

Modeling Tracer Gas Adsorption and Transport in the Vadose Zone with PFLOTRAN

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Introduction

Fluctuations in barometric pressure induce oscillatory flow of gases in the vadose zone. In a dual porosity system, this oscillatory flow can transport contaminant or tracer gas buried beneath the surface to the surface in a process known as barometric pumping. The efficiency of barometric pumping is dependent on the relative permeabilities and porosities of the fracture and matrix, as well as the frequency of the barometric pressure oscillation. However, gas adsorption in the matrix has often been neglected as tracer gases are generally assumed to be conservative.

Tracer Gas Transport Model

In the vadose zone, many volatile species can be present in more than one phase. Vapors are necessarily present in two phases while even so-called permanent gases can be solvated by liquid species. In addition, volatile species can appreciably adsorb onto the surfaces of the solid phase. Here, the concentration Ψ of a tracer species of the gas g , liquid l , and solid s phases can be expressed over a control volume. Porosity φ describes the fractional volume occupied by the fluid. In the first iteration of this model, the exposed solid surface area is modeled as being proportional to the degree of gas saturation S_g , which is complementary to the degree of liquid saturation S_l in a fluid system. The rate of phase transitions, for example $k_{\alpha \rightarrow \beta}$ are individually accounted for, in addition to advective and diffusive fluxes, represented by Ω_α .

$$\begin{aligned} \frac{\partial}{\partial t} \int \varphi S_l \Psi_l dV &= \int (-k_{l \rightarrow g} + k_{g \rightarrow l} - k_{l \rightarrow s} + k_{s \rightarrow l}) dV - \oint \Omega_l \cdot dA \\ \frac{\partial}{\partial t} \int \varphi S_g \Psi_g dV &= \int (+k_{l \rightarrow g} - k_{g \rightarrow l} - k_{g \rightarrow s} + k_{s \rightarrow g}) dV - \oint \Omega_g \cdot dA \\ \frac{\partial}{\partial t} \int (1 - \varphi) S_g \Psi_s dV &= \int (+k_{l \rightarrow g} - k_{g \rightarrow l} + k_{l \rightarrow s} - k_{s \rightarrow l}) dV - \oint \Omega_s \cdot dA \end{aligned}$$

In many simulations, it is impractical to model each phase directly as the rate of phase transitions within a control volume is far more rapid than the exchange of material between different control volumes. But, because the control volume exactly overlap on these mass balances, the three phases can be added exactly. Consequently, in this form, the total mass balance of a species in a control volume is independent of the phase transition kinetics.

$$\frac{\partial}{\partial t} \int (\varphi (S_l \Psi_l + S_g \Psi_g) + (1 - \varphi) S_g \Psi_s) dV + \oint (\Omega_l + \Omega_g + \Omega_s) \cdot dA = 0$$

Local Equilibrium Assumption

Whereas there is no fundamental relationship between the quantities in the various phases, chemical equilibrium is reached when the concentrations of all species in the phases are in a fixed proportion. Whereas gas solubility in liquids and gas adsorption on solids is frequently reported in terms of partial pressure of the gas phase, for gases modeled using the ideal gas equation of state, this is equivalent to the partition ratios K_D . This is often expressed in terms of Henry's Law solubility as it pertains to gas-liquid systems.

$$\frac{\Psi_g}{\Psi_l} = K_D$$

Per the Gibbs phase rule, if the phases are in equilibrium at a given temperature and pressure, the concentration of a given component in any one of the phases can fully determine the concentrations in the other phases. Consequently, for a tracer gas, there is a mean concentration $\bar{\Psi}$ in a control volume that is fully determined by the partition ratios (e.g. solubilities or adsorption isotherms), porosity, and the degree of saturation.

$$\bar{\Psi} = \frac{\int (\varphi (S_l \Psi_l + S_g \Psi_g) + (1 - \varphi) S_g \Psi_s) dV}{\int dV}$$

Figure 1 conceptually illustrates how the mean concentration determined by phase equilibria related to the finite volume mass transport model.

Retention Factor Approach

While an ideal gas is assumed to be evenly distributed volumetrically, because the solid phase alters the chemical potential near the interface, real gases accumulate in the vicinity of the solid interface. Where measurements of this are available for geologic materials, they are typically given in terms of gravimetric adsorption isotherms. That is, the ratio of the adsorbed quantity versus adsorbent mass. At low surface coverages, gas adsorption follows Henry's Law, but at higher surface coverages, where there is competition for adsorption sites or heterogeneity in the adsorption sites, gas adsorption may be nonlinear and follow Langmuir or Freundlich isotherms.

However, for a geologic matrix, there are frequently not one, but many minerals, each with a separate adsorption isotherm. While integration of the density and adsorption isotherm for each constituent mineral in a heterogeneous rock is possible, materials are rarely characterized in such detail. It is more efficient to model the mass averaged adsorption properties within a representative elementary volume, \bar{K}_D . In addition, because it is the ratio of quantities, and not concentration, that is important to a finite volume model, it is more computationally convenient to combine this with porosity, yielding a retention factor r analogous to that in gas chromatography.

$$r = \frac{\text{adsorbed quantity}}{\text{gas quantity}} = \frac{\int (1 - \varphi) S_g K_D \Psi_g dV}{\int \varphi S_g \Psi_g dV} = \bar{K}_D \frac{1 - \varphi}{\varphi}$$

In the limit of a gas saturated system, there is negligible material or transport in the liquid phase. Furthermore, simulations are generally designated to be in reference frame of the solid, which eliminates advection in the solid phase. Using the advective-diffusive model, $\Omega_g = u \Psi_g - D \nabla \Psi_g$, where u is the prevailing velocity of the gas phase and D is the Fickian diffusivity. Under these conditions, the model simplifies to the following partial differential equation:

$$\frac{\partial}{\partial t} \varphi (1 + r) \Psi_g dV - \nabla \cdot (u \Psi_g - D \nabla \Psi_g) = 0.$$

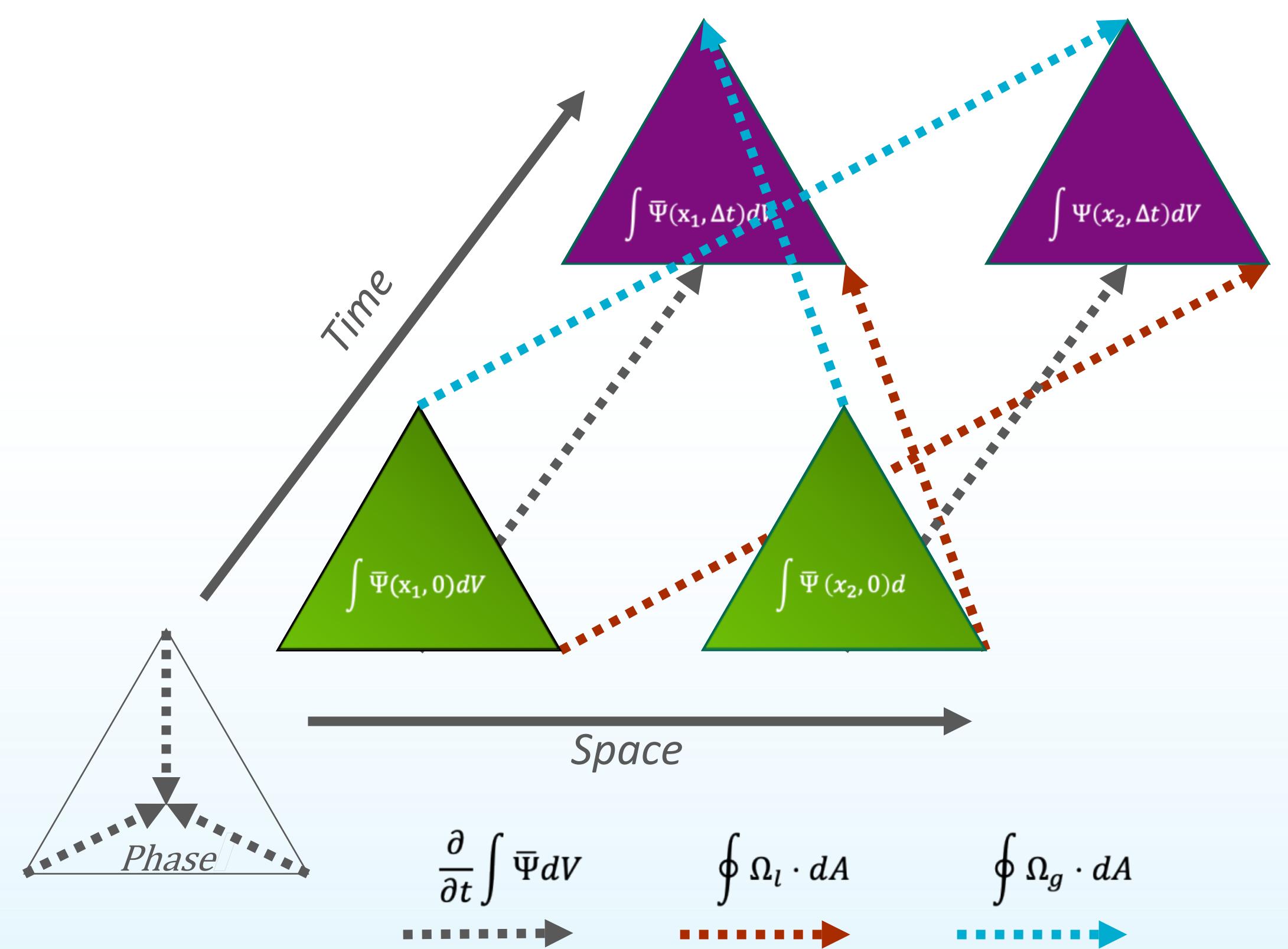


Figure 1. Conceptual figure of relationships in a three-phase local equilibrium approximation transport model using finite volume discretization

Validation and Verification

As the model in the gas-saturated limit has analytical solutions, it is being utilized for validation and verification purposes. Here, a finite quantity of a tracer gas m is inserted in a uniform mesh at an initial position x_0 . Steady state, uniform, and unidirectional flow has been established with fixed pressure boundary conditions in the PFLOTRAN flow model.

Under such conditions, a pulse of tracer gas undergoing advection, diffusion, dispersion, and equilibrium sorption must approach a Gaussian distribution. In the verification case, the distance travelled by the peak must approach $\frac{u}{1+r} t$, where u is the prevailing velocity in the flow field. Figure 2 below depicts the simulated displacement of a tracer peak using the development version of PFLOTRAN versus the expected analytical results. Other metrics being tested ensure proper gas phase partial pressure depression and reduces diffusive peak broadening.

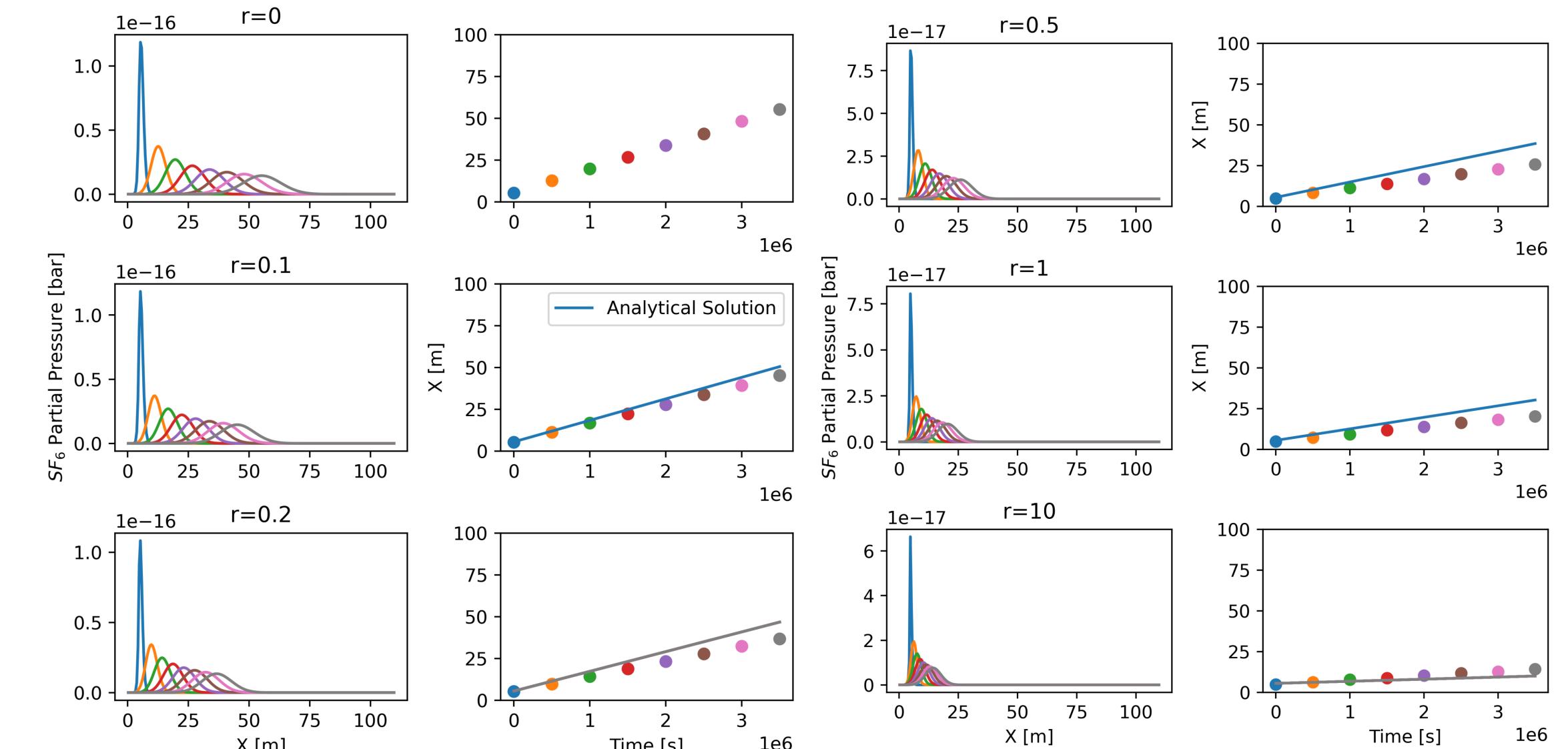


Figure 2. PFLOTRAN and analytical solution of peak displacement versus time under various gas retention factors

Continuing Development

For small values of r , the numerical approach implemented in PFLOTRAN is well aligned with the analytical solution. However, there is some deviation from the analytical solution at larger values of r . Debugging efforts are ongoing to identify the source of the deviation.

To support modeling of fracture-matrix interactions, the same underlying model is also being applied to the multi-continuum framework in PFLOTRAN. As this work is completed, its results will be compared to an analytical solution from Tang et al. (1981) modified to account for gas transport in the fracture and matrix.

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References

Tang, DH, EO Frind, and EA Sudicky (1981). Contaminant transport in fractured porous media: Analytical solution for a single fracture, *Water Resour. Res.*, **17**, 555-564.