

# Modeling Kinetic Adsorption in Porous Media by a Two-State Random Walk Particle Method

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**ABSTRACT.** In this paper, a stochastic approach to address linear kinetic adsorption mechanisms using a two-state particle tracking random walk theory is presented. During reactive solute transport in porous medium particles are assigned two states: either mobile (free) or immobile (adsorbed). By studying the exchange of particles' states, the mechanism of adsorption can be better understood. The kinetics of the particles is modeled with a Markov chain characterized by a transition probability matrix between the two states. The concept of exchange of particle states of the solute particles is more fundamental than that of relaxing the probability with a retardation factor and it is of great significance in modeling various reactive transport mechanisms. A computer code (called ADS\_2D) has been developed to perform numerical adsorption experiments. It has been shown from the experiments that adsorption with slow kinetics can not adequately be modeled using a retardation factor. The fundamental analytical solution deviates from the numerical solution, particularly the spreading of the solute plume. This is due to the fact that the fundamental analytical solution does not take into account the extra dispersion due to the kinetic reaction.

## **Introduction**

Field observations of contaminant plumes show very ragged plumes. This behavior is believed to be due to effects of physical heterogeneity of the medium, reactivity between solid matrix (sediments) and solutes (chemicals), and transient conditions of the flow system. In this research, reactivity in particular sorption desorption mechanisms is focused on. Other aspects such as transient conditions are treated elsewhere (Elfeki, 2003 and Elfeki, *et al.*, 2006) and heterogeneity will be addressed in the future. Some results on non reactive plumes in heterogeneous media are presented in Dagan, *et al.*, 1996, Uffink *et*

*al.*, 2005, Elfeki, 2006 a and b, However, reactive transport in heterogeneous medium under transient conditions is foreseen.

A large scale natural gradient experiment was conducted at Cape Cod, Massachusetts (LeBlanc *et al.*, 1991). Fig. 1 shows vertically averaged concentration of the tracer used (bromide, lithium and molybdate). The experiment was performed to investigate the applicability of stochastic transport theories (Gelhar and Axness, 1983; Dagan, 1984) which estimate macro-dispersivity from the statistical properties of the hydraulic conductivity distribution in aquifers and to study the reactive transport mechanisms in subsurface formations. Various studies have considered reactive transport modelling in porous media (e.g. Kinzelbach and Uffink, 1989, Tompson, 1993 and Gelhar, 1993). The purpose is to simulate the transport mechanisms in porous media and to get a deeper understating of the adsorption phenomenon. Table 1 summarises the difference in features between reactive and non-reactive transport from the visualization of the Cap Cod field experiment.

TABLE 1. Comparison between Reactive and Non-Reactive Plumes from the Cape Cod Site.

| <b>Feature</b>                 | <b>Non-reactive</b>        | <b>Reactive</b>                     |
|--------------------------------|----------------------------|-------------------------------------|
| Degree of dilution             | Less diluted               | More diluted                        |
| Location peak concentration    | In the middle of the plume | In the advancing edge               |
| Plume width                    | Wide                       | Thin                                |
| Retardation                    | Not retarded               | Retarded                            |
| Symmetry in the flow direction | Relatively symmetrical     | Non-symmetrical (negatively skewed) |

In this paper, a stochastic modelling of the kinetic adsorption process is presented. The model is based on a two-state random walk particle method where sorption desorption mechanisms are characterized by a two state Markov chain to model the exchange between the particle states.

### **Physics of Sorption and Desorption Processes**

Adsorption is the phenomenon of accumulation of a substance (component of a fluid phase; adsorbate) on the solid matrix (adsorbent) at a fluid-solid interface. In desorption, the amount of the substance on the solid matrix decreases. The exchange of the

substance between the solution and the soil matrix surface is a chemical process that is due to the positive and negative charges of the substance and the soil particles. Many factors are affecting this process such as the temperature, the solid surface configuration, the pH of the fluid phase, the chemical and physical characteristics of the substance and the solid matrix. If the adsorption process is fast compared to the typical time scale of flow, one can assume that the adsorbed concentration is always in equilibrium with the dissolved concentration, this means that:

$$S = f(C) \quad (1)$$

where  $S$  is the adsorbed concentration (often expressed in mg/kg for dry soil, or ppm),  $C$  is the fluid concentration (in mg/l), and  $f(C)$  is called the adsorption isotherm function (as it describes the distribution between mobile and immobile concentrations at constant temperature). Different adsorbate-adsorbent pairs have different isotherms.

- *Equilibrium isotherms*: which are based on the assumption that the quantities of the component on the solid and in the solution are continuously at equilibrium. Any change in the concentration of one of them produces an instantaneous change in the other.
- *Non-equilibrium isotherms (Kinetic adsorption)*: which assume that equilibrium is not achieved instantaneously, but rather that it is approached a certain rate, which, in general, depends on both  $S$  and  $C$ .

Following are some commonly used (equilibrium) isotherms:

- (a) Langmuir (1915, 1918) suggested the non-linear equilibrium isotherm by

$$S = \frac{k_1 C}{1 + k_2 C} \quad (2)$$

where  $k_1$ ,  $k_2$  are two constants and  $k_1/k_2$  represents the maximum adsorption capacity of the solid matrix.

- (b) Freundlich (1926), suggested the non-linear equilibrium isotherm

$$S = bC^m \quad (3)$$

where  $b$  and  $m$  are constants.

- (c) For  $m=1$  and replacing  $b = K_d$ , Eq. (3) reduces to

$$S = K_d C \quad (4)$$

where  $K_d$  is the distribution coefficient (partitioning coefficient). Adsorbed concentrations are linearly related to concentrations in the fluid phase. This is known as Henry's law (Appelo and Postma, 1993).

- (d) A more general formula of linear equilibrium isotherm is given by Appelo and Postma (1993),

$$S = k_3 C + k_4 \quad (5)$$

where  $k_3$  and  $k_4$  are constants.

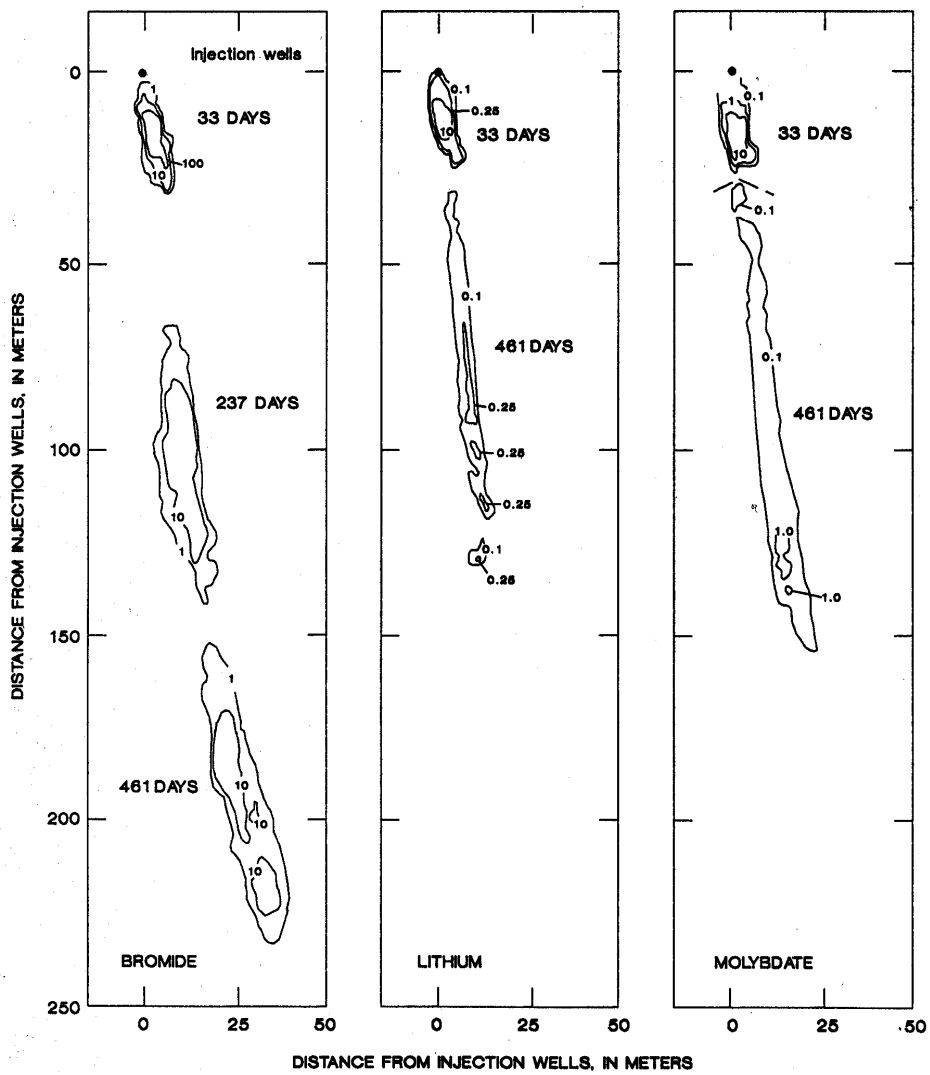
The first-order (linear) kinetic adsorption can be represented by,

$$\left( \frac{\rho_b}{\varepsilon} \right) \frac{\partial S}{\partial t} = k_a C - \left( \frac{\rho_b}{\varepsilon} \right) k_d S \quad (6)$$

where,  $\rho_b$  is the bulk mass density of the porous medium ( $M/L^3$ ),  $\varepsilon$  is the effective porosity,  $k_a$ , and  $k_d$  are adsorption desorption coefficients.

### Modelling Adsorption Kinetics as a Markov Chain

In this research, the interaction between the solid matrix and the chemicals under steady groundwater flow is highlighted. A stochastic approach to address linear adsorption mechanisms using a two-state particle tracking random walk theory is exhibited. During reactive solute transport, particles are assigned two states: either mobile (free) or immobile (adsorbed). By studying the change of particles states, the mechanism of adsorption can be better understood. The kinetics



**EXPLANATION**  
 — 10 — LINE OF EQUAL CONCENTRATION— Concentrations of bromide, lithium, and molybdate (as Mo) in milligrams per liter. Interval varies.

FIG. 1. Areal Distribution of Plume Concentrations of the Three Tracers Used at Cape Cod Site (after LeBlanc *et al.*, 1991).

between particles is modeled with a transition probability matrix in the form:

$$p_{lk} = \begin{matrix} & i & m \\ \begin{matrix} i \\ m \end{matrix} & \begin{bmatrix} 1-a & a \\ b & 1-b \end{bmatrix} \end{matrix}, \quad l = i, m \text{ and } k = i, m \quad (7)$$

where  $p_{lk}$  is the transition probability to change between state  $l$  (mobile  $m$  or immobile  $i$ ) and state  $k$  (mobile  $m$  or immobile  $i$ ).

The values of  $a$  and  $b$  (the off-diagonal elements of the chain) show how strong or weak the kinetics are. The stationary probability of the chain is given by:

$$\begin{bmatrix} w_m \\ w_{im} \end{bmatrix} = \begin{bmatrix} a(a+b)^{-1} \\ b(a+b)^{-1} \end{bmatrix} \quad (8)$$

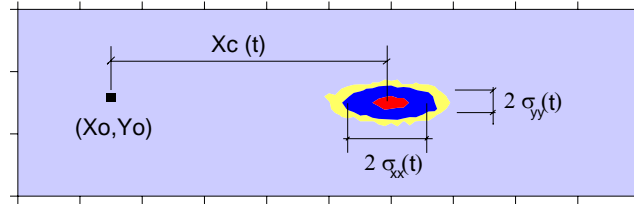
$w_m$  is the proportion of the mobile phase, and  $w_{im}$  is the proportion of the immobile phase.

Various transition probability matrices are investigated with symmetric and asymmetric transitions to describe various adsorption mechanisms (slow and fast reaction rates with different initial conditions of linear kinetic). Both linear and non-linear adsorption models could be addressed. However, the presentation in this research addresses only the linear case. The non-linear case will be presented in another paper. Comparison with analytical fundamental solution based on linear equilibrium adsorption with a retardation coefficient is presented in section 6.

### Numerical Modelling of Kinetic Adsorption

A computer code called “ADS\_2D” has been developed to perform numerical experiments on adsorption. Consider a flow domain that is rectangular in shape as shown in Fig. 2. The domain has a length  $L_x$  and a width  $L_y$ . A mean flow is driven in the horizontal direction ( $x$ -direction) from left to right by imposing a head gradient  $J_x = -\Delta\Phi/L_x$  obtained from a potential difference  $\Delta\Phi = 1.0$  over length  $L_x$  on the field. The lower and

upper boundaries are assumed impervious.



**FIG. 2. Definition Sketch of the Domain of Interest and Spatial Moments of a Pulse Injection in a Two-Dimensional Flow Field.**

The two-dimensional equation that describes solute transport, taking into account advection, hydrodynamic dispersion, and adsorption can be written in the following form (Freeze and Cherry, 1979):

$$\frac{\partial C}{\partial t} = -\left(\frac{\rho_b}{\varepsilon}\right) \frac{\partial S}{\partial t} - V_x \frac{\partial C}{\partial x} + D_{d,xx} \frac{\partial^2 C}{\partial x^2} + D_{d,yy} \frac{\partial^2 C}{\partial y^2} \quad (9)$$

where  $C$  is the aqueous concentration (mobile) at time  $t$ ,  $S$  is the adsorbed mass of chemical constituent on a unit mass of solid part of the porous medium (immobile) at time  $t$ ,  $\rho_b$  is the bulk mass density of the porous medium,  $\varepsilon$  is the effective porosity, and  $V_x$  is the Eulerian velocity field in  $x$  direction defined as follows:

$$V_x = -\frac{K}{\varepsilon} \nabla \Phi \quad (10)$$

where,  $K$  is the homogenous isotropic hydraulic conductivity,  $\nabla \Phi$  is the hydraulic gradient,  $D_{d,xx}$ , and  $D_{d,yy}$  are components of pore scale (micro-level) dispersion coefficients (Bear, 1972):

$$D_{d,xx} = \alpha_l |V|, D_{d,yy} = \alpha_t |V| \quad (11)$$

where  $\alpha_l$  is the longitudinal dispersivity,  $\alpha_t$  is the transversal dispersivity, and  $|V|$  is the magnitude of the resultant velocity which is  $V_x$  in our case.

The random walk particle model (RWPM) has been used to solve Eq. 9. The idea is that, the injected mass is discretized into a large number of particles. Each particle carries a part of the injected mass and a state (mobile or immobile) is convected with a deterministic velocity calculated from the flow system, and a random displacement calculated from the local micro-dispersion. The particle tracking algorithm used here is similar to the one described by Kinzelbach and Uffink (1989) and Uffink (1990). It provides an accurate way of tracking a large number of particles through a fine nodal grid discretizing the velocity field. The random walk equation of a particle in a two dimensional flow field is written explicitly as (Kinzelbach, 1986),

$$\begin{aligned} \text{for mobile particles: } X_p(t + \Delta t) &= X_p(t) + V_x(X_p(t), Y_p(t)) \cdot \Delta t \\ &+ Z \cdot \sqrt{2\alpha_t V_x(X_p(t), Y_p(t)) \cdot \Delta t} \\ Y_p(t + \Delta t) &= Y_p(t) + Z' \cdot \sqrt{2\alpha_t V_x(X_p(t), Y_p(t)) \cdot \Delta t} \end{aligned} \quad (12)$$

$$\begin{aligned} \text{for immobile particles: } X_p(t + \Delta t) &= X_p(t) \\ Y_p(t + \Delta t) &= Y_p(t) \end{aligned} \quad (13)$$

where,  $(X_p(t), Y_p(t))$  are the  $x$  and  $y$  coordinates of a particle at time  $t$ ,  $(X_p(t+\Delta t), Y_p(t+\Delta t))$  are the  $x$  and  $y$  coordinates of a particle at time  $t+\Delta t$ ,  $\Delta t$  is the time step of calculations,  $Z, Z'$  are two independent random numbers drawn from normal distribution with zero mean and unit variance.

The particle spatial moments are computed by averaging the mobile particle locations each time step and the spreading around the centre is also computed in both longitudinal and lateral direction to analyze the particles' cloud and the corresponding concentration field.

### Analysis of Simulation Results

The modelling parameters of the numerical experiments are displayed in Table 2. The adsorption probabilities are given in Table 3. Case A is a reference case with no adsorption. The rest are cases with



different degree of adsorption reactions described in the table by the values of  $a$  and  $b$ , the off-diagonal elements of the transition matrix.

TABLE 2. Parameters Used in the Modelling

| Parameter                          | Numerical Value |
|------------------------------------|-----------------|
| Domain dimensions                  | 100m × 30m      |
| Domain discretization              | 1.0m × 1.0m     |
| Time step                          | 3 day           |
| Upstream fixed head boundary       | 1.0 m           |
| Downstream head boundary           | 0.0 m           |
| Constant aquifer thickness         | 1 m             |
| Homogeneous hydraulic conductivity | 10 m/day        |
| Longitudinal dispersivity          | 0.1 m           |
| Lateral dispersivity               | 0.01 m          |
| Injected mass                      | 100 grams       |
| Number of particles                | 5000 particles  |
| Porosity                           | 0.3             |

TABLE 3. Adsorption Probabilities of the Different Cases

|                                     |                     |
|-------------------------------------|---------------------|
| Case (A) No-adsorption              | $a= 1.0$ , $b=0.0$  |
| Case (B) Highly adsorbed medium     | $a= 0.1$ , $b=0.9$  |
| Case (C) Moderate kinetic reaction  | $a= 0.5$ , $b=0.5$  |
| Case (D) Very slow kinetic reaction | $a= 0.1$ , $b=0.1$  |
| Case (E) Fast kinetic reaction      | $a= 0.9$ , $b= 0.9$ |
| Case (F) Poorly adsorbed medium     | $a= 0.9$ , $b=0.1$  |

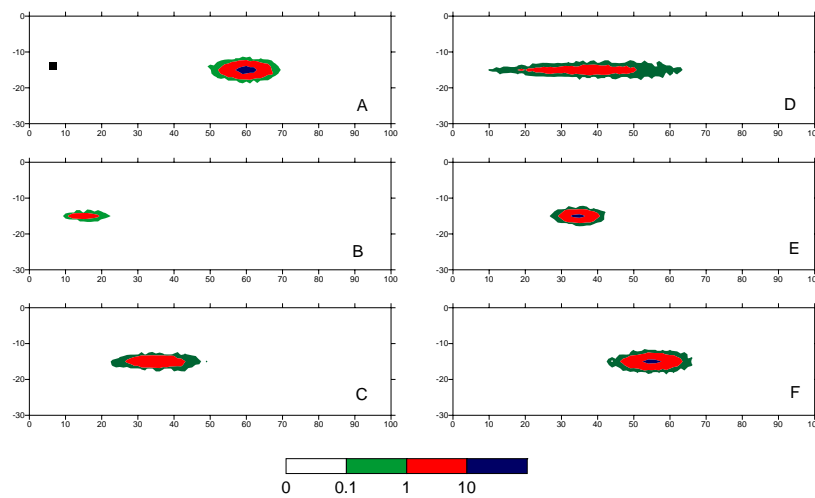


FIG. 3. Snapshot form the Numerical Modelling of Plume Concentration According to the Cases Mentioned in Table 2 after 147 days Since Release (Concentration Scale in mg/lit and Domain Dimensions are in Meters).

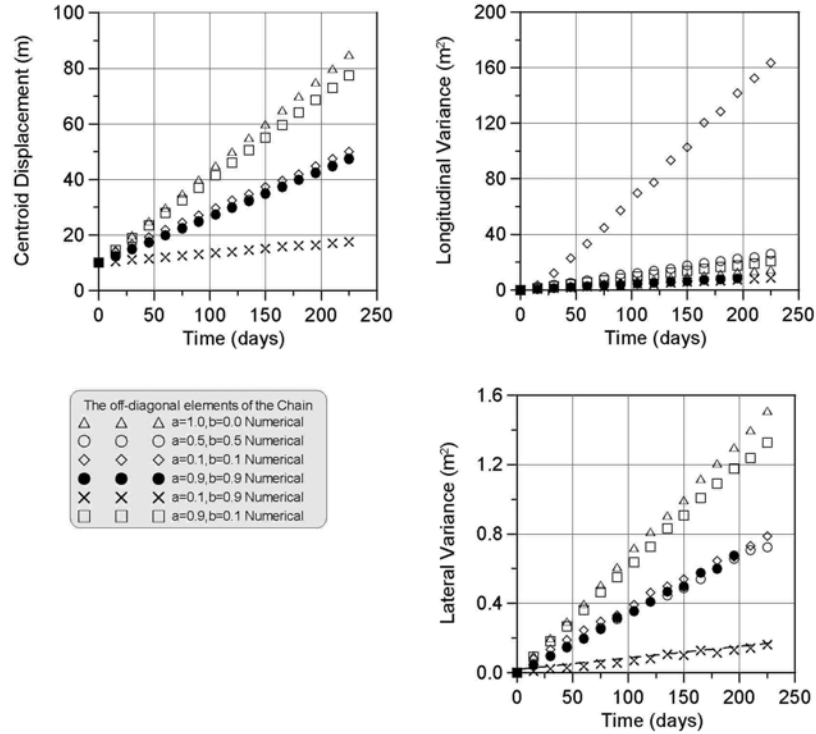


FIG. 4. Plume Spatial Moments for Cases Mentioned in Table 2. Top Left Corner: First Moment (Centroid displacement). Top Right Corner: Longitudinal second moment and Bottom Right Corner: Lateral Second Moment.

Fig. 3 shows plume snapshot at 147 days since release. When  $a$  and  $b$  have low values, it leads to slow kinetics (long plumes see case D) which mimics the Lithium plume in Fig 1 (middle). The reason is that the probability to change form mobile to immobile or vice versa is very slow; it takes long time to change leading to elongated plumes. While when  $a$  and  $b$  have high values one could obtain fast kinetics (see case E), the change is very fast leading to short plumes. The model as presented allows various adsorption mechanisms that could appear in nature. It does not stick to the use of retardation factor to model reactive transport. It provides a good tool

for fundamental understanding of the adsorption kinetics. Comparison with the fundamental analytical solution is given in the next section.

Fig. 4 describes plume spatial moments of the mobile phase. Fig 4 (top left corner) shows the evolution of the first moment of the plume in time. This figure shows the retardation of the plume centroid due to kinetics when compared with the reference case (no adsorption). This retardation is produced by the kinetics that is modeled by the chain.

Fig. 4 (top right corner) gives the evolution of the second moment of the plume in the longitudinal direction in time. This figure shows that the case of slow kinetics has the highest longitudinal spreading compared with the other cases. The reason is that the particles that are in certain state (mobile or immobile) stays for long time in that state leading to elongated plumes. The case mimics the observed Lithium plume in Fig. 1. However, the peak concentration is not peak concentration front as in the Lithium plume due to the non-linearity in the adsorption mechanism which is not considered in our model. The spreading in Case (D) is actually due to two mechanisms, the first is the pore-scale dispersion and the second is due to the particle kinetics. This extra mechanism is the cause of the plume elongation.

Fig. 4 (bottom right corner) shows the evolution of the lateral variance in time. The figure shows that the plumes get thinner by introducing kinetics. It is more pronounced in Cases B, C, and D at low values of the parameter "a" (slow change from immobile to mobile). This behavior is also present in the lithium plume in Fig. 1 (middle).

#### Comparison with Fundamental Analytical Solution

The initial concentration at  $t = 0$  is given by:

$$C(x, y, 0) = \frac{w_m M_o}{\varepsilon H} \delta(x) \delta(y) \quad (14)$$

where  $H$  is the aquifer thickness,  $M_o$  is the injected mass,  $\delta(x)$   $\delta(y)$  are the delta functions in  $x$  and  $y$  directions, and  $w_m$  is the portion of the mobile mass which is related to the transition probability by:

$$w_m = \frac{a}{a+b} \quad (15)$$

and the equation of boundary conditions could be written as:

$$C(\pm\infty, \pm\infty, t) = 0 \quad (16)$$

The solution is given by Bear (1979):

$$C(x, y, t) = \frac{w_m M_o / (\varepsilon H)}{\sqrt{4\pi\alpha_l \left(\frac{V_x}{R}\right) t} \sqrt{4\pi\alpha_l \left(\frac{V_x}{R}\right) t}} \exp \left[ -\frac{\left(x - X_o - \left(\frac{V_x}{R}\right) t\right)^2}{4\alpha_l \left(\frac{V_x}{R}\right) t} + \frac{(y - Y_o)^2}{4\alpha_l \left(\frac{V_x}{R}\right) t} \right] \quad (17)$$

where,  $R$  is the retardation factor which is related to the transition matrix and  $(X_o, Y_o)$  are the source coordinates.

$$R = 1 + \frac{b}{a} \quad (18)$$

The growth of the spatial moments (plume centroid, longitudinal and lateral variances respectively) in time is given by Elfeki (1996),

$$\begin{aligned} X_c(t) &= X_o + \frac{V_x}{R} t \\ \sigma_{xx}^2(t) &= 2 \frac{\alpha_l V_x}{R} t \\ \sigma_{yy}^2(t) &= 2 \frac{\alpha_l V_x}{R} t \end{aligned} \quad (19)$$

where,  $X_c(t)$  is the centroid displacement of the particle cloud,  $\sigma_{xx}^2(t)$  is the longitudinal variance of the cloud, and  $\sigma_{yy}^2(t)$  is the

lateral variance of the cloud.

Fig. 5 shows a comparison between the plume concentration for cases mentioned in Table 3 and the corresponding fundamental solution using the retardation factor given by Eq. 18, where  $a$  and  $b$  are obtained from the transition probability matrix. Case A is the reference case with no adsorption  $R = 1$  the solution is identical to the numerical modeling. However, in cases of reactive transport the fundamental solution deviates from the numerical solution particularly the spreading. This is due to the fact that the fundamental analytical solution does not take into account the dispersion due to the reaction.

### **Conclusions**

The numerical experiments show that adsorption which is characterized by slow kinetics can not adequately be modeled using a retardation factor. The analytical solution deviates from the particle numerical solution due to the fact that the analytical solution does not take into account the extra dispersion of the kinetic reaction. The particle simulations with slow kinetics were capable of mimicking some features (thin elongated plumes) that appeared in the lithium plume in Fig. 1 (middle), however, the peak concentration is located in the front of the lithium plume. This can be due non-linearity. This point will be considered in future research using the concept of Markov chains with limited capacity.

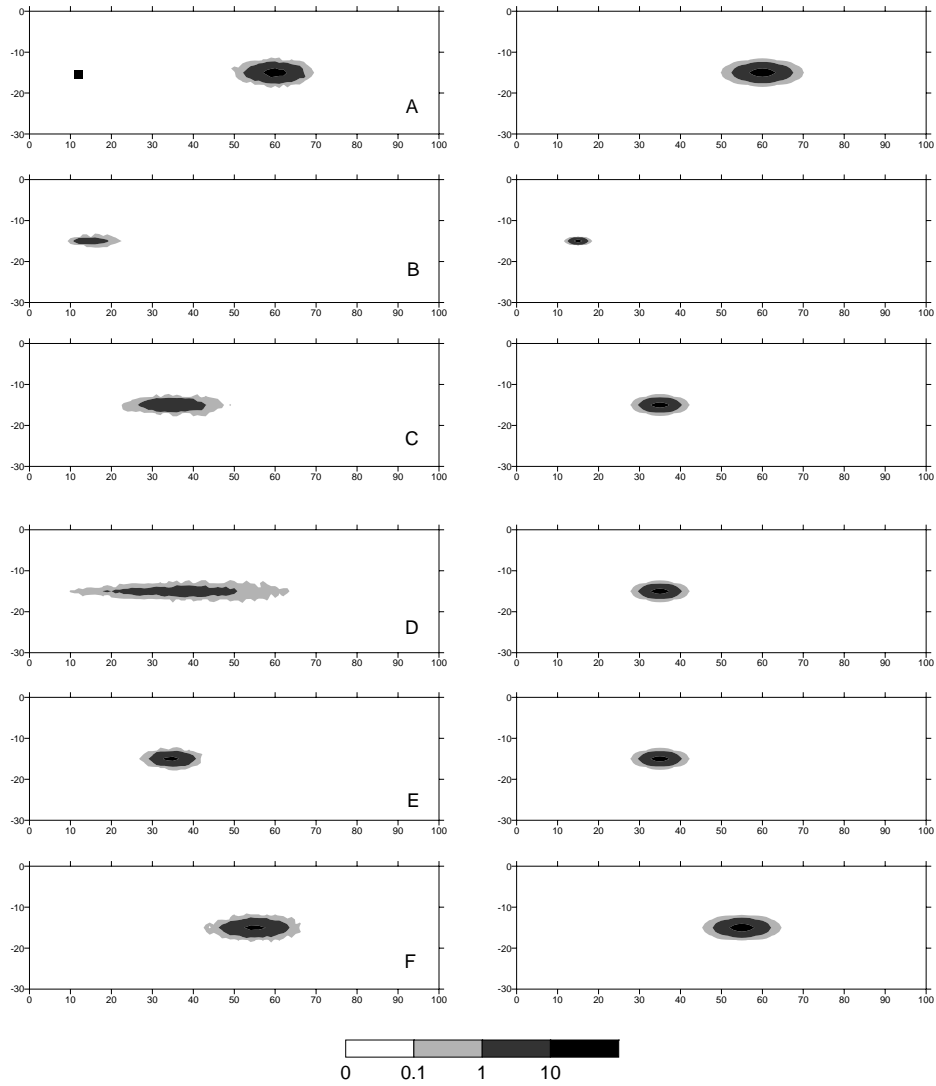
### **Acknowledgement**

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**FIG. 5. Comparison between Plume Concentration for the Cases Mentioned in Table 2 (left column) and the Corresponding Fundamental Solution (Eq. 17) Using a Retardation Factor  $R=1+(b/a)$  (right column).**

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(ADS\_2D)