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Initial Uncertainty Analysis of Carbon Tetrachloride Contamination and Remediation in the Ringold A and Lower Mud Units at the Central Plateau

September 2025

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U.S. DEPARTMENT
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Summary

The long-term effectiveness of groundwater cleanup at the Hanford Site Central Plateau depends on predictive models that can capture key uncertainties in contaminant fate and transport. Carbon tetrachloride (CCl₄), a persistent and toxic compound, presents particular challenges due to variability in degradation rates, uncertainty in initial plume distribution, and subsurface heterogeneity. These uncertainties directly influence plume persistence, migration pathways, and remedy performance, and thus must be systematically evaluated to support long-term remediation planning.

To address these gaps, a large-scale Monte Carlo analysis was conducted using the Plateau to River (P2R) model framework. The modeling approach parameterized three primary uncertainty factors: (1) degradation rate, (2) initial plume distribution, and (3) hydraulic conductivity. Degradation was represented as a first-order process, with half-lives ranging from 70 to 700 years. Initial plume distributions were created using a geostatistical simulation method (sgsim), which generates many equally plausible versions of how contaminants might be distributed underground. From this, 100 different scenarios were mapped onto the P2R grid. Variability in hydraulic conductivity was represented in a similar way, with 100 scenarios each for the Ringold Lower Mud and Ringold A units (layers 6 and 7), based on fitted exponential variograms and conditioned to well data. In total, more than 1000 realizations were simulated to assess plume behavior under uncertainty.

Results demonstrate that degradation kinetics exert the strongest control over plume persistence: Shorter half-lives produced rapid mass reduction, while longer half-lives yielded persistent plumes with limited attenuation. A nonlinear response was observed, with steep mass reductions at half-lives greater than 200 years and near-linear declines beyond this threshold, reflecting interactions between degradation and pumping. The initial plume distribution strongly influenced early transport patterns, with broader sources generating larger plume footprints, although pump-and-treat operations constrained plume migration to managed areas. By comparison, hydraulic conductivity variability in the Ringold units had only a secondary influence, modifying spreading behavior without altering the dominant migration pathways governed by source configuration and hydraulic controls.

Overall, the analysis highlights that uncertainty in degradation rate and initial plume configuration are the primary drivers of variability in plume predictions, while conductivity heterogeneity plays a limited role. These findings underscore the need for improved site-specific data on degradation processes and source characterization to enhance the reliability of long-term performance assessments and to better inform remedial decision-making at the Central Plateau.

Introduction

Effective cleanup of the Hanford Site Central Plateau requires predictive groundwater models that can guide decision-making by clarifying contaminant behavior, supporting the design of remediation

strategies, and ensuring efficient use of resources. Among the contaminants of concern, carbon tetrachloride (CCl₄) presents particular challenges. Its plume extends into the deeper aquifers of the Central Plateau, specifically within the Ringold A and Ringold Lower Mud units, where modeling efforts are complicated by significant uncertainties. These uncertainties arise from three of the major sources: (1) the distribution of the CCl₄ plume, shaped by complex geologic and hydrologic conditions; (2) the heterogeneous hydraulic properties of the aquifers, including permeability, porosity, and uncertain stratigraphic boundaries; and (3) the poorly constrained degradation rate of CCl₄, which can vary widely under different geochemical conditions, especially in anaerobic settings.

To address these challenges, we conducted an integrated uncertainty quantification study using a large ensemble of Monte Carlo simulations with the Plateau to River (P2R) model framework. More than 1000 realizations were generated to evaluate the combined impacts of plume distribution, aquifer heterogeneity, and contaminant degradation on plume migration and remedy performance. The degradation of CCl₄ was represented as a first-order decay process, with rate constants derived from reported half-lives ranging from 70 to 700 years. For plume distributions, 100 stochastic realizations were generated using a geostatistical simulation method (sgsim) based on field observations, while aquifer heterogeneity was captured through 100 hydraulic conductivity realizations for each of the Ringold Lower Mud and Ringold A units. These geostatistical simulations were carried out using the GSLIB software package (Deutsch and Journel, 1998). This integrated approach provides a robust basis for assessing uncertainty in groundwater flow and transport, and for evaluating the resilience of potential remediation strategies.

The following sections describe the general workflow for generating, processing, and integrating these realizations and present representative plume and hydraulic conductivity realizations to illustrate the variability encompassed within the Monte Carlo framework.

Model Setup

The P2R model (Budge and Nichols 2020) was configured to simulate groundwater flow and contaminant transport within the Central Plateau domain. Hydraulic properties were specified by layer, with stochastic conductivity realizations applied to the Ringold Lower Mud and Ringold A units (layers 6 and 7). Initial plume distributions generated by sgsim were mapped onto the model grid, and contaminant degradation was represented as a first-order decay process using rate constants derived from reported half-lives. Stress periods and simulation lengths were kept as-is (the same for each realization) to capture long-term plume migration and attenuation.

Parameterization of Contaminant Degradation Kinetics

The contaminant degradation process was parameterized as a first-order decay, where the rate constant k is related to the half-life ($t_{1/2}$) by:

$$k = \ln 2 / (t_{1/2} * 365) \quad (1)$$

Half-life values for carbon tetrachloride were bracketed from 70 to 700 years to represent plausible site conditions. The lower bound (70 years) is anchored by Hanford-specific kinetics reported in Amonette et al. (2008), whereas the upper bound (700 years) provides the baseline used in the native P2R configuration (~630 years). Ten values were sampled at uniform 70-year intervals across this range. Each half-life was converted to a corresponding first-order rate constant (k) using Eq. (1), with the results summarized in Table 1

Table 1. Contaminant degradation rates used in the simulations.

$t_{1/2}$ [year]	70	140	210	280	350	420	490	560	630	700
k [1/day]	2.71e-5	1.35e-5	9.04e-6	6.78e-6	5.43e-6	4.52e-6	3.87e-6	3.39e-6	3.01e-6	2.71e-6

Realizations of hydraulic conductivity fields

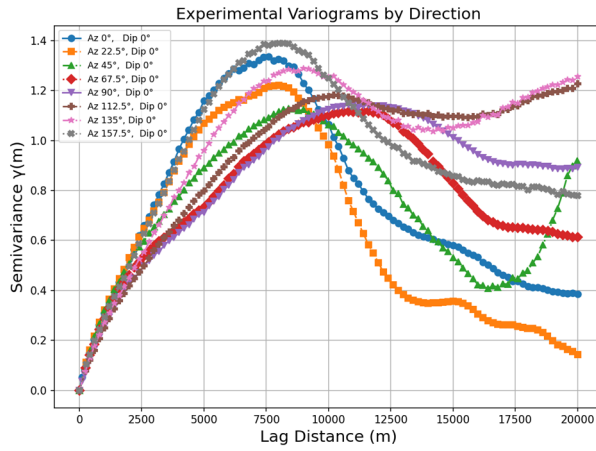
The generation of geostatistical realizations for the P2R model began with data preparation, which involved compiling hydraulic conductivity values from the existing P2R configuration, assembling their spatial coordinates, and performing quality control. Outliers were trimmed or capped, and the dataset was validated for suitability in geostatistical analysis.

A normal-score transformation (nscore) was then applied to the hydraulic conductivity data, converting raw values into a standard normal distribution (mean = 0, variance = 1). This transformation stabilized variance and allowed the use of Gaussian-based geostatistical methods. Both the transformed values and the back-transform lookup table were retained so that simulation results could later be mapped back into the original conductivity space for use in the P2R model.

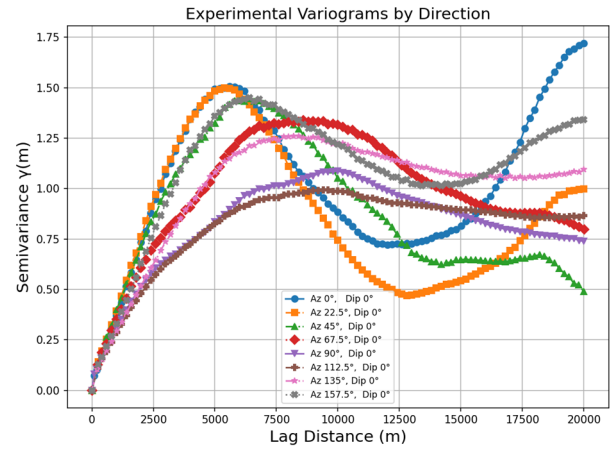
Next, experimental variograms (gamv) were computed directly from the P2R conductivity fields to quantify spatial continuity. Directional variograms were calculated at multiple lags, producing variogram clouds and averages that revealed anisotropy and correlation lengths relevant to subsurface heterogeneity. The results, shown in Figure 1(a) and (b), indicate that 90° and 112.5° are the primary directions of spatial continuity in the horizontal plane, for layers 6 and 7, respectively, which were subsequently adopted for model fitting and stochastic simulation.

The variograms were then fitted with theoretical models (vmodel) – spherical, exponential, or Gaussian – by calibrating nugget, sill, and range parameters to represent the spatial structure of the P2R conductivity fields. The fitted models were compared against the experimental variograms in the major directions, as shown in Figure 1(c) and (d). Among the candidate models, the exponential function provided the best fit and was therefore selected as the covariance model for subsequent stochastic simulations.

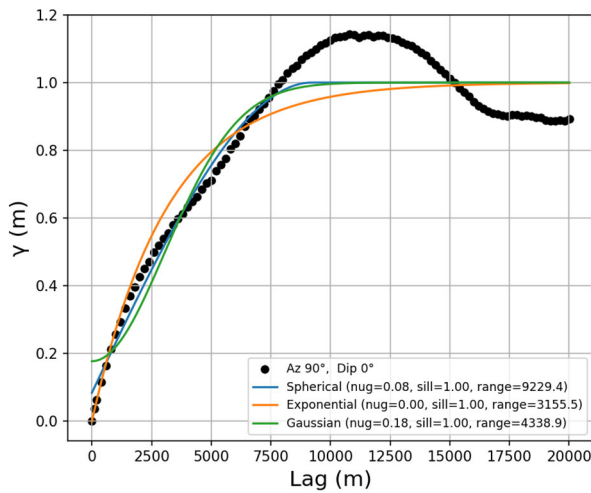
Finally, stochastic hydraulic conductivity fields for the Ringold Lower Mud and Ringold A units (layers 6 and 7 of the P2R model) were generated using sgsim with variogram parameters derived from the exponential model. Conditioning to monitoring well data ensured that local observations were honored while preserving the broader heterogeneity defined by the variogram. Figure 2 shows representative realizations illustrating the range of spatial variability in both hydrostratigraphic units.



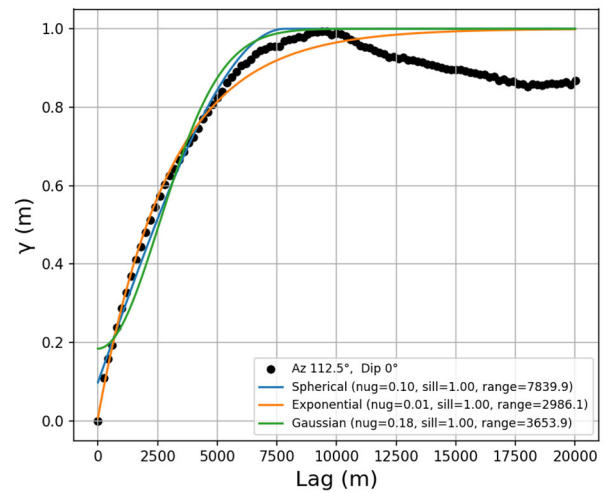
(a) Experimental variograms at layer 6



(b) Experimental variograms at layer 7



(c) Fitted models for the major direction in layer 6



(d) Fitted models for the major direction in layer 7

Figure 1. Experimental variograms of hydraulic conductivity for (a) layer 6 and (b) layer 7 of the P2R model. Fitted theoretical models (spherical, exponential, Gaussian) plotted against the experimental variogram along the principal directions of anisotropy for (c) layer 6 and (d) layer 7.

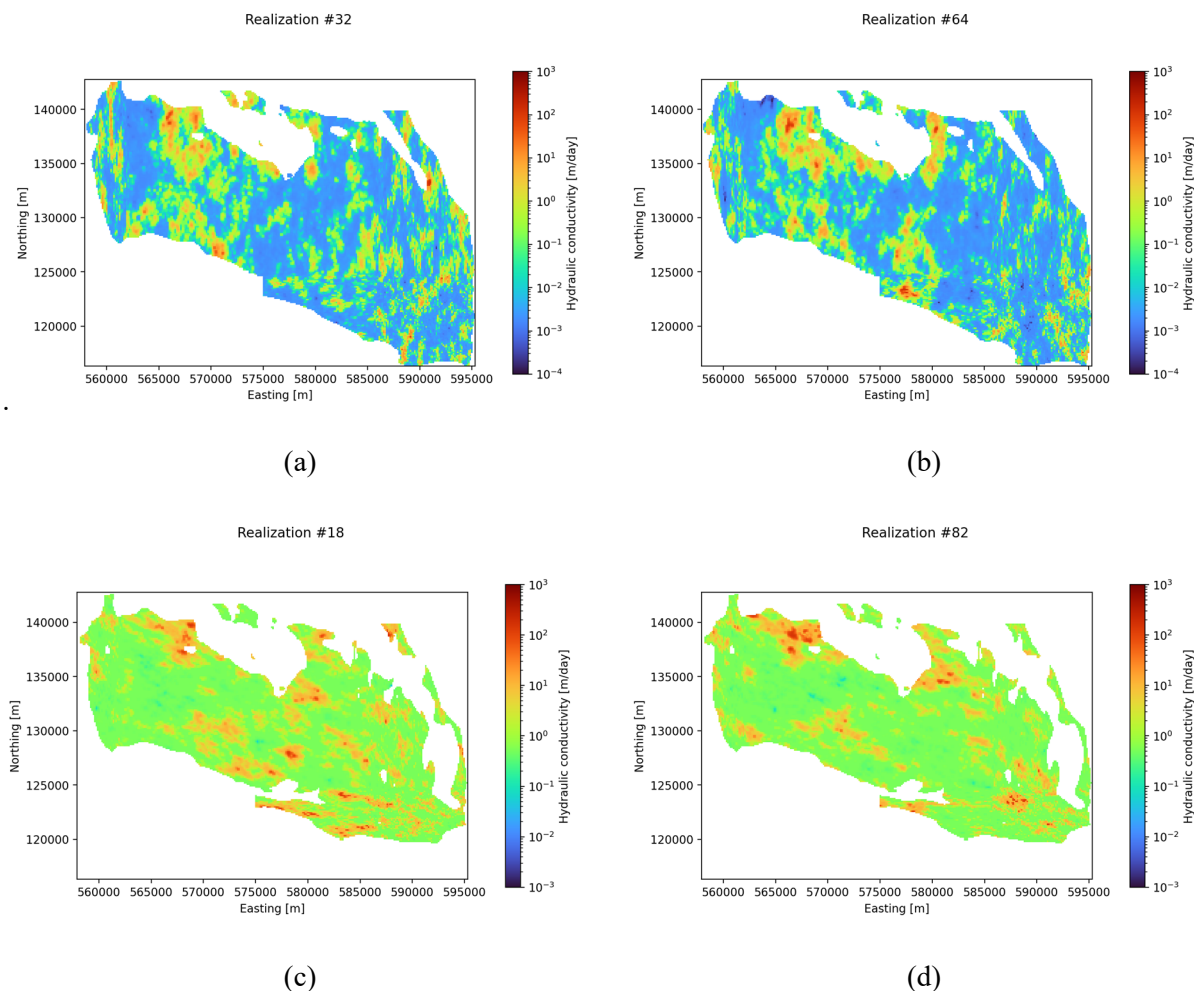


Figure 2. Examples of realizations for the hydraulic conductivities at layer 6 (a) and (b) and layer 7 (c) and (d).

Plume Realizations

Initial plume distributions were generated using the sgsim algorithm, following the same geostatistical workflow applied to hydraulic conductivity. The source dataset was obtained from SSPA¹, and 100 stochastic plume realizations were produced. Conditioning to monitoring data ensured that observed plume characteristics were honored, while the mapping of realizations onto the P2R model grid preserved spatial variability consistent with site-specific characterization. Figure 3 shows representative examples.

¹ SSPA = S. S. Papadopoulos and Associates, Inc., Environmental and Water Resource Consultants (<https://sspa.com/>)

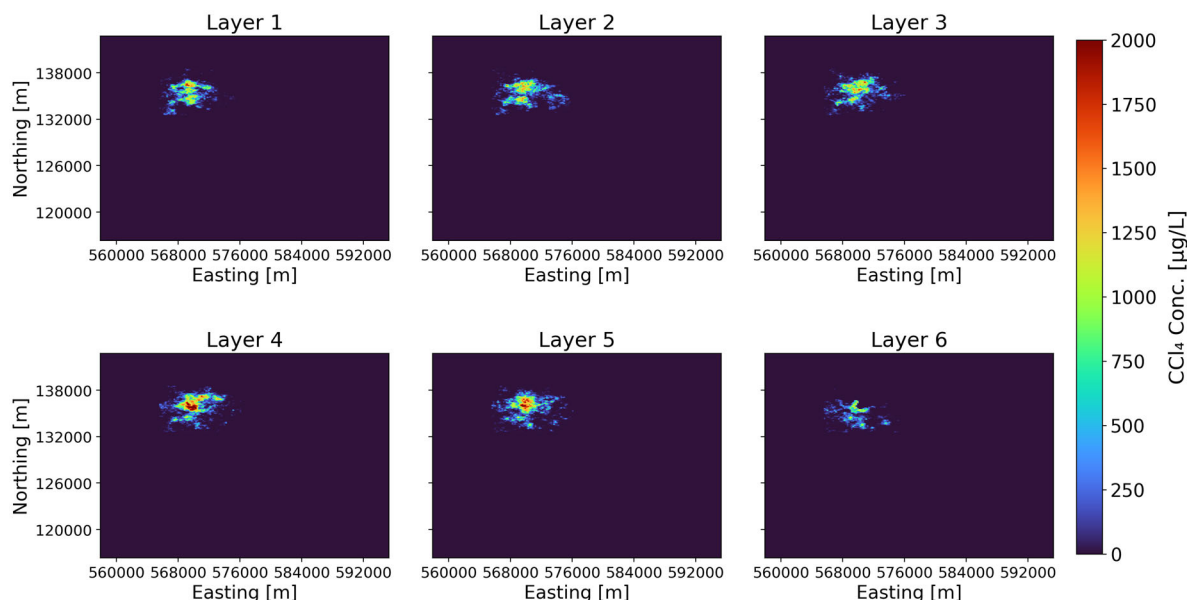


Figure 3. An example of the realizations for the initial CCl_4 plumes mapped onto P2R model domain.

Results and Discussion

The Monte Carlo simulation ensemble provided a comprehensive basis for evaluating the combined effects of degradation kinetics, initial plume configuration, and hydraulic conductivity variability on plume evolution within the P2R model framework. More than 1000 realizations were analyzed to assess uncertainty in predictions of contaminant fate and transport.

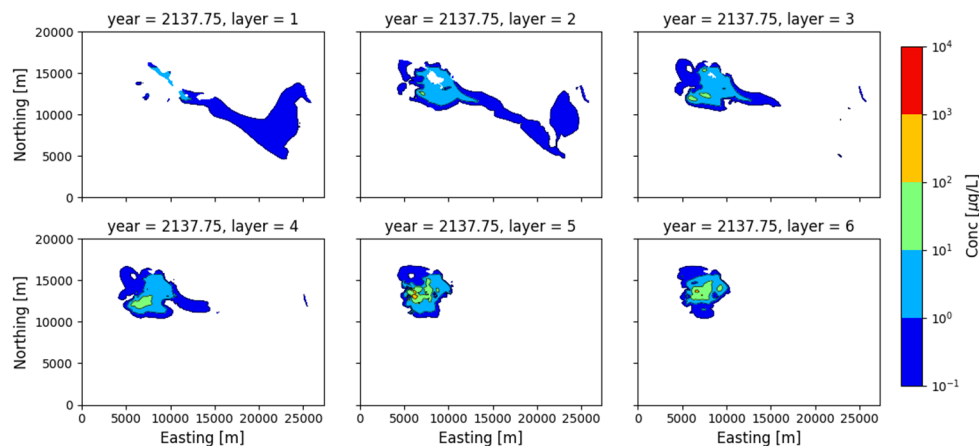
Results are presented in three parts. First, the impact of varying degradation half-lives on plume persistence and mass reduction is evaluated. Second, the influence of stochastic plume realizations on contaminant migration pathways is examined. Third, the role of hydraulic conductivity heterogeneity in the Ringold Lower Mud and Ringold A units is analyzed, with emphasis on its control over the overall transport behaviors of the contaminant plume.

Comparisons across realizations highlight the relative importance of each uncertainty factor and their interactions. Preliminary statistical analyses, including ensemble averages, variance fields, and probability exceedance maps, are used to quantify uncertainty and identify trends relevant to remedial performance.

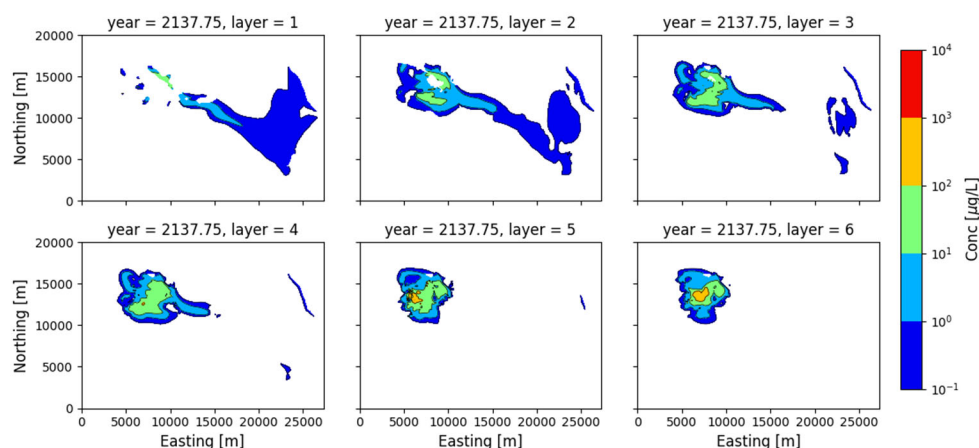
Effect of Degradation Rates

To evaluate the role of degradation kinetics, simulations were conducted in which only the first-order decay rate (k) was varied, while all other parameters and boundary conditions were fixed to the baseline P2R configuration. Decay rates were derived from half-lives ranging between 70 and 700 years, with 10 representative values selected at uniform 70-year increments, including the baseline half-life of ~630 years.

Figure 4 shows plume distributions at the end of the simulation for layers 1–6 for the cases corresponding to the smallest and largest half-lives. The overall plume shape did not change significantly across these scenarios; however, the plume magnitude exhibited strong sensitivity to the decay rate. Specifically, plumes simulated with shorter half-lives displayed noticeably reduced concentrations compared to those with longer half-lives.



(a)



(b)

Figure 4. CCl_4 plume distributions at layers 1~6 at year 2137 for cases with degradation rate at (a) $2.71\text{e-}5$ [1/day] and (b) $2.71\text{e-}6$ [1/day].

The total remaining mass of carbon tetrachloride in the domain was extracted from the simulation results and the results are plotted in Figure 5. As expected, a greater fraction of mass persisted in the domain under longer half-life scenarios. Interestingly, Figure 4 reveals a nonlinear relationship: When the half-life exceeds ~ 200 years, the remaining mass follows an approximately linear trend with increasing half-life, whereas for half-lives shorter than 200 years, the mass decreases much more rapidly. This nonlinear behavior may be related to the influence of pumping activities and associated hydraulic gradients, which enhance advective removal and plume flushing in cases with faster degradation.

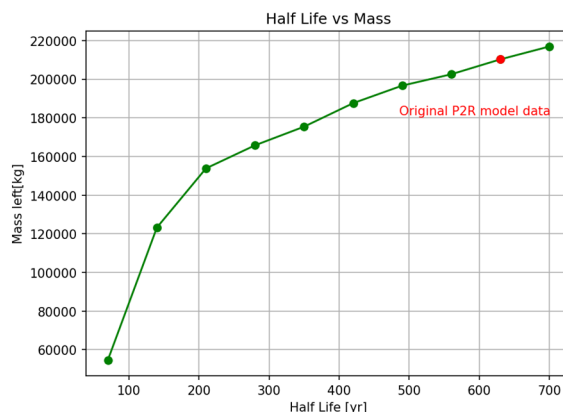


Figure 5. Relationship between CCl_4 half-life (degradation rate) and total mass remaining in the model domain at the end of simulation (year 2137).

Effect of Initial Plume Distributions

To assess the impact of source configuration uncertainty, 100 stochastic plume realizations were generated using sgsim and mapped onto the P2R grid, as described previously. All other model settings, including hydraulic conductivity and degradation rate, were maintained at their baseline values to isolate the effect of plume initialization.

Simulation results show that the initial plume distribution exerts a significant influence on transport behavior, particularly on predicted concentration patterns and the spatial extent of the plume in the first several hundred years. Plumes initialized with broader or more connected source zones tended to migrate more rapidly and sustain larger areal footprints, while those with more localized sources displayed limited spreading and lower concentrations downgradient. However, due to the pump-and-treat activities in this region, the major plumes remained largely constrained within a certain area, limiting the degree of divergence among realizations at later times.

Figure 6 shows examples of plume distributions at the end of the simulation (year 2137.75), demonstrating the influence of initial plume variability. To provide a quantitative measure of plume migration, spatial moments of plume concentrations (Rockhold and He 2022) were computed. The first spatial moment (plume centers of mass) was plotted in the model domain to track migration pathways. These results are shown in Figure 7, where plume tracks from different realizations are represented with a color gradient: Blue corresponds to earlier times (2015), while red corresponds to later times (2137.75). For comparison, the baseline case from the original P2R model is also shown as a solid thick red line. The tracks illustrate variability in plume migration among realizations while also highlighting the strong hydraulic control imposed by regional flow and pump-and-treat operations, which channel plume movement along preferred directions and limit spreading beyond the managed area.

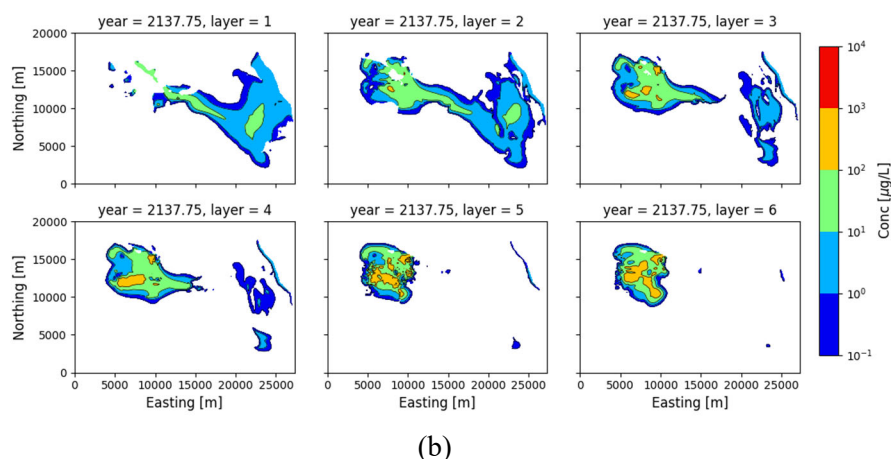
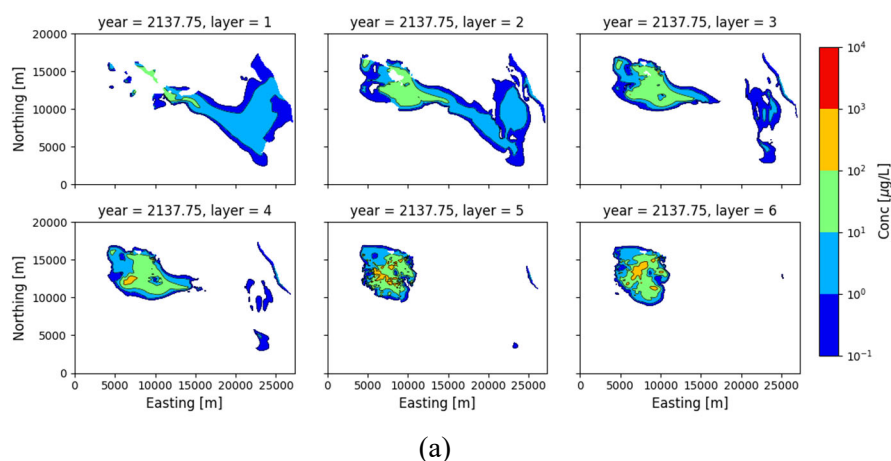


Figure 6. CCl_4 plume distributions at layers 1~6 at year 2137 using different initial plume realizations: (a) and (b) are two example realizations.

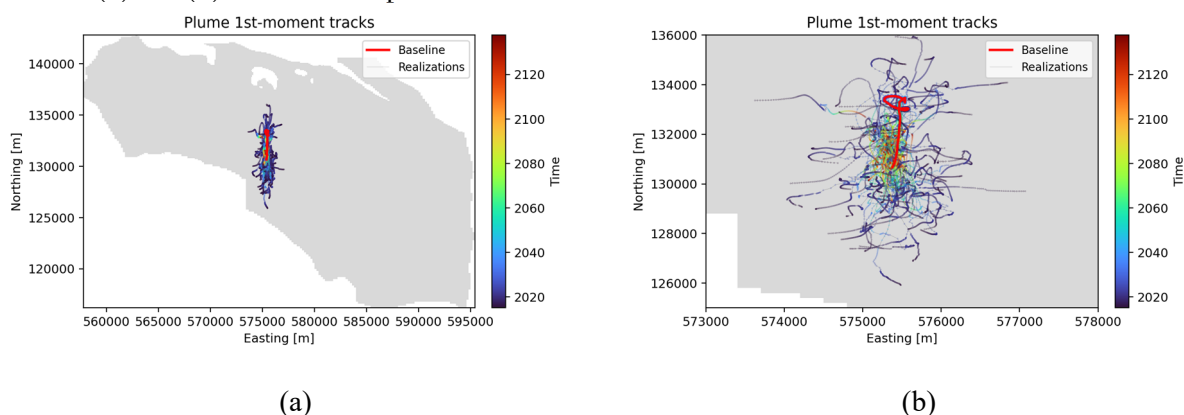


Figure 7. First spatial moments of CCl_4 plume concentrations from 100 realizations and the baseline case (original P2R model); (a) the full P2R model domain and (b) a zoomed-in view.

Effect of Hydraulic Conductivity

The realizations of hydraulic conductivity were randomly paired with the initial plume realizations to assess their combined effects. First, spatial moments (plume centers of mass) were computed and plotted to evaluate the influence of conductivity variability. The resulting migration pathways are shown in Figure 8 and are broadly similar to those in Figure 7, which were determined solely by initial plume variability.

This outcome suggests that the initial plume configuration primarily controls the overall migration pathways, while the hydraulic conductivities in layers 6 and 7 exert only a secondary influence, modifying plume behavior to some extent but not altering the dominant transport directions imposed by regional flow and pump-and-treat operations.

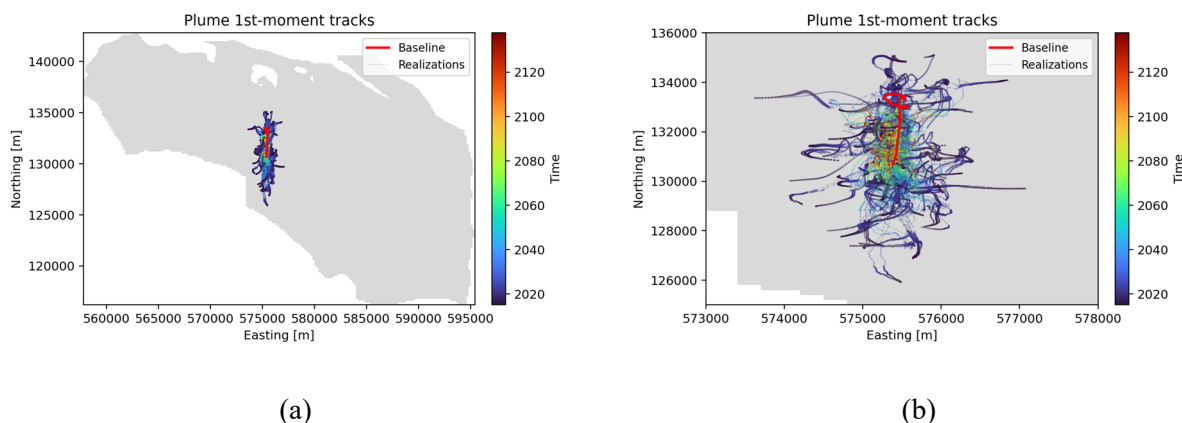


Figure 8. First spatial moments of CCl_4 plume concentrations from more than 1,000 realizations based on random pairings of hydraulic conductivity fields and initial plume distributions: (a) full P2R model domain and (b) zoomed-in view.

Remaining Evaluations

The results from the Monte Carlo analyses demonstrated that CCl_4 degradation rate and initial plume distribution are dominant factors influencing plume persistence and transport, while hydraulic conductivity exerts a secondary influence under current site conditions. Building on these findings, the next phase of the evaluation will include pumping schedule as an additional uncertainty factor, and will focus on more robust, quantitative evaluation of factor influences.

- **Robust Quantification of Factor Impacts:** Ensemble analyses will be extended to systematically evaluate the effects of degradation rate, initial plume distribution, hydraulic conductivity, and pumping schedule on key model outputs. Metrics such as plume mass, probability of concentration exceedance, and spatial moment variability will be used to quantify the relative magnitude of uncertainty associated with each factor.
- **Cross-Correlation Analysis:** The combined and interacting effects of these factors will be explicitly examined – for example, the interplay between pumping schedules and degradation kinetics on plume longevity or how conductivity variability modifies plume responses to different pumping regimes. Cross-correlation and variance decomposition methods (e.g., Sobol indices, ANOVA-style sensitivity analysis) will be applied to partition uncertainty contributions and identify synergistic or offsetting effects.

- **Factor Ranking and Sensitivity Prioritization:** A quantitative ranking of the three uncertainty factors will be developed to identify which factor exerts the greatest control over long-term plume predictions. Rankings will be based on sensitivity of plume longevity, contaminant mass remaining, plume extent, and compliance-point concentrations. This ranking will guide prioritization of future field investigations and model refinements.
- **Integration into Remedial Performance Assessment:** By including pumping schedules as a decision-variable factor, the analysis will provide insight into the robustness of current pump-and-treat operations and potential optimization strategies. Probability-based performance metrics (e.g., likelihood of containment, reduction in plume footprint under alternative pumping scenarios) will be developed to support adaptive remedy planning.

Collectively, this work will extend the current study by moving from qualitative observations to quantitative, multi-factor analysis, producing cross-correlated uncertainty assessments and factor rankings that directly inform site management and long-term remediation strategies.

Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory Nuclear Quality Assurance Program (NQAP). The NQAP complies with the DOE Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application*, as its consensus standard and NQA-1-2012, Subpart 4.2.1 as the basis for its graded approach to quality.

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