg et al.,
6 2004; Lewicki et al., 2005; 2007; Leuning et al., 2008; Cortis et al., 2008). The Zero Emissions
7 Research and Technology (ZERT) project established a CO₂ shallow-release facility on the Montana
8 State University campus to carry out experiments aimed at developing capabilities and testing
9 approaches for detecting and monitoring potential CO₂ seepage (Spangler et al., this issue). The 100
10 m-long horizontal well installed at the site was designed to model a line source of leakage from a
11 geologic carbon sequestration site such as could occur along a leaky fault.

12
13 One of the first observations from the experiment arising from careful measurements of CO₂ flux
14 using the accumulation chamber method was that emissions were patchy (i.e., expressed as localized
15 high-flux regions) above the horizontal well (Lewicki et al., 2007; Lewicki et al., this issue; Spangler
16 et al., this issue). This patchy nature of CO₂ emissions flux persisted over two field seasons with
17 little change in patch location. In this study, the origin of the patchy emission pattern observed in
18 the experiment above the nominally horizontal well was investigated. Specifically, numerical
19 experimentation was used to test the hypothesis that high-flux regions at the ground surface are
20 caused by relatively long slightly sloping runs of perforated pipe in which CO₂ flows slightly
21 upward until encountering a packer, at which point it enters the cobble-soil system and migrates
22 vertically upwards with little lateral spreading, to produce a persistent localized area of high CO₂
23 flux, i.e., a patchy emission pattern.

24

1 **Background**

2 *Observation*

3 Background and overview of the ZERT release facility and related research activities are described
4 fully in Spangler et al. (this issue). The focus of this paper is on numerical experiments that
5 investigate the origin of persistent localized emission regions referred to as patchy emissions. The
6 intriguing motivation for this study is illustrated in Figure 1. Figure 1b shows the elevation of the
7 nominally horizontal well with large vertical exaggeration to amplify the 0.50 m maximum vertical
8 deviation over the 70 m of horizontal injection zones. Also shown are the approximate locations of
9 the seven packers that separate the perforated pipe into the six zones into which CO₂ was injected
10 through tubing. In addition, the figure shows vertical dashed lines that highlight the spatial
11 relationship between packer locations in Figure 1b and soil CO₂ flux maxima measured using the
12 accumulation chamber method along the surface trace of the well (Figure 1a) (Lewicki et al., 2007).
13 A strong correlation is observed between packer locations and the patchy CO₂ emission pattern at
14 the ground surface. This observation led the ZERT team to speculate that the packers block flow
15 within each packed-off zone of the pipe and create effectively a local point-source of CO₂ injection
16 into the formation which then creates a persistent emission-flux and concentration hot spot at the
17 ground surface.

18

19 *Hypothesis*

20 Formalizing the observations of patchy emissions and their presumed cause discussed above, one
21 can propose the following testable hypothesis: the CO₂ that is injected into each zone of the well
22 flows within the pipe upward by buoyancy forces along the slightly sloping water-filled sections of
23 each zone until it encounters a packer, at which point it accumulates and flows through the

1 perforations of the pipe into the cobble-soil system effectively forming a local point source of
2 gaseous CO₂. Because the pipe is below the water table, the gas migrates vertically upwards initially
3 through the porous sediments strongly by buoyancy force and retains its focused flow pattern all the
4 way through the vadose zone to the ground surface.

5
6 To test this hypothesis, numerical experiments were carried out using a three-dimensional (3D)
7 model of the ZERT release facility. The Base Case model considers the system as it is installed with
8 six packed-off zones. An alternative scenario was simulated with 23 packed-off zones (Case 1), and
9 with effectively continuous injection from the pipe into the formation (Case 2). Both of these
10 alternative scenarios reduce the amount of along-pipe flow that can occur and effectively reduce or
11 eliminate the point-source geometry of the release.

12

13 **Methods**

14 *Numerical Simulation*

15 To carry out the numerical experiment outlined above, the multiphase and multicomponent
16 subsurface transport simulator TOUGH2 (Pruess et al., 1999) was used with EOS7CA, a research
17 module that models the chemical components of interest here, namely water, CO₂, and air (e.g.,
18 Oldenburg and Unger, 2003; Oldenburg et al., 2009). TOUGH2 solves implicitly the time-
19 dependent coupled flow and transport equations arising from the integral finite difference method.
20 Non-linearity is handled using Newton's method, and the large set of linear equations arising at each
21 Newtonian iteration is solved using a sparse conjugate gradient solver. Convergence is ensured by
22 the use of a residual-based convergence criterion at each time step. Table 1 presents the equations
23 solved in TOUGH2; full details of the methods used in TOUGH2 can be found in Pruess et al.
24 (1999) available online at the TOUGH2 website. Note the energy equation is omitted from Table 1

1 because isothermal conditions are assumed in this study. TOUGH2/EOS7CA is designed for near-
2 surface applications and uses Henry's Law for modeling CO₂ solubility. Other TOUGH2 modules
3 (e.g., ECO2N (Pruess, 2005) and EOS7C (Oldenburg et al., 2004) are available for deep subsurface
4 (high-pressure) systems.

5 *Model System and Discretization*

6 Prior simulation studies of the ZERT shallow-release facility (Oldenburg et al., 2009; Spangler et al.,
7 this issue) used a two-dimensional (2D) cross-section model (perpendicular to the pipe) known as
8 the transverse model. These prior transverse model simulations were appropriate because of the
9 long sub-horizontal dimension of the pipe and they were useful for estimating breakthrough times,
10 surface fluxes, and the degree of lateral spreading. For this study, aimed at testing the hypothesis
11 that variations in the pipe elevation are the origin of patchy surface emissions, a longitudinal (along-
12 the-pipe) geometry is needed. Furthermore, because the fundamental observation at the ground
13 surface is of patchy emissions, discretization in the transverse direction is also required resulting in
14 the need for a 3D grid.

15

16 A conceptual model of the longitudinal *XY* plane (vertical cross section) containing the pipe is
17 shown in Figure 2. As shown, the system consists of a gently sloping ground surface (gradient
18 ~1.7% downward to the northeast) with a 1.2 m-thick soil layer underlain by a cobbly sand (Mokwa,
19 2006) referred to here as cobble. The water table fluctuates seasonally and is approximated here to
20 be at the level shown in Figure 2 consistent with its location during the summers when experiments
21 have been carried out. Properties of the soil and cobble layers are given in Table 2.

22

1 The full 3D grid was generated using the WinGridder package (Pan, 2008). The grid was designed
2 to capture the details of the release of CO₂ from the horizontal well. Assuming for convenience that
3 the release is symmetric about the centerline of the pipe, a grid was constructed for the region to the
4 northwest of the pipe. It is assumed further for simplicity that the topography and soil and cobble
5 layer properties are invariant in the horizontal direction perpendicular to the pipe. The discretization
6 developed represents the horizontal well and its elevation variations in detail as shown by the *XY*
7 (vertical plane) cross section containing the pipe shown in Figure 3. Note in Figure 3 that the pipe is
8 fully within the cobble material in the southwest (SW, left-hand side) and at the cobble-soil interface
9 or within the soil on its northeast (NE, right-hand side) end. The 3D grid consists of 11 replications
10 of the grid shown in Figure 3. Though the pipe discretization is replicated in the direction
11 perpendicular to the pipe (*Z*-direction), there is no pipe material in the model anywhere except in the
12 plane at $Z = 8.975$ m (the mirror plane) and cobble or soil is specified as appropriate even where the
13 discretization mimics the pipe geometry. The resulting 3D grid is shown in Figure 4 with
14 independent scaling of the three axes (the *Z*-direction connections are not shown). Note the fine
15 spacing of the *XY* planes near the well intended to capture the details of processes near the well
16 while the plane spacing increases away from the well where the influence of the injection is much
17 smaller. Observations of the flux pattern from the 2007 release experiment guided our choice of the
18 variable spacing of the multiple vertical planes and the extent of the system perpendicular to the
19 pipe. Each *XY* plane contains 4779 grid blocks; there are 11 planes for a total of 52,569 gridblocks
20 and 147,486 connections.

21

22 Boundary conditions are no-flow at the bottom and atmospheric conditions at the top represented by
23 elevation-dependent pressure that is constant with time. The CO₂ concentration boundary condition

1 at the top is mass fraction in the aqueous phase equal to 5.76×10^{-4} which corresponds to a gas-
2 phase concentration of 380 ppmv and is also the initial condition throughout the system. The sides
3 ($X = 0.0$ and $X = 96.5$ m) are closed (no-flow boundary condition), while conditions at the rear XY
4 plane ($Z = 4.5$ m) are constant with time and equal to the initial condition. The front XY plane ($Z =$
5 8.975 m) is a no-flow boundary and serves as the mirror plane of the symmetric model system. All
6 simulations are isothermal at 15 °C.

7

8 *Flow Properties of the Materials*

9 The properties used for the two layers (soil and cobble) are given in Table 2. Capillary pressure and
10 relative permeability characteristic curves were approximated to give a higher capillary pressure in
11 the presumably finer-grained soil than in the cobble for a given liquid saturation. The porosity of
12 both layers was set to 0.35, while the permeabilities of the layers were assigned based on a
13 calibration from an earlier release (see Oldenburg et al., 2009; Spangler et al., this issue). Rainfall
14 infiltration was set to zero as the CO_2 releases from the horizontal well were carried out in summer
15 months for which there is little precipitation. The steady-state gravity-capillary equilibrium moisture
16 profile used as the initial condition is shown in Figure 5. Note the dry region around $X = 15$ m, $Y =$
17 8.7 m which arises from a capillary barrier effect (local region of high liquid saturation above lower
18 liquid saturation) that develops in unsaturated systems where finer-grained materials overlies coarser
19 materials (e.g., Oldenburg and Pruess, 1993).

20

21 The pipe was approximated as a high-porosity and high-permeability porous medium with low
22 capillarity. This assumption clearly does not allow a rigorous modeling of intra-well flow processes,
23 but will capture the key effect of faster flow and transport of CO_2 within the well and stronger

1 capillary suction of the formation than the pipe in unsaturated conditions. This is critical as one
2 aspect of the hypothesis being tested is that along-well flow of CO₂ accumulates against packers in
3 the high-elevation regions of each packed-off section. As shown below, the processes of flow in the
4 well are believed to be adequately modeled using the porous-medium approach. The total injection
5 rate of CO₂ into the pipe is 100 kg/d distributed evenly into each packed-off section and divided by
6 two to honor the mirror symmetry of the system. Note that not all zones are the same length and
7 therefore this injection specification differs slightly from that in the field experiment which injected
8 the same amount of CO₂ per unit length. This difference does not affect the conclusions of the
9 numerical experiments presented here.

10 **Results**

11 The basic flow and transport processes involved in the injection of CO₂ beneath the water table into
12 the cobble-soil system at the ZERT release facility have already been described (Oldenburg et al.,
13 2009; Spangler et al., this issue). To summarize briefly, injected CO₂ first displaces water in the
14 saturated zone and forms bubbles which then move upwards by buoyancy into the vadose zone. The
15 buoyancy driving force in the saturated zone is sufficiently large to make CO₂ move upward without
16 significant spreading. In the vadose zone, CO₂ is the dense gas relative to air and therefore tends to
17 spread out, especially in the unsaturated cobble, as it moves upward by pressure gradient forces.
18 Below are presented results of the testing of the hypothesis of the packer origin of patchy emissions
19 for the 3D system, and some observations about moisture redistribution as injected CO₂ creates
20 unsaturated conditions.

21

22 Figure 6 presents a 3D view of results for the Base Case at $t = 3$ days of the mass fraction of CO₂ in
23 the gas phase ($X_g^{CO_2}$). This figure shows the right-hand (northwest) side of a symmetric system with

1 patchy emissions on the ground surface (approximated as a uniformly sloping surface). The first-
2 order observation is that the Base Case model is able to produce, at least qualitatively, patchy
3 emission patterns similar to those observed in the field. The overall average measured CO₂ flux at t
4 = 9 days is $1.8 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$ ($1500 \text{ g m}^{-2} \text{ d}^{-1}$) while the modeled average flux is $2.2 \times 10^{-5} \text{ kg m}^{-2}$
5 s^{-1} ($1900 \text{ g m}^{-2} \text{ d}^{-1}$). The modeled mean fluxes along the projection of the pipe at the ground surface
6 are presented in Table 3 (see also Lewicki et al., 2007). Note that this agreement is considered
7 adequate for purposes here, and system properties are not altered from those used in Oldenburg et
8 al. (2009) to match the measured fluxes. From this point of qualitative match of model and field
9 systems, a numerical experiment may be conducted to test whether packer location and along-pipe
10 flow are the cause of patchy emissions.

11

12 The first experimental case (Case 1) considered is one in which there are four times as many packers
13 as actually installed. The idea is to test the possibility that more packers will create more patches.
14 For convenience, results are presented for mass fraction of CO₂ in the gas phase only in the plane
15 containing the pipe, although all of the results presented are from the full 3D model. Shown in
16 Figure 7 are results for the Base Case (six zones) and Case 1 (23 zones) at five times ($t = 0.06, 0.5,$
17 $1.0, 1.5,$ and 2.0 days). In the Base Case, there is an early breakthrough at $X = 61$ m, followed by a
18 breakthrough at $X = 84$ m. Both of these breakthroughs occur at the upper ends of packer sections
19 suggesting the hypothesis that along-pipe flow of CO₂ and subsequent blocking of flow by the
20 packers produce essentially point-sources. At these locations, the pipe is also very shallow. Other
21 point sources produced by packer locations create additional patches of high CO₂ emissions later in
22 time. It is speculated that the breakthrough at $X = 84$ m (Zone 1) is not as fast as the one at $X = 61$ m
23 (from Zone 2) because it has no neighboring zone to the right-hand side and therefore does not

1 receive any lateral CO₂ flow as occurred at the Zone 2-3 packer. Finally, note that the injection at X
2 > 61 m is into pipe that is within soil, which has larger permeability than cobble as determined by
3 calibration (Oldenburg et al., 2009; Spangler et al., this issue). These factors, namely proximity to
4 surface and pipe installed in high-permeability soil, appear to play a role in the early breakthrough.
5 The patchy emission pattern appears to result from the packer blocking along-pipe flow and causing
6 an effective point-source release.

7
8 Results for Case 1 (23 zones) show some of the same behavior as the base case, e.g., tendency for
9 early breakthrough at $X = 61$ m and 84 m. But the Case 1 results also show clearly the tendency for
10 multiple packers to produce multiple point sources as evidenced by the numerous finger-like CO₂
11 plumes generated by each packer. From this result, the hypothesis of a packer origin of patchy
12 emissions is confirmed.

13
14 The hypothesis is further tested by running a Case 2 with effectively an infinite number of packers in
15 the pipe. This condition is achieved by setting the horizontal permeability of the pipe to 10^{-18} m²
16 (effectively zero). Results are shown in Figure 8. Comparing Figures 7 and 8 shows that the more
17 packers used, the less pronounced are any given upward-flowing plumes of CO₂ because each
18 effective point source is weaker. However, the proximity of the pipe to the ground surface still
19 produces early breakthroughs (e.g., at $X = 61$ m), and the effect of injecting into pipe that is
20 embedded within the soil in the model is to create an area where early breakthrough is independent
21 of packer location or number.

22

1 Patchy emissions in the field experiment were persistent throughout the periods of injection. In the
2 model, the patches tend to merge more than in the field experiment. Figure 9 presents results at $t = 5$
3 and 9 days showing more merging but also persistence of some patches for the Base Case. This
4 greater persistence of patches in the field suggests that there are features or processes in the field that
5 are not captured in the model. It is speculated that the model system may have a larger horizontal
6 permeability than the actual site, especially if the high permeability of the soil is due to cracks which
7 would tend to be subvertical. The implication of these results for actual GCS seepage monitoring
8 and modeling is that persistent patchy emission patterns may be the expected form of seepage at
9 GCS sites under similar conditions where unexpected low-level CO₂ migration to the near-surface
10 occurs.

11

12 Finally, there are some observations of moisture evolution in the 3D system that are worthy of note.
13 The initial moisture distribution in the 3D model changes in two ways as CO₂ is injected. First, CO₂
14 injected into the pipe increases CO₂ mass fraction in the aqueous phase and eventually exceeds the
15 solubility limit causing two-phase conditions with CO₂ gas displacing water. Second, once
16 unsaturated conditions develop due to CO₂ injection, variations in capillary suction properties of the
17 pipe and adjacent materials affect moisture retention and gas-entry properties. These differences
18 appear along the length of the pipe as shown in Figure 10 by the different liquid saturations present
19 in the pipe in the left-hand side (SW region) and right-hand side (NE region). On the left-hand side
20 of the system (SW region of pipe), the horizontal well pipe is installed at a greater depth and it is in
21 the cobble below the water table prior to CO₂ injection. On the right-hand side of the system (NE
22 end of pipe), the horizontal well is installed shallower and it is in the soil very near the water table.
23 The soil has a stronger capillary suction than the cobble, which all other things being equal, would

1 result in greater pressure needed by the CO₂ gas to displace water from the soil than from the cobble.
2 In this case, the soil also has higher permeability (see Table 2) and the pipe in the NE region is at
3 higher elevation than the SW region. These effects combine to cause more water to be expelled
4 from the pipe as injection occurs than in the SW regions where the pipe is installed in cobble. The
5 result of these differences is a stronger drying of the pipe material as shown in Figure 10. Note that
6 these effects play no role in the gravity-capillary equilibrium in which the pipe is below the water
7 table because both soil and pipe materials are fully saturated and therefore not subject to different
8 strengths of capillary suction. Because the actual pipe consists of slotted steel rather than porous
9 media as modeled here, the contribution of capillarity to this effect is believed to be largely relevant
10 only to the model and does not play a significant role in controlling the amount of water in the pipe
11 in the field system.

12

13 **Conclusions**

14 Numerical experiments using TOUGH2/EOS7CA with a 3D grid of the ZERT release facility
15 suggest that along-pipe CO₂ flow in the open injection zones is blocked at packers and enters the
16 cobble or soil effectively as a point source. From these effective point sources, early breakthroughs
17 and persistent patchy emission patterns emerge as observed in two summers of field experiments.
18 Early breakthrough occurs where the pipe is shallow and is enhanced when the pipe is in contact
19 with the high-vertical-permeability soil. An implication of this work for actual GCS leakage
20 monitoring and modeling is that patchy emissions may be the expected style of emission from
21 potential low-flux leakage that might occur from GCS sites under conditions of similar soil and
22 moisture as at the ZERT site. The effects of different capillary suction properties, elevation, and

1 permeability of materials are manifest as differences in liquid saturation in the pipe when injected
2 CO₂ creates unsaturated conditions in the model system.

3

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|----|---------------|--|----------------------------------|
| 1 | Nomenclature | | |
| 2 | d | molecular diffusivity | $\text{m}^2 \text{s}^{-1}$ |
| 3 | \mathbf{g} | acceleration of gravity vector | m s^{-2} |
| 4 | \mathbf{F} | Darcy flux vector | $\text{kg m}^2 \text{s}^{-1}$ |
| 5 | k | permeability | m^2 |
| 6 | k_r | relative permeability | |
| 7 | M | mass accumulation term | kg m^{-3} |
| 8 | \mathbf{n} | outward unit normal vector | |
| 9 | NK | number of components | |
| 10 | NPH | number of phases | |
| 11 | P | total pressure | Pa |
| 12 | P_c | capillary pressure | Pa |
| 13 | q | mass flux | $\text{kg m}^{-2} \text{s}^{-1}$ |
| 14 | q_v | volumetric source term | $\text{kg m}^{-3} \text{s}^{-1}$ |
| 15 | S | saturation. | |
| 16 | t | time | s |
| 17 | T | temperature | $^{\circ}\text{C}$ |
| 18 | V | volume | m^3 |
| 19 | X | mass fraction with phase subscript and component superscript | |
| 20 | X | X -coordinate | |
| 21 | Y | Y -coordinate | |
| 22 | Z | Z -coordinate (positive upward) | |
| 23 | | | |
| 24 | Greek symbols | | |
| 25 | α | l/P_0 in van Genuchten's capillary pressure function | Pa^{-1} |
| 26 | β | phase index (subscript) | |
| 27 | Γ | surface area | m^2 |

| | | | |
|----|-----------------------------|--|----------------------------------|
| 1 | θ | exponent for temperature dependence of diffusivity | |
| 2 | κ | mass components (superscript) | |
| 3 | λ | van Genuchten's m | - |
| 4 | μ | dynamic viscosity | $\text{kg m}^{-1} \text{s}^{-1}$ |
| 5 | ρ | density | kg m^{-3} |
| 6 | τ | tortuosity | |
| 7 | ϕ | porosity | |
| 8 | | | |
| 9 | | | |
| 10 | Subscripts and superscripts | | |
| 11 | g | gas | |
| 12 | l | liquid | |
| 13 | s | satiated (saturation) | |
| 14 | max | maximum | |
| 15 | r | residual | |
| 16 | w | water | |
| 17 | o | reference value | |
| 18 | | | |
| 19 | | | |
| 20 | | | |
| 21 | | | |

1 **Tables**

2 Table 1. Governing equations solved in TOUGH2/EOS7CA for isothermal problems.

| Description | Equation |
|---|--|
| Conservation of mass | $\frac{d}{dt} \int_{V_n} M^\kappa dV = \int_{\Gamma_n} \mathbf{F}^\kappa \cdot \mathbf{n} d\Gamma + \int_{V_n} q_v^\kappa dV$ |
| Mass accumulation | $M^\kappa = \phi \sum_{\beta=1}^{NPH} S_\beta \rho_\beta X_\beta^\kappa$ |
| Phase flux | $\mathbf{F}_\beta = -k \frac{k_{r\beta} \rho_\beta}{\mu_\beta} (\nabla P_\beta - \rho_\beta \mathbf{g})$ |
| Component flux | $\mathbf{F}^\kappa = \sum_{\beta=1}^{NPH} (X_\beta^\kappa \mathbf{F}_\beta - \phi \tau_o \tau_\beta \rho_\beta d_\beta^k \nabla X_\beta^\kappa)$ |
| Pressure and capillary pressure | $P_\beta = P + P_{c\beta}$ |
| Henry's law | $P_g^\kappa = K_H X_{aq}^\kappa$ |
| Relative permeability (liquid after van Genuchten, 1980; gas after Corey, 1954) | $\text{if } S_l < S_{ls}, \quad k_{rl} = \sqrt{S^*} \left\{ 1 - \left(1 - [S^*]^{1/\lambda} \right)^\lambda \right\}^2$ $\text{if } S_l \geq S_{ls} \quad k_{rl} = 1$ $\text{if } S_{gr} = 0 \quad k_{rg} = 1 - k_{rl}$ $\text{if } S_{gr} > 0 \quad k_{rg} = (1 - \hat{S})^2 (1 - \hat{S}^2)$ <p>where $S^* = (S_l - S_{lr}) / (S_{ls} - S_{lr})$,</p> $\hat{S} = (S_l - S_{lr}) / (1 - S_{lr} - S_{gr})$ |
| Capillary pressure (after van Genuchten, 1980) | $P_c = P_0 \left([S^*]^{1/\lambda} - 1 \right)^{1-\lambda}$ <p>subject to $-P_{\max} \leq P_c \leq 0$</p> |
| Molecular diffusion | $f_\beta^\kappa = -\phi \tau_o \tau_\beta \rho_\beta d_\beta^k \nabla X_\beta^\kappa$ <p>where $\tau_o \tau_\beta = \tau_o k_{r\beta}(S_\beta)$</p> <p>and</p> $d_\beta^k(P, T) = d_\beta^k(P_0, T_0) \frac{P_0}{P} \left[\frac{T + 273.15}{273.15} \right]^\theta$ |

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1 Table 2. Properties of the materials in the model.

| | Soil | Cobble | Pipe |
|--|---|---|---|
| Temperature (T) | 15 °C | 15 °C | 15 °C |
| Porosity (ϕ) | 0.35 | 0.35 | 0.99 |
| Permeability (k) | $5 \times 10^{-11} \text{ m}^2$ | $3.2 \times 10^{-12} \text{ m}^2$ | $1 \times 10^{-10} \text{ m}^2$ |
| Capillary Pressure (P_c) | van Genuchten ^{1,2} $\lambda = 0.291, S_{lr} = 0.15, \alpha = 2.04 \times 10^{-4} \text{ Pa}^{-1}, P_{max} = 5 \times 10^5 \text{ Pa}, S_{ls} = 1.$ | van Genuchten ^{1,2} $\lambda = 0.627, S_{lr} = 0.10, \alpha = 1.48 \times 10^{-3} \text{ Pa}^{-1}, P_{max} = 5 \times 10^5 \text{ Pa}, S_{ls} = 1.$ | No capillary pressure |
| Relative permeability (k_r) | Liquid: van Genuchten ^{1,2} ; Gas: Corey ³ $S_{lr} = 0.17, S_{gr} = 0.05$ | Liquid: van Genuchten ^{1,2} ; Gas: Corey ³ $S_{lr} = 0.12, S_{gr} = 0.05$ | Linear with saturation ¹ $S_{lr} = 0.1, S_{gr} = 0.05$ |
| Molec. diffusivity coefficients (d_{β}^K) | Liquid: $10^{-10} \text{ m}^2 \text{ s}^{-1}$ Gas: $10^{-5} \text{ m}^2 \text{ s}^{-1}$ $\theta = 1.0, P_0 = 10^5 \text{ Pa}$ | Liquid: $10^{-10} \text{ m}^2 \text{ s}^{-1}$ Gas: $10^{-5} \text{ m}^2 \text{ s}^{-1}$ $\theta = 1.0, P_0 = 10^5 \text{ Pa}$ | Liquid: $10^{-10} \text{ m}^2 \text{ s}^{-1}$ Gas: $10^{-5} \text{ m}^2 \text{ s}^{-1}$ $\theta = 1.0, P_0 = 10^5 \text{ Pa}$ |
| Tortuosity (τ_0) | 1.0 | 1.0 | 1.0 |
| Saturation-dependent tortuosity (τ_{β}) | Equal to relative permeability | Equal to relative permeability | Equal to relative permeability |

2 ¹Pruess et al. (1999)

3 ² λ is m in van Genuchten, 1980.

4 ³Corey (1954)

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7 Table 3. Measured and modeled ground-surface fluxes above the pipe at $t = 9$ days.

| Zone | Measured surface flux $\text{kg m}^{-2} \text{ s}^{-1}$ | | Modeled surface flux $\text{kg m}^{-2} \text{ s}^{-1}$ | |
|------|--|----------|---|----------|
| | Mean | Maximum | Mean | Maximum |
| 1 | 9.88E-07 | 3.22E-06 | 5.52E-06 | 1.17E-05 |
| 2 | 2.32E-06 | 7.05E-06 | 4.64E-06 | 2.65E-05 |
| 3 | 2.56E-06 | 1.71E-05 | 2.87E-06 | 6.63E-06 |
| 4 | 2.36E-06 | 5.75E-06 | 1.14E-06 | 1.85E-06 |
| 5 | 1.18E-06 | 1.21E-05 | 8.56E-07 | 2.01E-06 |
| 6 | 1.45E-06 | 6.53E-06 | 1.91E-06 | 2.53E-06 |

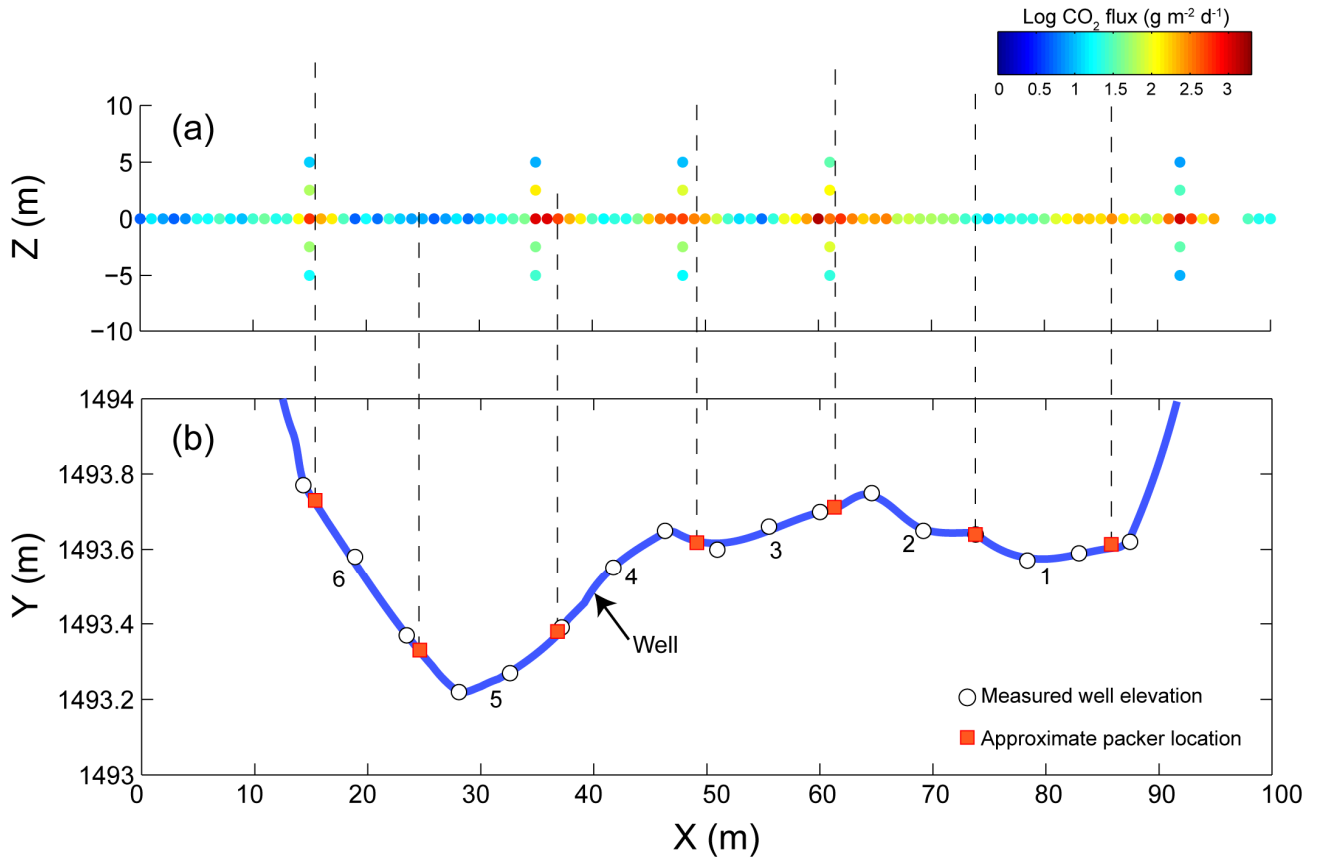
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2 **Figures**

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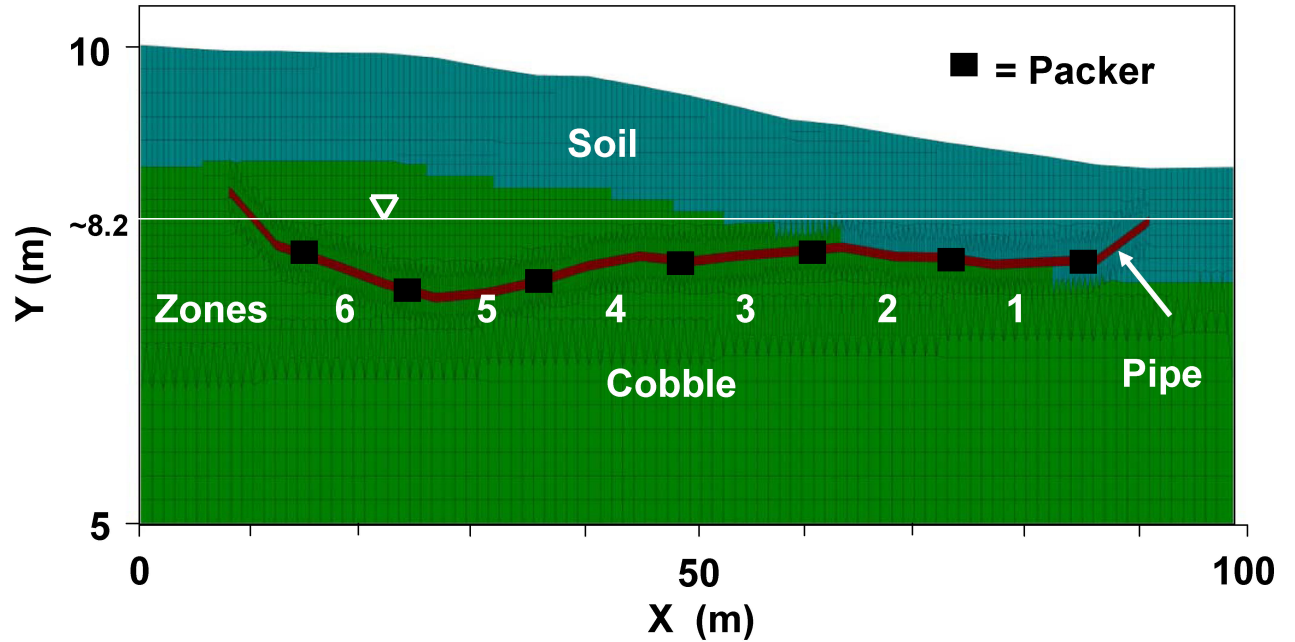


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5 Figure 1. (a) Log soil CO₂ fluxes measured along surface trace of well on day 9 of the first CO₂
6 release carried out in 2007 (see Lewicki et al., 2007). (b) Elevation of nominally horizontal well
7 (note vertical exaggeration) and packer locations (figure after Amonette, pers. commun.). Focused
8 areas of high CO₂ flux (patches) are generally correlated with packer locations.

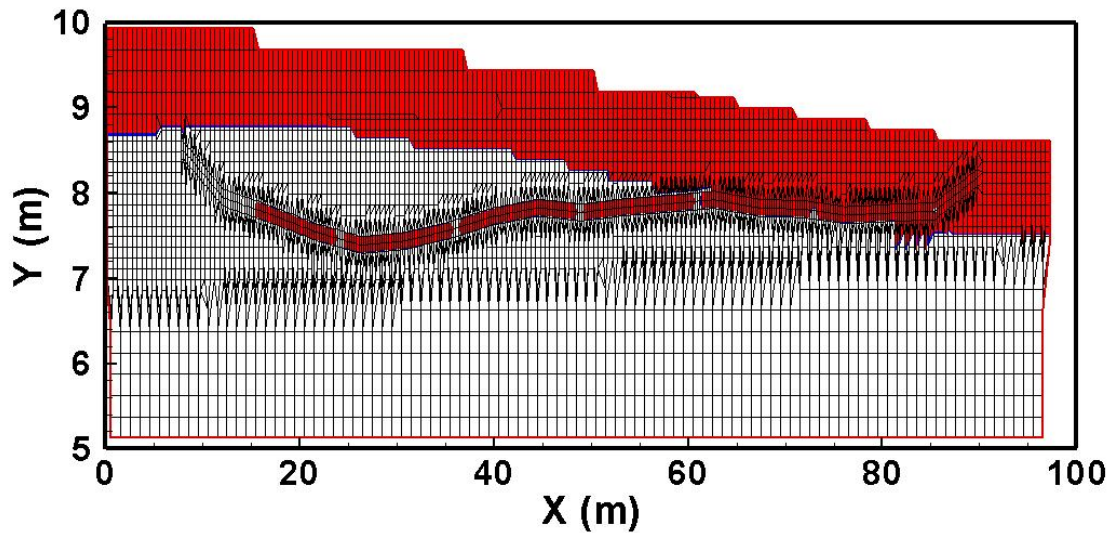
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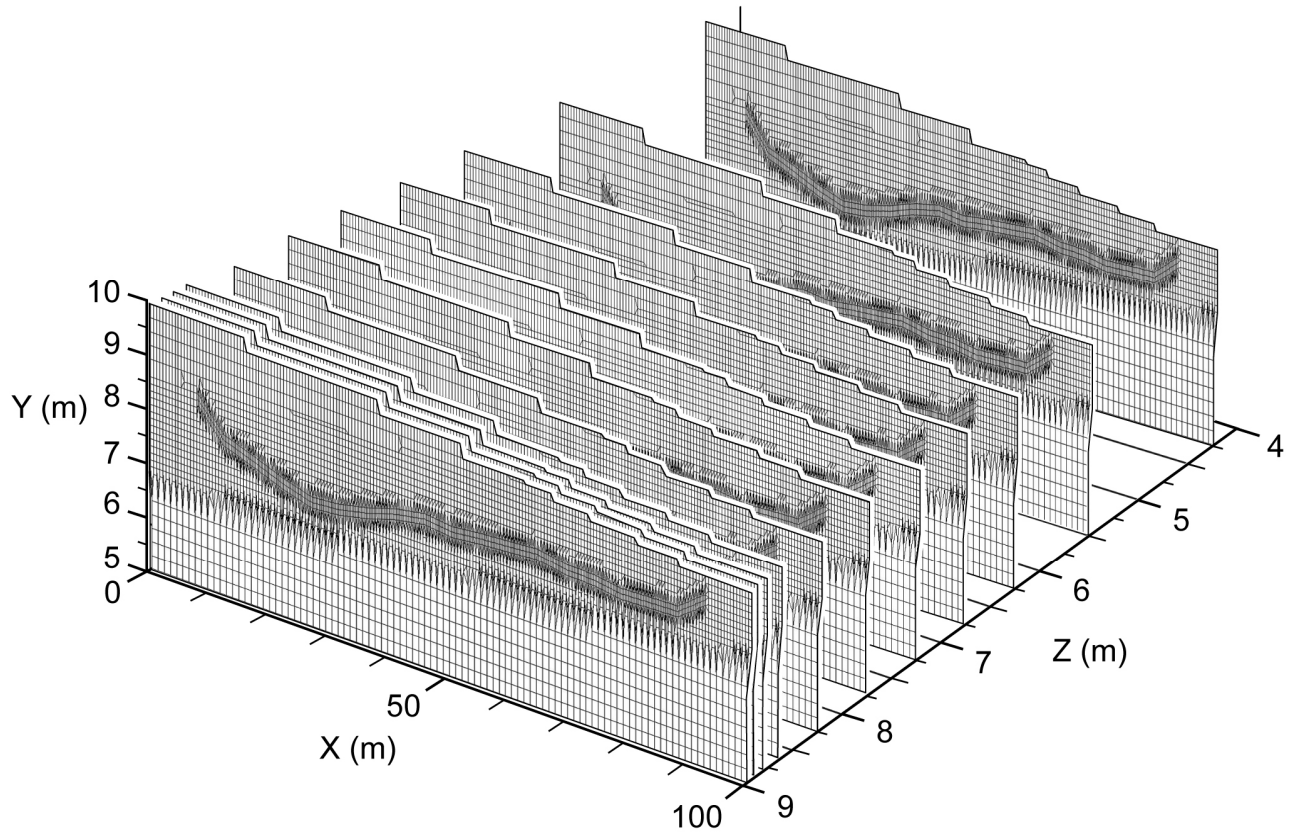
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Figure 2. Two-dimensional slice of the three-dimensional model showing soil and cobble layers, water table, packer locations, and injection zone numbering.



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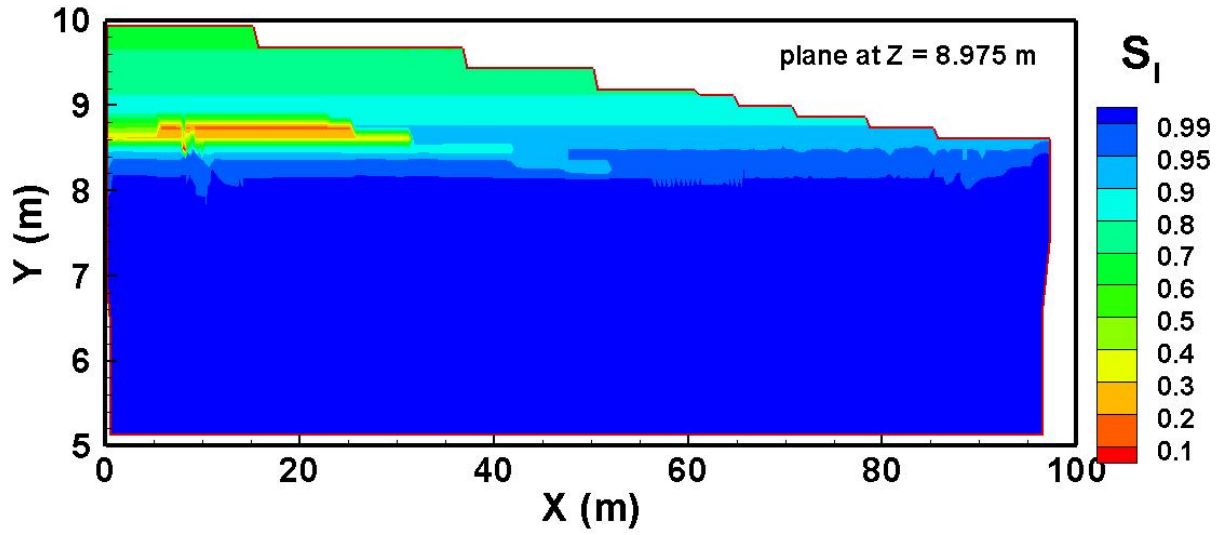
Figure 3. Two-dimensional slice of the three-dimensional model showing the connections between gridblocks. High-permeability regions are shaded (red) showing the open sections of the pipe and the soil layer.



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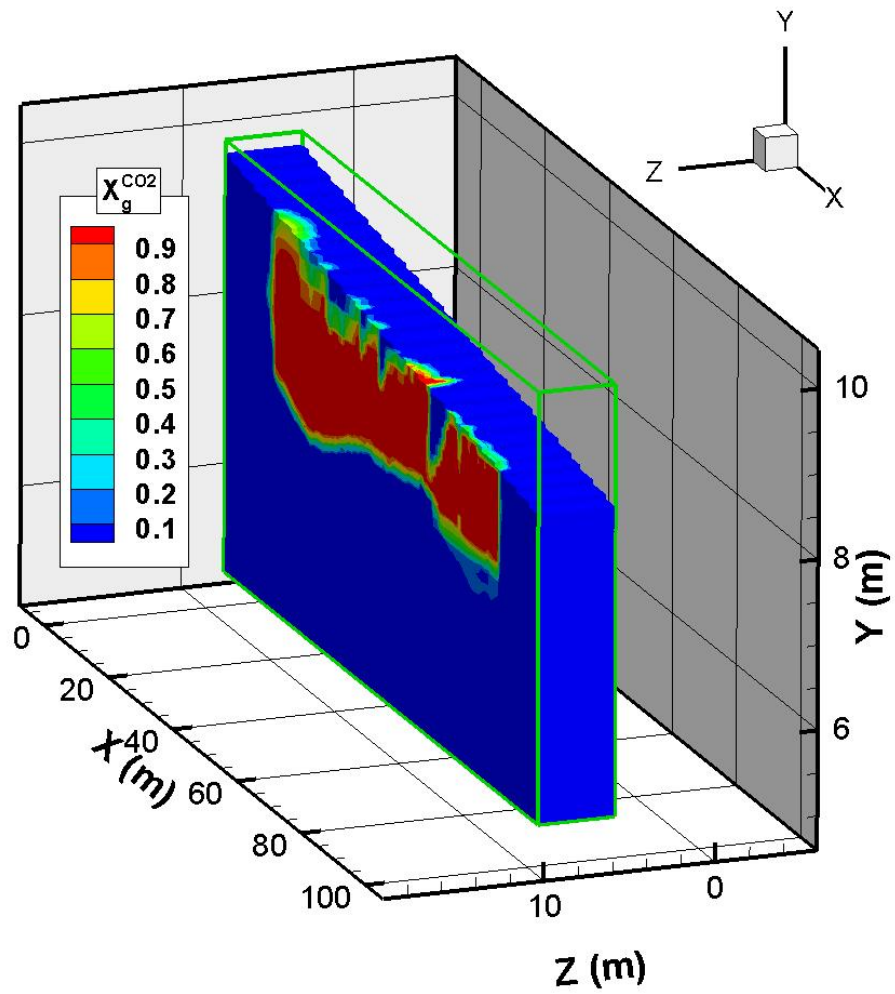
Figure 4. Three-dimensional grid showing the plane at $Z = 8.975$ m (mirror plane) that contains the pipe and the ten planes to the right-hand side (northwest). Horizontal Z -direction connections between planes are not shown. Note that the pipe discretization is in all planes. However, the only pipe material is in the plane at $Z = 8.975$ m, while all other planes consist of either soil or cobble depending on location.

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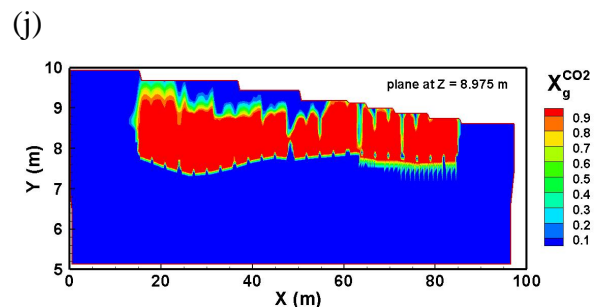
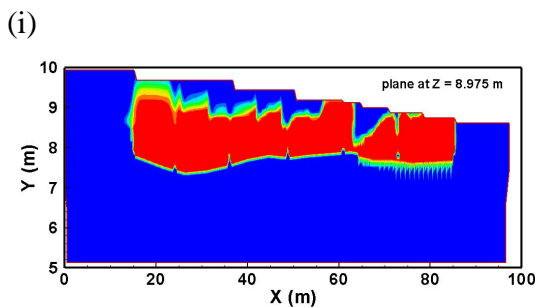
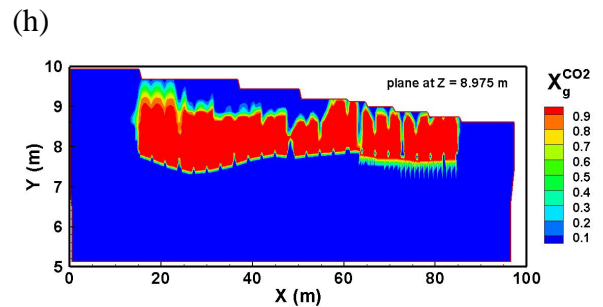
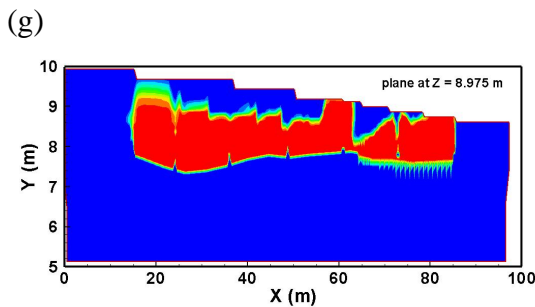
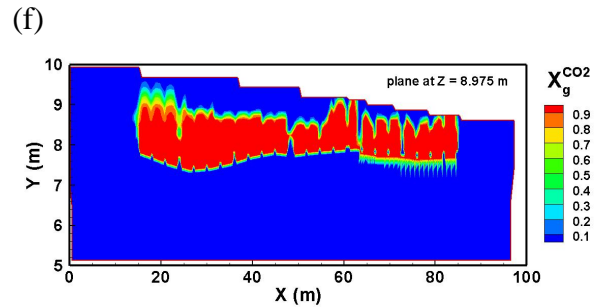
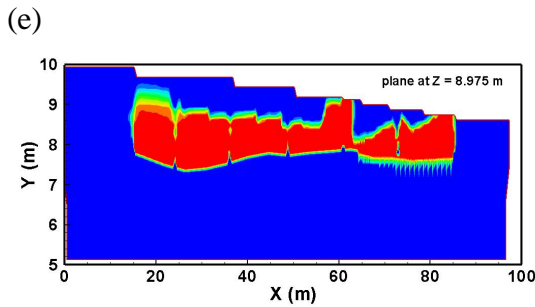
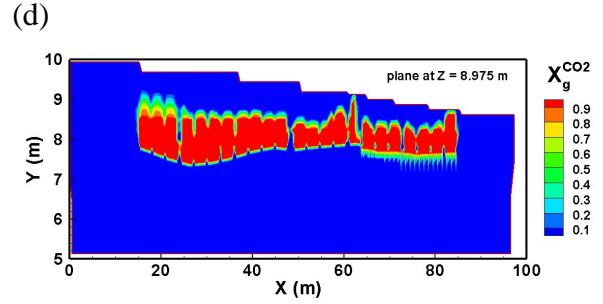
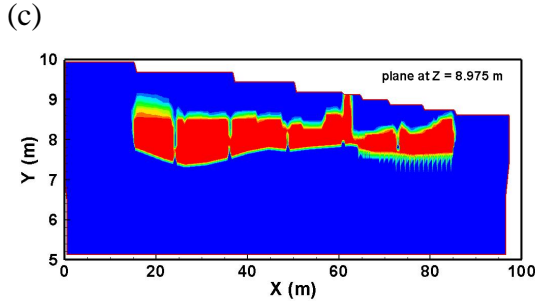
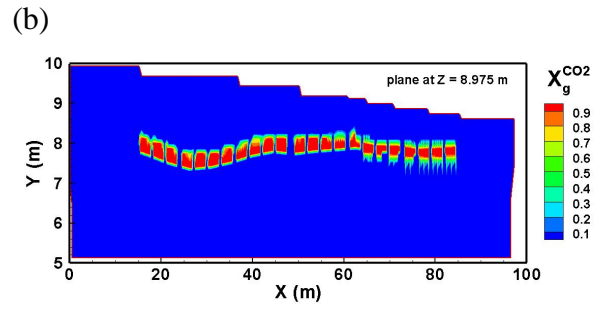
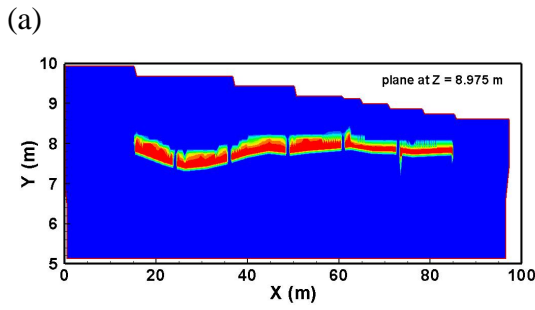
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Figure 5. Initial condition of water saturation. Conditions are assumed uniform in the third dimension (Z -direction, into the page).

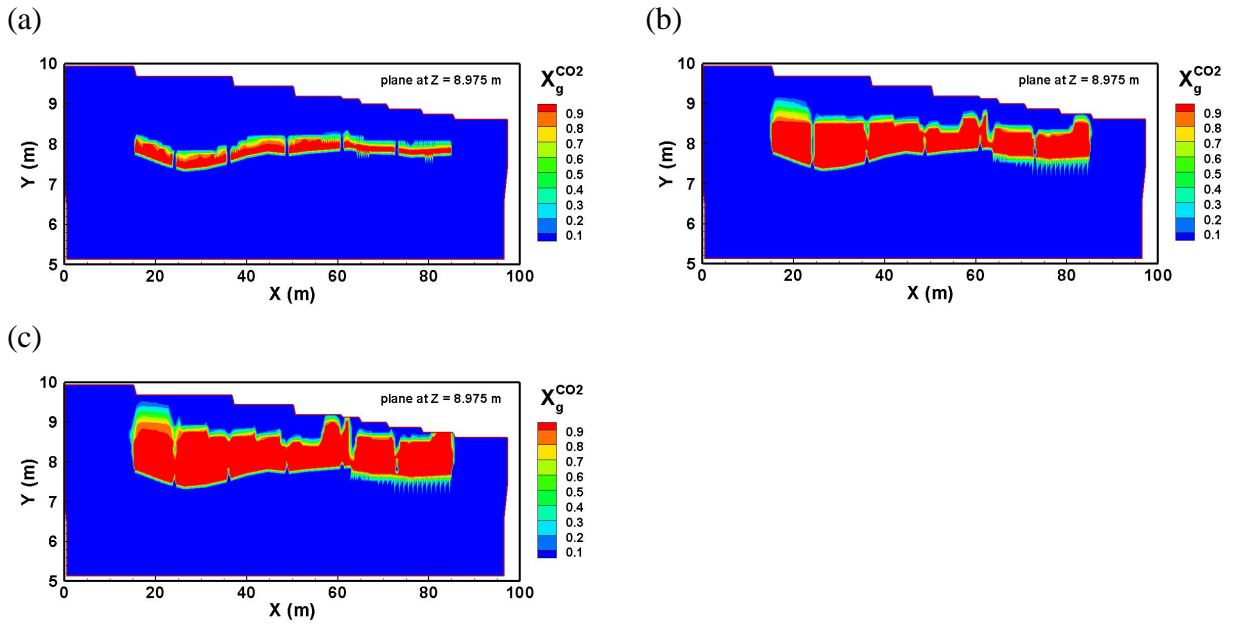


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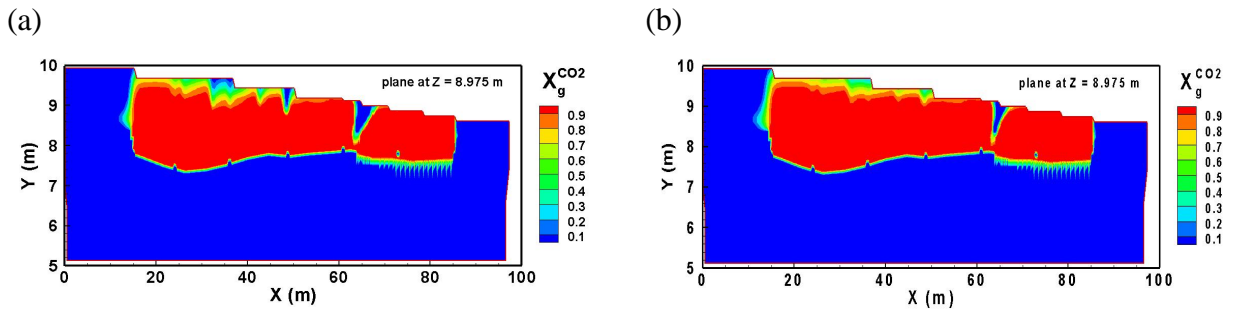
Figure 6. Three-dimensional result of the Base Case showing mass fraction of CO₂ in the gas phase ($X_g^{CO_2}$) in a patchy emission pattern at $t = 3$ days.



1 Figure 7. Mass fraction of CO₂ in the gas phase at $t = 0.06, 0.5, 1, 1.5,$ and 2 days for the case of
 2 injection into six zones (right-hand side(a, c, e, g, i) and 23 zones (left-hand side (b, d, f, h, j)).
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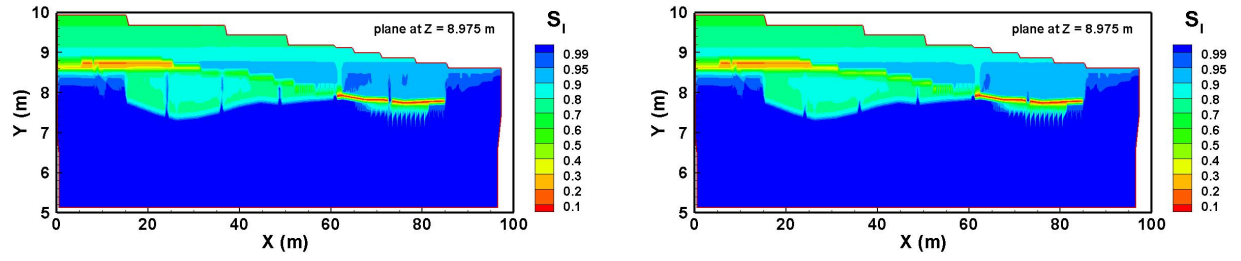


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 6 Figure 8. Mass fraction of CO₂ in the gas phase at $t = 0.06, 0.5,$ and 1 days for the case of injection
 7 into an infinite number of zones (spatially continuous injection).
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 11 Figure 9. Mass fraction of CO₂ in the gas phase at $t = 5,$ and 9 days for the Base Case showing the
 12 merging of some early patches but also patchy emission persistence.
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Figure 10. Liquid saturation in the plane $Z = 8.975$ m at $t = 0.5$ and 2 days.