Supplementary Material

Representative elementary volume estimation and neural network based prediction of change rates of DNAPL saturation and DNAPL-water interfacial area in porous media

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Text S1. The spatial moment

The spatial moment method is utilized to analyze the spatial movement of PCE plume (Fig. 2a) and associated characteristics. The spatial moment is defined as (Zheng et al., 2015; Natarajan and Kumar, 2018):

$$M_{ij}(t) = \int_{x_0}^{x_1} \int_{z_0}^{z_1} \theta(x,z) S_0(x,z,t) \, x^i z^j \, dx dz \tag{S1}$$

where M_{ij} is the spatial moment of PCE plume at time t; $S_o(x,z,t)$ is PCE saturation at place (x, z) when time is t; i and j are the orders of moment along x and z directions, respectively.

The first moments of PCE plume is expressed as:

$$\sigma_x = \frac{M_{10}}{M_{00}} \tag{S2}$$

$$\sigma_Z = \frac{M_{01}}{M_{00}} \tag{S3}$$

where σ_x and σ_z are first moments along x and z directions, respectively; M_{10} is calculated based on Eq. (5) that i=1, j=0.

The distribution range of PCE plume around the mass centroid can be characterized by the second moments:

$$\sigma_{xx} = \frac{M_{20}}{M_{00}} - \sigma_x^2 \tag{S4}$$

$$\sigma_{zz} = \frac{M_{02}}{M_{00}} - \sigma_z^2 \tag{S5}$$

where σ_{xx} and σ_{zz} are second moments along x and z directions, respectively.

Text S2. GTP analysis

Ganglia-to-pool ratio (GTP) characterizing architecture of contaminant plume is derived as the ratio of ganglia mass to pool mass (Christ et al., 2006). The ganglia PCE and pooled PCE usually is dominated by a threshold saturation equal to maximum residual PCE saturation.

Text S3. REV estimation

The relative gradient error (ε_g^i) (Costanza-Robinson et al., 2011; Wu et al., 2020) is used to estimate REVs of S_o rate and A_{OW} rate:

$$\varepsilon_g^i = \left| \frac{\varphi^{i+1} - \varphi^{i-1}}{\varphi^{i+1} + \varphi^{i-1}} \right| \frac{1}{\Delta L} \tag{S6}$$

where φ is the variable such as S_o rate or A_{OW} rate; i is the increment number of measured length; ΔL is the increment length.

Table S1. Experimental conditions

Experiment	I	II	III	IV
Sandbox dimensions (cm)	60×45	60×45	60×45	60×45
Packed translucent silica sand	F20/30	F20/30	F20/30	F20/30 and lenses
Medium condition	Homogeneity	Homogeneity	Homogeneity	Heterogeneity
Sodium chloride concentration (g/L)	0.585	32	0.585	0.585
Tween 80 concentration (mg/L)	0.0	0.0	20.0	0.0
V_{PCE} (ml)	32	32	20	40
Injection rate (ml/min)	0.5	0.5	0.5	0.5

Table S2. The fitted models between average REV of S_o rate, A_{OW} rate and d_I, d_m

Experiment		d_I	d_M
I	SR-REV	$\overline{REV} = -2.83 \times 10^{-10} \cdot d_I^2 + 1.33 \times 10^{-7} \cdot d_I - 7.95 \times 10^{-6}$ (R²=0.45)	$\overline{REV} = 3.54 \times 10^{-10} \cdot d_M^2 + 8.16 \times 10^{-8} \cdot d_M + 1.91 \times 10^{-6}$ (R²=0.44)
	AR-REV	$\overline{REV} = -3.31 \times 10^{-8} \cdot d_I^2 + 3.16 \times 10^{-5} \cdot d_I + 9.60 \times 10^{-4}$ (R²=0.31)	$\overline{REV} = 1.71 \times 10^{-7} \cdot d_M^2 - 3.76 \times 10^{-5} \cdot d_M + 3.52 \times 10^{-3}$ (R²=0.41)
II	SR-REV	$\overline{REV} = 1.11 \times 10^{-10} \cdot d_I^2 - 1.54 \times 10^{-8} \cdot d_I + 5.47 \times 10^{-6}$ (R²=0.38)	$\overline{REV} = 1.87 \times 10^{-10} \cdot d_M^2 - 5.03 \times 10^{-8} \cdot d_M + 7.51 \times 10^{-6}$ (R²=0.51)
	AR-REV	$\overline{REV} = 8.24 \times 10^{-9} \cdot d_I^2 + 4.72 \times 10^{-6} \cdot d_I + 2.58 \times 10^{-3}$ (R²=0.24)	$\overline{REV} = 5.33 \times 10^{-8} \cdot d_M^2 - 1.54 \times 10^{-5} \cdot d_M + 4.02 \times 10^{-3}$ (R²=0.39)
III	SR-REV	$\overline{REV} = 1.77 \times 10^{-10} \cdot d_I^2 - 6.68 \times 10^{-8} \cdot d_I + 1.53 \times 10^{-5}$ (R²=0.40)	$\overline{REV} = 2.35 \times 10^{-9} \cdot d_M^2 - 8.82 \times 10^{-7} \cdot d_M + 8.24 \times 10^{-5}$ (R²=0.71)
	AR-REV	$\overline{REV} = 8.56 \times 10^{-8} \cdot d_I^2 - 2.38 \times 10^{-5} \cdot d_I + 4.32 \times 10^{-3}$ (R²=0.16)	$\overline{REV} = 1.26 \times 10^{-6} \cdot d_M^2 - 5.64 \times 10^{-4} \cdot d_M + 6.07 \times 10^{-2}$ (R²=0.66)
IV	SR-REV	$\overline{REV} = -4.88 \times 10^{-11} \cdot d_I^2 + 2.86 \times 10^{-8} \cdot d_I - 4.98 \times 10^{-6}$ (R²=0.33)	$\overline{REV} = 4.17 \times 10^{-10} \cdot d_M^2 - 1.15 \times 10^{-7} \cdot d_M + 2.61 \times 10^{-6}$ (R²=0.80)
	AR-REV	$\overline{REV} = 3.62 \times 10^{-10} \cdot d_I^2 + 6.79 \times 10^{-7} \cdot d_I - 1.48 \times 10^{-4}$ (R²=0.48)	$\overline{REV} = 2.21 \times 10^{-8} \cdot d_M^2 - 5.89 \times 10^{-6} \cdot d_M + 1.93 \times 10^{-4}$ (R²=0.84)

*$\overline{REV}$ is the average value of REV size, d_m is the distance from mass center of PCE plume to the cell contained in PCE plume, d_I is the distance from injection point to the cell contained in PCE plume

Table S3. The predicted frequency of SR-REV by BP neural network

Time (min)	I	II	III	IV
5	$F = 2.26 \times 10^{-7} + \dfrac{1}{2\pi \times 3.09}e^{-\frac{(REV-8.37)^2}{2\times 3.09^2}}$ (R^2=0.36)	$F = 2.36 \times 10^{-8} + \dfrac{1}{2\pi \times 2.62}e^{-\frac{(REV-5.57)^2}{2\times 2.62^2}}$ (R^2=0.29)	$F = 8.78 \times 10^{-8} + \dfrac{1}{2\pi \times 4.64}e^{-\frac{(REV-7.56)^2}{2\times 4.64^2}}$ (R^2=0.15)	$F = 2.30 \times 10^{-8} + \dfrac{1}{2\pi \times 4.04}e^{-\frac{(REV-7.94)^2}{2\times 4.04^2}}$ (R^2=0.16)
21	$F = 3.25 \times 10^{-8} + \dfrac{1}{2\pi \times 4.32}e^{-\frac{(REV-8.85)^2}{2\times 4.32^2}}$ (R^2=0.33)	$F = 1.50 \times 10^{-7} + \dfrac{1}{2\pi \times 3.96}e^{-\frac{(REV-7.92)^2}{2\times 3.96^2}}$ (R^2=0.38)	$F = 9.49 \times 10^{-9} + \dfrac{1}{2\pi \times 3.60}e^{-\frac{(REV-8.19)^2}{2\times 3.60^2}}$ (R^2=0.25)	$F = 1.94 \times 10^{-8} + \dfrac{1}{2\pi \times 3.87}e^{-\frac{(REV-8.54)^2}{2\times 3.87^2}}$ (R^2=0.17)
80	$F = 5.06 \times 10^{-9} + \dfrac{1}{2\pi \times 4.34}e^{-\frac{(REV-8.96)^2}{2\times 4.34^2}}$ (R^2=0.29)	$F = 6.41 \times 10^{-8} + \dfrac{1}{2\pi \times 3.81}e^{-\frac{(REV-9.94)^2}{2\times 3.81^2}}$ (R^2=0.34)	$F = 1.15 \times 10^{-7} + \dfrac{1}{2\pi \times 3.71}e^{-\frac{(REV-9.50)^2}{2\times 3.71^2}}$ (R^2=0.36)	$F = 2.01 \times 10^{-8} + \dfrac{1}{2\pi \times 3.92}e^{-\frac{(REV-9.26)^2}{2\times 3.92^2}}$ (R^2=0.25)
1523	$F = 1.01 \times 10^{-8} + \dfrac{1}{2\pi \times 3.29}e^{-\frac{(REV-10.72)^2}{2\times 3.29^2}}$ (R^2=0.50)	$F = 1.30 \times 10^{-8} + \dfrac{1}{2\pi \times 3.75}e^{-\frac{(REV-9.85)^2}{2\times 3.75^2}}$ (R^2=0.38)	$F = 7.13 \times 10^{-9} + \dfrac{1}{2\pi \times 3.86}e^{-\frac{(REV-9.81)^2}{2\times 3.86^2}}$ (R^2=0.28)	$F = 4.13 \times 10^{-7} + \dfrac{1}{2\pi \times 3.50}e^{-\frac{(REV-10.32)^2}{2\times 3.50^2}}$ (R^2=0.50)

[*]F represents the frequency of REV

Table S4. The predicted frequency of AR-REV by BP neural network

Time (min)	I	II	III	IV
5	$F = 2.43 \times 10^{-8}$ $+ \dfrac{1}{2\pi \times 3.29} e^{-\frac{(REV-8.65)^2}{2\times3.29^2}}$ (R^2=0.33)	$F = 5.69 \times 10^{-9}$ $+ \dfrac{1}{2\pi \times 0.56} e^{-\frac{(REV-14.09)^2}{2\times0.56^2}}$ (R^2=0.97)	$F = 3.09 \times 10^{-8}$ $+ \dfrac{1}{2\pi \times 3.31} e^{-\frac{(REV-7.65)^2}{2\times3.31^2}}$ (R^2=0.16)	$F = 4.93 \times 10^{-8}$ $+ \dfrac{1}{2\pi \times 3.53} e^{-\frac{(REV-9.92)^2}{2\times3.53^2}}$ (R^2=0.22)
21	$F = 1.15 \times 10^{-8}$ $+ \dfrac{1}{2\pi \times 3.62} e^{-\frac{(REV-9.15)^2}{2\times3.62^2}}$ (R^2=0.40)	$F = 4.32 \times 10^{-9}$ $+ \dfrac{1}{2\pi \times 4.11} e^{-\frac{(REV-8.96)^2}{2\times4.11^2}}$ (R^2=0.17)	$F = 1.42 \times 10^{-7}$ $+ \dfrac{1}{2\pi \times 3.26} e^{-\frac{(REV-10.03)^2}{2\times3.26^2}}$ (R^2=0.37)	$F = 9.10 \times 10^{-8}$ $+ \dfrac{1}{2\pi \times 3.44} e^{-\frac{(REV-10.91)^2}{2\times3.44^2}}$ (R^2=0.40)
80	$F = 5.12 \times 10^{-10}$ $+ \dfrac{1}{2\pi \times 3.61} e^{-\frac{(REV-9.48)^2}{2\times3.61^2}}$ (R^2=0.46)	$F = 1.63 \times 10^{-7}$ $+ \dfrac{1}{2\pi \times 3.84} e^{-\frac{(REV-9.83)^2}{2\times3.84^2}}$ (R^2=0.32)	$F = 4.30 \times 10^{-7}$ $+ \dfrac{1}{2\pi \times 3.58} e^{-\frac{(REV-9.86)^2}{2\times3.58^2}}$ (R^2=0.49)	$F = 1.21 \times 10^{-7}$ $+ \dfrac{1}{2\pi \times 3.35} e^{-\frac{(REV-10.96)^2}{2\times3.35^2}}$ (R^2=0.50)
1523	$F = 9.52 \times 10^{-8}$ $+ \dfrac{1}{2\pi \times 3.47} e^{-\frac{(REV-10.08)^2}{2\times3.47^2}}$ (R^2=0.50)	$F = 2.09 \times 10^{-8}$ $+ \dfrac{1}{2\pi \times 3.70} e^{-\frac{(REV-9.54)^2}{2\times3.70^2}}$ (R^2=0.38)	$F = 5.63 \times 10^{-9}$ $+ \dfrac{1}{2\pi \times 4.10} e^{-\frac{(REV-8.88)^2}{2\times4.10^2}}$ (R^2=0.36)	$F = 4.63 \times 10^{-9}$ $+ \dfrac{1}{2\pi \times 3.53} e^{-\frac{(REV-9.91)^2}{2\times3.53^2}}$ (R^2=0.54)

[*]F represents the frequency of REV

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