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Pacific Northwest
National Laboratory
Operated by Battelle for the
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Recent Site-Wide Transport Modeling Related to the Carbon Tetrachloride Plume at the Hanford Site

M. P. Bergeron
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September 2004

Prepared for the U.S. Department of Energy
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Executive Summary

The Hanford Carbon Tetrachloride Innovative Treatment Remediation Demonstration (ITRD) Program provided an initial evaluation of the nature and extent of carbon tetrachloride contamination in the unconfined aquifer in the 200 West Area of the Hanford Site (Truex et al. 2001). After the ITRD program ended, subsequent studies more closely examined the transport of carbon tetrachloride (CCl4) in the unconfined aquifer system. Those studies were undertaken to support strategic planning and provide guidance for the more robust modeling needed to obtain a final record of decision (ROD) for the carbon tetrachloride plume. This report documents the technical approach and results of those studies.

The ITRD modeling study examined carbon tetrachloride concentrations at an arbitrary boundary between the 200 East and 200 West Areas (Truex et al. 2001). After that work was completed, questions arose concerning the concentrations reaching the Columbia River as well as about the impact of remediation options involving source removal or absence. To address those questions, additional modeling studies were conducted using the site-wide groundwater model (SGM) with the modeling domain extended to the Columbia River. This modeling analysis resulted in the following conclusions:

With the assumption of a continuing source with no sorption or abiotic degradation (Case 1a), we observed:

- Development and migration of a substantial carbon tetrachloride plume from source areas in the 200 West Area to the Columbia River. Predicted concentrations reached about 200 µg/L at the arbitrary boundary chosen for this analysis and about 34 µg/L along the Columbia River during the 1000-year period of analysis. Both of these values exceed the benchmark maximum concentration limit (MCL) of 5 µg/L
- The equilibrium carbon tetrachloride release estimate in the source area was about 73 kg/yr.
- Initial conditions yielded an initial mass of about 542 kg in the aquifer, which grew to 58,050 kg after 1000 years (the year 3000).

With the assumption of a continuing source with median value estimates of sorption and abiotic degradation (Case 1b), we observed:

- Limited development and migration of a carbon tetrachloride plume from source areas within the general vicinity of the 200 West Area. Predicted concentrations reached about 4.5 µg/L at the arbitrary boundary chosen for this analysis. Concentrations at discharge areas along the Columbia River did not reach any substantial levels during the 1000-year period of analysis.
- The combination of sorption and abiotic degradation rate significantly limits aquifer source loading and the aquifer area and volume affected by the carbon tetrachloride plume migration. The more important parameter of the two is the abiotic degradation rate because retardation alone will not reduce concentrations other than through dilution because of hydrodynamic dispersivity.

Without a continuing source of carbon tetrachloride and no sorption or abiotic degradation, we observed results that were very similar whether the source area with the highest concentrations in the

plume (i.e., above 3000 µg/L) was assumed to be removed from the aquifer (Case 2) or the existing plume was considered an initial condition of aquifer contamination (Case 3). In both cases we observed:

- A more limited development and migration of a carbon tetrachloride plume outside the 200 West Area toward the Columbia River than with the continuing source assumption evaluated in Case 1a.
- A predicted concentration profile reaching about 6.5 µg/L at the arbitrary boundary over a period of about 600 years between 2100 and 2700. This contrasts with the rapidly rising and plateauing profile of carbon tetrachloride concentrations predicted under the continuing source assumption evaluated in Case 1a.
- A concentration profile at discharge areas along the Columbia River that is well below the benchmark MCL level of 5 µg/L during the 1000-year period of analysis.

In summary, the results of these analyses illustrate the importance of developing field-scale estimates of K_d and K_a for carbon tetrachloride. With K_d and K_a of zero, carbon tetrachloride concentrations will exceed the compliance limit of 5 µg/L outside the 200 Area Plateau waste management area, and the aquifer source loading and area of the aquifer affected will continue to grow until river arrival rates equal source release rates of an estimated 33 kg/yr. Results of this modeling analysis show that natural attenuation parameters K_d and K_a are critical (especially K_a) in predicting the future movement of carbon tetrachloride from the 200 West Area. Results also show the significant change in predictions between continual source release from the vadose zone and complete source removal.

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1.0 Introduction

The Hanford Carbon Tetrachloride Innovative Treatment Remediation Demonstration (ITRD) Program provided an initial evaluation of the nature and extent of carbon tetrachloride contamination in the unconfined aquifer in the 200 West Area of the Hanford Site (Truex et al. 2001). After the ITRD program ended, subsequent studies more closely examined the transport of carbon tetrachloride (CCl4) in the unconfined aquifer system. Those studies were undertaken to support strategic planning and provide guidance for the more robust modeling needed to obtain a final record of decision (ROD) for the carbon tetrachloride plume. This report documents the technical approach and results of this modeling. Section 1.1 provides an overview of the carbon tetrachloride plume, and Section 1.2 provides the scope of the report and the modeling studies performed.

1.1 Overview of the Hanford Carbon Tetrachloride Plume

In the 200 West Area at Hanford, carbon tetrachloride was disposed to the soil at several sites adjacent to the Z Plant (Plutonium Finishing Plant) during operations from 1955 to 1973. The carbon tetrachloride had been used in mixtures with other organics to recover plutonium from aqueous streams at Z Plant. The resultant organic liquid waste stream discharged to the disposal sites consisted primarily of carbon tetrachloride in mixtures with tributyl phosphate, dibutyl butyl phosphate, and lard oil.

The areal extent of the dissolved carbon tetrachloride plume is approximately 10 km^2. Concentrations of dissolved carbon tetrachloride detected in the groundwater have been estimated to account for approximately 2% of the original carbon tetrachloride inventory.

Previous work (Swanson et al. 1999) considered an order-of-magnitude estimate of the 1990 inventory of carbon tetrachloride remaining in the subsurface using available groundwater concentration data, soil-gas concentration data, and well venting data. For the rough-order-of-magnitude estimates, it was assumed that 750,000 kg of carbon tetrachloride was discharged to the soil between 1955 and 1973. Total atmospheric losses were estimated to be 21%; the unsaturated zone inventory (in soil gas, soil moisture, and adsorbed phases) accounted for 12%; and the dissolved phase in the aquifer was estimated at 2%, leaving 65% of the original volume unaccounted for. However, the estimates did not consider nonaqueous-phase liquid (NAPL) organic residual saturation in the unsaturated zone, perched organic liquid on low-permeability lenses, or separate organic liquid present within the unconfined aquifer. Any or all of these forms of concentrated carbon tetrachloride may be present within the subsurface, though none has been observed.

1.2 Scope of Report

This report summarizes recent site-wide modeling studies that were part of an analysis that consisted of four model runs for analysis of the transport of the carbon-tetrachloride plume. The modeling approach, results, and general conclusions are described in Sections 2 and 3. Conclusions are presented in Section 4 and cited references in Section 5. Supporting documentation is provided in the appendix.

2.0 Technical Approach of Modeling Analysis

The ITRD modeling study examined carbon tetrachloride concentrations at an arbitrary boundary between the 200 East and 200 West Areas (Truex et al. 2001). After that work was completed, questions arose concerning the concentrations reaching the Columbia River as well as the impacts of remediation options involving the removal or absence of the source. To address those questions, additional modeling studies were conducted using the site-wide groundwater model (SGM) with the modeling domain extended to the Columbia River. The original SGM grid and the arbitrary compliance boundary are shown in Figure 2.1 along with other details of the ITRD analysis (Truex et al. 2001).

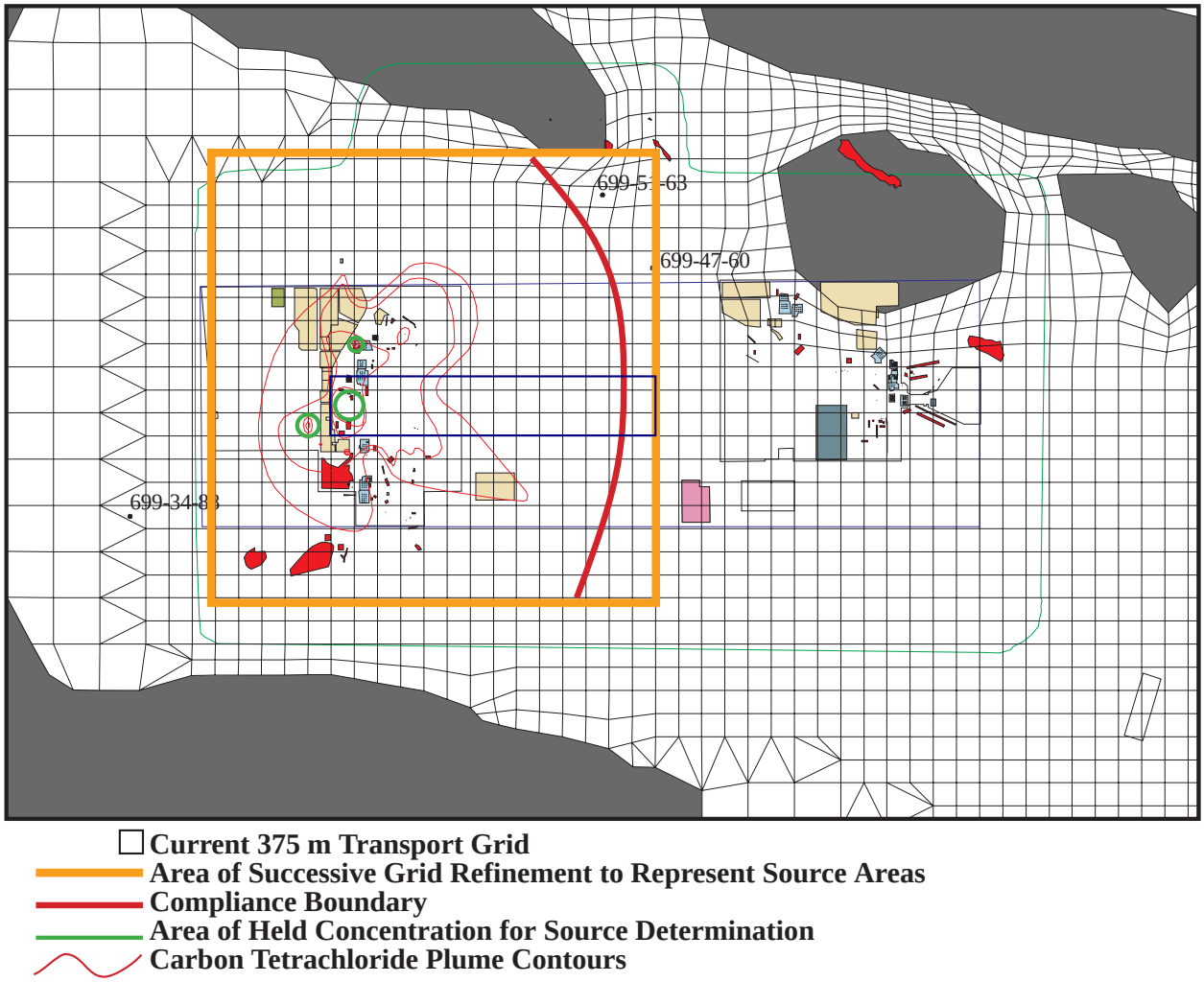


Figure 2.1. SGM Model Grid of 200 East and West Areas. Overlays illustrate 1) the areal extent of carbon tetrachloride (thin red lines), 2) the area of grid refinement for the ITRD study (orange line), 3) the compliance analysis boundary for ITRD study (thick red line), and 4) the flow tube used for the one-dimensional modeling to examine the effect of parameter uncertainty and develop sampling strategies to minimize the number of three-dimensional model runs (blue box).

2.1 Cases Simulated

Three general cases were evaluated as part of this modeling analysis:

- **Case 1** (Continuing Source) involves a run to examine the effects of a continuing source. For this case the same assumptions used in the ITRD modeling are made (i.e., the groundwater system near the source is in equilibrium with the source). As a result, the continuing source can be simulated by holding all of the aquifer volume with concentrations at or above 3,000 μg/L at existing concentration levels until the remaining source inventory has been released (487,500 kg, or ~65% of the estimated unaccounted for disposal mass of 750,000 kg). Two variations of this case were investigated, each involving different assumptions for the controlling transport parameters to bound possible outcomes.
  - Conservative variation with the natural attenuation parameters set to zero (i.e., $K_d = 0$ and $K_a = 0$), where K_a is the abiotic degradation rate and K_d is the soil/water equilibrium sorption coefficient.
  - Best-estimate variation using median values for the K_a =0.00956 yr^{-1} (reaction halftime = 72.5 yr) and K_d = 0.000322 m^3/kg (retardation factor = 2.6) determined from the *Literature Review: Natural Attenuation Mechanisms and Rates for Chloromethane Subsurface Contamination at Hanford* provided to the ITRD Technical Advisory Group and included as Appendix C in the ITRD report (Truex et al. 2001).
- **Case 2** (Source Removal) simulates the effects of source removal. For this case the entire aquifer volume at or above the 3,000 μg/L contour was set to zero, simulating complete source removal. Thus, only the effects related to continued migration of the plume outside the source area were evaluated. For this case the conservative values for natural attenuation parameters were used ($K_d = 0$ {retardation factor =1.0} and $K_a = 0$ {no abiotic reactions}).
- **Case 3** (No Source and No Removal) is a run to simulate the effects of the assumption that the only remaining unaccounted-for inventory is in the existing plume. For this run the existing plume provides the initial conditions, and only the effects of the plume's migration without further source additions are simulated. As with Case 2, only the conservative variation for natural attenuation parameters was investigated (i.e., $K_d = 0$ and $K_a = 0$).

2.2 Initial Conditions—Three-Dimensional Interpretation of Plume

A geostatistical analysis of the existing carbon tetrachloride measurements performed as part of the initial ITRD modeling study (Truex et al. 2001) provided the three-dimensional (3-D) data set on carbon tetrachloride distribution used to approximate the 3-D initial conditions and source-term concentrations for the modeling analysis described in this report.

A 3-D distribution of carbon tetrachloride in 1993 was needed to provide the initial conditions for flow and transport modeling. This was developed from data collected from the wells shown in Figure 2.2 (Truex et al. 2001). The geostatistical approach is fully discussed in the ITRD report. Information on the distribution of carbon tetrachloride with depth was not available for most of the wells, and only one measurement was available near the water table. Carbon tetrachloride concentrations for these 121 wells are from the Groundwater Monitoring Project database and restricted to measurements from 1993. Data for distribution of carbon tetrachloride with depth were taken from Swanson et al. (1999, Appendix A).

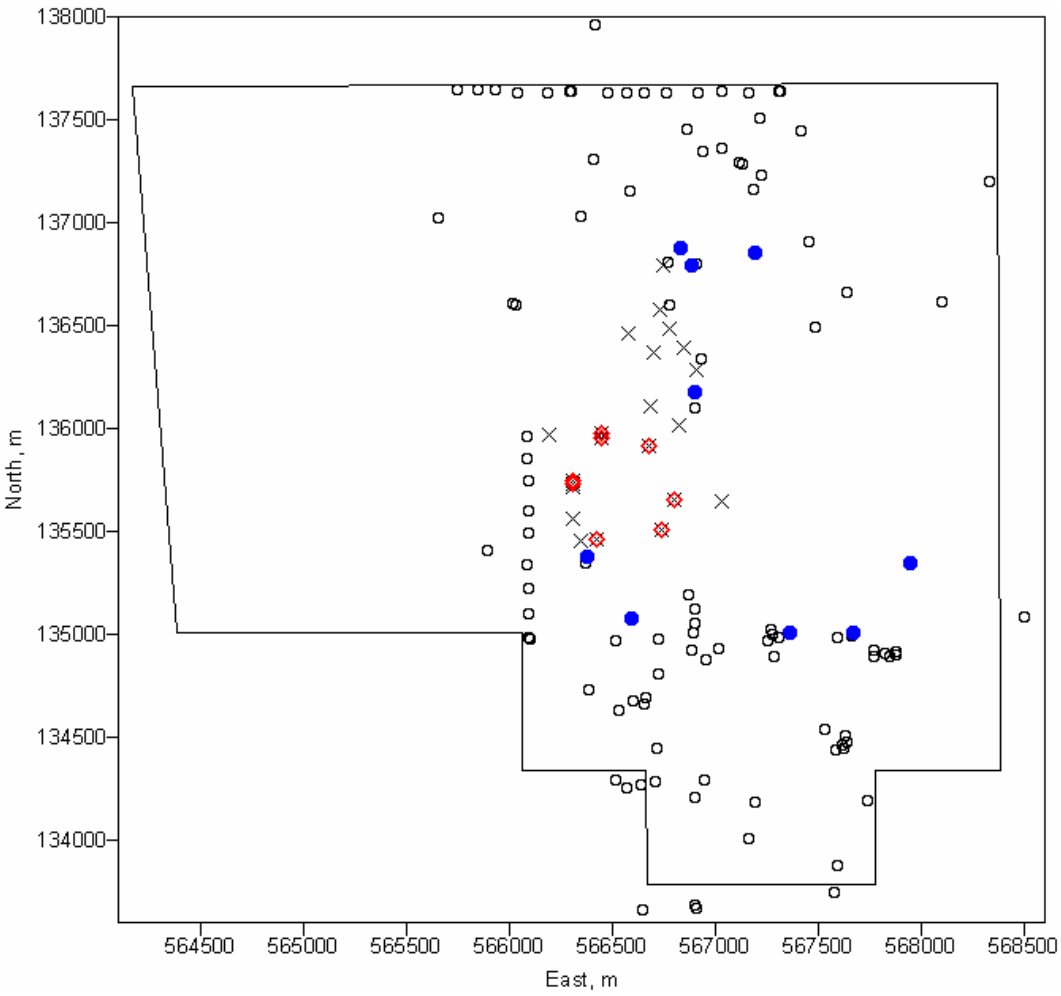


Figure 2.2. Map of Carbon Tetrachloride Concentration Data Used in Geostatistical Analysis. The blank circles and crosses represent the 2-D outer and central wells; the blue solid circles represent the nine 3-D outer wells and red diamonds the eight 3-D central wells. Central wells have concentrations exceeding 1000 μg/L; 3-D wells have carbon tetrachloride concentration data at depths greater than 5 m (from Truex et al. 2001).

Only eight central wells and nine outer wells have available 3-D carbon tetrachloride data in that data set. Because of the scarcity of deep carbon tetrachloride data where the location of the measurement is known with any confidence, it was impossible to restrict the data to 1993 for deep measurements, so the average of all measurements made at various times at a given 3-D location (i.e., for a given well and depth) were used. Even so, only 58 data points are available where the depth of the measurement was more than 5 m below the water table. The 58 data points are distributed among the 17 locations (eight central and nine outer wells) with deep carbon tetrachloride measurements.

One hundred realizations were generated of the 3-D spatial distribution of the carbon tetrachloride concentration at a grid node spacing of 50 by 50 m horizontally and 5 m vertically. A total of 65,280 (51 by 64 by 20) grid nodes were simulated in each realization. Horizontal and vertical displays of the median carbon tetrachloride from the first 100 realizations are shown in Figure 2.3.

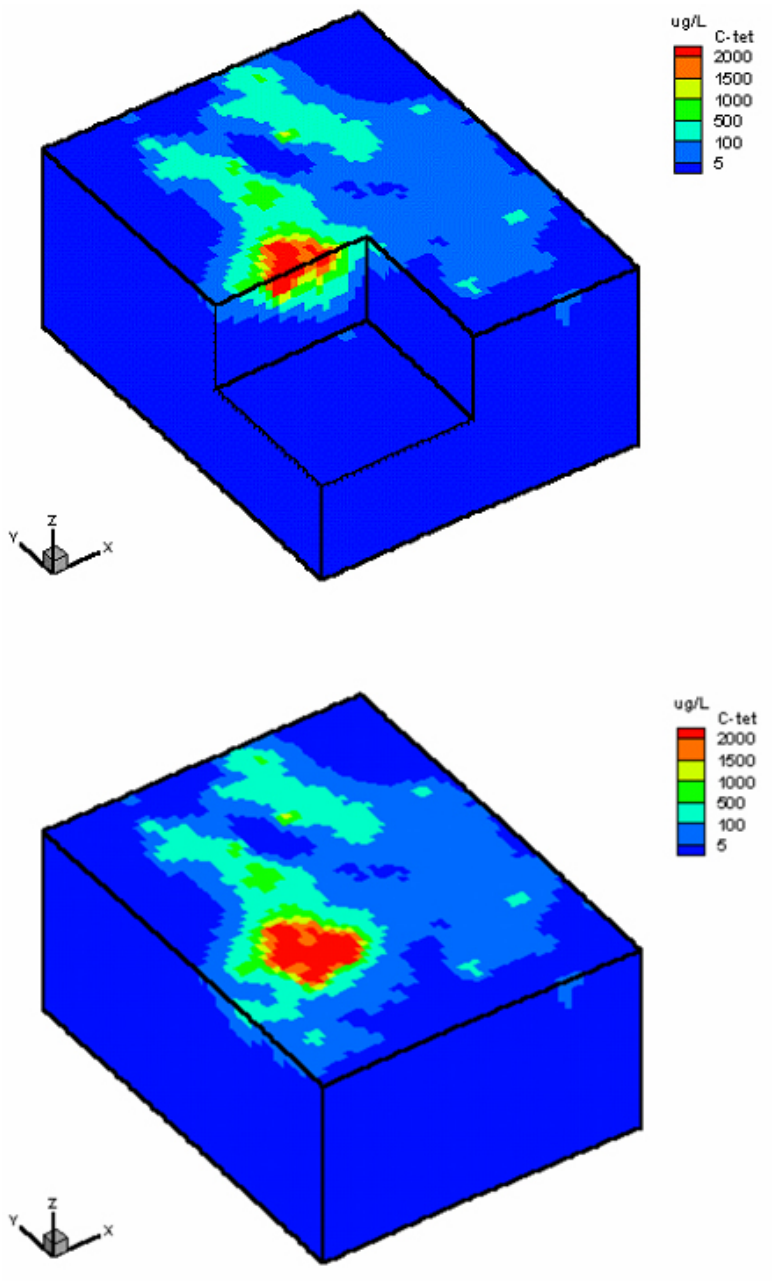


Figure 2.3. Block Diagrams Showing Median of First 100 Geostatistical Simulations of 3-D Carbon Tetrachloride Distribution

Figure 2.4 from the ITRD study shows the simulation median concentrations and the 2-D carbon tetrachloride inventory from vertical summation of simulated 3-D median carbon tetrachloride. An analysis of three possible source areas, labeled Block 1, Block 2, and Block 3 in Figure 2.4, identified Block 1 as the main source with an area approaching 1 km^2. The proportion of carbon tetrachloride inventory in Blocks 2 and 3 together is less than 0.1 of the total inventory; Block 1 contains nearly 0.8 of the total.

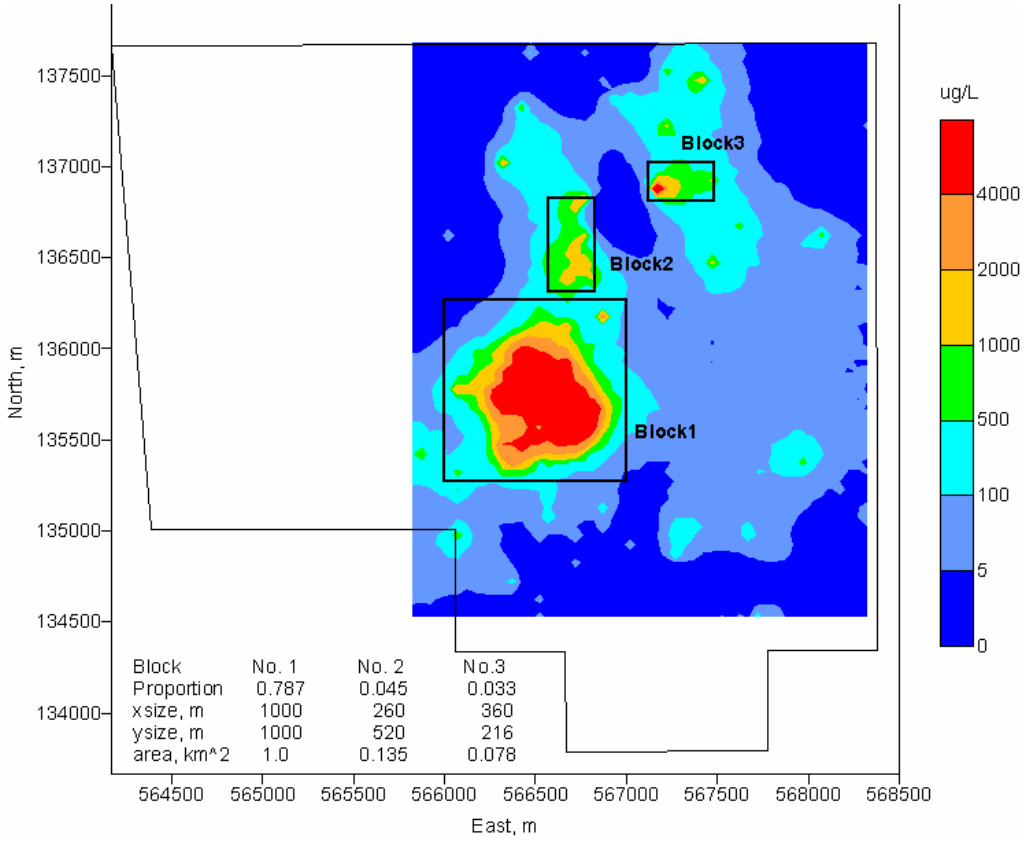


Figure 2.4. Vertical Summation of Simulated Median Carbon Tetrachloride Concentration and Proportion Within Three Source Blocks to Total Summed Concentration

2.3 Model, Grid, and Hypothetical Points of Analysis

Several hypothetical points and boundaries in the current and previous ITRD analyses are shown in Figure 2.1. These include the areal extent of carbon tetrachloride (thin red lines), the area of grid refinement for the original ITRD study (orange line), the arbitrary compliance analysis boundary (thick red line) for the original ITRD study, and the flow tube (blue box) used for the 1-D modeling to examine the effects of parameter uncertainty and to develop sampling strategies to minimize the number of 3-D model runs. The thin green line in Figure 2.1 illustrates the outer boundaries of the proposed core zone around the 200 Area Plateau WMA. The other important boundary is the Columbia River, which is not shown in the figure.

The initial conditions and refined grid for the smaller-scale subregion model used in the previous ITRD modeling study (orange boundary of Figure 2.1) are shown in Figure 2.5. This previous modeling, as well as that documented in this report, used the model from the earlier site-wide plume analysis (Cole et al. 1997). The background grid in Figure 2.1 is the transport grid for the previous modeling. It can be seen that the existing grid in the area of the source is the same scale as the primary source area (i.e., the central dark-green circle of Figure 2.1), and as a result some refinement was needed to properly represent the source area for evaluating the three cases investigated in this study. Figure 2.6 shows the slightly refined SGM grid with expanded sections that illustrate the refinement for the source areas and the median realization for initial conditions.

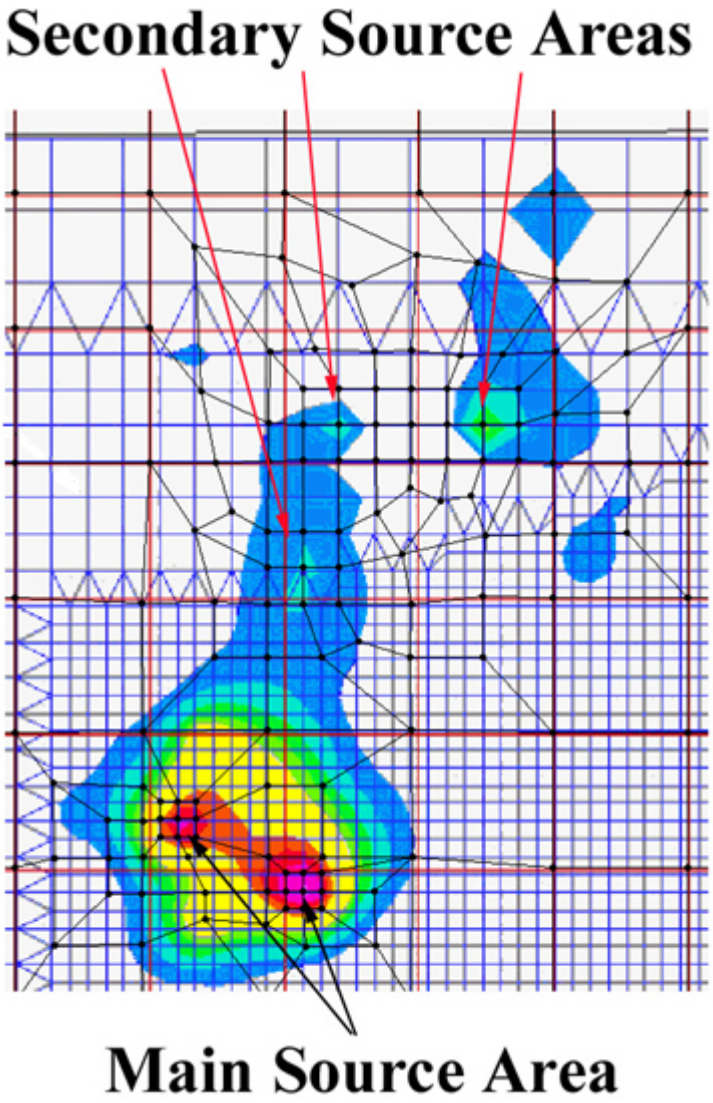


Figure 2.5. Initial Conditions (upper 5 M) for Current and Previous ITRD Modeling with Fine Grid Used in Previous ITRD Subregion Modeling (orange boundary in Figure 2.1); also shows the main and secondary source areas.

2.4 Natural Attenuation Modeling Parameters

In addition to the geostatistical simulations of the carbon tetrachloride source volumes, the ITRD study examined realizations of several other modeling parameters needed for the 1-D Monte Carlo flow and transport study (Truex et al. 2001). That analysis examined the best-estimate values for two parameters, the K_d for carbon tetrachloride and the abiotic degradation rate of carbon tetrachloride, or K_a, which were used in this study. Truex et al. (2001) identified the minimum, maximum, and most likely values of each parameter, which were then used to characterize the probability distributions. These values and distributions are shown in Table 2.1 and Figure 2.7, respectively.

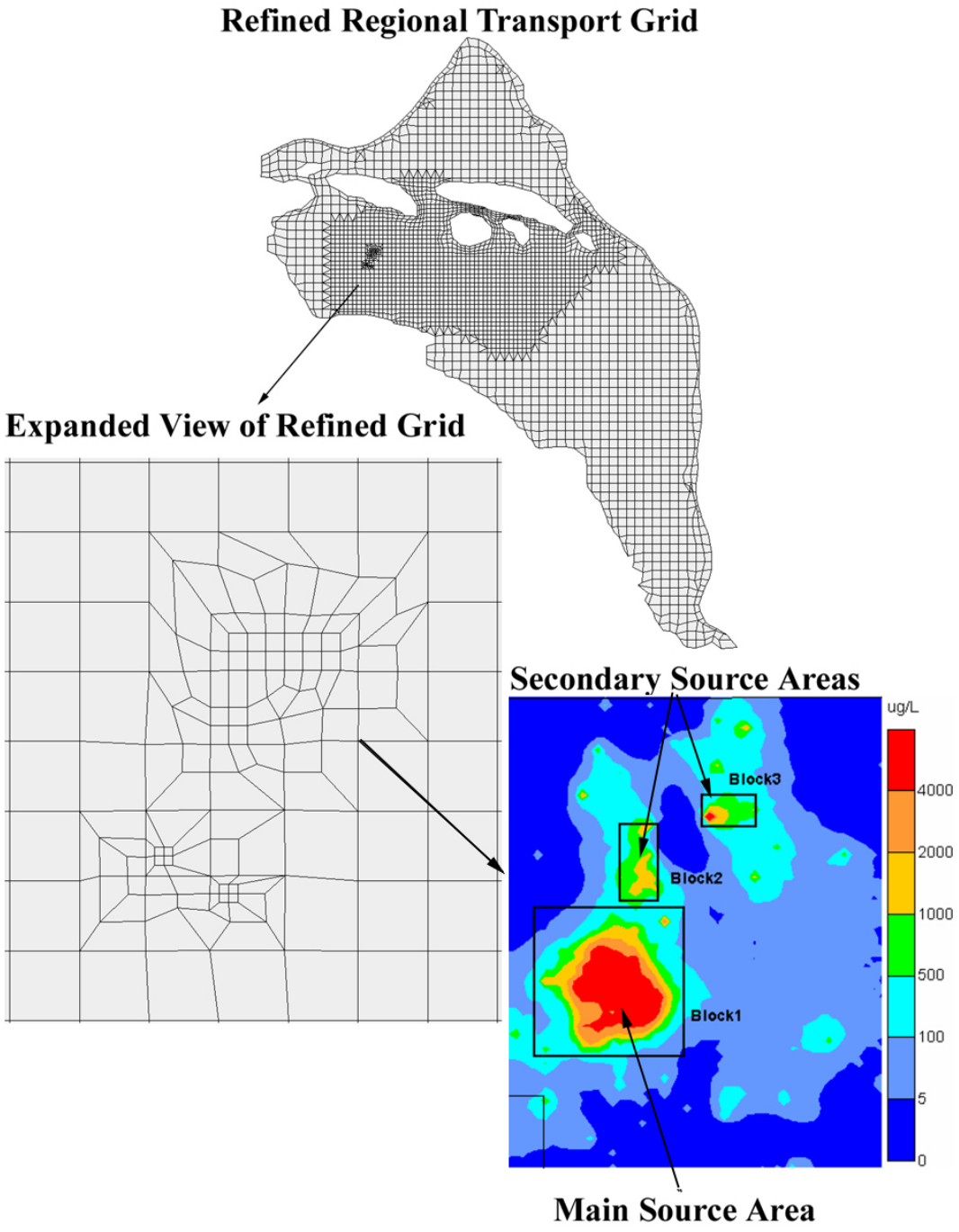


Figure 2.6. Refined SGM Grid Used in this Study with Expanded Sections to Illustrate the Refinement for Source Areas and Matching Realization Used for Initial Conditions

Table 2.1. Modeling Parameter Probability Distributions Used in ITRD Modeling Study

Parameter	Distribution Type	Minimum	Maximum	Most Probable
CCl_4 K_d (L/kg)	Triangular	0.016	0.83	0.12
CCl_4 K_a (per day)	Triangular	6.50E-06	5.30E-05	1.90E-05

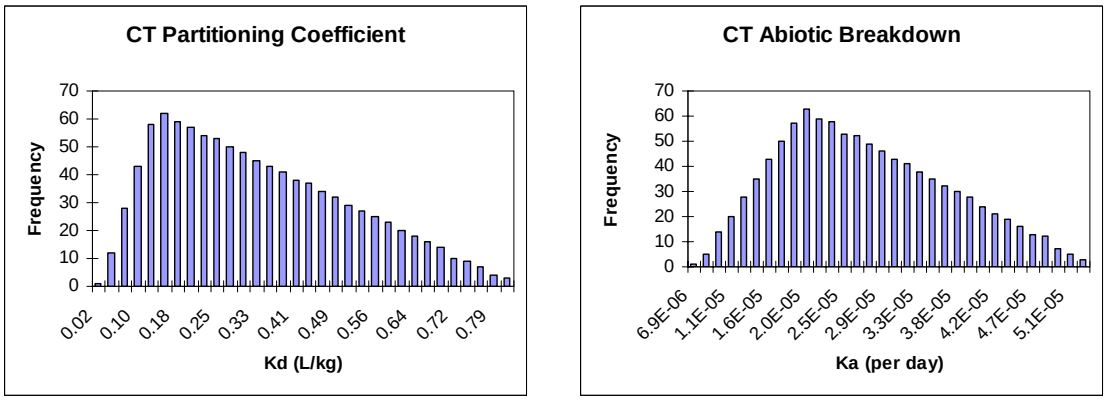


Figure 2.7. Histograms of 1000 Simulated Values of Each of the Four Input Parameters Used in the ITRD Flow and Transport Modeling

2.5 Other Modeling Considerations

The model used the same future disposal assumptions and addressed a transient time period extending from current conditions to the next ~1500 years. Results include plots of maximum concentration versus time at selected locations and plan view concentration distribution plots at various times (e.g., 5, 10, 50 100, 200...years) until intersection with the Columbia River.

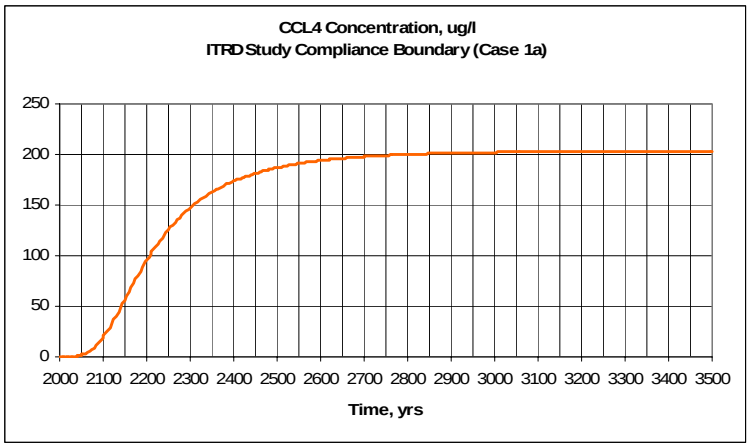
3.0 Results

This section presents results for the three general simulation cases used in this modeling study. Key results for Case 1a, assuming a continuing source and K_d and K_a equal to zero, are discussed in Section 3.1, and Case 1b, with a continual source and a median K_d and K_a, is presented in Section 3.2. Case 2, which assumes no continuing source, but source removal and K_d and K_a equal to zero, is discussed in Section 3.3, and Case 3, assuming no continuing source, no source removal, and K_d and K_a equal to zero, is presented in Section 3.4.

3.1 Case 1a

Key results for Case 1a, assuming a continuing source and K_d and K_a equal to zero, are discussed in this section and illustrated in Figures 3.1 through 3.4. Simulation results for this case indicated that maximum predicted carbon tetrachloride concentrations would exceed the current benchmark maximum concentration limit (MCL) of 5 µg/L at the arbitrary analysis boundary (Figure 3.1a). Within the regional

(a)



(b)

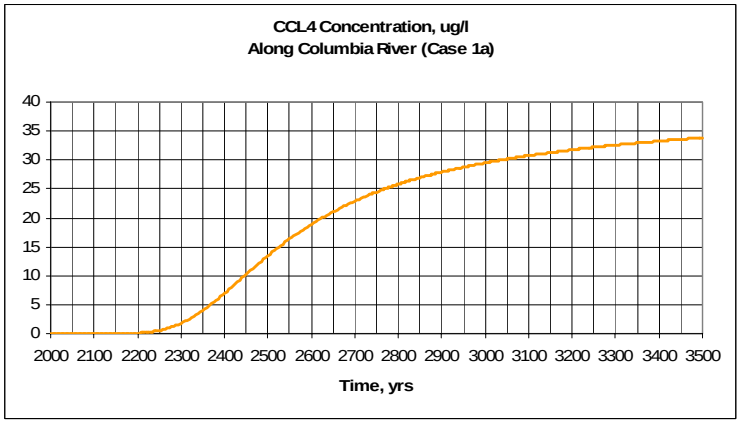


Figure 3.1. Carbon Tetrachloride Concentrations at ITRD Study Compliance Boundary (a) and Along Columbia River (b) for Case 1a

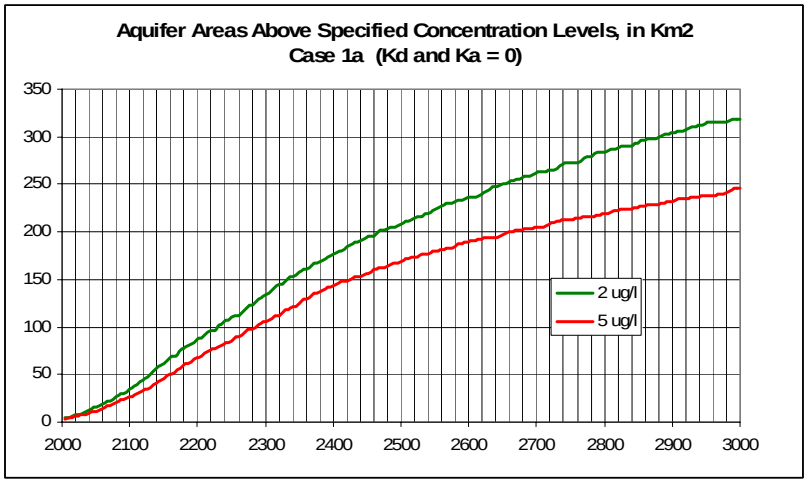
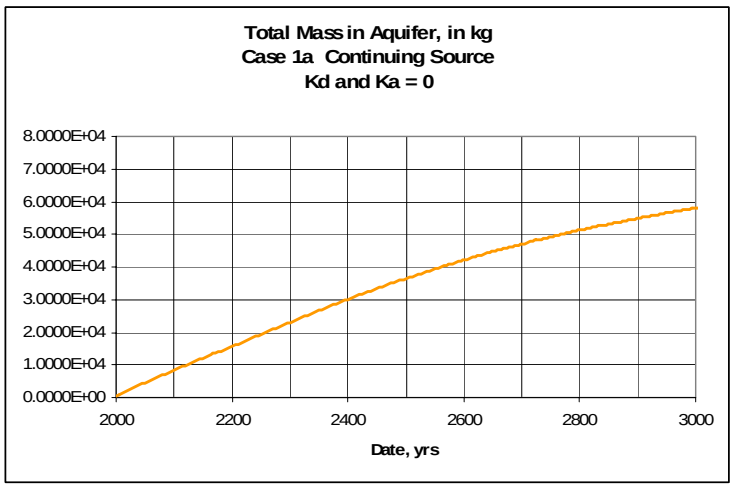


Figure 3.2. Aquifer Areas Above Specified Concentration Levels (km^2) for Case 1a

(a)



(b)

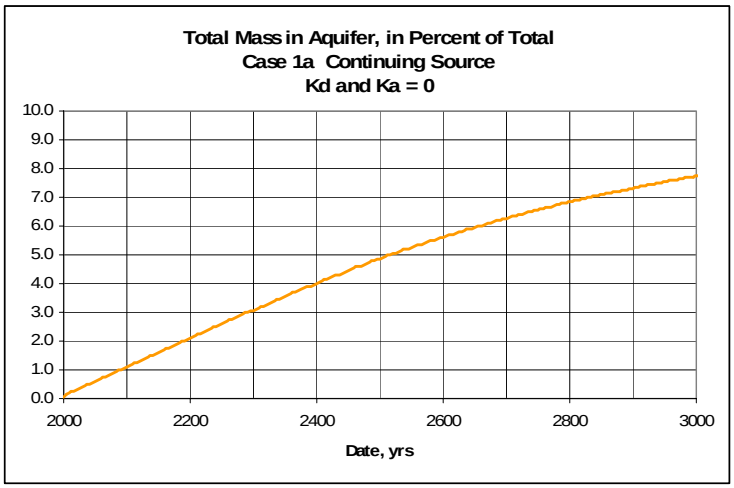


Figure 3.3. Total Mass in Aquifer (a = kg; b = % of total), Case 1a

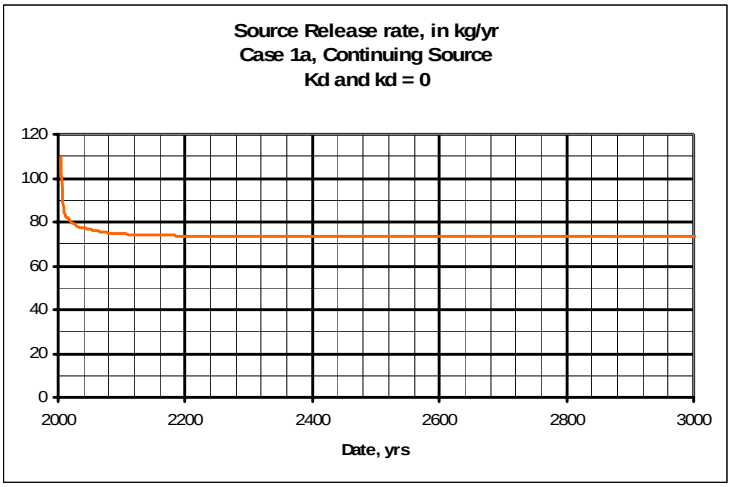


Figure 3.4. Source Release Rate (kg/yr) for Case 1a

scale model presented here, maximum concentrations at the analysis boundary would reach about 200 µg/L ~1000 years after the start of simulations (Figure 3.1a). Maximum concentrations estimated in the regional scale model just before discharging into the Columbia River near the Hanford Town Site exceed the benchmark MCL (5 µg/L) less than 400 years after the start of the simulation, reaching about 30 µg/L at 1000 years and about 34 µg/L at 1500 years (Figure 3.1b). The resulting aquifer area that would exceed the benchmark MCL (5 µg/L) in the regional scale was estimated at about 247 km^2 (95.4 mi^2) 1000 years after simulations began (Figure 3.2). The resulting aquifer area that would exceed a 2 µg/L concentration level was estimated to be about 318 km^2 (122.8 mi^2) 1000 years after the start of simulation (Figure 3.2).

Mass in the aquifer ranged from an initial condition of about 542 kg at the start of the simulation to about 58,050 kg in the year 3000 (Figure 3.3a). These mass estimates (Figure 3.3b) represent about 0.07 and 7.8 percent of the total estimated historical inventory release (that is, ~750,000 kg).

With the assumption of a continuing source, as analyzed in this case, estimated mass loading from the source zone would reach a maximum loading rate of about 73 kg/yr (Figure 3.4). This loading rate indicates that, with this simplifying assumption, only a very small percentage (0.00973%) of the total estimated historical inventory release (that is, ~750,000 kg) would be released each year from the highest concentration volumes within the groundwater source zones.

3.2 Case 1b

Key results for Case 1b, which assumes a continual source and median K_d and K_a, are discussed in this section and illustrated in Figures 3.5 through 3.8. Simulations for this case (Figure 3.5) produced a maximum predicted concentration of ~4.5 µg/L, which would not exceed the current benchmark MCL of 5 µg/L at the arbitrary analysis boundary. Thus, the maximum predicted concentration would not reach the Columbia River at any substantial level within the 1000-year period of analysis and would never be close to MCL. The resulting aquifer area (Figure 3.6) that would exceed the benchmark MCL (5 µg/L) was estimated to be about 13.6 km^2 (5.3 mi^2) ~600 years after the start of simulations. The resulting aquifer area that would exceed a 2 µg/L concentration level was estimated to be about 20.8 km^2 (8.0 mi^2)

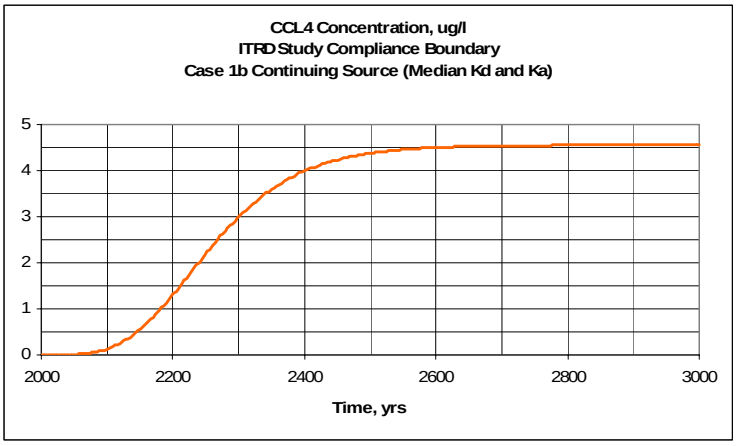


Figure 3.5. Carbon Tetrachloride Concentration at ITRD Study Compliance Boundary (µg/L) for Case 1b

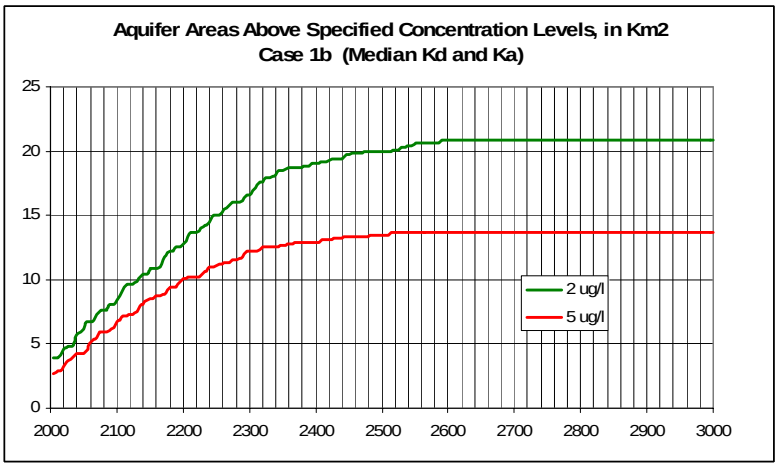


Figure 3.6. Aquifer Areas Above Specified Concentration Levels (km^2) for Case 1b

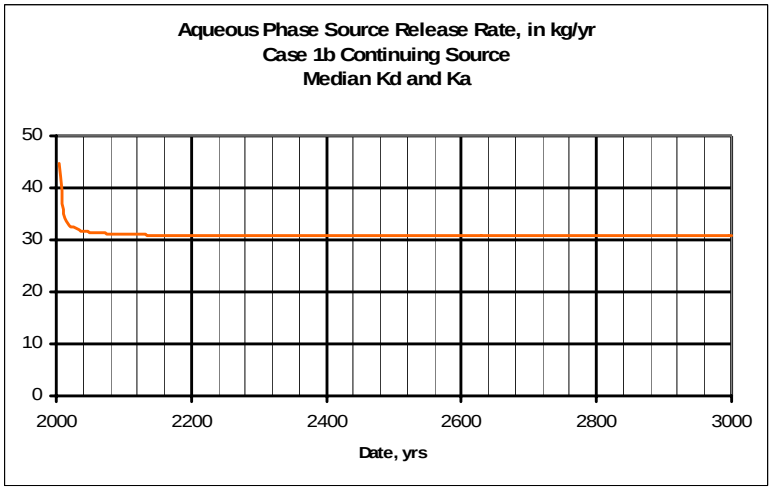
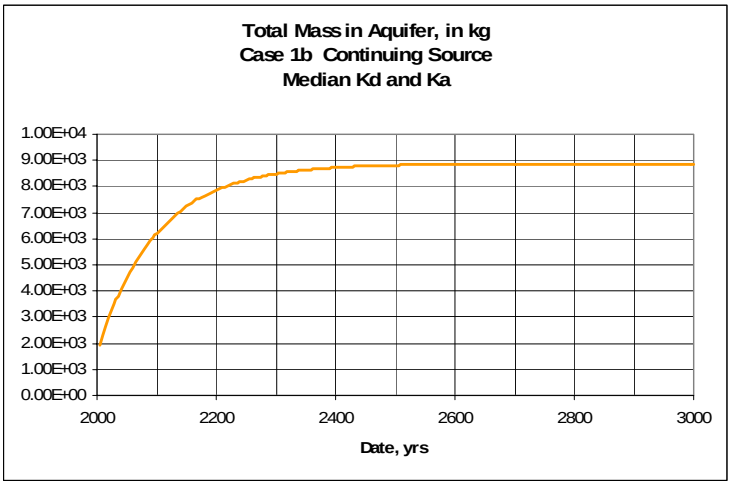


Figure 3.7. Aqueous Phase Source Release Rate (kg/yr) for Case 1b

(a)



(b)

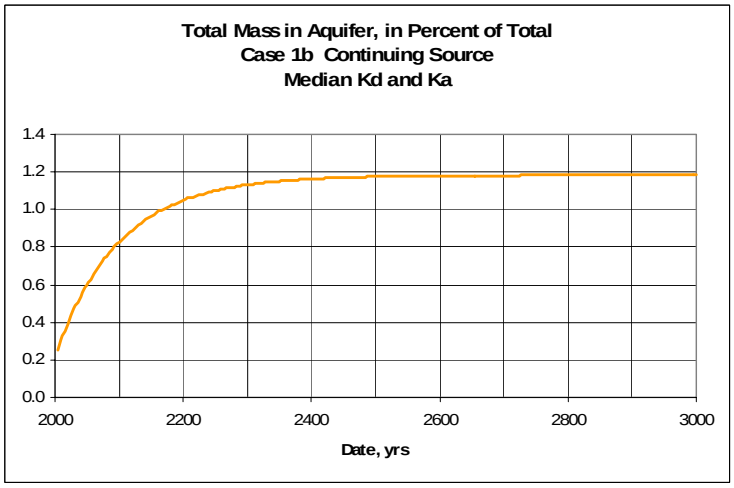


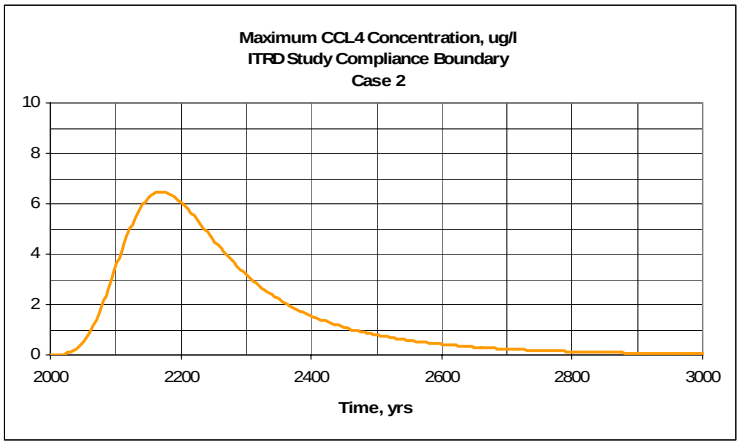
Figure 3.8. Total Mass in Aquifer (a = kg; b = % of total) for Case 1b

~600 years after the start of simulation. These areas of elevated concentrations reached a steady-state condition ~600 years after the simulation began, when the decay due to abiotic degradation within the plume reached equilibrium with mass production rates in the source areas of ~30.9 kg/yr (Figure 3.7). This loading rate indicates that, with this simplifying assumption, only a very small percentage (0.0041%) of the total estimated historical inventory (~750,000 kg) would be released each year from the highest concentration volumes in the groundwater source zones. Mass in the aqueous phase of the aquifer ranged from an initial condition of ~500 kg to ~3372 kg in the year 3000 (Figure 3.8a). These mass estimates (Figure 3.8b) represent 0.07 and 0.45% of the total estimated historical inventory release (~750,000 kg).

3.3 Case 2

Key results for Case 2, which assumes no continuing source, source removal, and K_d and K_a equal to zero, are discussed in this section and illustrated in Figures 3.9 through 3.11. Simulation results of this case (Figure 3.9a) predicted a concentration maximum that slightly exceeds (~6.25 µg/L) the current benchmark MCL of 5 µg/L at the arbitrary analysis boundary between the 200 East and West Areas in

(a)



(b)

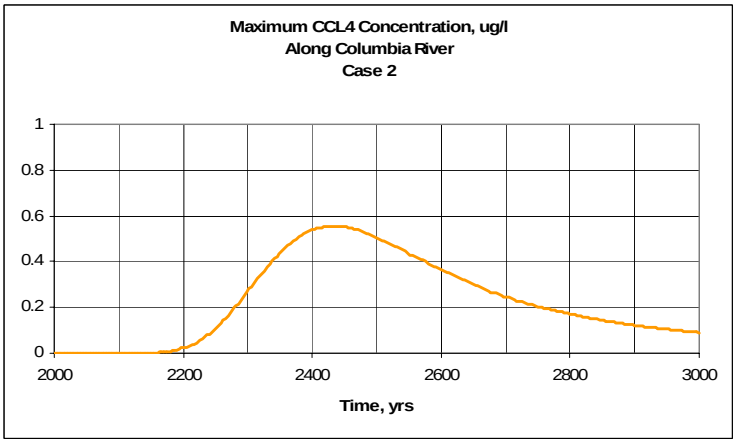


Figure 3.9. Maximum Carbon Tetrachloride Concentration (µg/L) at (a) ITRD Study Compliance Boundary and (b) Along Columbia River for Case 2

about 180 years. Estimated concentrations at discharge areas near the Columbia River (Figure 3.9b) are not predicted to come close to reaching the benchmark MCL of 5 µg/L—they reach a maximum concentration of about 0.5 µg/L a little over 400 years after the start of the simulation. The resulting aquifer area that would exceed the benchmark MCL (5 µg/L) in the regional scale was estimated to be about 10.8 km^2 (4.2 mi^2) 115 years after the start of simulations (Figure 3.10). The aquifer area that would exceed a 2 µg/L concentration level was estimated to be about 18.4 km^2 (7.1 mi^2) approximately 180 years after the start of simulation, and groundwater concentrations were predicted to drop below 5 and 2 µg/L about 320 and 520 years, respectively, after the start of simulations (Figure 3.10).

Mass in the aquifer ranged from an initial condition of about 543 kg at the start of the simulation to about 200 kg in the year 3000 (Figure 3.11a). These mass estimates represent 0.07 and 0.03% (Figure 3.11b) of the total estimated historical inventory release (that is, ~750,000 kg).

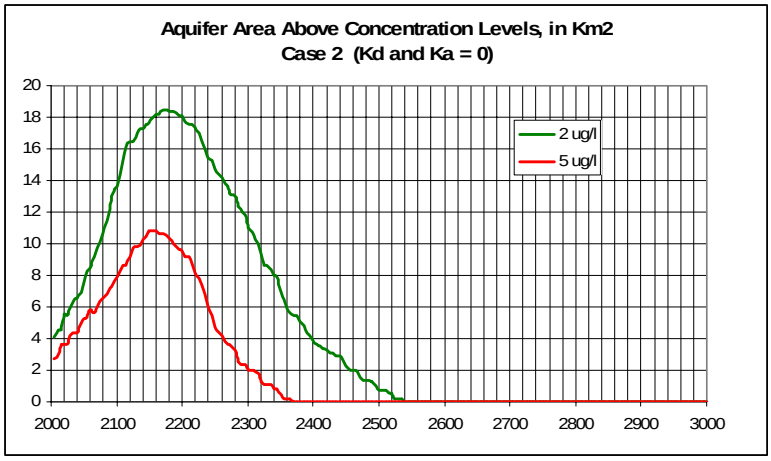
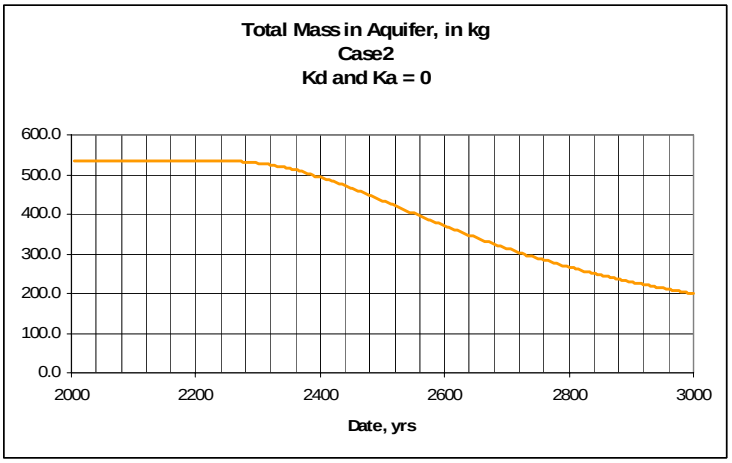


Figure 3.10. Aquifer Area Above Concentration Levels (km^2) for Case 2

(a)



(b)

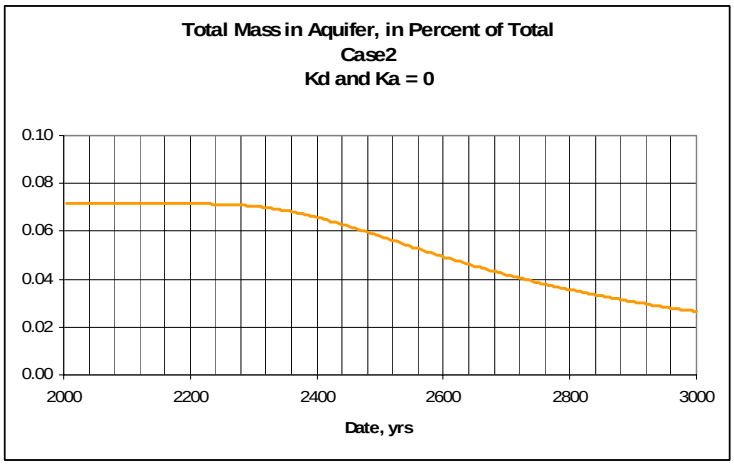


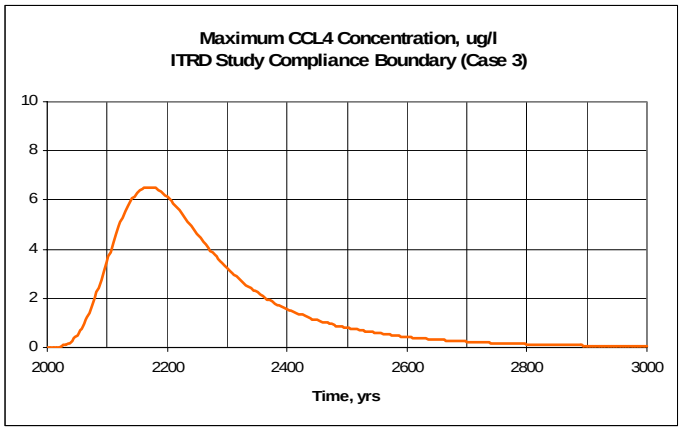
Figure 3.11. Total Mass in Aquifer (a = kg; b = % of total) for Case 2

3.4 Case 3

Key results for Case 3, which assumes no continuing source, no source removal, and K_d and K_a equal to zero, are discussed in this section and illustrated in Figures 3.12 through 3.14. Simulation results for this case (Figure 3.12a) predicted concentrations slightly exceeding the current benchmark MCL of 5 µg/L at the arbitrary analysis boundary between the 200 East and West Areas. Maximum concentrations at the arbitrary analysis boundary would reach about 6.25 µg/L 180 years after the start of the simulation. Like Case 2, estimated concentrations at discharge areas near the Columbia River are predicted to be about 0.5 µg/L, which is well below the benchmark MCL of 5 µg/L within the period of analysis (Figure 3.12b). The resulting aquifer area that would exceed the benchmark MCL (5 µg/L) is ~10.8 km^2 (4.2 mi^2) about 150 years after the start of simulations (Figure 3.13). The resulting aquifer area that would exceed a 2 µg/L concentration level was estimated to be about 18.4 km^2 (7.1 mi^2) about 180 years after the start of simulations (Figure 3.13). As in Case 2, groundwater concentrations were predicted to drop below 5 and 2 µg/L about 320 and 520 years, respectively, after the start of simulations.

Mass in the aquifer ranged from initial conditions of ~536 kg at the start of the simulation to ~199 kg in the year 3000 (Figure 3.14a). These mass estimates represent 0.07 and 0.03% (Figure 3.14b) of the total estimated historical inventory release (~750,000 kg).

(a)



(b)

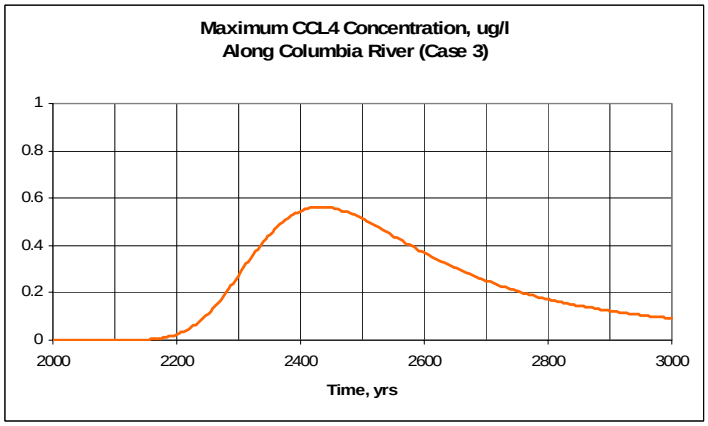


Figure 3.12. Maximum Carbon Tetrachloride Concentration (µg/L) at (a) ITRD Study Compliance Boundary and (b) Along Columbia River for Case 3

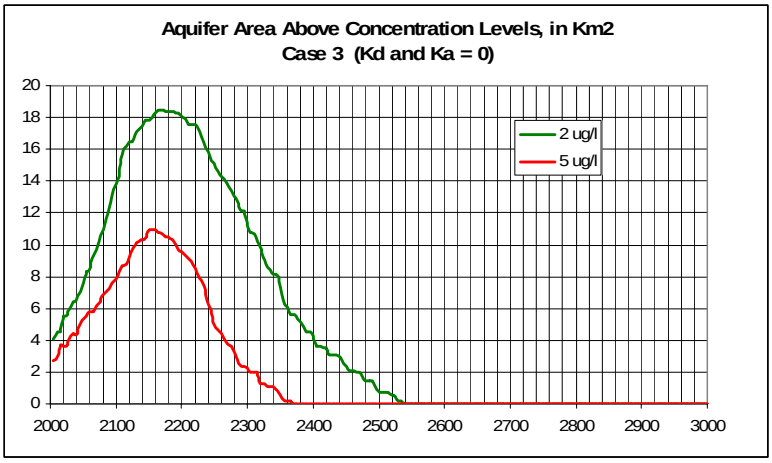
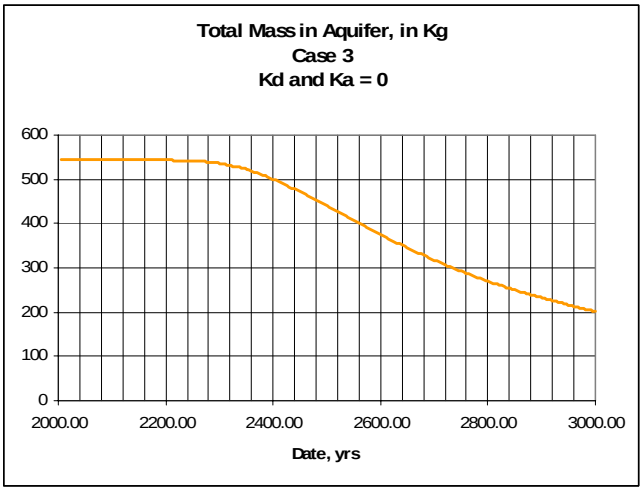


Figure 3.13. Aquifer Area Above Concentration Levels (km^2) for Case 3

(a)



(b)

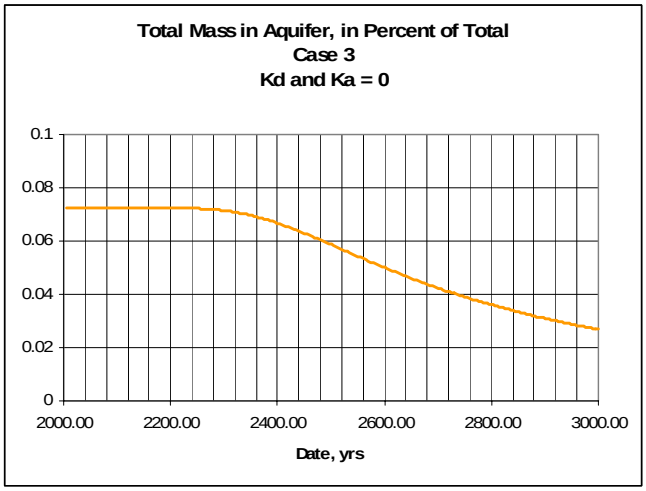


Figure 3.14. Total Mass in Aquifer for Case 3 (a = kg; b = % of total)

4.0 Results and Conclusions

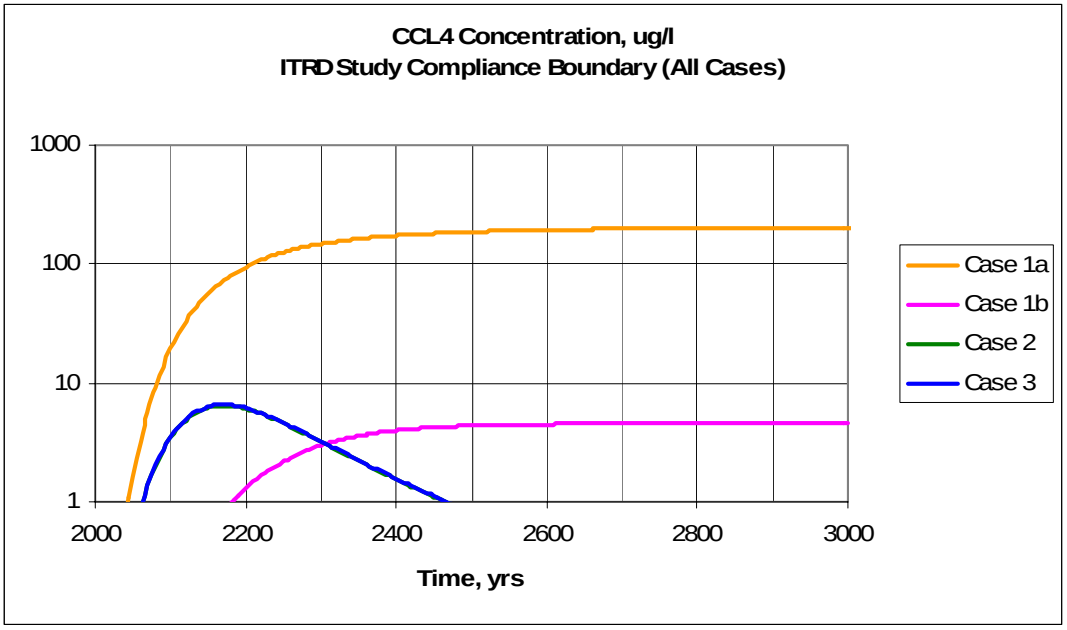
Key results of the modeling analysis are discussed in detail in Section 3 and summarized in Table 4.1 and Figure 4.1. These results of this modeling analysis gave rise to the following conclusions:

- Case 1a, which was based on assumptions of a continuing source with no sorption or abiotic degradation, resulted in:
  - Development and migration of a substantial carbon tetrachloride plume from source areas in the 200 West Area to the Columbia River. Predicted concentrations exceeded the benchmark MCL of 5 µg/L reached about 200 µg/L at the arbitrary boundary chosen for this analysis and about 30 µg/L at discharge points along the Columbia River during the 1000-year period of analysis.
  - An equilibrium carbon tetrachloride release estimate of about 73 kg/yr in the source area.
  - Mass in the aquifer ranged from an initial condition of about 542 kg at the start of the simulation to about 58,050 kg in the year 3000.
- Case 1b, which was based on assumptions of median value estimates for sorption and abiotic degradation, resulted in:
  - Limited development and migration of a carbon tetrachloride plume from source areas within the general vicinity of the 200 West Area. Predicted concentrations were just below the benchmark MCL of 5 µg/L, reaching 4.5 µg/L at the arbitrary boundary chosen for this analysis. Concentrations were well below MCL at the discharge areas along the Columbia River during the 1000-year period of analysis.

Table 4.1. Results of Analyses

Case	Max. Concentration in µg/L (time of max)		Max. aquifer area above 5 µg/L in km^2 (time of max)	Loading rate to aquifer in kg/yr (percent of estimated total inventory)	Total mass in aquifer in kg (percent of estimated total inventory)
	Arbitrary boundary between 200 E and W Areas	Columbia River boundary			
Case 1a	200 (yr 3000)	30 (yr 3000)	250 (yr 3000)	73.3 (0.0098)	542 (0.07)[(a)] 58050 (7.8)[(b)]
Case 1b	4.5 (yr 3000)	n/a[(c)]	13.6 (yr 3000)	30.9 (0.0041)	500 (0.07) 3372(0.4)[(b)]
Case 2	6.5 (yr 2180)	0.5 (yr 2440)	10.8 (yr 2200)	n/a	543 (0.07)[(a)] 200 (0.03)[(b)]
Case 3	6.5 (yr 2180)	0.5 (yr 2440)	3.7 (yr 2200)	n/a	536 (0.07)[(a)] 199 (0.03)[(b)]

(a) Estimated mass in aquifer at start of simulation (yr 2000).
(b) Estimated mass in aquifer at yr 3000.
(c) n/a = not applicable.



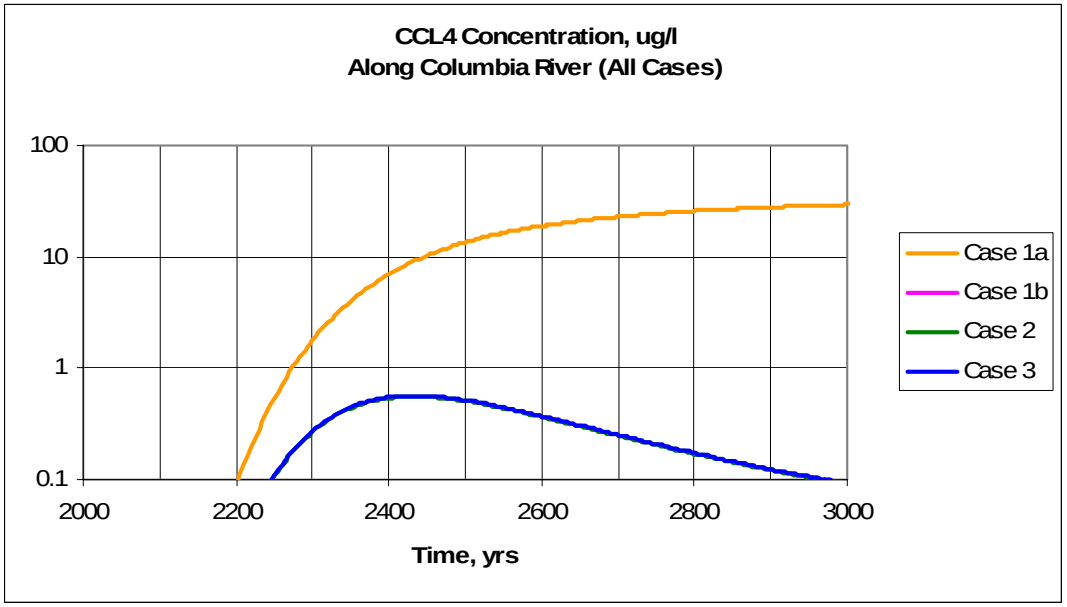


Figure 4.1. Carbon Tetrachloride Concentration for All Cases (µg/L); (a) at ITRD Study Compliance Boundary and (b) Along Columbia River. Plots of results at the ITRD Study Compliance Boundary and along the Columbia River for Cases 2 and 3 are nearly identical and plot on top of one another. Concentration results for Case 1b along the Columbia River are well below the levels of interest and below the minimum concentration level in the plot.

- The combination of sorption and abiotic degradation significantly limits aquifer source loading and aquifer area and volume affected by the migration of the carbon tetrachloride plume.

- Cases 2 and 3 evaluated the combined effects of removal and no removal of sources from the highest concentrations in the plume, and both assumed there was no continuing source of carbon tetrachloride feeding the aquifer. They used conservative estimates (zero) of sorption and abiotic degradation. Results of both of these cases showed:
  - A much more limited development and migration of a carbon tetrachloride plume outside 200 West Area toward the Columbia River than predicted under the continuing source assumption evaluated in Case 1a..
  - A predicted concentration profile reaching 6.5 µg/L and exceeding the benchmark MCL of 5 µg/L at the arbitrary boundary between 200 East and West Areas over a period of about 600 years between 2100 and 2700. This contrasts with the rapidly rising and plateauing profile of carbon tetrachloride concentrations predicted under the continuing source assumption evaluated in Case 1a.
  - Concentrations at discharge areas along the Columbia for these cases were predicted to be well below the benchmark MCL level of 5 µg/L during the 1000-year period of analysis.
  - The effect of simulating complete source removal (Case 2, evaluation of estimated initial aquifer concentration levels after concentrations at or above the 3,000 µg/L contour are set to zero) and no source removal (Case 3, evaluating transport of the estimated initial aquifer concentrations) was difficult to distinguish using the metrics established in these analyses (i.e., predicted concentrations at the arbitrary compliance boundary location and along the Columbia River and the total aquifer areas above specified concentration levels).

In summary, the results of these analyses illustrate the importance of developing field-scale estimates of K_d and especially K_a appropriate for carbon tetrachloride in the Hanford sediments. With K_d and K_a of zero, carbon tetrachloride concentrations will exceed the compliance limit of 5 µg/L outside the 200 Area Plateau WMA, and the aquifer source loading and area of the aquifer affected will continue to grow until river arrival rates equal source release rates. Results of this comparative modeling showed that natural attenuation parameters K_d and especially K_a are critical in predicting the future movement of carbon tetrachloride from the 200 West Area. Results also show the significant change in predictions if source release from the vadose zone is assumed to be a continual long-term source of contaminant or if no long-term source release is assumed.

5.0 References

Cole CR, SK Wurstner, MP Bergeron, MD Williams, and PD Thorne. 1997. *Three-Dimensional Analysis of Future Groundwater Flow Conditions and Contaminant Plume Transport in the Hanford Site Unconfined Aquifer System: FY 1996 and 1997 Status Report.* PNNL-11801, Pacific Northwest National Laboratory, Richland, WA.

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Truex MJ, CJ Murray, CR Cole, RJ Cameron, MD Johnson, RS Skeen, and CD Johnson. 2001. *Assessment of Carbon Tetrachloride Groundwater Transport in Support of the Hanford Carbon Tetrachloride Innovative Technology Demonstration Program*. PNNL-13560, Pacific Northwest National Laboratory, Richland, WA.

Appendix

Predicted Distributions of Carbon Tetrachloride Derived from Modeling Studies After Initial ITRD Investigations

Appendix

Predicted Distributions of Carbon Tetrachloride Derived from Modeling Studies After Initial ITRD Investigations

This appendix contains a series of selected time plane plots (Figures A.1 through A.11) to illustrate results of simulation cases used in this modeling study. The three general cases evaluated as part of the follow-on modeling analysis were as follows:

- **Case 1** (Continuing Source) involves a run to examine the effects of a continuing source. For this case the same assumptions used in the ITRD modeling are made (i.e., the groundwater system near the source is in equilibrium with the source). As a result, the continuing source can be simulated by holding all of the aquifer volume with concentrations at or above 3,000 μg/L at existing concentration levels until the remaining source inventory has been released (487,500 kg ~65% of the estimated unaccounted-for disposal mass of 750,000 kg). Two variations of this case were investigated. Each involves different assumptions for the controlling transport parameters in order to bound possible outcomes.
  - Conservative variation with the natural attenuation parameters set to zero (i.e., $K_d = 0$ and $K_a = 0$), where K_a is the abiotic degradation rate and K_d is the soil/water equilibrium sorption coefficient.
  - Best-estimate variation using median values for the K_a =0.00956 yr^{-1} (reaction halftime = 72.5 yr) and K_d = 0.000322 m^3/kg (retardation factor = 2.6) determined from the *Literature Review: Natural Attenuation Mechanisms and Rates for Chloromethane Subsurface Contamination at Hanford* provided to the ITRD Technical Advisory Group and included as Appendix C in the ITRD report (Truex et al. 2001).
- **Case 2** (Source Removal) simulates the effects of source removal. For this case all of the aquifer volume at or above the 3,000 μg/L contour was set to zero, simulating complete source removal. Thus, only the effects related to continued migration of the plume outside the source area were evaluated. For this case the conservative values for natural attenuation parameters were used ($K_d = 0$ {retardation factor =1.0} and $K_a = 0$ {no abiotic reactions}).
- **Case 3** (No Source and No Removal) simulates the effects of the assumption that the only remaining inventory unaccounted for is in the existing plume. For this run the existing plume provides the initial conditions and only the effects of the plume's migration without further source additions are simulated. Like Case 2, only the conservative variation for natural attenuation parameters was investigated (i.e., $K_d = 0$ and $K_a = 0$).

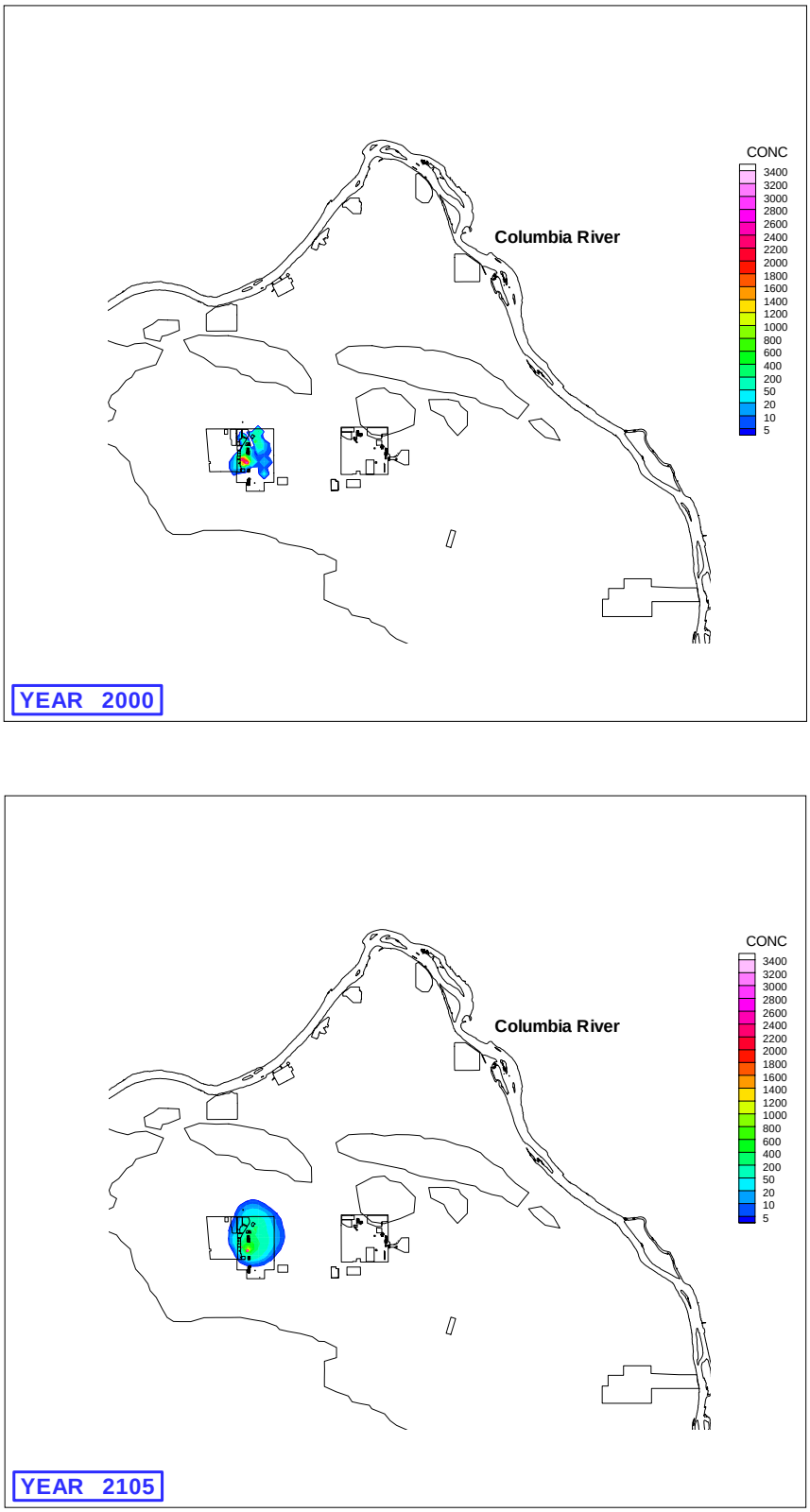
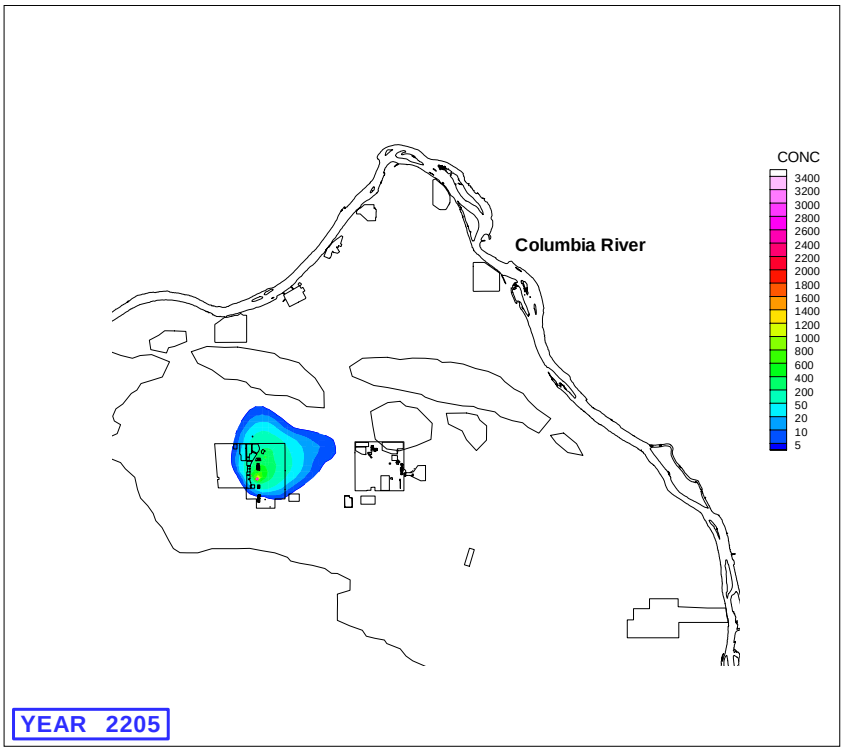


Figure A.1. Case 1a, Continuing Source, K_d and K_a = 0 (yr 2000 and 2105)



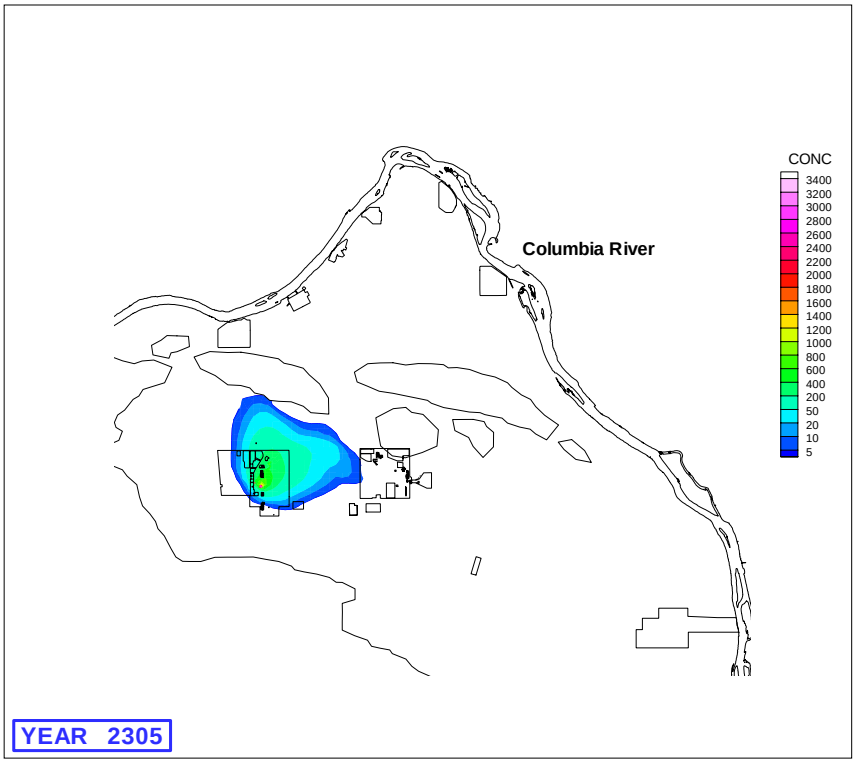


Figure A.2. Case 1a, Continuing Source, K_d and K_a = 0 (yr 2205 and 2305)

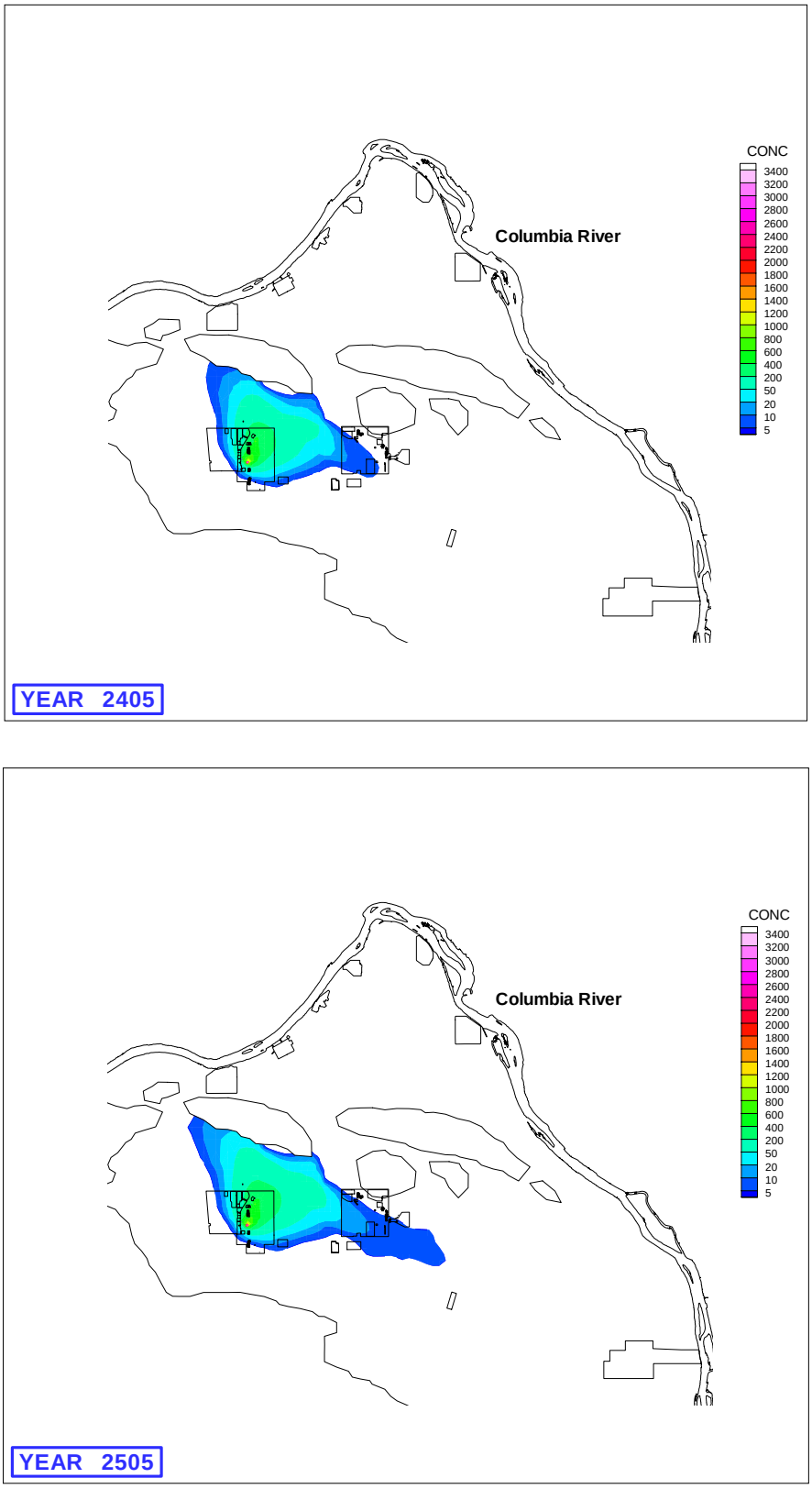
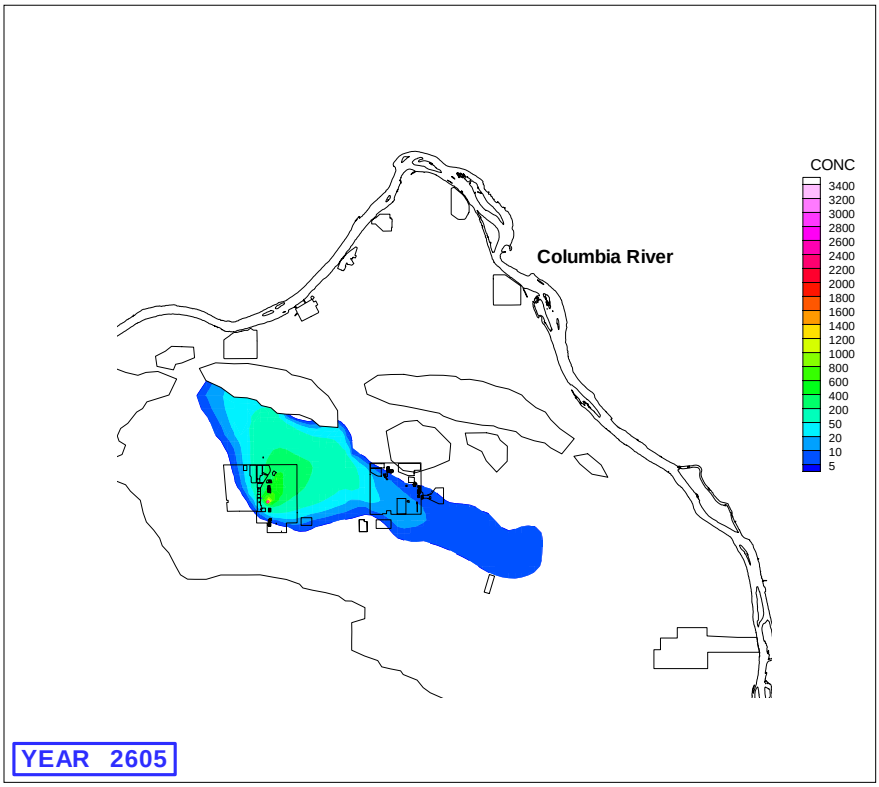


Figure A.3. Case 1a, Continuing Source, K_d and K_a = 0 (yr 2405 and 2505)



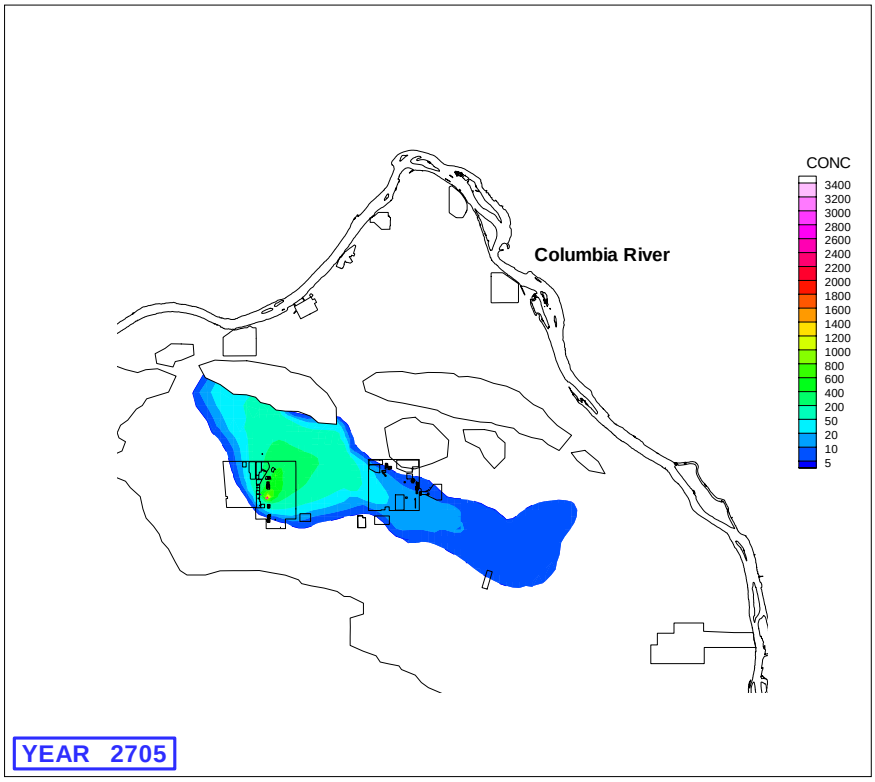
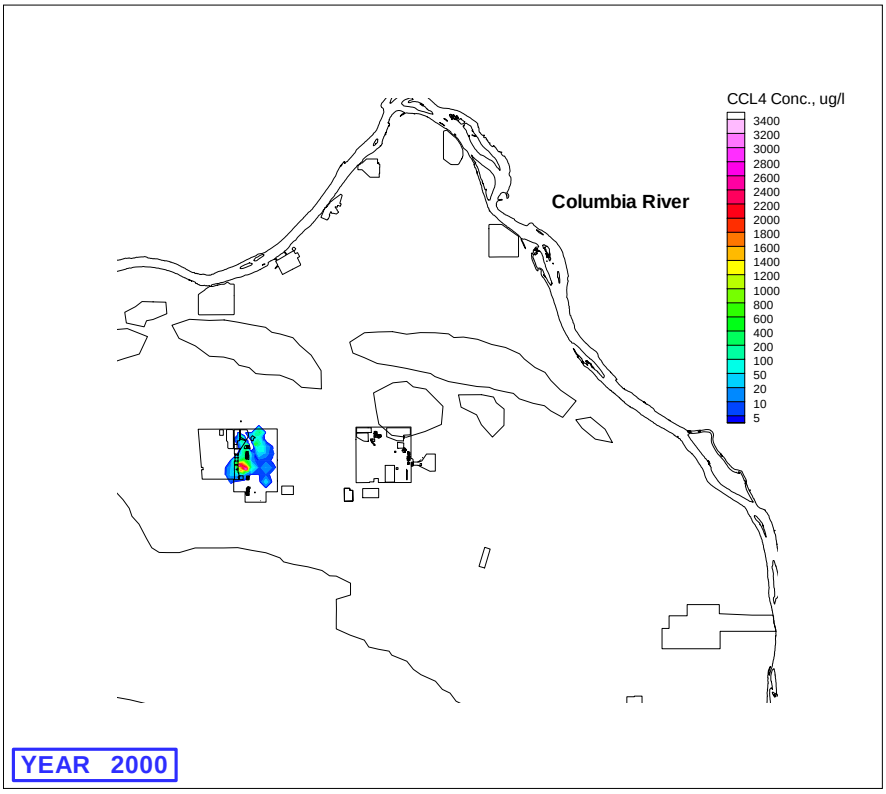


Figure A.4. Case 1a, Continuing Source, K_d and K_a = 0 (yr 2605 and 2705)



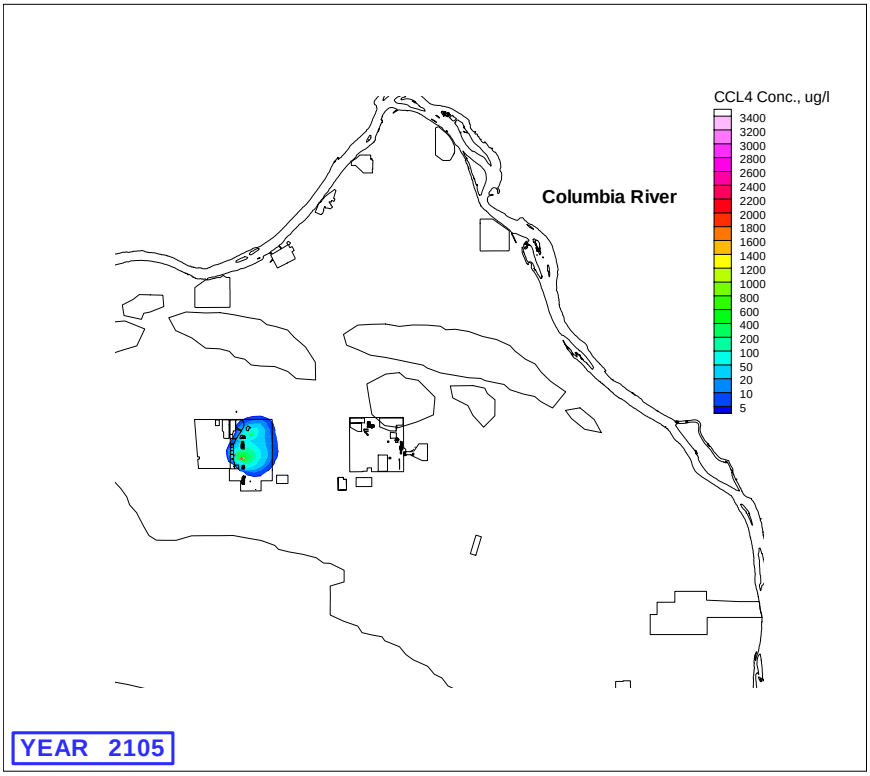
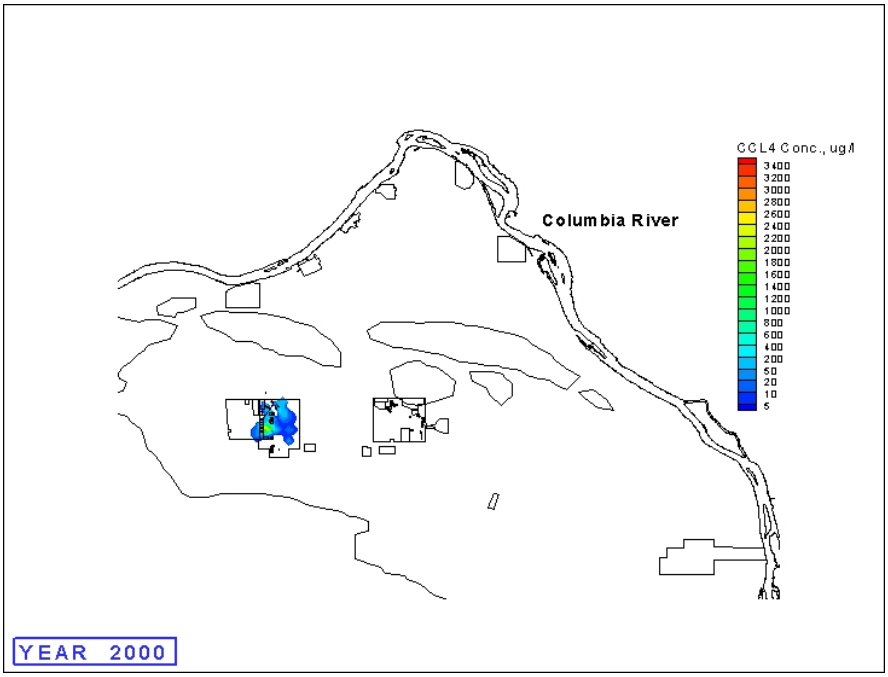


Figure A.5. Case 1b, Continuing Source, Median K_d and K_a (yr 2000 and 2105)



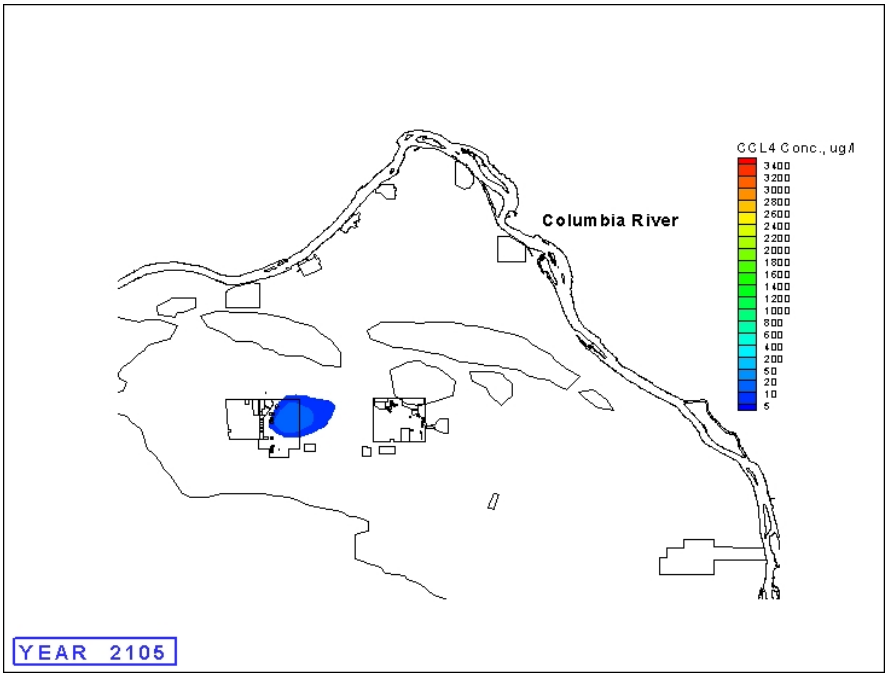


Figure A.6. Case 2, No Continuing Source, Limited Removal of Source Area, K_d and K_a = 0 (yr 2000 and 2105)

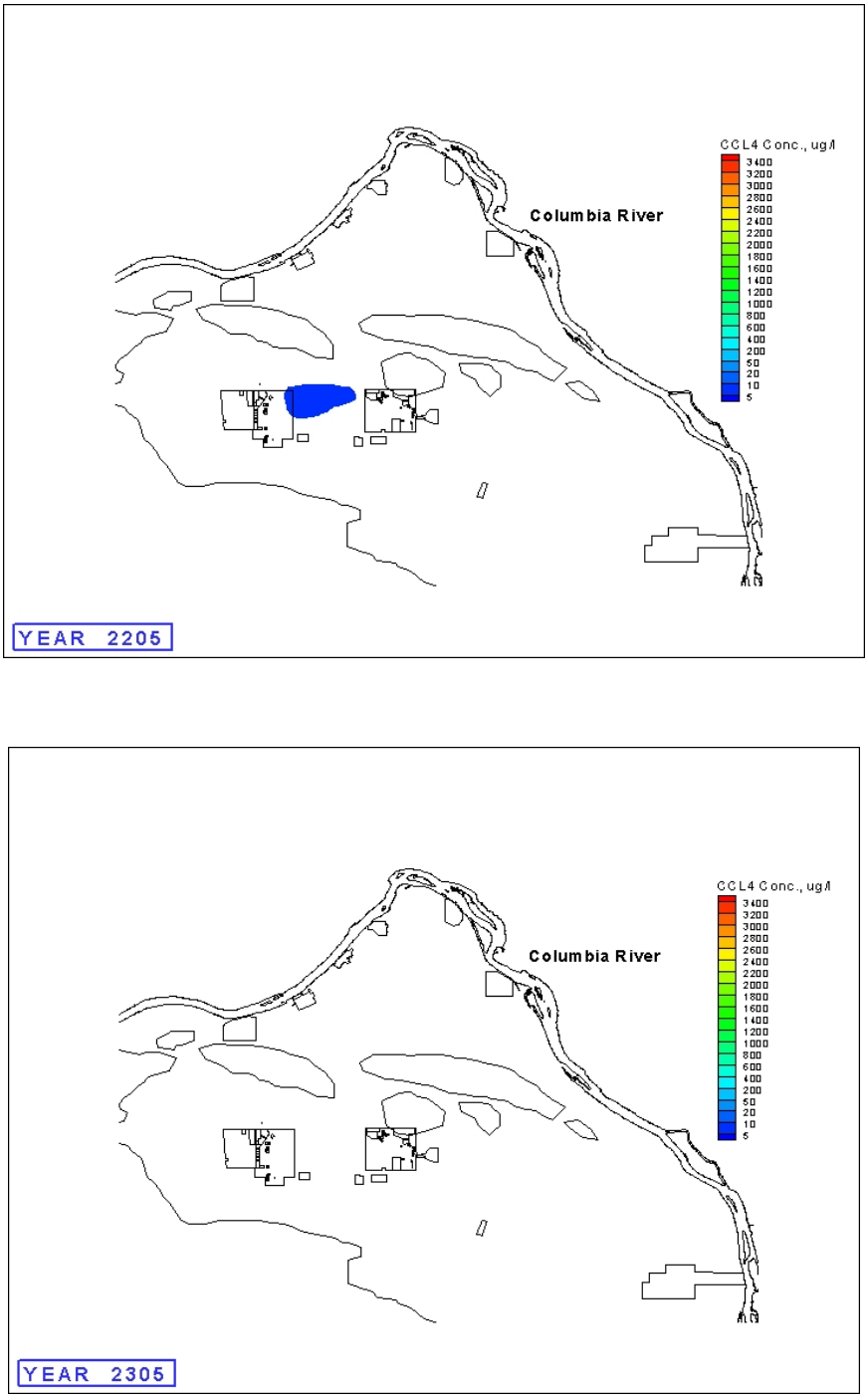
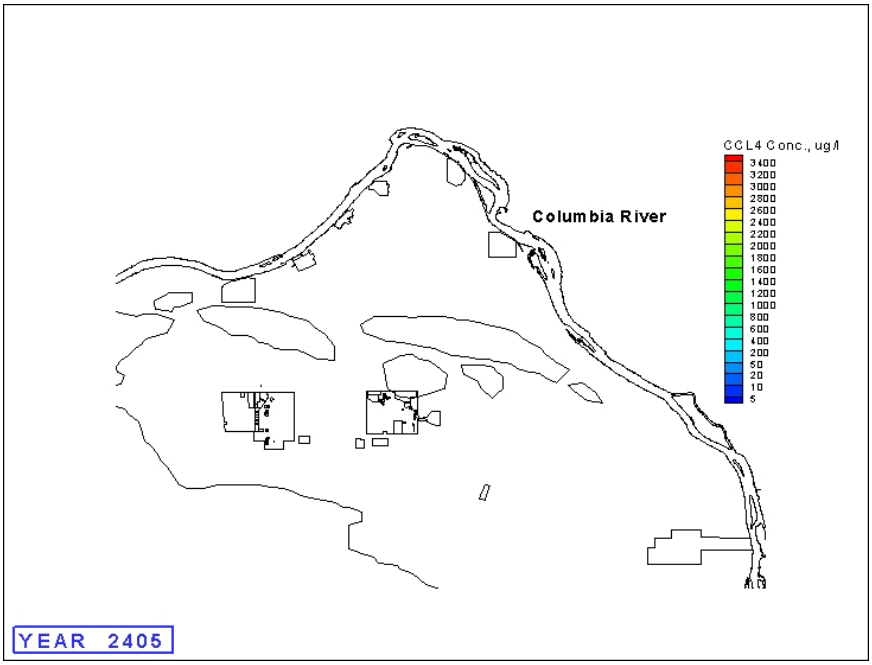


Figure A.7. Case 2 - No Continuing Source, Limited Removal of Source Area, K_d and K_a = 0 (yr 2205 and 2305)



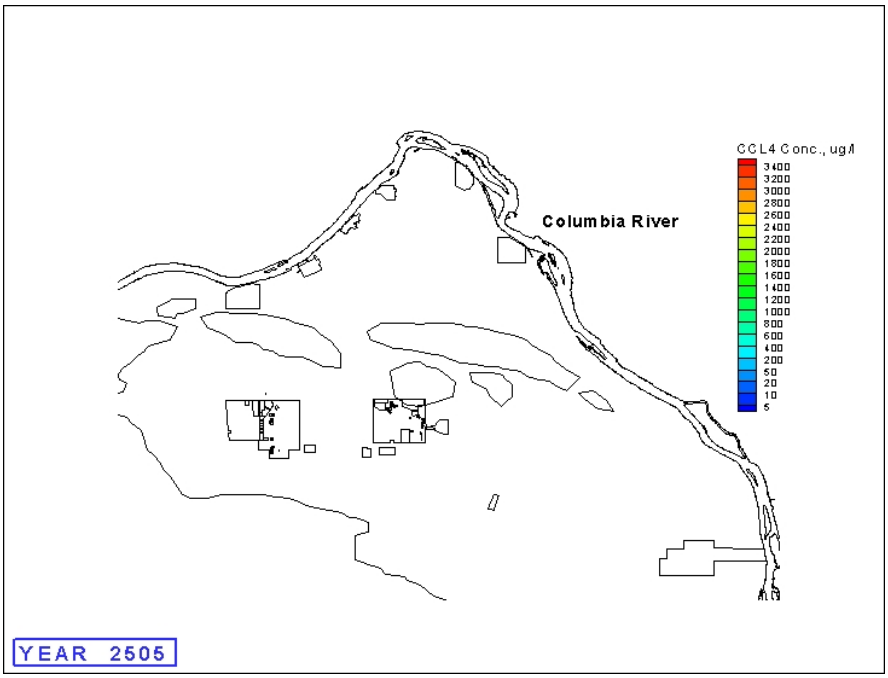


Figure A.8. Case 2, No Continuing Source, Limited Removal of Source Area, K_d and K_a = 0 (yr 2405 and 2505)

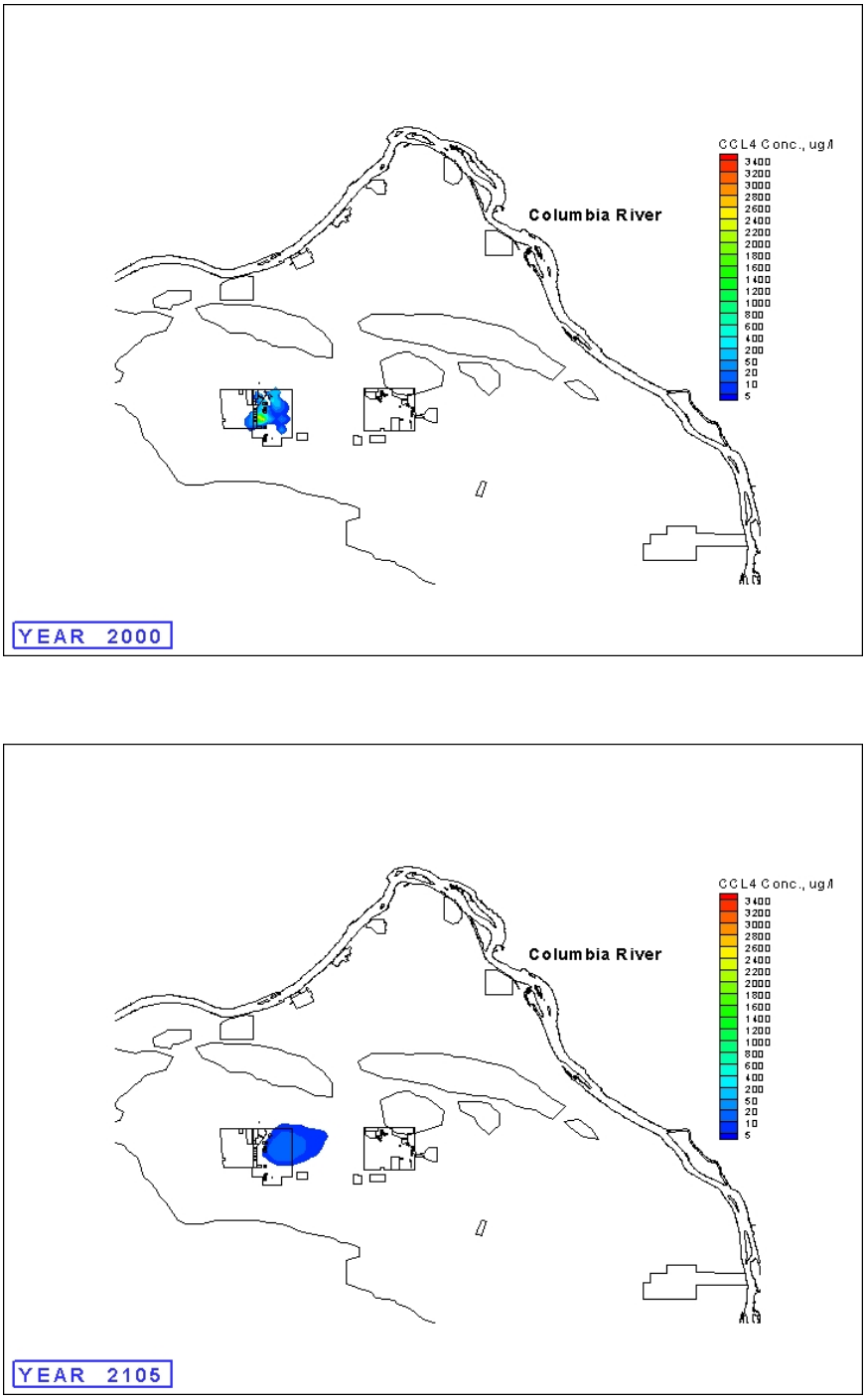


Figure A.9. **Case 3,** No Continuing Source, No Limited Removal of Source Area, K_d and K_a = 0 (yr 2000 and 2105)

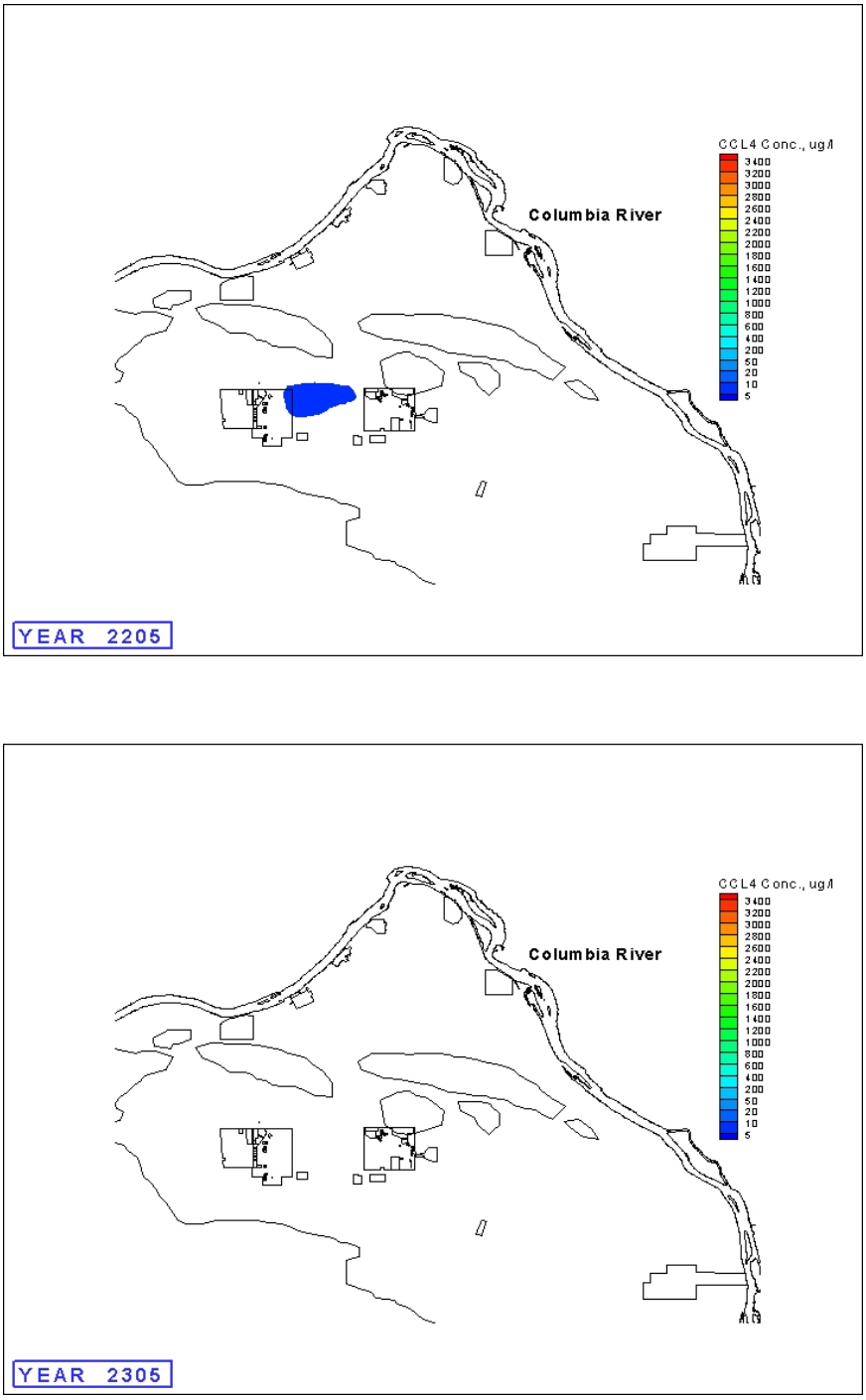


Figure A.10. **Case 3,** No Continuing Source, No Limited Removal of Source Area, K_d and K_a = 0 (yr 2205 and 2305)

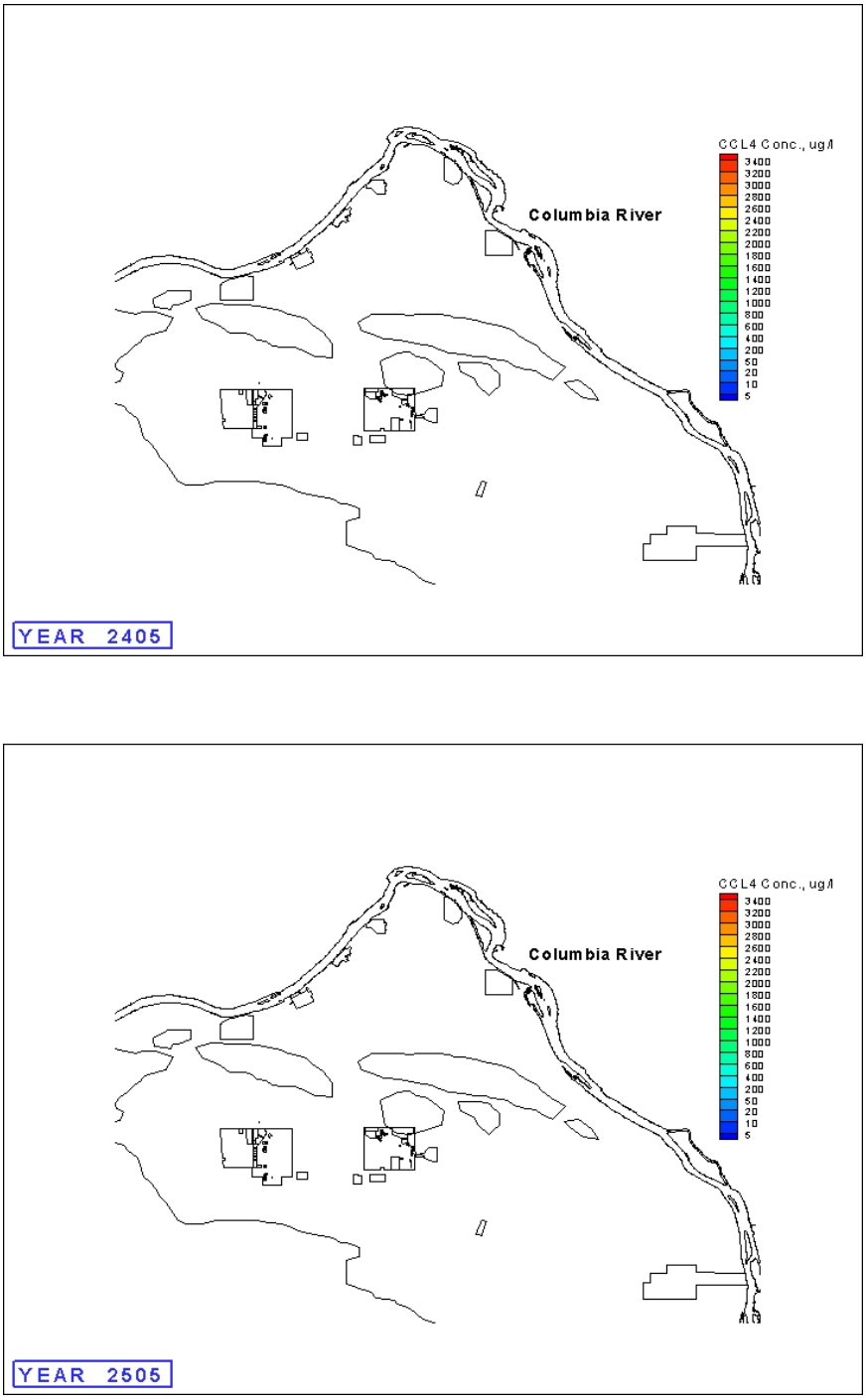


Figure A.11. **Case 3,** No Continuing Source, No Limited Removal of Source Area, K_d and K_a = 0 (yr 2405 and 2505)

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