

VOC Modeling in Support of 300 Area FF-5 RI/FSS Document

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

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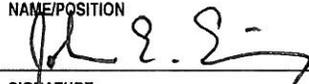
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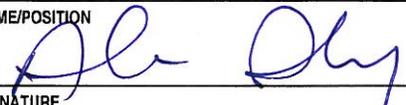
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1. Purpose

Beginning in 1987, elevated concentrations of tetrachloroethene (PCE) and its biodegradation products, trichloroethene (TCE) and *cis* 1,2-dichloroethene (cDCE) have been observed in well 399-1-16B. The source for these concentrations is unclear. It has been posited that spills occurring in the 300 Area Process Trenches near well 399-1-23 may be a potential source of the concentrations in well 399-1-16B.

The purpose of the analysis presented here is two-fold. The first goal is to assess whether it is plausible that PCE-DNAPL which was spilled in the 300 Area Process Trenches would infiltrate through the Hanford Formation and penetrate into the Ringold Formation. The second objective is to assess the plausibility of PCE-DNAPL trapped in the Ringold Formation beneath the 300 Area Process Trenches could be the source of PCE, TCE, and cDCE concentrations observed in well 399-1-16B. The potential source location was assumed to be well 399-1-23.

2. Methodology

Feasibility of DNAPL Penetration into Ringold Formation

The primary parameter governing whether a pool of DNAPL is capable of entering an adjacent portion of uncontaminated soil is the entry pressure of that soil. For a DNAPL pool overlying a stratum of finer-grained sediments, the pool thickness (T) necessary to overcome the entry pressure of the underlying sediments can be presented by Pankow and Cherry (1996, p. 102):

$$\Delta\rho g T = P_d \quad \rightarrow \quad T = \frac{P_d}{\Delta\rho g} \tag{1}$$

where P_d is the entry (displacement) pressure of the underlying sediment, $\Delta\rho$ is the difference in densities between the DNAPL and water, and g is gravitational acceleration.

Pankow and Cherry (1996, p. 102) also present a correlation between entry pressure and hydraulic conductivity:

$$P_d = 9.6 \left(\frac{\sigma}{\sigma_{aw}} \right) \left(\frac{K}{\Phi} \right)^{-0.403} \tag{2}$$

where K is the hydraulic conductivity (cm/s), Φ is the porosity, σ is the interfacial tension of the fluid pair of interest, and σ_{aw} is the interfacial tension of water against air.

Combining these two equations, Pankow and Cherry (1996, p. 102) presented a simple equation for calculating the DNAPL pool thickness that can be sustained by an underlying, lower-permeability soil:

$$T = 9.6 \left(\frac{\rho_w}{\Delta\rho} \right) \left(\frac{\sigma}{\sigma_{aw}} \right) \left(\frac{K}{\Phi} \right)^{-0.403} \quad (3)$$

where T is the DNAPL pool thickness (cm) and K is the hydraulic conductivity (cm/s). An infiltrating non-wetting phase will tend to invade an uncontaminated soil through the largest pore throats of that soil. Accordingly, it will be the portions of the Ringold Formation beneath the PCE spill location that have the highest hydraulic conductivity (and largest pore throats) which will be invaded most easily by the PCE-DNAPL. Aquifer tests tend to represent a volume of soil at a considerably larger scale (meters) than is applicable to DNAPL invasion into uncontaminated sediments (centimeters). The reported hydraulic conductivity likely represents an average value of both higher and lower values present in the volume of soil included in the aquifer test. It should also be noted that the scales at which anisotropy is evident in hydraulic conductivity values (meters) are considerably larger than the scale applicable to entry pressure (centimeters). For these reasons, it is important to focus on the highest reported values of hydraulic conductivity of the Ringold Formation.

Plume Simulations

The PCE-DNAPL entrapped in the Ringold will act as a source zone for dissolved PCE in groundwater. This will result in a downstream plume of PCE and, in the presence of reductive dechlorination, its daughter products TCE, cDCE, and VC.

To simulate the transport of dissolved PCE and its daughter products, the analytical simulator REMChlor (Falta et al., 2007a) was employed. REMChlor takes information about the source zone, groundwater velocity, and transport processes and simulates the downstream concentrations of the solutes of interest. Because many aspects of the PCE source zone and transport processes are uncertain, sensitivity simulations were conducted to evaluate results under a variety of conditions.

3. Assumptions and Inputs

Feasibility of DNAPL Penetration into Ringold Formation

The pertinent parameters for calculating the PCE pool thickness required to penetrate the Ringold Formation are summarized in Table 1.

Table 1. Parameters for Pool Thickness Calculation

Parameter	Value	Units	Reference	Comment
Porosity, ϕ	0.25	--	Williams et al., 2008, p. 3.25	model input
	0.267	--	Last et al., 2009, p. 14	sitewide average
Hydraulic Conductivity, K	40	m/d	Williams et al., 2008, p. 3.26	model input, K_{xy}
	4	m/d	Williams et al., 2008, p. 3.26	model input, K_z
	4.13e-4	cm/s	Last et al., 2009, p. 18	sitewide average
Water Density, ρ_w	998.2	kg/m ³	Potter and Wiggert, 1991, p. 655	20 °C
PCE Density, ρ_n	1.63	g/cm ³	Pankow and Cherry, 1996, p. 508	25 °C, note: 1 g/cm ³ = 1e3 kg/m ³
Water Surface Tension, σ_{aw}	0.0736	N/m	Potter and Wiggert, 1991, p. 655	20 °C, note: 1 N/m = 1e3 dyn/cm
PCE-Water Interfacial Tension, σ_{nw}	47.5	erg/cm ²	Horvath, 1982, p. 153	20 °C, note: 1 erg/cm ² = 1 dyn/cm

Using Equation 3 and the parameters from Table 1, a range in DNAPL pool thicknesses from 19 cm to 133 cm is estimated. The value of 19 cm was calculated using the highest hydraulic conductivity and lowest porosity in Table 1 and the value of 133 cm was calculated using the lowest hydraulic conductivity and highest porosity in Table 1. For the reasons discussed above, the lower end of the range for estimated pool height can be expected to be most realistic.

As PCE-DNAPL infiltrates through the Hanford Formation, some of the PCE will be trapped by capillary forces and remain behind as a residual saturation. Assuming a three-phase residual PCE saturation of 5% for the 10 m of vadose zone (Peterson et al., 2008, p. 2.5) and 20% for the 6.5 m of saturated zone (Peterson et al., 2008, p.2.5) above the Ringold Formation beneath the 300 Area Process Trenches and an assumed PCE infiltration column diameter of 10 cm, 3.5 L of PCE can be expected to remain as residual saturation. For a 120 gallon (454 L) spill of PCE (Peterson et al., 2008, p. 3.1), that would leave 451 L of PCE available to pool at the Hanford-Ringold Formation contact. A 451 L pool with a pool height of 19 cm would result in a pool diameter of 345 cm. This would involve a diameter to height ratio of 18 for the pool. It appears very plausible that such a pool could form in the Hanford formation and therefore it is plausible that PCE infiltrating beneath the 300 Area Process Trenches would penetrate the Ringold Formation.

Plume Simulations

Explanation of the REMChlor input parameters can be found in the REMChlor User's Manual (Falta et al., 2007b). Additional description of the methods or rationale used to determine the values for the input parameters is included in the accompanying spreadsheet "PCE calculations_rev1.xlsx."

Because no measurements of the initial source concentration exist, two scenarios were considered for input into REMChlor. First, it was assumed that the source concentration was equal to the equilibrium solubility of PCE in water. This represents the maximum concentration possible and corresponds to PCE covering the entire source width and depth and a source residence time sufficient that the groundwater

would reach equilibrium with the PCE. Lower concentrations are also possible and can be considered depending on the results from the simulations.

The source mass of PCE is simply assumed to correspond to the entire volume of PCE spilled. The PCE mass is primarily important in dictating the persistence of the source zone over time and is of arbitrary importance to this study so long as the source geometry, source function and source concentration do not result in depletion of the source during the time period of interest.

The source function exponent (γ) in REMChlor describes the dissolved concentration emitting from the source zone as a function of the depletion of source mass. While this is a very important parameter in dictating the long-term fate of a DNAPL source, it does not play such an important role in the qualitative evaluation of whether a particular source could plausibly produce concentrations in a downstream observation well. A typical γ value of 1.0 (Falta et al., 2007b) was used. An exponent of 1.0 results in a source concentration that declines exponentially with time. If necessary, other possible source function exponents of 0.0, 1.0 or 2.0 can be investigated. The exponent of 0.0 means that the source concentration will always remain at C_0 until the mass is depleted, at which point the concentration will go to zero. An exponent of 0.5 leads to a source concentration that declines linearly with time. This is indicative of a source zone in which the DNAPL mass is distributed primarily in the higher permeability regions as would be expected for a non-wetting DNAPL. An exponent of 2.0 is indicative of a source zone in which the DNAPL mass is distributed primarily in the lower permeability regions.

The source width and depth are primarily important in dictating the persistence of the DNAPL source zone. For example, a larger width and depth would result in a shorter duration for the DNAPL source mass to deplete. The source is assumed to have a width of 10 meters and a depth of 3 meters.

The Darcy velocity was determined by estimating the distance between the 105.9 m and 105.8 m contours in the vicinity of well 399-1-23 from the June 2009 Ringold water levels found in Environmental Calculation ECF-300FF5-11-0151. The 40 m/d value for hydraulic conductivity reported by Williams et al. (2008, p. 3.26) was then used along with Darcy's law to calculate the Darcy velocity. The porosity value of 0.25 reported in Williams et al. (2008, p. 3.25) is used by REMChlor to calculate the pore velocity.

Source zone remediation parameters were set to zero to reflect that no remediation has been done on the source. Retardation factors primarily impact the timing of the downstream concentrations and have little impact on their magnitude. A retardation factor of 1, corresponding to no retardation, was used.

Two values for the velocity field coefficient of variation (σ_{mv}) were chosen to correspond to scale dependent longitudinal dispersivities of $x/100$ and $x/10$, where x is the longitudinal distance from the source to the solute front. A longitudinal distance of 170 m was estimated along the groundwater flow direction from the source zone to the plane transecting well 399-1-16B. This length was then used to estimate constant x -direction dispersivity coefficients corresponding to the two values chosen for the σ_{mv} parameter. The y -direction dispersivity coefficient was initially assumed to be $1/10^{\text{th}}$ the x -direction value. No dispersion was considered in the z -direction in keeping with a two-dimensional x - y solute plume.

The value for the minimum normalized streamtube velocity (vMin) of 0 suggested in the REMChlor User's Manual was used. Similarly, the suggested method of calculating the maximum normalized streamtube velocity $v_{Max} = 1 + 4 * \text{Sig}mav$ was used. Because the analytical solution can be solved relatively quickly by modern computers, a large number of stream tubes was selected to focus on a smooth solution over run speed.

The mass of TCE created by first order decay of one unit of mass of PCE was calculated as the molecular weight of TCE divided by the molecular weight of PCE. This yield is typical for reductive dechlorination (Falta et al., 2007b). Similarly, the mass of cDCE created by first order decay of one unit of mass of TCE was calculated as the molecular weight of cDCE divided by the molecular weight of TCE. Because no VC was observed in any of the groundwater samples, a yield coefficient of 0 was assumed for the transformation from cDCE to VC.

While REMChlor allows up to 9 different reaction rates for each chemical species, a single reaction rate for each component based on the mean reaction rates reported in Aziz et al. (2002, p. 3) was assumed. The reaction rate for cDCE was assumed to be zero since no VC was observed in groundwater samples.

Spatial discretization values were chosen so that output would be produced at the location of wells 399-1-16B and 399-1-8. Output were taken from the model grid cell with an x-value of 168.1 m and a y-value of 135 m for well 399-1-16B and with an x-value of 188.1 m and a y-value of 27 m for well 399-1-8. Time discretization was chosen such that yearly simulation output was produced.

The input parameters used in the base case REMChlor simulations are summarized in Table 2.

Table 2. Summary of REMChlor Model Inputs

Parameter	Value(s)	Units	Comments
Concentration	0.15	g/L	Equilibrium solubility for PCE
Mass	740	kg	Entirety of PCE spilled, calculated as mass = volume * density
Gamma	1	--	Exponentially decaying source function ^(a)
Source Width	10	m	Assumed
Source Depth	3	m	Assumed
Darcy Velocity	10	m/yr	Calculated from $q = -K \text{ dh/dl} = 40\text{m/d} * 365.25\text{d/yr} * 0.1\text{m}/140\text{m}$ ^(b)
Porosity	0.25	--	Williams et al., 2008, p. 3.25
Percent Removed	0	%	Not used as remediation was not pertinent to this study
Start Time	0	yr	
End Time	0	yr	
Source Decay	0	1/yr	
Retardation Factor	1	--	Assume no retardation
Sigmav	0.14	--	Corresponds to dispersivity of $\text{alphax} = x/100$ ^(c)
vMin	0	--	Typical value from p. 41 of User's Manual
vMax	1.6	--	$v_{Max} = 1 + 4 * \text{Sig}mav$ as recommended on p. 41 of User's Manual
# Stream Tubes	100	no.	Large number to achieve smooth solution
alphay	0.17	m	$\text{alphax}/10$ or alphax ^(d)
alphaz	0	m	Assume two-dimensional x-y plume so no dispersion in z
Yield 2 from 1	0.79	--	Calculated as MW_{TCE}/MW_{PCE}
Yield 3 from 2	0.74	--	Calculated as MW_{cDCE}/MW_{TCE}
Yield 4 from 3	0	--	Assumed to be zero since no VC observed

Time Period 1	30	yr	Time since PCE spill
Time Period 2	50	yr	One period so irrelevant but larger than Time Period 1
X1	400	m	Encompassing the x-dimension of the region of interest
X2	700	m	One zone so irrelevant but larger than X1
PCE decay rate	1.4	1/yr	Mean values from Table 2. of Aziz et al. (2002), p. 3
TCE decay rate	1.5	1/yr	
cDCE decay rate	0	1/yr	No observed VC so assume no cDCE decay or VC
VC decay rate	0	1/yr	
X (Int, Min, Max)	101, 0.1, 200.1	m	Discretization to have output at well 399-1-16B location
Y (Int, Min, Max)	33, -144, 144	m	Discretization to have output at well 399-1-16B location
Z (Int, Min, Max)	1, 0, 0	m	Assume two-dimensional x-y plume
t (Int, Min, Max)	30, 0, 30	yr	Yearly output for 30 years

^(a) See p. 39 of the User's Manual

^(b) $K = 40$ m/d (Williams et al., 2008, p. 3.26), $d_l = 140$ m from Ringold contours in Environmental Calculation ECF-300FF5-11-0151), and $d_h = -0.1$ m (contour interval in Environmental Calculation ECF-300FF5-11-0151)

^(c) From lookup table on page 41 in the User's Manual

^(d) Assumed α_x equal to distance from source (399-1-23) to observation pt (399-1-16B) along flow direction of 167.56 m divided by 100

4. Software Applications

The plume simulations were performed using the approved utility calculation software REMChlor (Remediation Evaluation Model for Chlorinated Solvents) Version 1.0 code, Hanford Information System Inventory (HISI) identification number 2948. The REMChlor code provides an analytical solution for simulating the transient effects of ground water source and plume remediation on the transport of chlorinated solvents with biotransformation between solvents (PCE → TCE → DCE → VC). The contaminant source model is based on a power-function relationship between source mass and source discharge, and serves as a time dependent, mass-flux boundary condition to the analytical plume model, where flow is assumed to be one dimensional. The plume model simulates first-order sequential decay and production of several species, and the decay rates and parent/daughter yield coefficients are variable functions of time and distance.

The REMChlor code has been graded as Level D software in accordance with PRC-PRO-IRM-309, *Controlled Software Management*. REMChlor is not designated as a Safety System Software. This application of REMChlor within the 300 Area is limited to exploratory work to validate or invalidate a hypothesis regarding potential source location for chlorinated solvents. The use of this software was consistent with its purpose, used within its limitations, and was a valid application of REMChlor consistent with the functional requirements identified in CHPRC-01455 Rev 0, *REMChlor Software Management Plan*.

The REMChlor code was executed for this calculation on a Dell® Optiplex® 780 with a 2.83-GHz Intel® Core Quad CPU Q9550 processor and 8 GB of RAM loaded with the 64-Bit Windows 7 Professional Service Pack 1 operating system.

Microsoft Excel 2007® spreadsheets were used to calculate the feasible DNAPL pool height and DNAPL pool diameter and relevant inputs for REMChlor. This use of Excel® is in the spreadsheet category and all calculations are subject to checking as part of this Environmental Calculation File.

5. Calculations

Feasibility of DNAPL Penetration into Ringold Formation

Calculations for the DNAPL penetration analysis are attached in the spreadsheet “PCE calculations_rev1.xlsx”. Calculations of a sustainable pool height are in the “Pool Height” worksheet. Calculations of an estimated pool diameter are in the “Pool Diameter” worksheet. Descriptions of the methodology and equations used are included in the worksheets.

Plume Simulations

Calculation of the interwell distances from the presumed source well 399-1-23 to the observation wells 399-1-16B and 399-1-8 are detailed in the “Interwell Info” worksheet within the “PCE calculations_rev1.xlsx” spreadsheet. Derivation of the REMChlor model input parameters listed in Table 2 is included in the “REMChlor Inputs” worksheet within the “PCE calculations_rev1.xlsx” spreadsheet.

6. Results/Conclusions

Feasibility of DNAPL Penetration into Ringold Formation

Pool height and pool diameter calculations indicate that it is plausible that PCE infiltrating beneath the 300 Area Process Trenches would penetrate the Ringold Formation.

Plume Simulations

The locations of wells within the 300 Area are shown in Figure 1. The water level elevation contours, indicating the flow direction during June and December of 2009, are depicted in Figure 2. The results for the simulation using the base case parameters are shown in Figures 3 through 7. Figures 3 through 5 depict the PCE, TCE, and cDCE plumes, respectively, after a period of 28 years. This duration corresponds roughly to the time between the latest groundwater observations and the spill date of November 1982 (Peterson et al., 2008, p. 3.1). Figures 6 and 7 depict the simulated and observed concentrations at well 399-1-16B and well 399-1-8, respectively. The observed data for wells 399-1-16B and 399-1-8 were downloaded from the HE15 database on August 31, 2010. Note that simulated concentrations are zero at well 399-1-16B. These figures indicate that the base case parameters – particularly a longitudinal dispersion coefficient corresponding to $x/100$ (where x is the distance to the transport front) and a transverse dispersion coefficient $1/10^{\text{th}}$ the longitudinal dispersion – produce a plume that is too narrow to result in VOC concentrations reaching well 399-1-16B. Note that simulated

concentrations can be seen in well 399-1-8 (Figure 7) but are somewhat higher than the observed concentrations.

To test the sensitivity of the dispersion coefficients, additional sensitivity simulations were conducted. These sensitivity simulations are summarized in Table 3 along with the base case simulation. For simulation case R1, the σ_{yav} parameter was increased from 0.14 to 0.45, corresponding in an increase in the longitudinal dispersion coefficient from $x/100$ to $x/10$, where x is the distance to the transport front. The α_{y} parameter was also increased accordingly but still corresponds to a ratio of $1/10$ between the transverse and longitudinal dispersion coefficients. The simulation results for case R1 are given in Figures 8 through 12. The increased dispersion results in the plume reaching well 399-1-16B but at extremely low concentrations (Figure 11). The simulated concentrations at well 399-1-8 are higher than those observed (Figure 12).

Simulation case R2 involves increasing the transverse dispersivity to be one-half of the longitudinal dispersivity. The simulation results are shown in Figures 13 through 17. This increased transverse dispersivity results in concentrations of the same order of magnitude as those observed at well 399-1-16B (Figure 16). The simulated concentrations are considerably higher than those observed at well 399-1-8, however (Figure 17).

Table 3. Description of Sensitivity Runs

Case	Comments	Plausibility
R0	Base case parameters from Table 2. Corresponds to $\alpha_{\text{max}} = x/100$ and $\alpha_{\text{y}} = \alpha_{\text{max}}/10$.	Plume is too narrow to reach the lateral extents of well 399-1-16B. Concentrations zero at well 399-1-16B and somewhat high at well 399-1-8.
R1	$\sigma_{\text{yav}} = 0.45$, $v_{\text{Max}} = 2.8$, $\alpha_{\text{y}} = 1.7$. Corresponds to $\alpha_{\text{max}} = x/10$ and $\alpha_{\text{y}} = \alpha_{\text{max}}/10$.	Plume crosses through well 399-1-16B. Concentrations far lower than those observed at well 399-1-16B and high at well 399-1-8.
R2	$\alpha_{\text{y}} = 8.5$. Corresponds to $\alpha_{\text{y}} = \alpha_{\text{max}}/2$. $\sigma_{\text{yav}} = 0.45$, $v_{\text{max}} = 2.8$	Plume crosses through well 399-1-16B. Concentrations plausible at well 399-1-16B but much too high at well 399-1-8.

Given the number of uncertainties regarding the DNAPL source zone location and geometry and the transport parameters of the Ringold Formation, a wide array of possible concentration outcomes can be simulated. It is certainly possible to simulate concentrations consistent with those observed at well 399-1-16B using what can be considered reasonable parameters and assumptions. There is no combination of parameters, however, that can simultaneously simulate the observed concentrations at both well 399-1-16B and well 399-1-8 using the described derivation of the groundwater flow direction of 40° south of east. Because well 399-1-8 is closer to the centerline of the groundwater flow direction than well 399-1-16B, it will always have higher simulated concentrations than well 399-1-16B for any REMChlor parameter combinations. The only way for the simulated concentrations in well 399-1-8 to be lower than those in well 399-1-16B, as is the case with the observed concentrations, would be for well 399-1-16B to be closer to the centerline of the groundwater flow direction. This would require a groundwater flow direction almost due east, which is inconsistent with the water level measurements in

the Ringold Formation. These findings indicate that it does not appear plausible that the source for the concentrations observed in well 399-1-16B is the 300 Area Process Trenches.

The model presented here is of a simplistic, scoping nature. The model assumes homogeneity with a one dimensional flow field. Furthermore, many of the model parameters are assumed and poorly constrained. None of the limitations of the model, however, change the basic conclusion that it does not appear plausible that concentrations at well 399-1-16B and well 399-1-8 can result from a source at the 300 Area Process Trenches given the current understanding of the groundwater flow direction.

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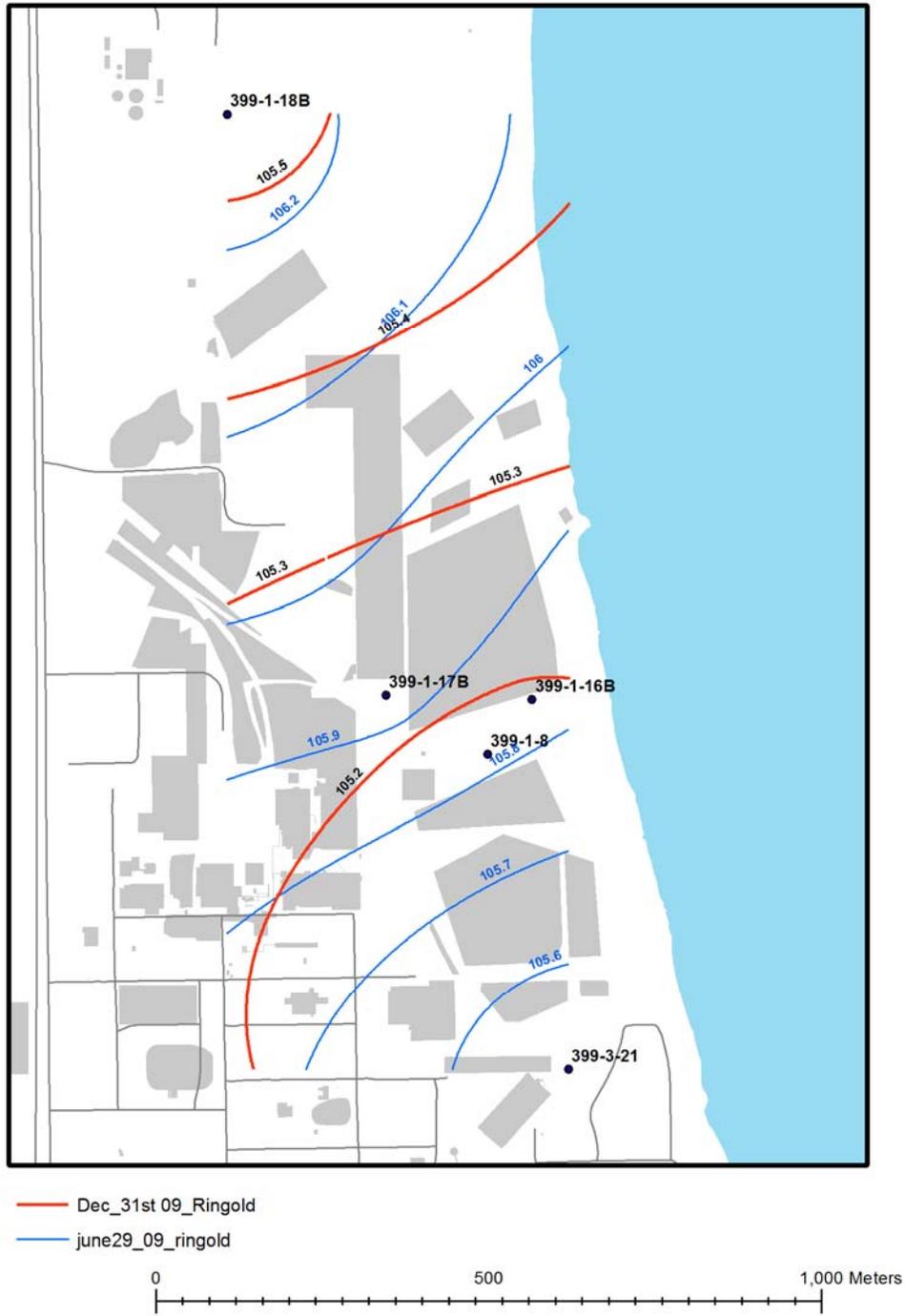


Figure 2. Ringold Formation water-level elevations during June and December 2009.

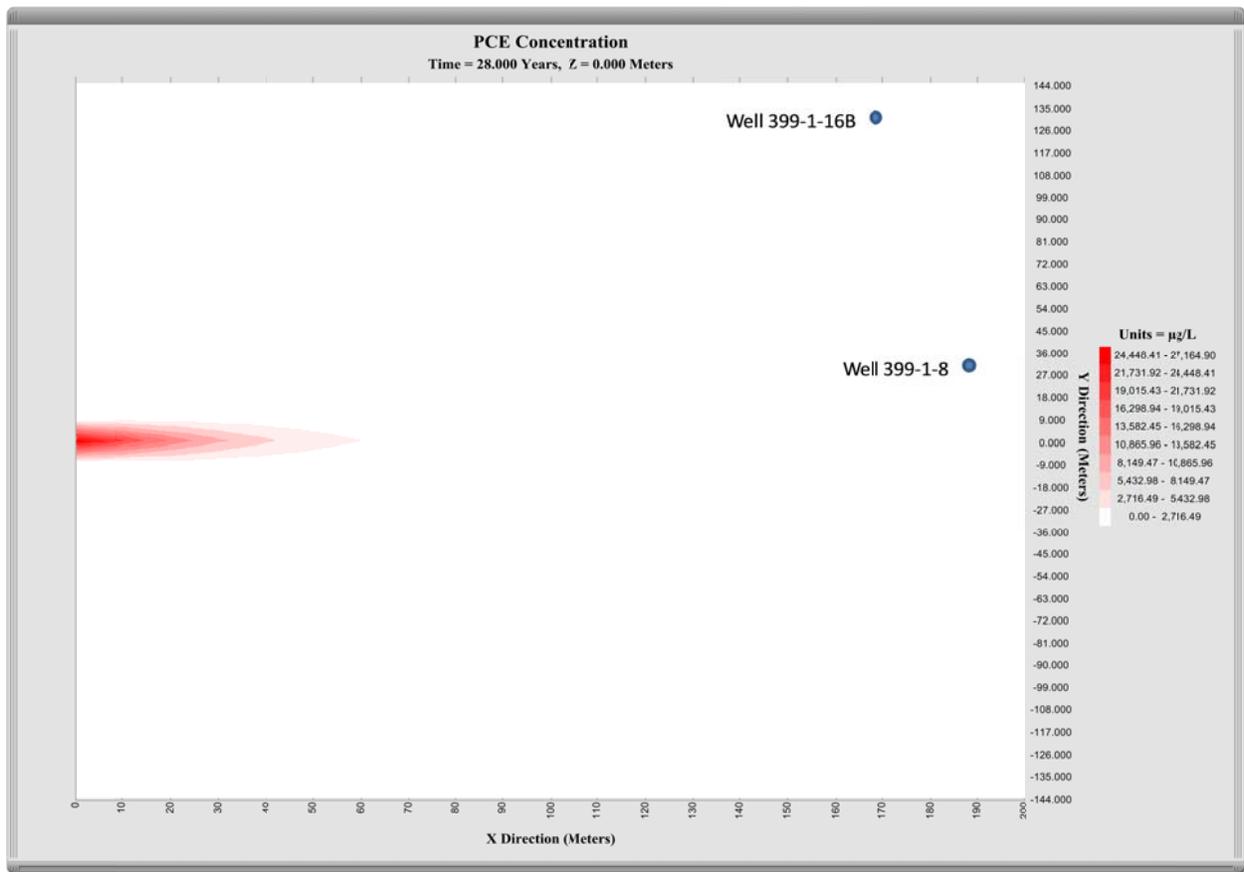


Figure 3. Case R0: simulated PCE concentrations after 28 years.

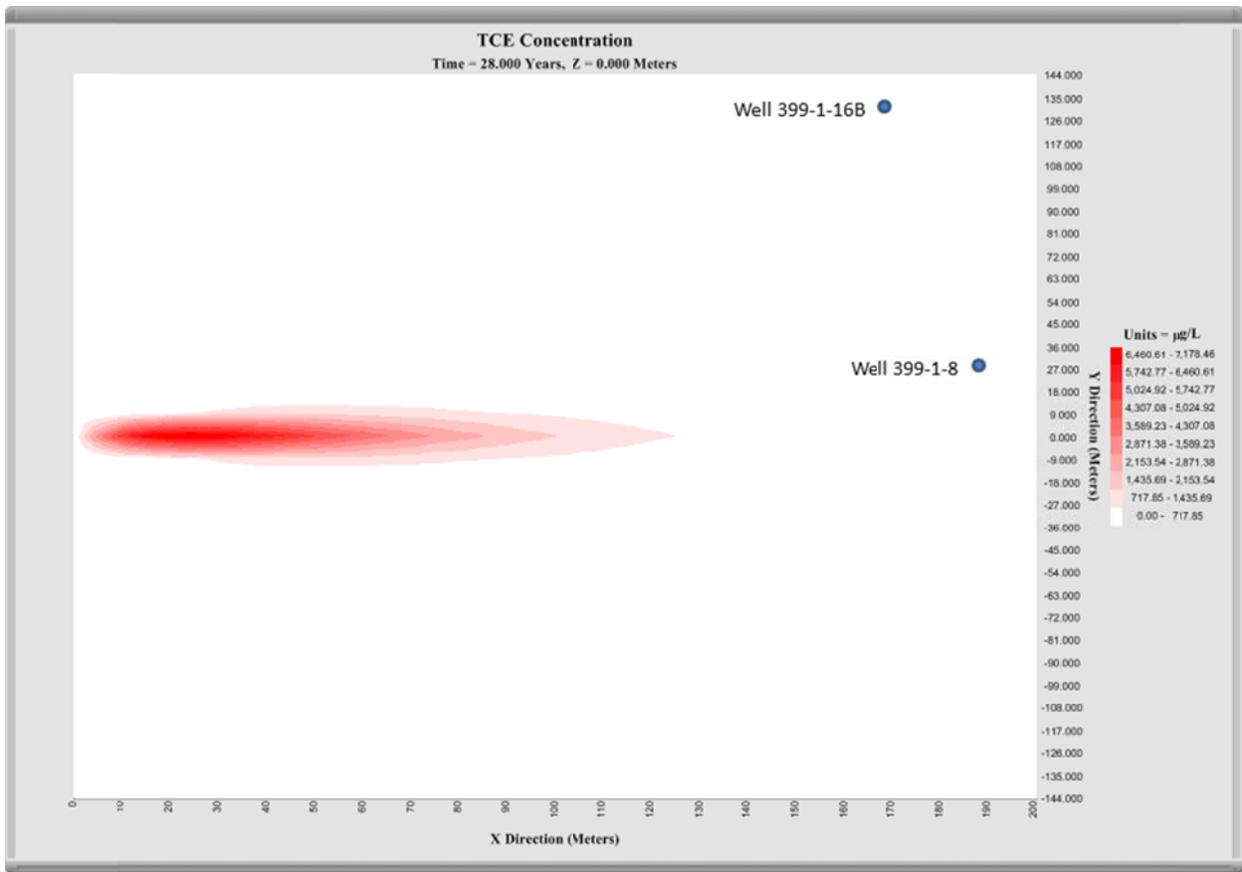


Figure 4. Case R0: simulated TCE concentrations after 28 years.

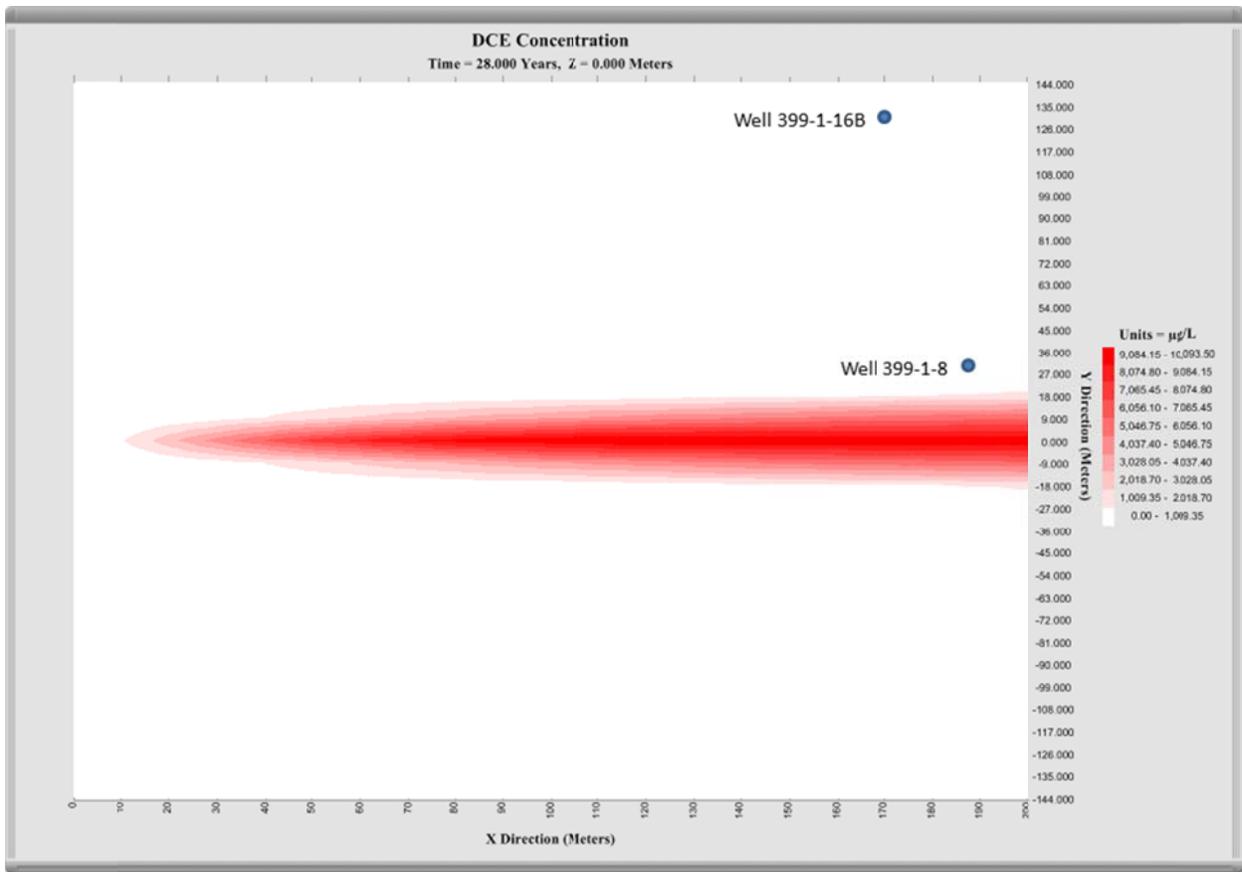


Figure 5. Case R0: simulated cDCE concentrations after 28 years.

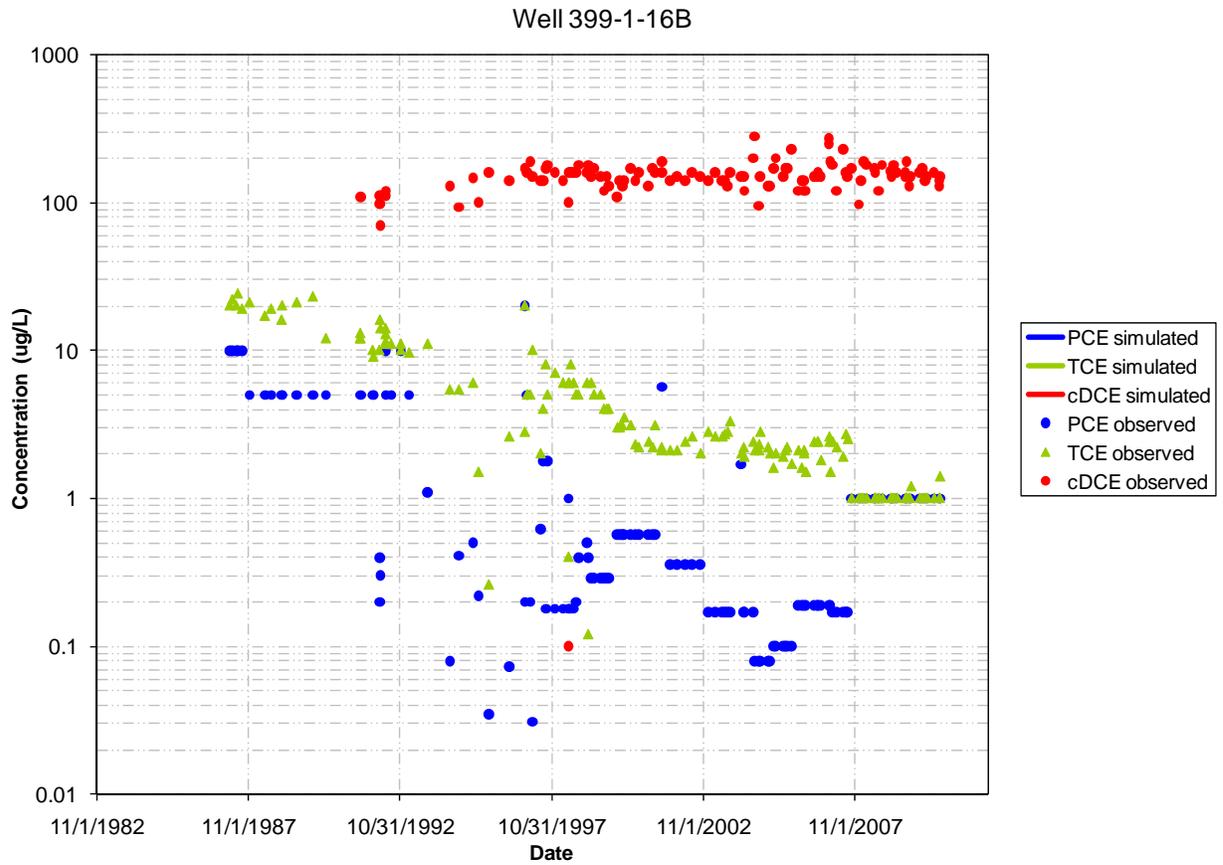


Figure 6. Case R0: simulated and observed concentrations in Well 399-1-16B.

Well 399-1-8

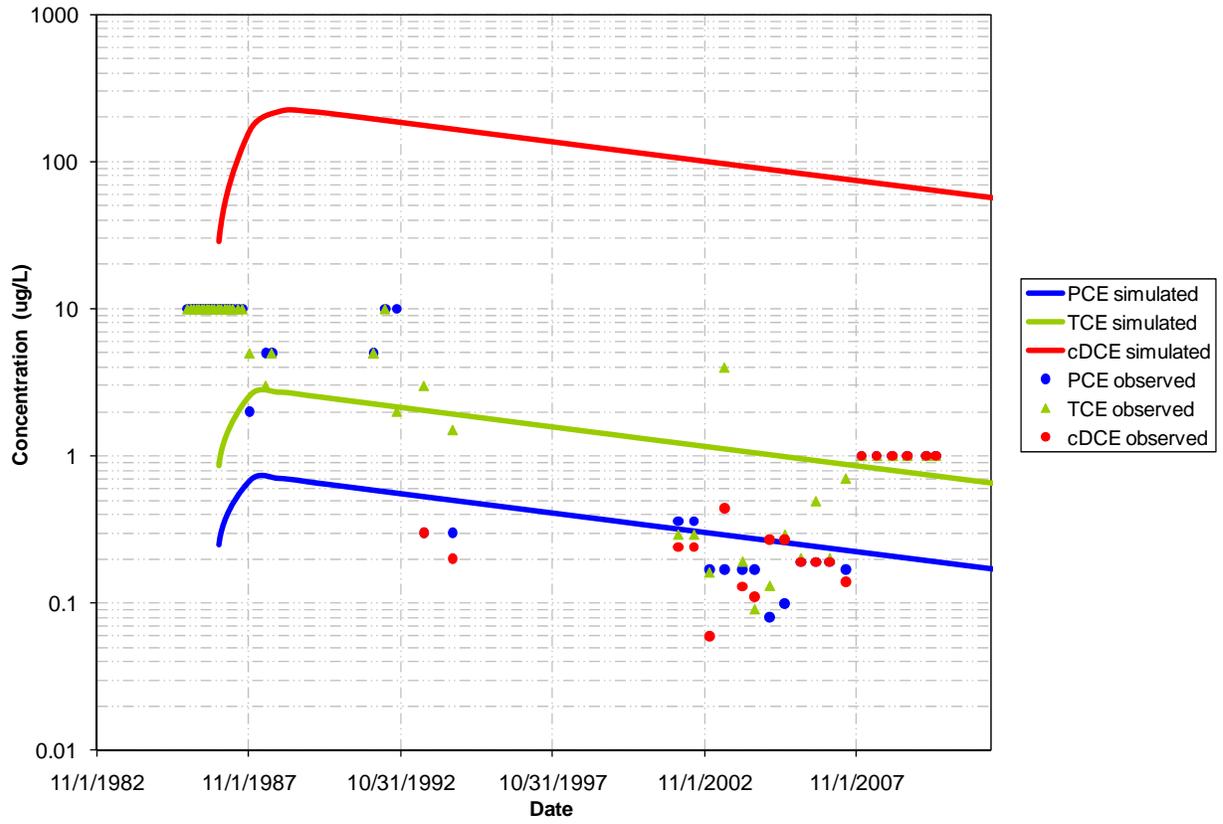


Figure 7. Case R0: simulated and observed concentrations in Well 399-1-8.

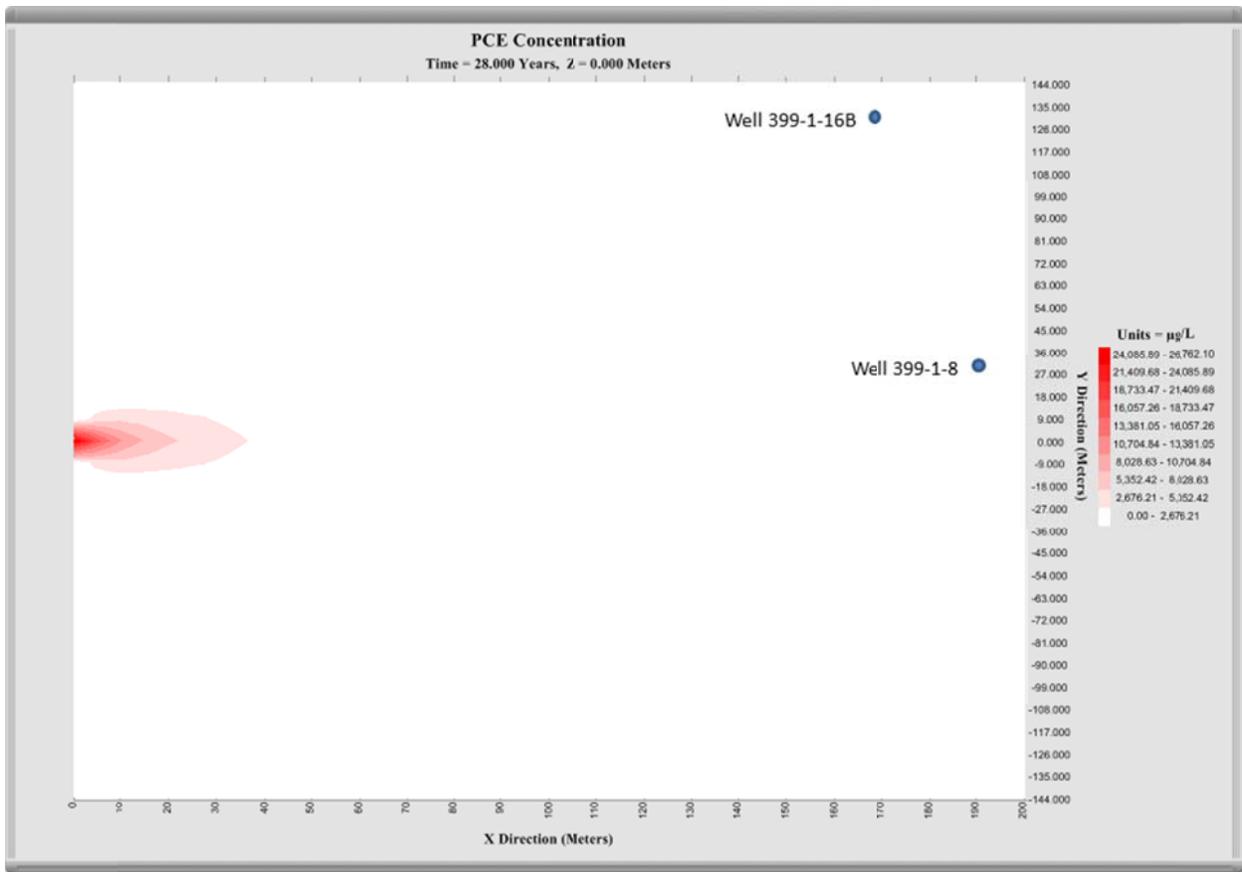


Figure 8. Case R1: simulated PCE concentrations after 28 years.

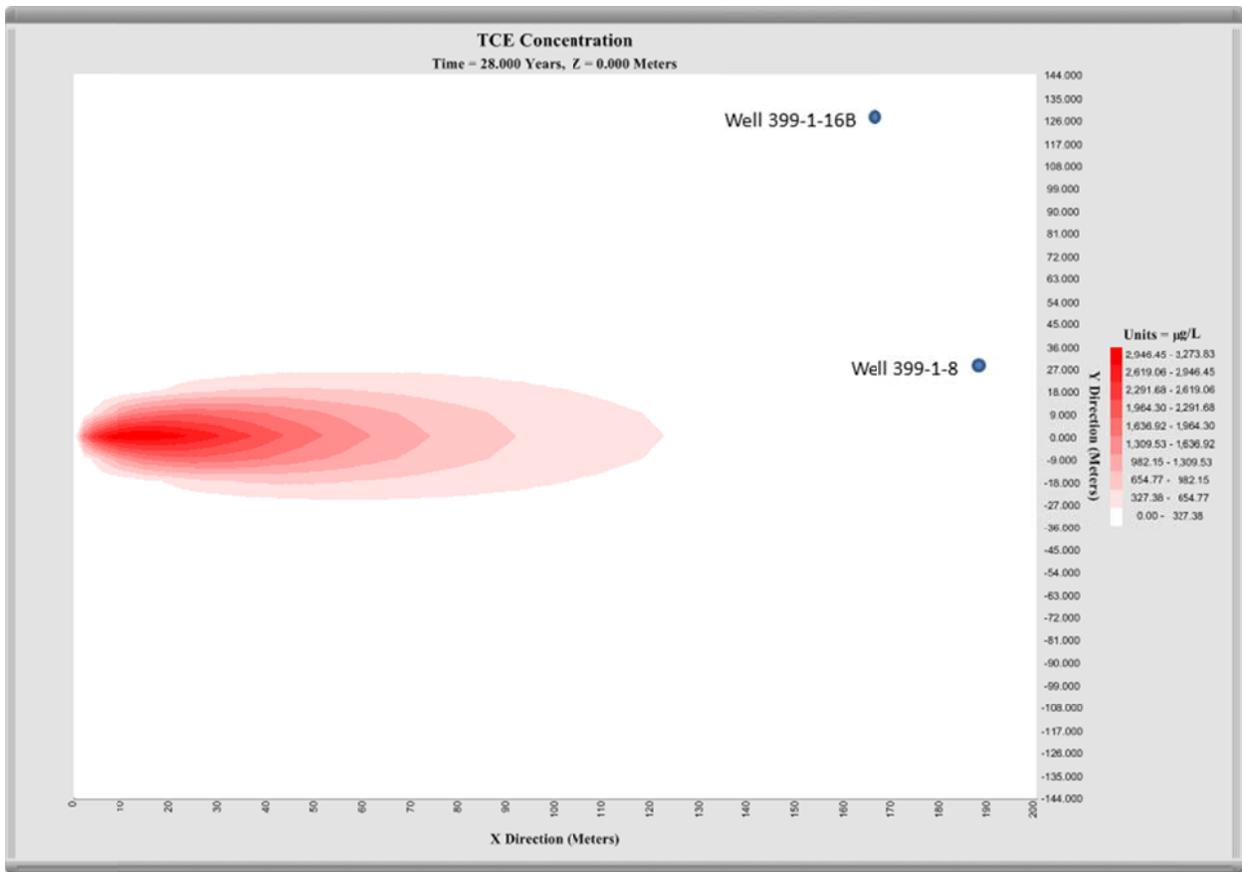


Figure 9. Case R1: simulated TCE concentrations after 28 years.

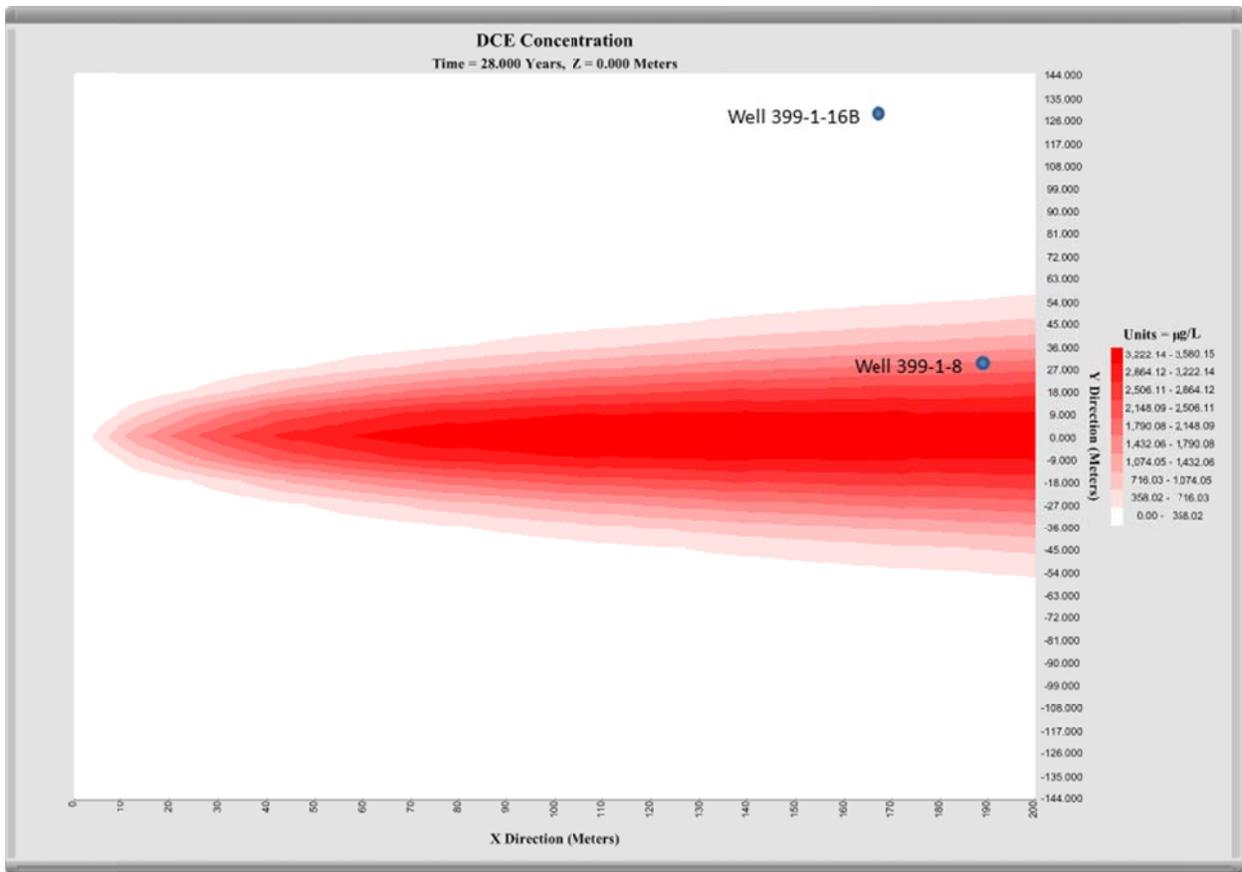


Figure 10. Case R1: simulated TCE concentrations after 28 years.

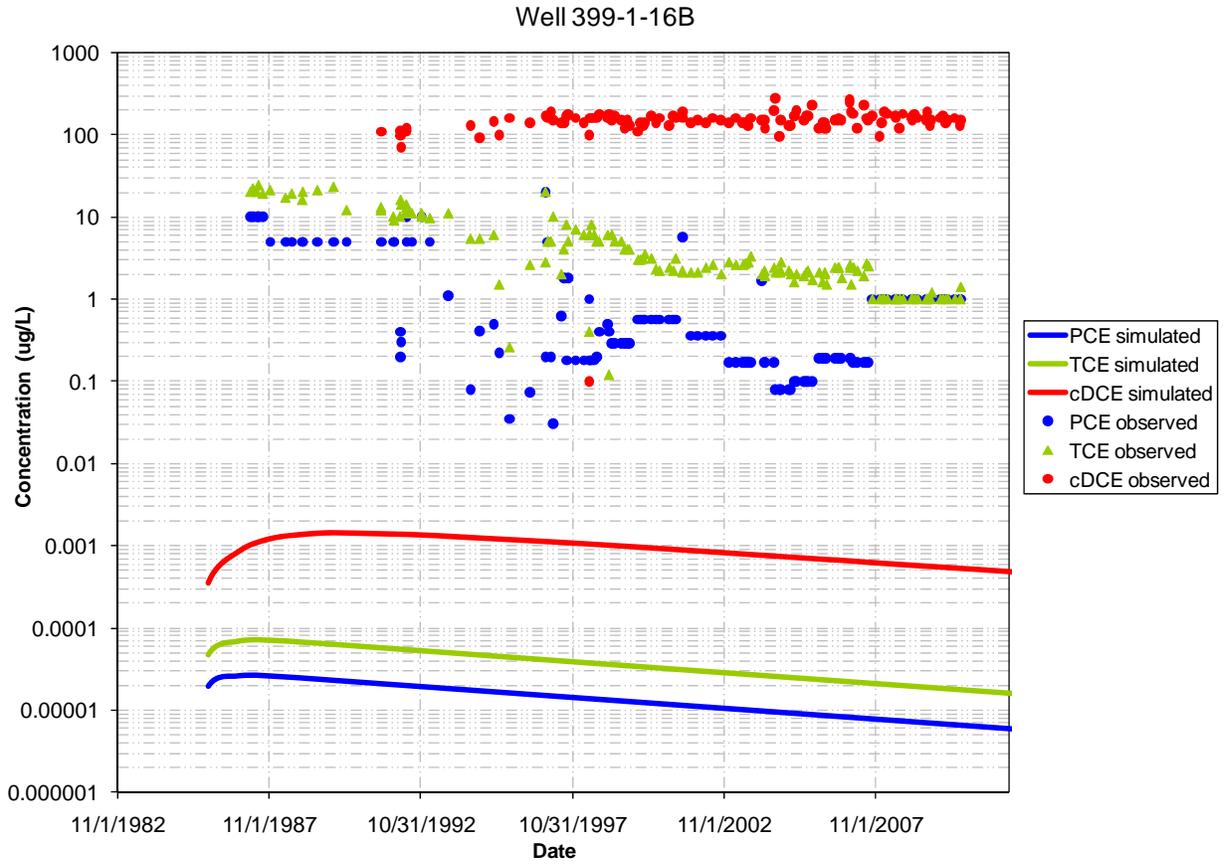


Figure 11. Case R1: simulated and observed concentrations in Well 399-1-16B.

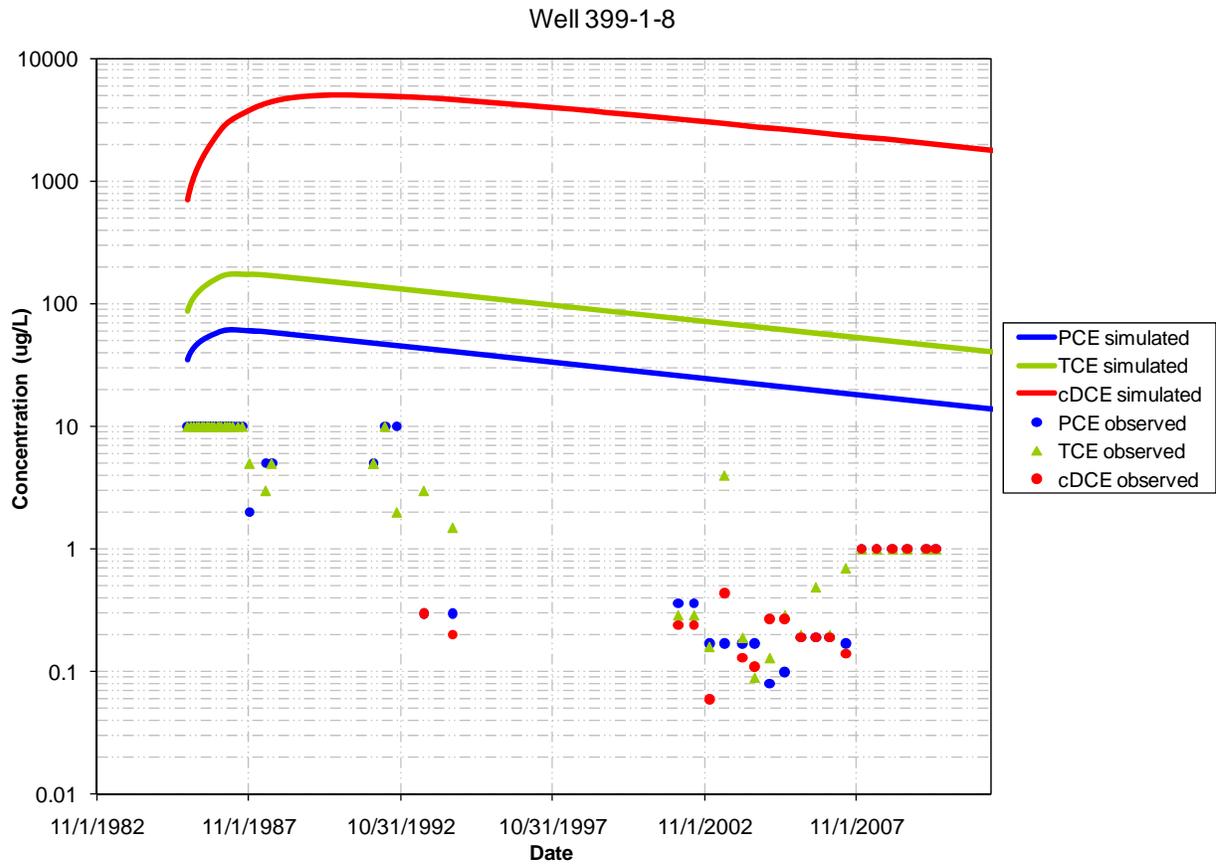


Figure 12. Case R1: simulated and observed concentrations in Well 399-1-8.

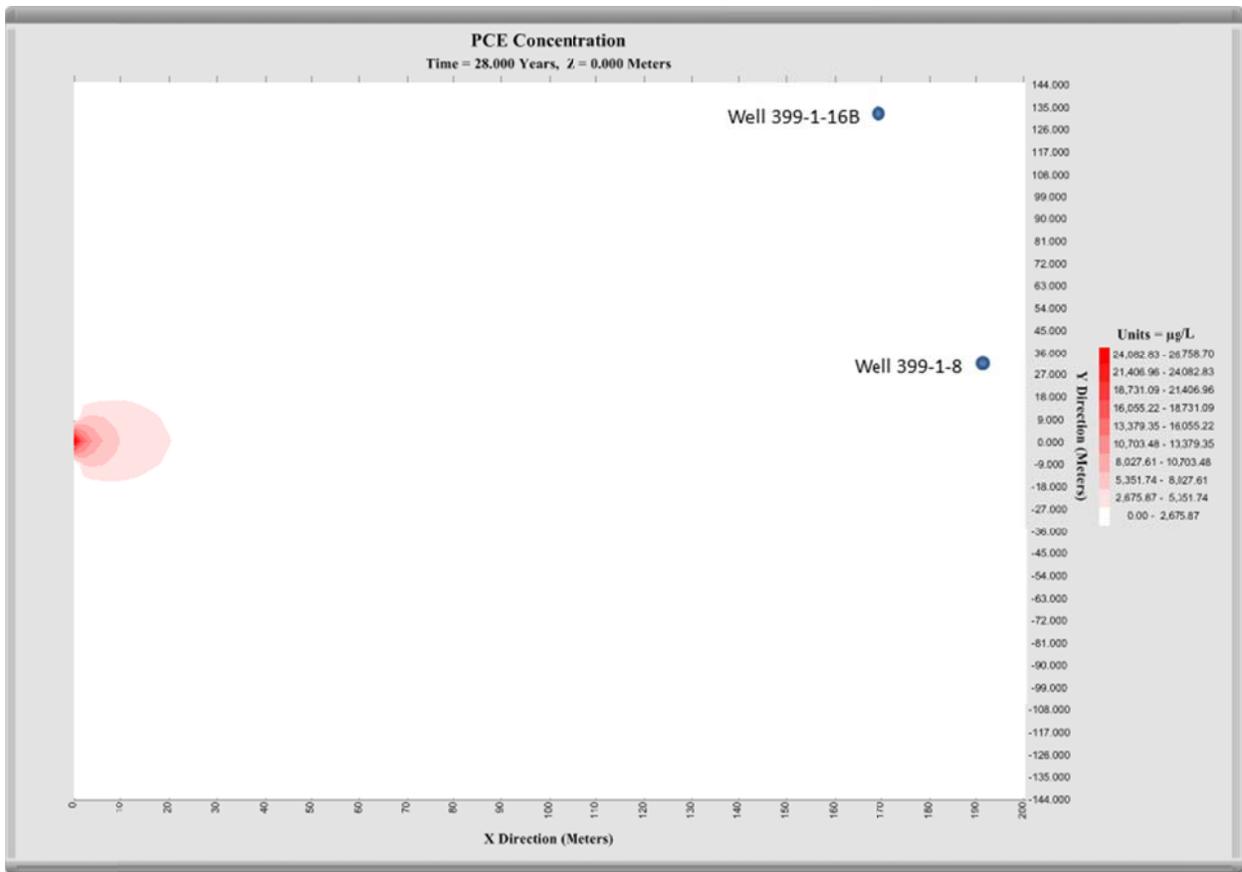


Figure 13. Case R2: simulated PCE concentrations after 28 years.

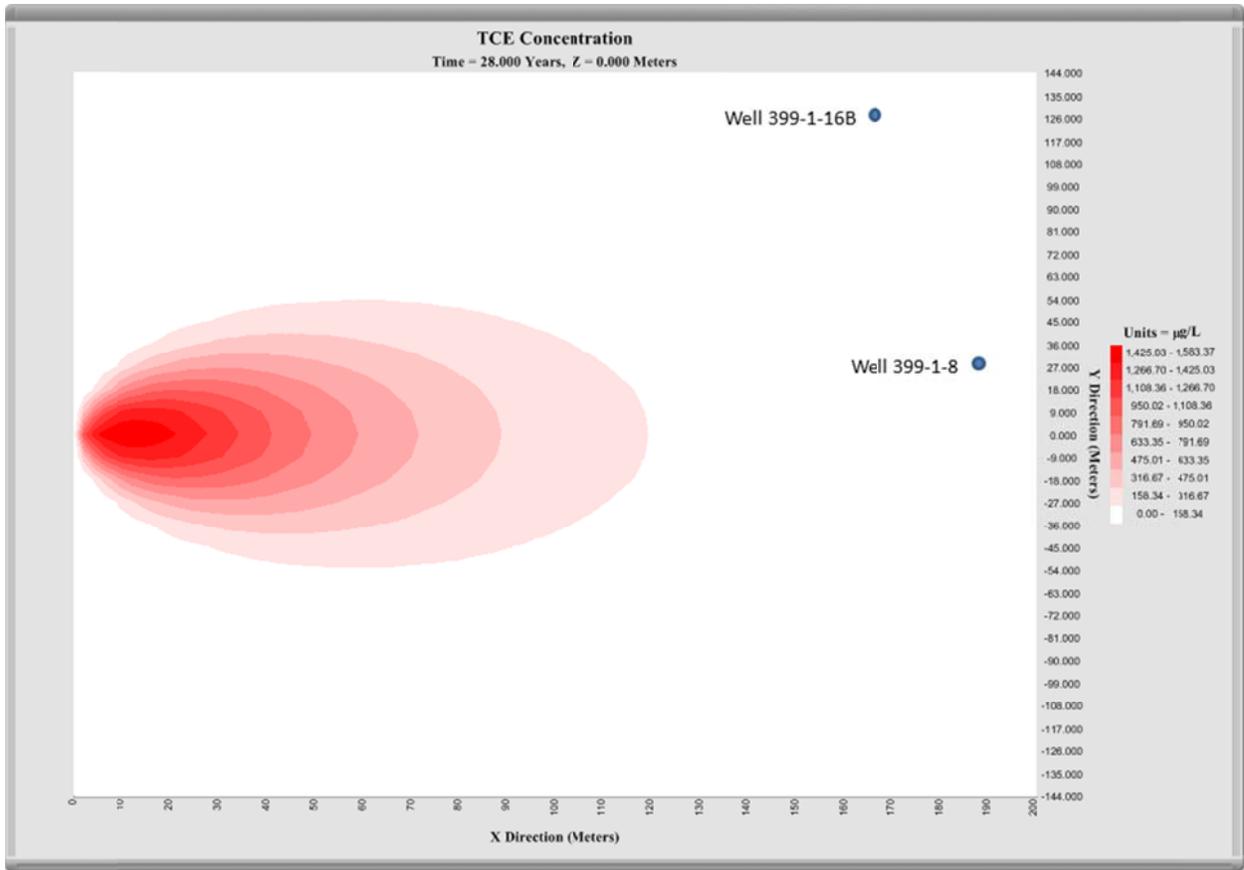


Figure 14. Case R2: simulated TCE concentrations after 28 years.

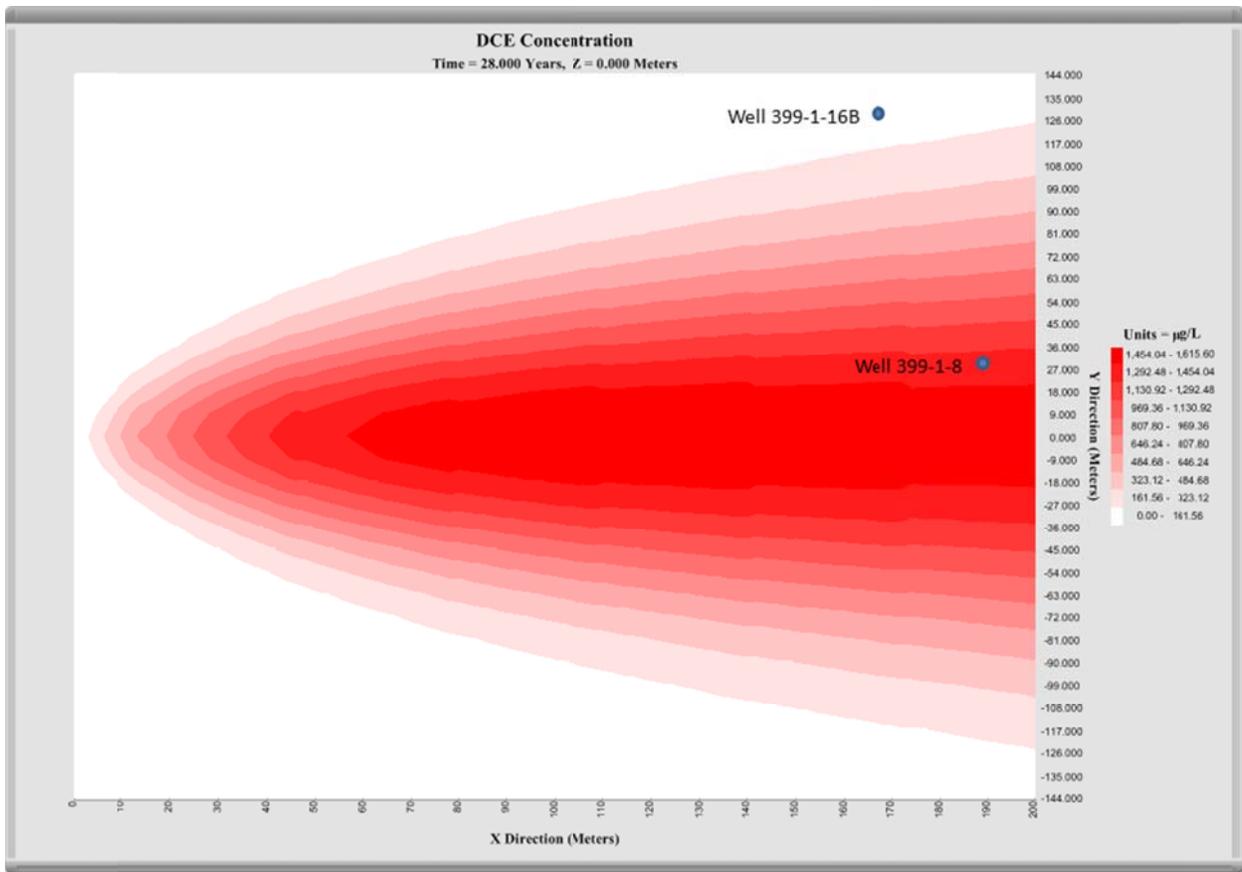


Figure 15. Case R2: simulated cDCE concentrations after 28 years.

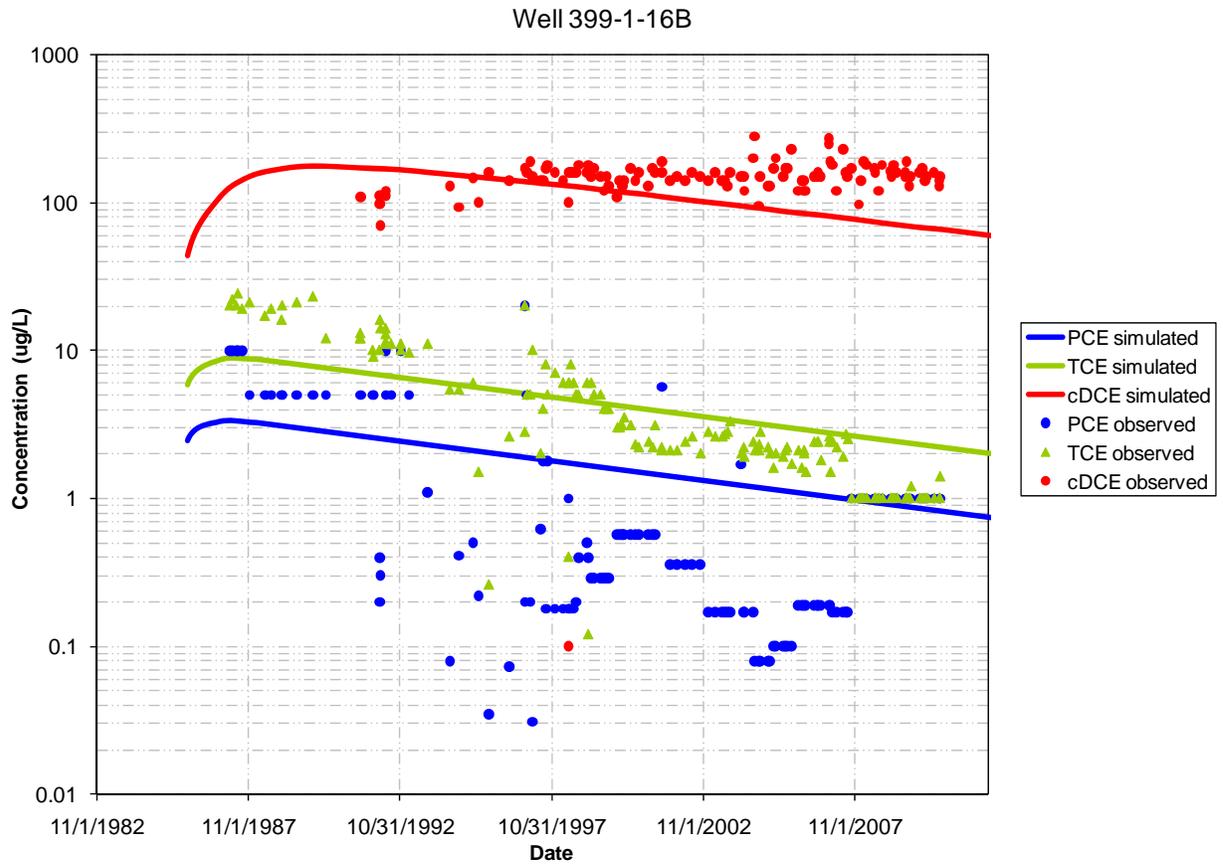


Figure 16. Case R2: simulated and observed concentrations in Well 399-1-16B.

Well 399-1-8

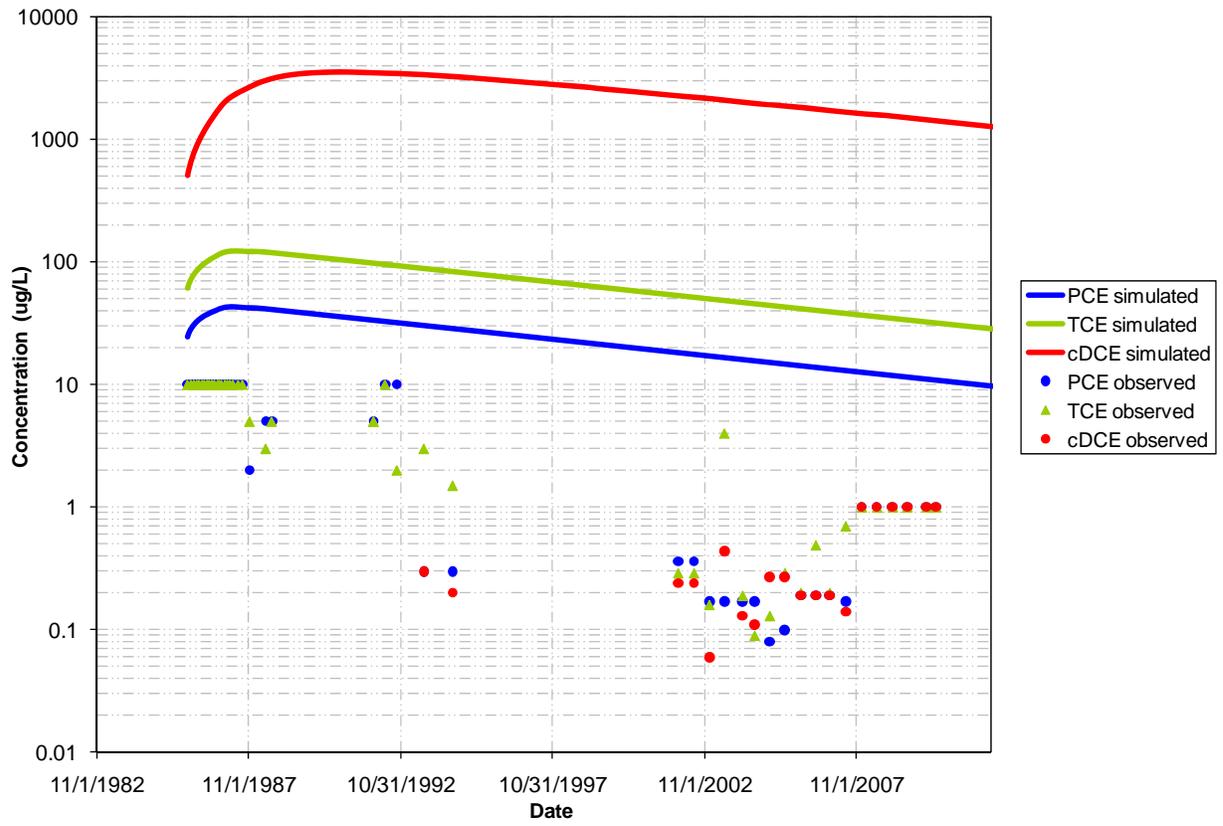


Figure 17. Case R2: simulated and observed concentrations in Well 399-1-8.