Supplemental Information: Numerical modeling and data-worth analysis for characterizing the architecture and dissolution rates of a multicomponent DNAPL source

Andres E. Prieto-Estrada, Mark A. Widdowson, Lloyd D. Stewart

Mathematical Model

Solute Transport Equation

$$-\frac{\partial}{\partial x_i}(v_i C^k) + \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C^k}{\partial x_j}\right) + \frac{q_s C_s^k}{n_e} + R^{N,k} = \left(1 + \frac{K_d^k \rho_b}{\theta}\right)\frac{\partial C^k}{\partial t} \qquad (1)$$

C^k	**M L^{-3}**	*Aqueous phase concentration of species k*
x_i	**L**	*Distance along cartesian coordinate axis*
t	**T**	*Time*
v_i	**L T^{-1}**	*Average pore water velocity*
D_{ij}	**L^2 T^{-1}**	*Hydrodynamic dispersion coefficient tensor*
q_s	**T^{-1}**	*Volumetric flux of water per unit volume of aquifer representing fluid sources (positive) and sinks (negative)*
C_s^k	**M L^{-3}**	*Concentration of the source or sink flux for species k*
K_d^k	**L^3 M^{-1}**	*Distribution coefficient*
ρ_b	**M L^{-3}**	*Bulk density*
θ	**L^3 L^{-3}**	*Aquifer porosity*
$R^{N,k}$	**M L^{-3} T^{-1}**	*Source term representing NAPL dissolution for species k*

NAPL mass balance term

$$\frac{\partial C^{N,k}}{\partial t} = -\frac{\theta}{\rho_b} R^{N.k} \qquad (2)$$

$C^{N,k}$	**M L^{-3}**	*NAPL phase concentration of species k*

NAPL source term

$$R^{N.k} = k^{N,k}\left(C_{eq}^k - C^k\right) \qquad (3)$$

$k^{N,k}$	**T^{-1}**	*Lumped mass transfer coefficient of species k*
C_{eq}^k	**M L^{-3}**	*Aqueous-phase equilibrium concentration of species k calculated using Raoult's Law*

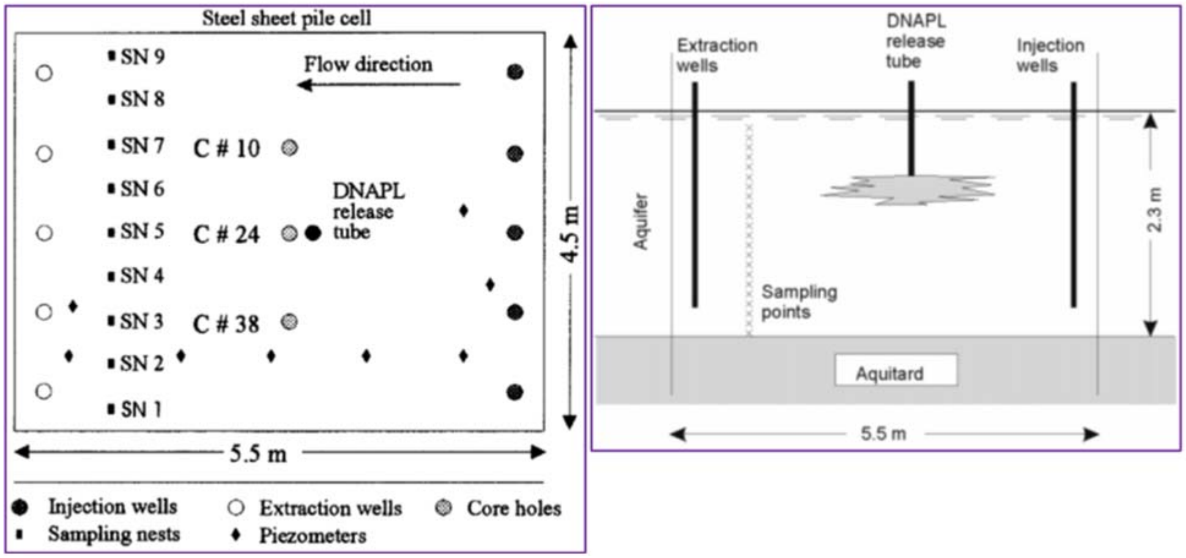

Figure S1. Plan and cross-sectional views of aquifer test cell (adapted from Broholm et al. 1999).

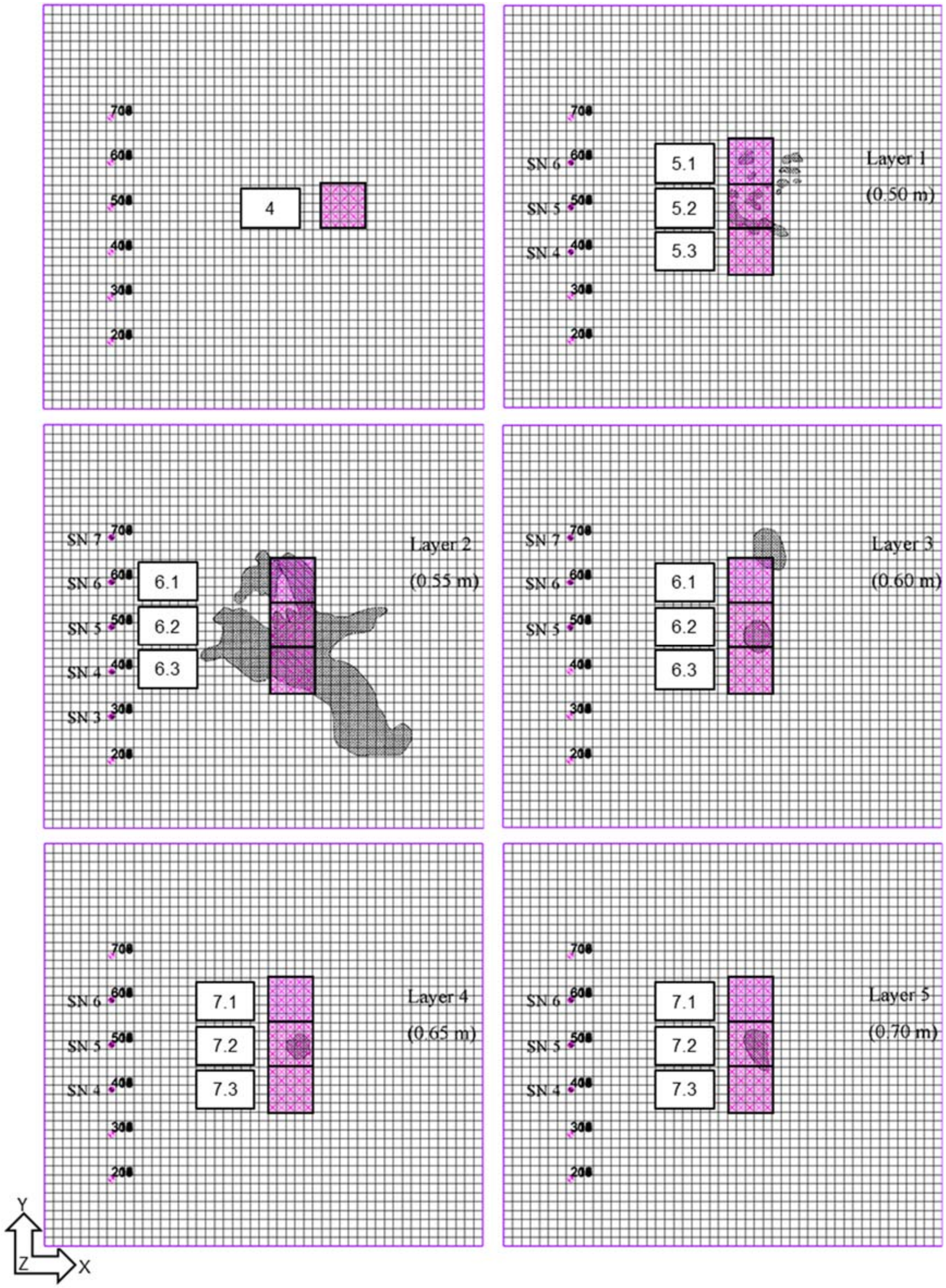

Figure S2. Grid-scale NAPL zones in model layers 4 through 7. All NAPL zones measured 0.5 m x 0.5 m on the horizontal plane, encompassing 25 grid blocks. Model layers measured 0.1 m along the Z-axis representing the vertical spacing between MLS ports. The post-experimental NAPL footprint mapped in 0.05-m vertical increments (excavation layers) by Broholm et al. (1999) was included for reference.

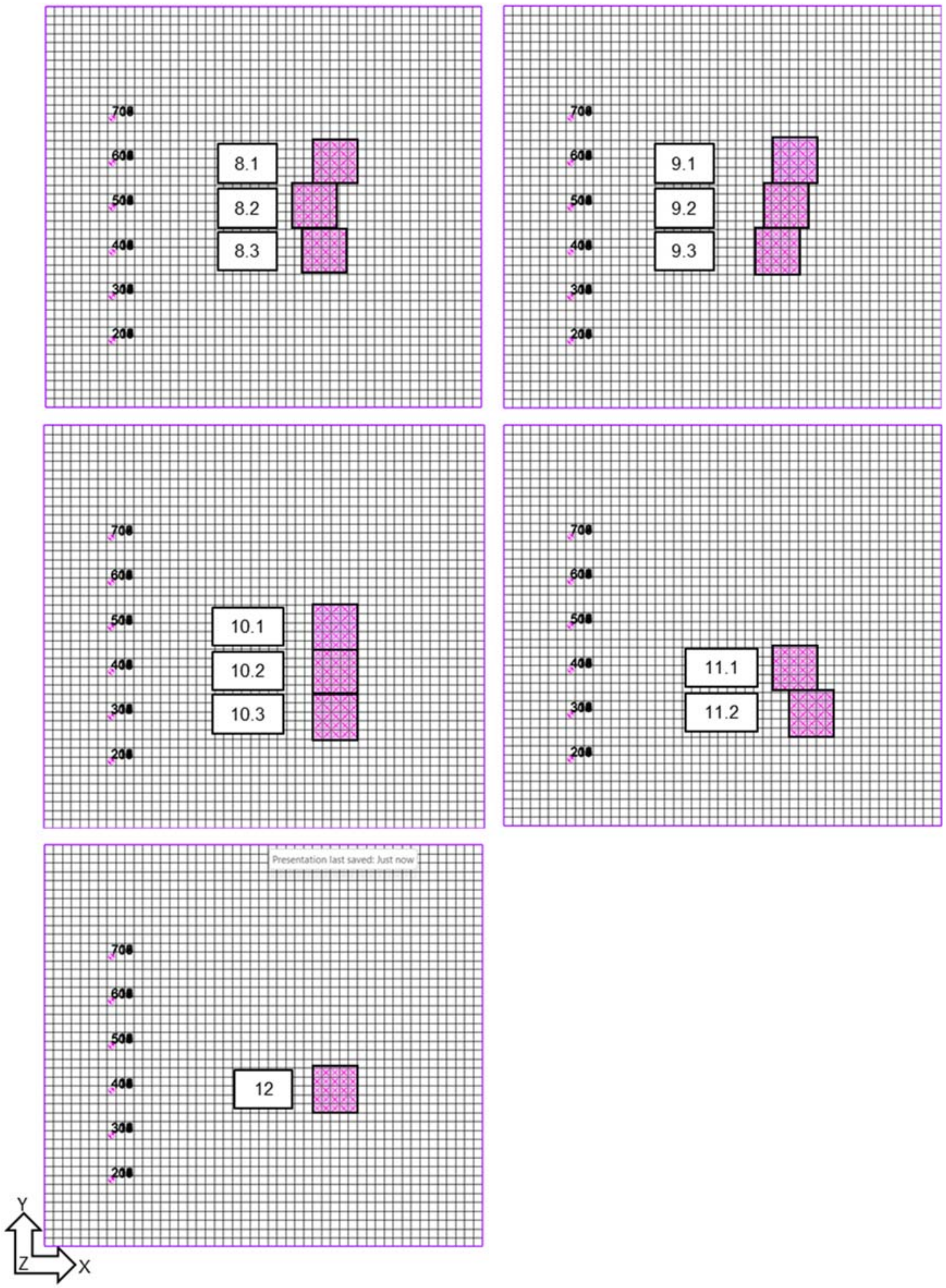

Figure S3. Grid-scale NAPL zones in model layers 8 through 12.

Andres E. Prieto-Estrada, Mark A. Widdowson, Lloyd D. Stewart

Table S1. Input parameters of groundwater flow and solute transport model including NAPL properties

Model Parameter	Value	Data Source
Hydraulic conductivity (m/d)	2.0	Broholm et al. 1999
Porosity (%)	33.0	Broholm et al. 1999
Longitudinal dispersivity (cm)	5.0	Mobile et al. 2012
Transverse horizontal dispersivity (cm)	0.5	Mobile et al. 2012
Transverse vertical dispersivity (cm)	0.05	Mobile et al. 2012
TCM sorption coefficient (m^3/g)	3.0×10^{-8}	Mobile et al. 2012
TCE sorption coefficient (m^3/g)	5.0×10^{-8}	Mobile et al. 2012
PCE sorption coefficient (m^3/g)	1.3×10^{-7}	Mobile et al. 2012
Soil bulk density (g/m^3)	1.65×10^{6}	Mobile et al. 2012
TCM initial NAPL mass fraction (%)	9.60	Broholm et al. 1999
TCE initial NAPL mass fraction (%)	37.9	Broholm et al. 1999
PCE initial NAPL mass fraction (%)	52.5	Broholm et al. 1999
TCM ideal solubility (mg/L)	8700	Broholm et al. 1999
TCE ideal solubility (mg/L)	1400	Broholm et al. 1999
PCE ideal solubility (mg/L)	240	Broholm et al. 1999
TCM molecular weight (g/mol)	119.4	Rivett et al. 2001
TCE molecular weight (g/mol)	131.4	Rivett et al. 2001
PCE molecular weight (g/mol)	165.8	Rivett et al. 2001
TCM density (g/cm^3)	1.48	Broholm et al. 1999
TCE density (g/cm^3)	1.46	Broholm et al. 1999
PCE density (g/cm^3)	1.62	Broholm et al. 1999

Table S2. Parameter values used to calculate percentages of initial NAPL mass removed by natural dissolution and methanol flushing presented in Table 5.

Parameter	TCM	TCE	PCE	Total	Source
Initial NAPL (L)	0.48	1.895	2.625	5	Mobile et al. (2012)
Initial NAPL (g)	739.2	2918.3	4042.5	7700	Mobile et al. (2012)
Remaining NAPL (L) (1)	0.001	0.34	1.24	1.58	Broholm et al. (1999)
Remaining/Initial NAPL (1)	0.002	0.179	0.472	0.32	Calculated
Remaining NAPL (g) (1)	**1.54**	**523.6**	**1909.6**	**2434.74**	**Calculated**
Remaining NAPL Fractions (1)	0.0006	0.2151	0.7843	1	Calculated
Remaining NAPL (L) (2)	0.002	0.532	1.940	2.47^	Calculated / Broholm et al. (1999)
Remaining/Initial NAPL (2)	0.0033	0.2807	0.7390	0.49	Calculated
Remaining NAPL (g) (2)	**2.4**	**819.1**	**2987.3**	**3808.8**	**Calculated**

(1) Post-excavation volumes (L) of each NAPL component provided by Broholm et al. (1999) assuming a homogeneous 3.6% NAPL saturation of the pore space in all excavation layers. ^Total post-excavation NAPL volume (L) provided by Broholm et al. (1999) assuming a 20% NAPL saturation in excavation layer 2 and a 3.6% saturation in other soil layers. (2) Remaining volume (L) and mass (g) calculated for each NAPL component using the individual remaining fractions in (1) reported by Broholm et al. (1999), applied to the total remaining NAPL volume of ^2.47 L also reported by Broholm et al. (1999).