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Numerical Analysis of Carbon Tetrachloride Movement in the Saturated and Unsaturated Zones in the 200 West Area, Hanford Site

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Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Bechtel Hanford, Inc.
Richland, Washington

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Numerical Analysis of Carbon Tetrachloride Movement in the Saturated and Unsaturated Zones in the 200 West Area, Hanford Site

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EXECUTIVE SUMMARY

From 1955 to 1973, carbon tetrachloride (CCl_4) was used in processing operations at Z Plant, located in the 200 West Area of the Hanford Site. Large quantities of CCl_4 were discharged to the 200 West Area soils via crib and trench disposal facilities during this period.

The main purpose of this report is to describe the numerical modeling that was used to estimate the effects of CCl_4 volatilization in the vadose zone and CCl_4 absorption by water in both the vadose zone and aquifer on the flow or movement of the immiscible liquid CCl_4 in both the vadose zone and aquifer near the 216-Z-9 Trench site. Another purpose is to show the differences in results from two different models (and computer codes).

In summary, absorption of CCl_4 in water appears to have a small effect on the immiscible liquid CCl_4 flow in the vadose zone and in an aquifer with nonflowing (horizontally) groundwater but a very large effect in an aquifer with flowing groundwater, even if the pore velocity is only 1 m/yr. The solubility of CCl_4 in water is about 800 mg/L, which is higher than the solubilities of many other volatile organic compounds; therefore, even slowly moving groundwater is sufficient to completely absorb (dissolve) all of the CCl_4 reaching the groundwater from the 216-Z-9 Trench. In other words, the CCl_4 from the 216-Z-9 Trench that reaches the aquifer does not reach the bottom of the aquifer because the flowing groundwater absorbs most of the CCl_4 in the top 10 m of the aquifer. However, if the aquifer has stagnant (or extremely slow moving) groundwater, liquid CCl_4 does reach the bottom of the aquifer, which is about 69 m deep. In stagnant groundwater, enough clean water is not available to keep absorbing the liquid CCl_4, whereas in an aquifer with flowing groundwater, there is. Similarly, the vadose water does not offer enough clean water to absorb the liquid CCl_4 significantly, and the flow of liquid CCl_4 is not affected much. Furthermore, volatilization of CCl_4 in the vadose zone does not appear to affect the liquid CCl_4 flow significantly under isothermal and static barometric pressure conditions.

The results of this report also show that the CCl_4 from the 216-Z-9 Trench could have reached the aquifer in less than 8 years if the CCl_4 residual in the vadose zone is very small. Thus, the 216-Z-9 Trench may have continuously been releasing CCl_4 into the aquifer since 1963. However, the travel time to the aquifer could easily have been longer than 8 years, depending primarily on the residual CCl_4 saturation value, the source term volume, and the porosities of the soil formations. All of these parameters are very important in determining the flow in the vadose zone. For example, if the source term volume were smaller than the upper-bounding value used in this report, the travel-time would increase significantly (i.e., flow would be much slower). On the other hand, if the porosities of the soils were smaller than the upper-bounding values used in this report, the travel-time would decrease significantly (i.e., flow would be much faster). Hence, accurate predictions of CCl_4 flow require accurate residuals, source term, and porosities.

The results of modeling performed for this report indicate that at least 66% and perhaps as much as 90% of the total CCl_4 released from the 216-Z-9 Trench remains in the vadose zone today. If the source term volume of CCl_4 were smaller, an even higher percentage of the CCl_4 could be expected to be in the vadose zone today. The residual saturation value of CCl_4 is an important parameter in determining the amount remaining in the vadose zone. If a high percentage of the CCl_4 mass is still in the vadose zone today, it would be very beneficial to remove the CCl_4 in the vadose zone before more reaches the groundwater. However, based on the modeling performed here, vadose-zone removal methods other than vapor extraction need to be investigated.

The modeling results indicate that vapor extraction (mechanical suction) of gaseous CCl_4 is not very effective; the one suction well in the model removed less than 0.5% of the total CCl_4 over 6 years. However, any two-dimensional model, including the model used in this report, would be biased against vapor extraction processes, especially when the extraction well is placed on the edge of the modeling domain. This is because only one side of the two-dimensional rectangular well is exposed to the gases, whereas in reality, gases completely surround the well. Furthermore, the single well in this model was placed 26 m from the edge of the trench on the end boundary, which is relatively far from the source to be very effective. Also, an impermeable air cover was not included in the model, which would also enhance vapor extraction. Hence, the effectiveness of vapor extraction processes in removing CCl_4 from the vadose zone is not conclusive in this report. Additional modeling with the extraction well closer to the trench should be performed, and the effects of an air cover should be included.

Based on the analyses in this report, a compositional (fully coupled flow transport) model is needed to determine the amount of immiscible liquid CCl_4 in the aquifer. However, an independent flow model with transport capability is easier to use, faster on a computer, and produces results similar to the more complicated compositional model, except for the amount of immiscible CCl_4 in the aquifer.

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1.0 INTRODUCTION

From 1955 to 1973, carbon tetrachloride (CCl_4) was used in processing operations at the Z Plant (currently called the Plutonium Finishing Plant) in the 200 West Area of the Hanford Site. Large quantities of CCl_4, a dense, nonaqueous-phase liquid, were discharged to the 200 West Area soils via trench and crib disposal facilities during this period. The liquid discharges also included significantly larger amounts of aqueous-phase fluids. As the nonaqueous- and aqueous-phase liquids migrated down through the vadose zone water, some of the CCl_4 was absorbed in vadose zone water, some volatilized in the vadose zone air-filled pore spaces, and some was retained in the vadose zone as residual saturation. Soil vapor extraction was initiated in 1992 as the preferred remedial alternative of the carbon tetrachloride expedited response action (ERA) for removal of CCl_4 from the vadose zone beneath the disposal facilities (DOE-RL 1991).

Numerical modeling is being used to estimate the extent and concentration of the CCl_4 contamination and to attempt to identify the phase in which it may be found. This information is to provide guidance for the ERA in remediation of the vadose zone and protection of the groundwater.

Thermal effects are expected to have been present at the time of discharge. However, thermal effects were not addressed in this study because no known heat sources exist in the vadose zone and the initial thermal gradients were expected to dissipate very quickly as a result of the large soil volume around and below the discharge trenches (or cribs). However, some of the CCl_4 discharged in the trench (or crib) was definitely lost to the atmosphere as a result of thermal effects at the time of discharge.

CCl_4 is an organic compound that does not mix easily with water (i.e., it is immiscible with water). However, some of the CCl_4 is absorbed by water, and that which is absorbed will always diffuse and probably disperse (if velocities are not zero) in the water just as any other contaminant does (i.e., concentration gradients will drive the absorbed CCl_4 mass to locations with lower concentrations). The term "absorption," which is more general than "dissolution" (Parker 1984), is used in this report to refer to the taking up of the CCl_4 in bulk by water.

As the liquid (generally immiscible) CCl_4 moved through the vadose zone, some was absorbed by water, volatilized, or retained as residual CCl_4 along the way; eventually, the remaining liquid CCl_4 reached the water table and entered the aquifer. When the liquid CCl_4 entered the aquifer, more pore water was available to absorb the CCl_4 and carry it away in the aqueous phase. The absorbed CCl_4 diffused and dispersed, which spread it out more in the groundwater. The amount of CCl_4 absorbed and carried away depends on the rate of groundwater flow. If the groundwater is flowing fast enough, the entire liquid CCl_4 entering the aquifer could be completely absorbed and carried away.

The main purpose of this report is to numerically show the effects of water absorption of CCl_4 and volatilization of CCl_4 on the flow of the immiscible liquid CCl_4 in both the unsaturated and

saturated zones around and below the 216-Z-9 Trench, one of the primary CCl_4 disposal facilities in the 200 West Area. Another purpose is to gain an understanding of the following questions.

1. How fast must the groundwater flow in order to absorb all of the liquid CCl_4 entering the aquifer?

2. How much time did it take for the discharged CCl_4 to reach water table?

3. How fast is the CCl_4 entering the aquifer?

4. How much CCl_4 is still in the vadose zone today?

5. How effective is a vapor extraction well in removing CCl_4 from the bottom of the vadose zone?

6. What are the important parameters and processes governing migration of CCl_4 in the subsurface?

Version 3.0 of the multiphase MAGNAS code (HydroGeologic 1994) appeared to be capable of answering the above questions and was the code used to perform the modeling for this report. Another purpose of this report is to compare the new version (3.0) of MAGNAS with an earlier version (2.1) of the code. The flow calculations for CCl_4, water, and air used in Version 2.1 of the MAGNAS code are not as rigorous as those used in Version 3.0. Version 2.1 calculated the amount of CCl_4 absorbed by water and volatilized into the air only after the immiscible liquid CCl_4 flow velocities as well as water and air velocities were calculated for the entire time period of interest. As a result, the earlier version (2.1) of the code did not slow the downward flow of immiscible liquid CCl_4 resulting from these absorption and volatilization losses. Version 3.0 couples the absorption and volatilization processes with the flow calculations at every iteration of each time step. Such a fully coupled model is referred to as a compositional model (Corapcioglu and Baehr 1987). Version 3.0 of MAGNAS adjusts the velocities at every iteration; therefore, the velocities should be more accurate than those calculated using Version 2.1 of MAGNAS (or other similar codes). However, the compositional model runs more slowly, is more difficult to use, and cannot handle a very large number of grid cells. Hence, the more conventional independent flow model is still a useful tool if the results are accurate enough.

A description of the conceptual model is given in Section 2.0, followed by the mathematical/ numerical model description in Section 3.0. The source-term data are provided with the conceptual model description in Section 2.0. All of the other data values are provided in Section 3.0. Section 4.0 provides the results (saturations and concentrations) for six different cases. In four cases (two groundwater flow rates with two CCl_4 residual values), the compositional model was used (Version 3.0 of the MAGNAS code); and in two cases (two groundwater flow rates with one CCl_4 residual value), the independent flow model (Version 2.1 of the MAGNAS code) was used.

2.0 CONCEPTUAL MODEL

The conceptual model is based on relatively well-known information, such as the aqueous-phase liquid and nonaqueous-phase liquid (NAPL) source terms, the location of the disposal facility, the geologic environment and its hydrologic properties, and the pertinent properties of the organic compound of interest (CCl_4).

2.1 LOCATION AND STRATIGRAPHY

A plan view of the 216-Z-9 Trench and vicinity in the 200 West Area is shown in Figure 2-1. The location and length (depth is shown in Figure 2-2) of the two-dimensional model domain is indicated by the north-south line intersecting the 216-Z-9 Trench in Figure 2-1. Even though the model is considered two-dimensional, it does have a width of 1 m in the third dimension, with no-flow boundary conditions on each side of the 1-m width. Hence, the model is really three-dimensional, but no flow takes place in the third dimension, the width of which is 1 m. The model is intended to show trends, as detailed in Chapter 1.0, rather than predicting absolute real quantities. Hence, in the two-dimensional model, the groundwater is assumed to flow from south to north, which may not be the actual flow direction at this location. To be realistic and predict absolute results, a three-dimensional model is probably needed because planar tilts are known to exist in the stratigraphy in this location but are ignored in the two-dimensional model.

A cross section of the model domain, shown in Figure 2-2, illustrates the stratigraphy used in the two-dimensional model of the subsurface beneath the 216-Z-9 Trench. The model domain is 276 m long and extends from ground surface to the bottom of the unconfined aquifer, a vertical distance of 129 m; the uppermost 60 m is unsaturated (Figure 2-2).

The major geologic units that lie above the water table beneath the 216-Z-9 Trench are, in descending order, the Hanford formation, the early Palouse soil, the Plio-Pleistocene unit (often referred to as "caliche"), and the Middle Ringold formation (Ringold Unit E). The Hanford formation, deposited as a result of cataclysmic flood waters, is composed of glaciofluvial gravels, sands, and silts. For this study, the Hanford formation was considered homogeneous, although the upper part is sometimes characterized as the gravel or coarse sequence, and the lower part is sometimes characterized as the sandy or fine sequence (Johnson 1993). Because both sequences are rather porous, liquid CCl_4 flows quickly through them. Hence, the effects of the Hanford formation heterogeneity (not addressed in this study) on CCl_4 migration is expected to be minimal as the heavy (dense) CCl_4 liquid tends to flow straight down. The early Palouse soil consists of eolian silt and fined-grained sand. The Plio-Pleistocene unit consists of basaltic detritus and a carbonate-rich paleosol. The Ringold Unit E is a series of alluvial gravels and sands, overbank deposits, and lacustrine deposits. The model domain used in the simulation stops at the Ringold lower mud unit. Detailed information on the surfaces of these geologic units in the vicinity of the 216-Z-9 Trench was obtained from data collected during the initial site

Figure 2-1. The 216-Z-9 Trench Site and Surrounding Area in 200 West Area.

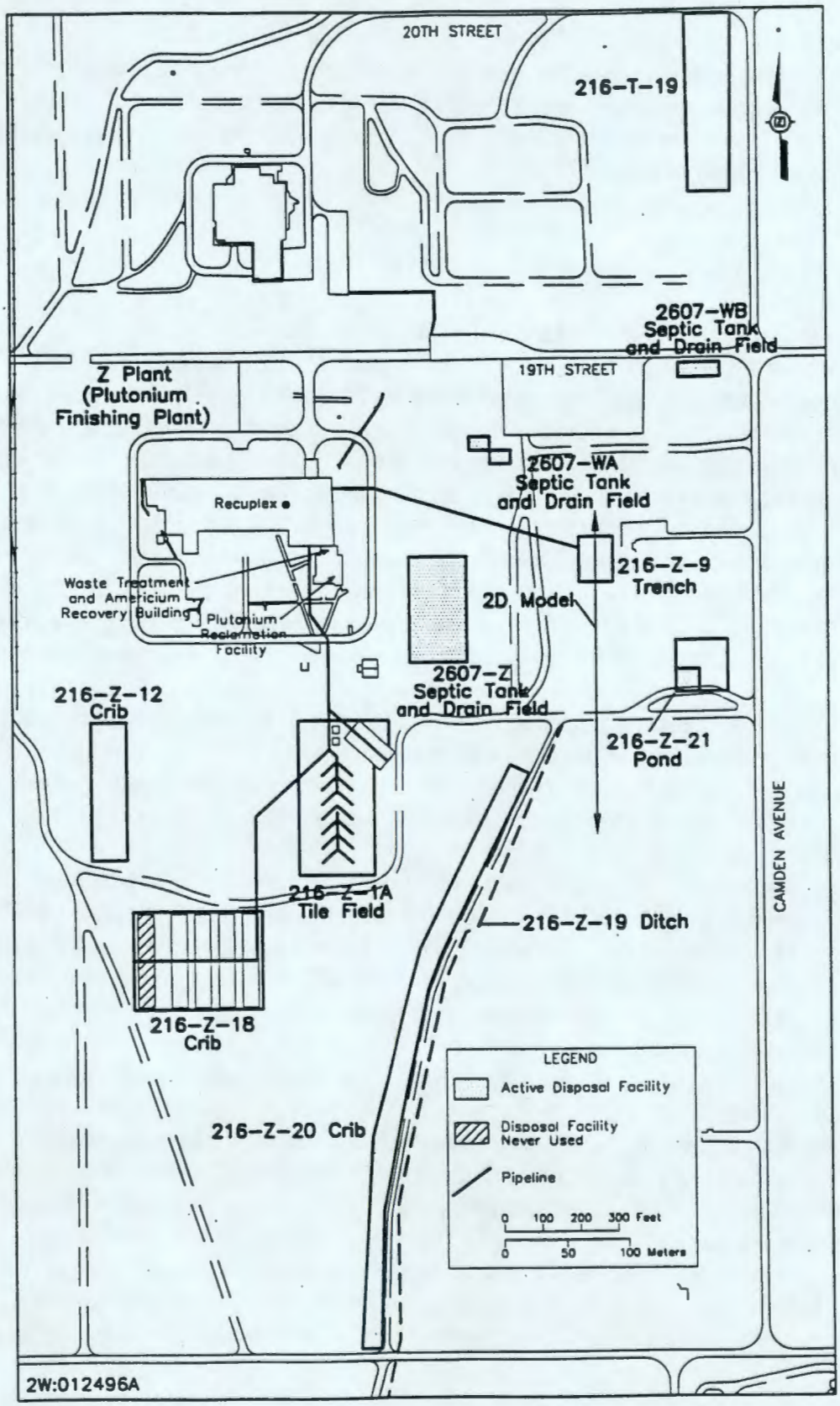
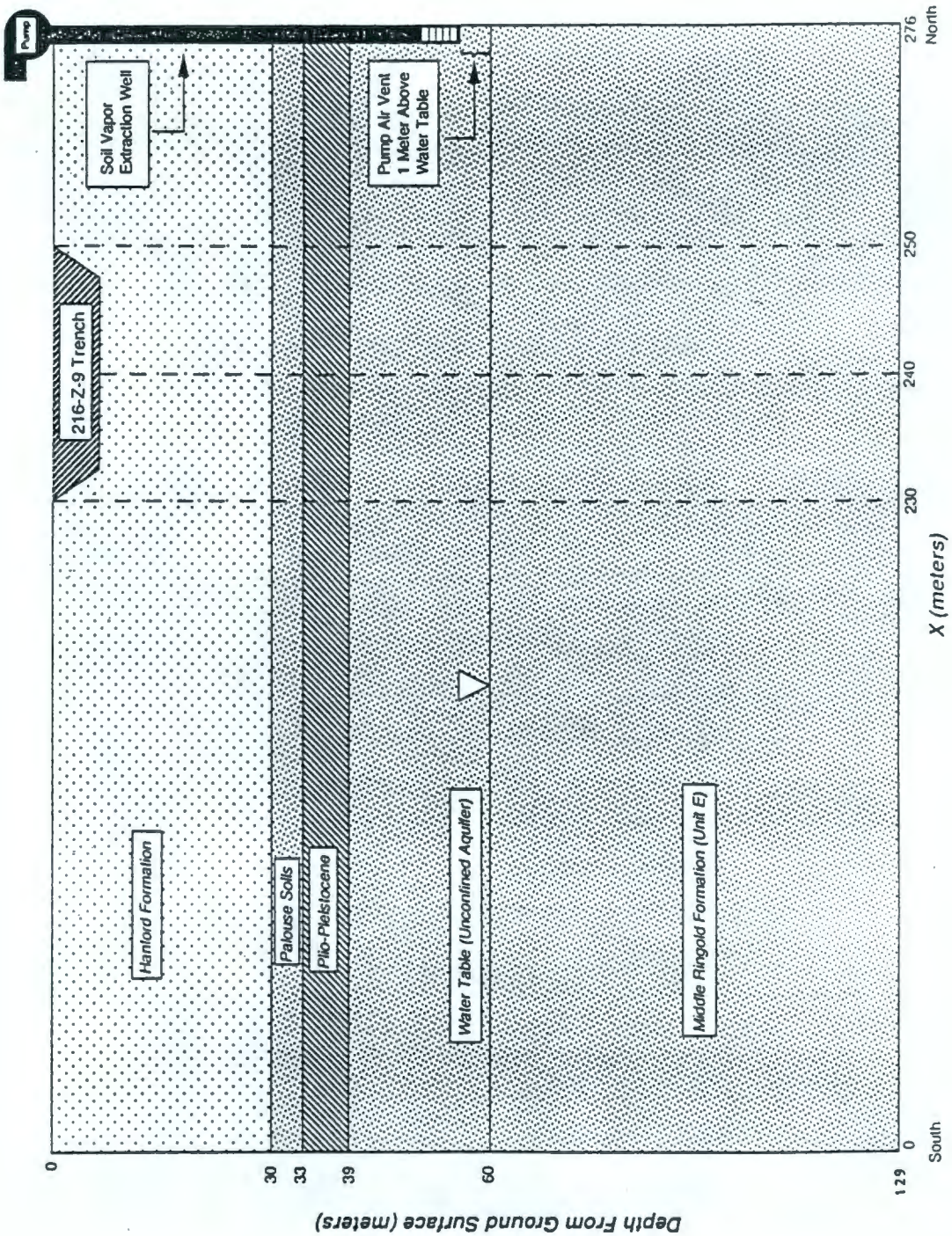


Figure 2-2. Stratigraphy Underlying 216-Z-9 Trench in Two-Dimensional Model Domain.



investigation to support CCl_4 remediation (Hagood and Rohay 1991). Additional information on the geology is included in DOE-RL (1991), Johnson (1993), and Rohay et al. (1994).

2.2 SOURCE TERM

In order for the numerical model to predict the movement of fluids into the vadose zone, the types of fluids introduced into the trench must be established. The 216-Z-9 Trench operated from 1955 to 1962 and is estimated to have received the amounts of aqueous fluid and CCl_4 listed in Table 2-1. To simplify the model, the discharged aqueous fluid was assumed to have water properties. A graphical representation of the volumes of aqueous fluid (water) and CCl_4 discharged to the 216-Z-9 Trench is shown in Figure 2-3. The 216-Z-1A Tile Field and the 216-Z-18 Crib also received NAPL effluents (DOE-RL 1991). The 216-Z-9 Trench was selected for numerical modeling because this facility, which has the smallest area of the three facilities, received the largest quantity of CCl_4 per unit of area and possibly the largest total quantity.

Table 2-1. Aqueous and NAPL Effluents Discharged to the 216-Z-9 Trench.

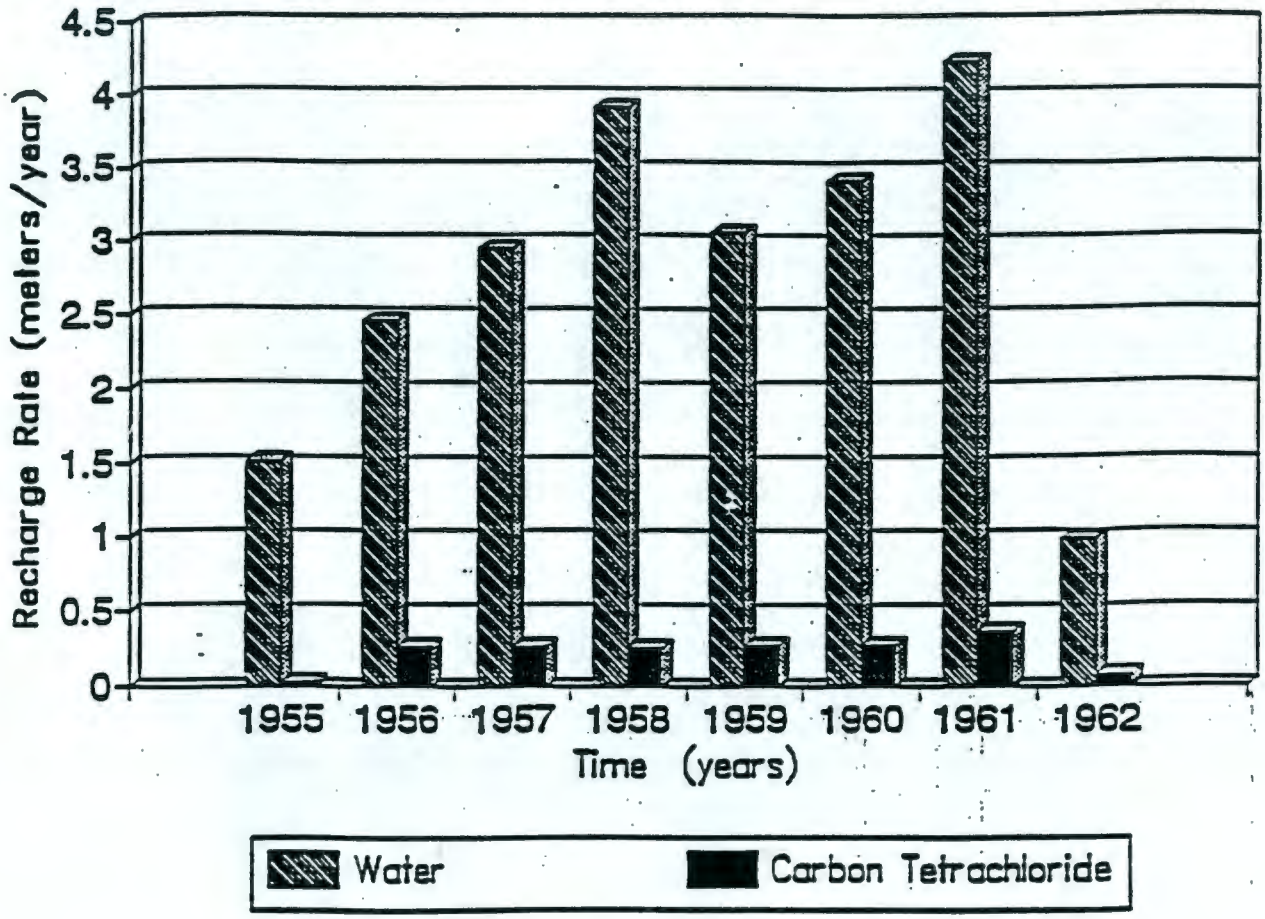
Year	Total Liquid Discharged (m^3)	Water Discharged (m^3)	CCl_4 Discharged		Recharge of Water[a] ($m^3/m^2/yr$)	Recharge of CCl_4[a] ($m^3/m^2/yr$)
			m^3	kg		
1955	260	254.88	5.12	8.14E+3	1.52	0.031
1956	460	413.6	46.4	7.38E+4	2.47	0.277
1957	540	493.6	46.4	7.38E+4	2.95	0.277
1958	700	655.8	44.2	7.03E+4	3.92	0.264
1959	560	512.7	47.3	7.52E+4	3.07	0.283
1960	620	572.2	47.8	7.69E+4	3.42	0.286
1961	770	706.63	63.37	1.01E+5	4.23	0.379
1962	180	165.19	14.81	2.35E+4	0.99	0.089
Total	**4,090**	**3774.6**	**315.4**	**5.015E+5**		

[a]Annual recharge (either water or CCl_4) was calculated by dividing the annual discharge (for either water or CCl_4) by the area of the trench: length of 18.3 m by width of 9.1 m = area of 167.2 m^2.

The bottom of the 216-Z-9 Trench is estimated to be 18.3 m long and 9.1 m wide. The 1-m width of the third dimension in the model domain intersects 1/9.1 of the entire trench. Thus, the source terms shown in Table 2-1 were multiplied by 1/9.1 in order to obtain the source term for the two-dimensional model.

The lowest annual amount of discharge to the 216-Z-9 Trench over the 8-year disposal period occurred in 1955, which was the first year of discharge. This was partly because the discharges

Figure 2-3. Aqueous and NAPL Sources Over Time for the 216-Z-9 Trench.



started after mid-year. The year with largest amount of discharge, which was over 100 metric tons of CCl_4, was 1961, which was just before the discharges were stopped in 1962. Over the entire 8-year span, more than 500 metric tons of CCl_4 were discharged to the 216-Z-9 Trench. These discharge volumes are at the high end of the range of volumes estimated to have been discharged to the 216-Z-9 Trench (DOE-RL 1991). However, the upper bound of discharged CCl_4 was used in the simulations to be conservative.

Based on earlier work (Piepho et al. 1993), the CCl_4 residual saturation is expected to play an important role in the CCl_4 movement in both the vadose zone and aquifer. The CCl_4 residual saturation is the volume of immovable fluid divided by the volume of pore space for a given volume of soil. In other words, the capillary forces in the vadose zone and the water pressures in the aquifer cannot move the residual CCl_4, which is trapped in closed-end pore spaces or adsorbed (held) by organic carbon compounds. Of course, a larger residual value means that less fluid is available for flowing. Also, not all of the movable fluid flows because some fluid is held in place by the capillary forces. Essentially, the fluid (both aqueous and nonaqueous) content is almost always larger than the residual content of the fluid.

2.3 INITIAL CONDITIONS AND BOUNDARY CONDITIONS

The initial conditions were obtained from a steady-state simulation with only water infiltrating the top boundary at a constant rate (0.5 cm/yr), with the barometric pressure head constant at one atmosphere (10 m of water column).

The boundary conditions on the aquifer consisted of constant pressure heads on both ends (north and south) so that fluid could flow in or out of these boundaries, which is what the groundwater was doing for cases with flowing groundwater. A no-flow boundary condition was used for liquid CCl_4 because, if the liquid CCl_4 were allowed to flow out, it would be lost from the system and unrepresented in figures summarizing the CCl_4 distribution. Instead, CCl_4 that would have flowed out of the model domain was forced to pond at the end of the model domain. The air pressure was fixed at one atmosphere on the land surface, with no barometric pressure oscillations included. A vapor extraction well with a mechanical suction of 130 in. of water column was screened at the bottom of the vadose zone on the north end of the model domain 32 years after the first effluent discharges in 1955.

3.0 MATHEMATICAL/NUMERICAL MODEL

For multiphase flow, the constitutive relationships for single-phase flow, which includes only liquid water, have to be extended to account for the additional NAPL and air phases. The air phase in single-phase flow is passive, whereas in three-phase flow, all phases are active. A passive air phase just means that an air pressure is not calculated, and the air content in the unsaturated zone is simply the complement of the water content.

3.1 MULTIPHASE CONSTITUTIVE RELATIONSHIPS AND PARAMETERS

The van Genuchten parameters for multiphase flow may be extended by the method presented in Lenhard and Parker (1987, 1988) to obtain saturations for each phase. This extension requires the computation of scaling parameters that are calculated from the interfacial tension parameters. The scaling parameters permit the expression of the capillary pressure-soil saturation relations for the combinations of fluid pairs (e.g., air-water, air-CCl_4, water-CCl_4) as appropriate in a given problem. Only two-phase relationships can be measured experimentally, so several theories exist for extending the two-phase relationships to the three-phase relationships, which are required for the CCl_4-water-air phases that are present in the 216-Z-9 Trench problem.

Parker (1989) developed a method for extending Mualem's theory to get the relative permeabilities in each cell (based on formation properties) as a function of capillary pressure (which can vary for each cell at each time step) for multiphase flow. The constitutive relations referred to above have been used successfully for the transmission oil simulations reported in Piepho and Runchal (1991). This approach also appeared to be better than other methods examined in Piepho et al. (1993).

The functional relationships that were used for multiphase flow are listed below. First, the relative permeabilities for two-phase flows using the van Genuchten/Mualem theory are given (van Genuchten 1978, Mualem 1976). Then the capillary pressure functions are given based on van Genuchten's theory, which is the theory that the MAGNAS code uses for capillary pressures. Finally, the extended van Genuchten/Mualem theory for the NAPL relative permeability (k_m) for a three-phase (water, NAPL, air) system is given.

3.1.1 Two-Phase Relative Permeabilities

The Mualem relative permeabilities (which vary from cell to cell and change over time), with van Genuchten retention, are calculated by the following equations:

$$
\begin{aligned}
k_{rw} &= (\overline{S}_w)^{1/2}\,[1-(1-\overline{S}_w^{\,1/m})]^2 \\
k_{ra} &= (\overline{S}_a)^{1/2}\,[1-\overline{S}_L^{\,1/m}]^{2m} \\
k_{rn}^{wn} &= (1-\overline{S}_w-\overline{S}_{nr})^{1/2}\,(1-\overline{S}_w^{\,1/m})^{2m} \\
k_{rn}^{na} &= (1-\overline{S}_w-\overline{S}_{nr})^{1/2}\,[1-(1-\overline{S}_L^{\,1/m})^m]^2
\end{aligned}
\qquad (1)
$$

where:

k_{rw} = relative permeability to water in an air-water system

k_{ra} = relative permeability to air in an air-water system

k_{rn}^{wn} = relative permeability to NAPL in a water-NAPL system (a function of water saturation)

k_{na}^{rn} = relative permeability to NAPL in an air-NAPL system (a function of air saturation)

$\overline{S}_i$ = effective wetting phase saturation, $S_i/(1 - S_{wr})$, where i = w(water), wr(water residual), a(air), n(NAPL), L(liquid), nr(NAPL residual)

S_L = $1 - S_a$ = effective liquid saturation (including both NAPL and water), $S_w + S_n$

S_w = absolute water saturation = total volume of water in a cell divided by volume of pore space in the cell

S_{wr} = residual water saturation = volume of immovable water divided by volume of pore space

S_a = absolute air saturation = volume of air divided by volume of pore space

S_n = absolute NAPL saturation = volume of NAPL divided by volume of pore space

S_{nr} = residual NAPL saturation = volume of immovable NAPL divided by volume of pore space

m = 1 - 1/n

n (superscript) = van Genuchten curve-fitting parameter (dimensionless).

3.1.2 Van Genuchten Capillary Pressure Functions

The capillary pressure functions of van Genuchten as used in MAGNAS are

$$P_{cnw} = \frac{\sigma_{nw}\rho_{fw}g}{\alpha\sigma_{aw}}\left[(\overline{S_w})^{-1/m}-1\right]^{1/n}$$

$$P_{can} = \frac{\sigma_{an}\rho_{fw}g}{\alpha\sigma_{aw}}\left[(1-\overline{S_a})^{-1/m}-1\right]^{1/n} \qquad (2)$$

$$P_{caw} = \frac{\rho_{fw}g}{\alpha}\left[(1-\overline{S_a})^{-1/m}-1\right]^{1/n}$$

which, upon substitution for ρ_{fw}, g, σ_{nw}, and σ_{an} in units using centimeter, gram, and second (CGS), become

$$P_{cnw} = \frac{605.345}{\alpha}\left[(\overline{S_w})^{-1/m}-1\right]^{1/n}$$

$$P_{can} = \frac{361.886}{\alpha}\left[(1-\overline{S_a})^{-1/m}-1\right]^{1/n} \qquad (3)$$

$$P_{caw} = \frac{980.66}{\alpha}\left[(1-\overline{S_a})^{-1/m}-1\right]^{1/n}$$

where:

P_c	=	capillary pressure (dynes/cm^2), calculated by code
σ	=	interfacial tension (dynes/cm), Table 3-1
α	=	van Genuchten curve-fitting parameter (cm^{-1}), Table 3-2
n (superscript)	=	van Genuchten curve-fitting parameter (dimensionless), Table 3-2
m	=	1 - 1/n
ρ	=	density of water, Table 3-1
g	=	acceleration due to gravity (980 cm/sec^2).

The subscript "nw" relates to NAPL and water, "an" relates to air and NAPL, and "aw" relates to air and water.

Table 3-1. Useful Physical and Chemical Properties of Carbon Tetrachloride.*

Property	CCl_4	Water
Solubility in water	800 mg/L @ 20°C	N/A
Vapor pressure	113.8 mm Hg @ 25°C	24 mm Hg @ 25°C
Saturated vapor concentration	754 mg/L @ 20°C	N/A
Henry's Law Constant, K_h, (dimensionless)	0.94	N/A
Liquid density	1.59 g/mL @ 20°C	0.998 g/mL @ 4°C
Vapor specific gravity	1.65	0.62 (air = 1.0)
Dielectric constant (dimensionless)	2.2	78.5
Surface tension	26.8 dynes/cm @ 20°C	72.2 dynes/cm @ 20°C
Interfacial tension (water-CCl_4)	45.0 dynes/cm	

* Adapted from DOE-RL (1991).

Table 3-2. Van Genuchten Single-Phase Parameters for Flow Model.

Parameter[a]	Hanford Formation	Palouse Soils	Plio-Pleistocene	Middle Ringold
S_r (Θ_r/Θ_s)	0.1026	0.1098	0.0869	0.0396
Porosity, Θ_s	0.3792	0.4745	0.4328	0.4140
α (1/cm)	0.0724	0.0054	0.0199	0.0662
n	1.60	3.0619	1.5635	1.3957
Ksat (vertical)	2.39E-3	1.4E-4	3.87E-5	2.1E-3
Ksat (horiz.)	2.39E-2	1.4E-3	3.87E-4	2.1E-2

[a]Note: Θ_r = residual volumetric water content (cm^3/cm^3)
Θ_s = saturated volumetric water content (cm^3/cm^3)
α = van Genuchten curve-fitting parameter (cm^{-1})
n = van Genuchten curve-fitting parameter (dimensionless)
m = 1 - 1/n
Ksat = saturated conductivity (cm/sec)

3.1.3 Three-Phase NAPL Relative Permeability

The van Genuchten/Mualem three-phase extension is given by the following equation:

$$k_{rn} = (\overline{S_L} - \overline{S_w} - \overline{S_{wr}})^{1/2}[(1 - \overline{S_w}^{1/m})^m - (1 - \overline{S_L}^{1/m})^m] \quad (4)$$

The van Genuchten parameters for each stratigraphic unit are given in Table 3-2 for the draining (drying) case. Because the multiphase models include air as an active phase, the wetting curves were not applicable. The wetting curves have smaller porosities than the drying curves because the trapped air in the wetting curves was subtracted from the total porosities. Both wetting and drying curves were studied and reported earlier (Piepho et al. 1993).

In addition to the hydraulic properties that are required for modeling, Table 3-1 lists other basic physical and chemical properties of CCl_4.

The grid used for numerical simulations with MAGNAS contained 1,680 nodes (i.e., 1,577 grid cells or elements), 83 grid cells (84 nodes) in vertical direction, and 19 grid cells (20 nodes) in horizontal direction. The vertical discretization is shown in Table 3-3. The water table is located at 69 m above the bottom boundary, which is the bottom of the unconfined aquifer. Because the computer code requires that the axis values be monotonic increasing, the vertical axis' zero value (origin) is placed at the bottom of the aquifer or model domain rather than at the top of the vadose zone or model domain during calculations. In the figures in this report summarizing the results of the numerical modeling, the zero value is placed at ground surface to conform with the model cross section (Figure 2-2).

Table 3-3. Vertical Discretization Data for Lithologic Units.

Layer	Depth (m)		Thickness (m)	No. of Grid Cells
	Top	Bottom		
Hanford formation	0	30	30	30
Palouse soils	30	33	3	3
Plio-Pleistocene	33	39	6	6
Middle Ringold (Unsaturated)	39	60	21	21
Middle Ringold (Saturated)	60	129	69	23

3.2 GOVERNING EQUATIONS

As discussed in Section 1.0, one of the purposes of this report is to compare the two types of models represented by the two versions of the MAGNAS code. The differences between the two types of models (compositional and independent flow) relate to whether the transport processes, such as absorption, diffusion, dispersion, and volatilization, are fully coupled with the advection calculations (compositional model), or are not coupled back to the advection calculations (independent flow model). The details of the governing equations, which are variations of Darcy's Law using the three-phase constitutive relations described in the preceding section, are described in the MAGNAS code documentation (HydroGeologic 1994) and by Ponday et al. (1994). Because of their detailed complexity, they are not presented here.

3.3 BOUNDARY CONDITIONS

For all scenarios, the recharge rate was 0.5 cm/yr. A larger recharge value of 5 cm/yr was used in a previous report (Piepho et al. 1993) and was not considered an important parameter because the flow of the CCl_4 seems to be controlled more by its own volume and properties. Also, the recharge value in the 200 West Area is not expected to exceed 1 cm/yr. The groundwater flow rate used in the simulations was relatively slow with a pore velocity of about 1 m/yr from south to north (left to right in Figure 2-2). The actual groundwater could have a pore velocity larger than 100 m/yr.

The vadose-zone end (north-south) boundary conditions were fixed heads for water and liquid CCl_4, so water and CCl_4 were allowed to flow past the end boundaries in the model. The aquifer end boundary conditions were fixed heads for water and no flow for liquid CCl_4. The boundary condition at the bottom of the model domain, which represents the impermeable bottom of the unconfined aquifer, was no flow for water and CCl_4. For the stagnant (nonflowing) groundwater cases, some water was allowed to flow out of the modeling domain on the bottom, left, and right boundaries. This water leakage was very small and equal to the recharge (0.5 cm/yr) entering the modeling domain from the top boundary. If no water were allowed to flow out of the model domain, the recharge would saturate the entire model domain. No immiscible (unabsorbed) liquid CCl_4 was allowed to flow out of the aquifer under conditions of stagnant groundwater, but some CCl_4, which was absorbed by the water, was allowed to flow out under conditions of both stagnant and flowing groundwater.

In all simulations, an extraction well with mechanical suction was turned on approximately 32 years after the start of the transient simulation (1955) on the north (right) end of vadose zone modeling domain. The suction was about one-third of an atmosphere (about 130 in. of water column) and was based on having a high suction pump to better show the effect of the soil vapor extraction removal of CCl_4 vapor from the vadose zone. Also, no impermeable air barrier was assumed to be placed over any of the land surface. Placement of an impermeable air barrier on

the land surface around the extraction well can enhance the effects of soil vapor extraction. For simplification, the barometric pressure changes were excluded from this analysis. The barometric pressure was kept constant at one atmosphere (10 m of water column).

3.4 INITIAL CONDITIONS

The initial conditions were obtained by simulating a 0.5-cm/yr recharge of water at the top boundary for 1,000 years. No NAPL existed during the initial condition simulation. Hence, the first NAPL appeared in the soils in 1955 when NAPL effluents were discharged to the 216-Z-9 Trench.

3.5 SOURCE TERM

The source term discharged to the 216-Z-9 Trench was defined in Section 2.0 in the presentation of the conceptual model. Even though the NAPL and water source terms consisted of mostly batch discharges, they were modeled as continuous sources with respect to time in this analysis. The effect of this simplification diminishes as the NAPL and water sources migrate downward through the vadose zone. The vadose zone acts to buffer or hold up the effluents such that the effluents in future batches can catch up with the preceding ones. Hence, the batch discharges are expected to have the greatest effect on the upper part of the Hanford formation just below the trench. Future work could investigate this effect in detail to determine the depth at which the NAPL flow becomes uniform.

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4.0 MULTIPHASE RESULTS

4.1 BRIEF DESCRIPTION OF THREE SCENARIOS

Groundwater flow and CCl_4 residual saturation uniquely define different scenarios that can be analyzed using numerical models. The following three scenarios were analyzed in this study:

- Scenario 1: Groundwater flowing and CCl_4 residual saturation at 0.0001
- Scenario 2: Groundwater flowing and CCl_4 residual saturation at 0.01
- Scenario 3: Groundwater stagnant (not flowing in a horizontal direction) and CCl_4 residual saturation at 0.01.

The residual saturation for CCl_4 is the volume of immovable CCl_4 (i.e., the amount that is not controlled by pressure gradients) divided by the volume of the pore space (porosity). This immovable or stationary CCl_4 is assumed to exist in both the vadose zone and aquifer. One reason some CCl_4 can be stationary is that organic carbon in the soil will tend to hold onto the CCl_4, keeping it from moving. At the CCl_4 site, the amount of organic carbon in the soils is very small at less than 0.07% (Yonge et al. 1996). Hence, small values (0.0001 and 0.01) of residual CCl_4 saturation were used in all numerical simulations. Small pore entrapment of fluid is also possible, causing larger residual values, but this process is more common for water than for CCl_4 because water, the wetter fluid and first fluid, will tend to fill the small pores, making them unavailable for CCl_4 to be trapped.

The three scenarios were run with both the compositional model and the independent flow model, providing the following six simulations or cases:

Case 1: Compositional model with groundwater flowing right (north) and CCl_4 residual saturation at 0.0001

Case 2: Compositional model with groundwater flowing right (north) and CCl_4 residual saturation at 0.01

Case 3: Compositional model with stagnant groundwater and CCl_4 residual saturation at 0.01

Case 4: Independent flow model with groundwater flowing right (north) and CCl_4 residual saturation at 0.0001

Case 5: Independent flow model with groundwater flowing right (north) and CCl_4 residual saturation at 0.01

Case 6: Independent flow model with stagnant groundwater and CCl_4 residual at 0.01.

The six cases provide upper and lower bounds on residual values and groundwater flow rates for analysis using the two different flow models.

These six simulations, or cases, are compared/contrasted with each other for four major aspects:

- The effects of CCl_4 residual values on CCl_4 plume with flowing groundwater
- The effects of stagnant and flowing groundwater on CCl_4 plume with very small residual
- The effects of compositional and independent flow models on absorbed and immiscible CCl_4 with flowing groundwater
- The effects of compositional and independent flow models on absorbed and immiscible CCl_4 with stagnant groundwater.

The results of the numerical analyses are shown in a series of graphs for each case. Different pairs of cases are compared in the following sections of this chapter. To aid in comparison of results between different pairs of cases, selected graphs may be shown in more than one section.

The graphs for each case show the distribution of CCl_4 in a particular phase (water or air) using weighted CCl_4 concentrations. The weighted CCl_4 concentrations are mass concentrations (mass per phase volume) that have been weighted (multiplied) by the amount of water (or air) content in the cell. In other words, the weighted concentrations represent the mass of CCl_4 in a particular phase in a computational cell divided by the cell volume in units of milligrams of CCl_4 per liter of subsurface. For example, the mass concentration of CCl_4 absorbed in water in a cell would be weighted by the water content in the cell:

$$\text{weighted concentration} = \frac{\text{mg } CCl_4}{\text{L water}} \times \text{water content,}$$

$$\text{where water content} = \frac{\text{water volume in cell}}{\text{pore volume in cell}} \times \frac{\text{pore volume in cell}}{\text{total volume in cell}}.$$

This means that the weighted concentrations are based on CCl_4 mass, not CCl_4 volume as CCl_4 saturations are. The mg/L unit is often considered equal to one part per million (ppm), but the ppm unit is not used here since it usually refers to number of moles of contaminant (or volume, not mass) per million moles of water. Hence, mg/L was chosen as the preferred unit for CCl_4 weighted concentration here.

The main advantage in showing the weighted concentrations in the graphs is that the total mass of CCl_4 in a unit square (1 m by 1 m) on the graph can be easily calculated. The total CCl_4 mass in a unit square (recall that the model domain has unit thickness) is equal to the average CCl_4 concentration (mg/L) in the unit square times 1,000 L/m^3. This is the case for concentrations in the water phase in both the vadose zone and aquifer and for the air phase in the vadose zone.

The actual CCl_4 concentration in the aqueous phase volume (i.e., CCl_4 mass per unit volume of water), instead of the total volume, can be calculated by dividing the weighted concentrations in the graphs by the volumetric water content in that region. The initial (steady-state) volumetric water content is about 0.08 in the upper vadose zone or Hanford formation, 0.30 in the Plio-Pleistocene and Palouse formations, 0.25 in the Ringold Formation, and about 0.41 in the aquifer. The last three water contents are high because the Plio-Pleistocene, Palouse, and Ringold Formations all have tight moisture-retention characteristics (see Table 3-2) and large porosities (and the aquifer is 100% saturated). For actual concentrations in the air phase, divide the weighted concentrations in the graph by the volumetric air content in that region. The volumetric air content is about 0.92 in the upper vadose zone, 0.15 in the Plio-Pleistocene and Palouse formations, and 0.16 in the unsaturated Ringold Formation. There is no air phase in the aquifer. The above prescription is not recommended in the vadose zone as the transient moisture content is much greater than the initial (or steady-state) moisture contents due to the large effluent discharges of water and CCl_4 into the trench. However, the above method for estimating CCl_4 mass concentrations in the water is very appropriate and accurate for the concentrations in the groundwater because the aquifer always has a moisture content of 0.414, which is equal to the porosity of the aquifer.

4.2 EFFECTS OF CARBON TETRACHLORIDE RESIDUAL SATURATION VALUES WITH FLOWING GROUNDWATER - CASES 1 AND 2

Figure 4-1 (Case 1 with 0.0001 CCl_4 residual saturation) shows more CCl_4 penetration in the aquifer and faster movement through the vadose zone than does Figure 4-2 (Case 2 with 0.01 CCl_4 residual saturation) as a result of the effects of a smaller CCl_4 residual saturation in Case 1 (0.0001 versus 0.01 in Case 2). The smaller CCl_4 residual means that a larger percentage of the CCl_4 is movable, which tends to enhance the CCl_4 flow rate to the aquifer. In mathematical/ physical terms, a larger percentage of CCl_4 volume (i.e., larger saturation) has a larger relative permeability that causes the CCl_4 to flow faster (see Equation 4 in Section 3.1.3). Recall that the relative permeability is a multiplicative factor in the total hydraulic conductivity used in Darcy's Law.

The concentrations in the vadose zone for the two cases are very similar with higher concentrations in the Plio-Pleistocene and Palouse formations due to their higher fluid-retention properties. Also, in both cases, the CCl_4 plume reaches the aquifer in less than 8 years, which means that some CCl_4 mass was reaching the aquifer while discharges into the 216-Z-9 Trench were still taking place in 1962. However, the amount of CCl_4 reaching and penetrating the aquifer is not enough to actually reach the bottom of the aquifer and form a CCl_4 pool. The amount of mass is small enough that the flowing groundwater can absorb all of the CCl_4 mass that enters the aquifer. If the CCl_4 source term volume were not at its upper bound, the travel time to the water table would be longer.

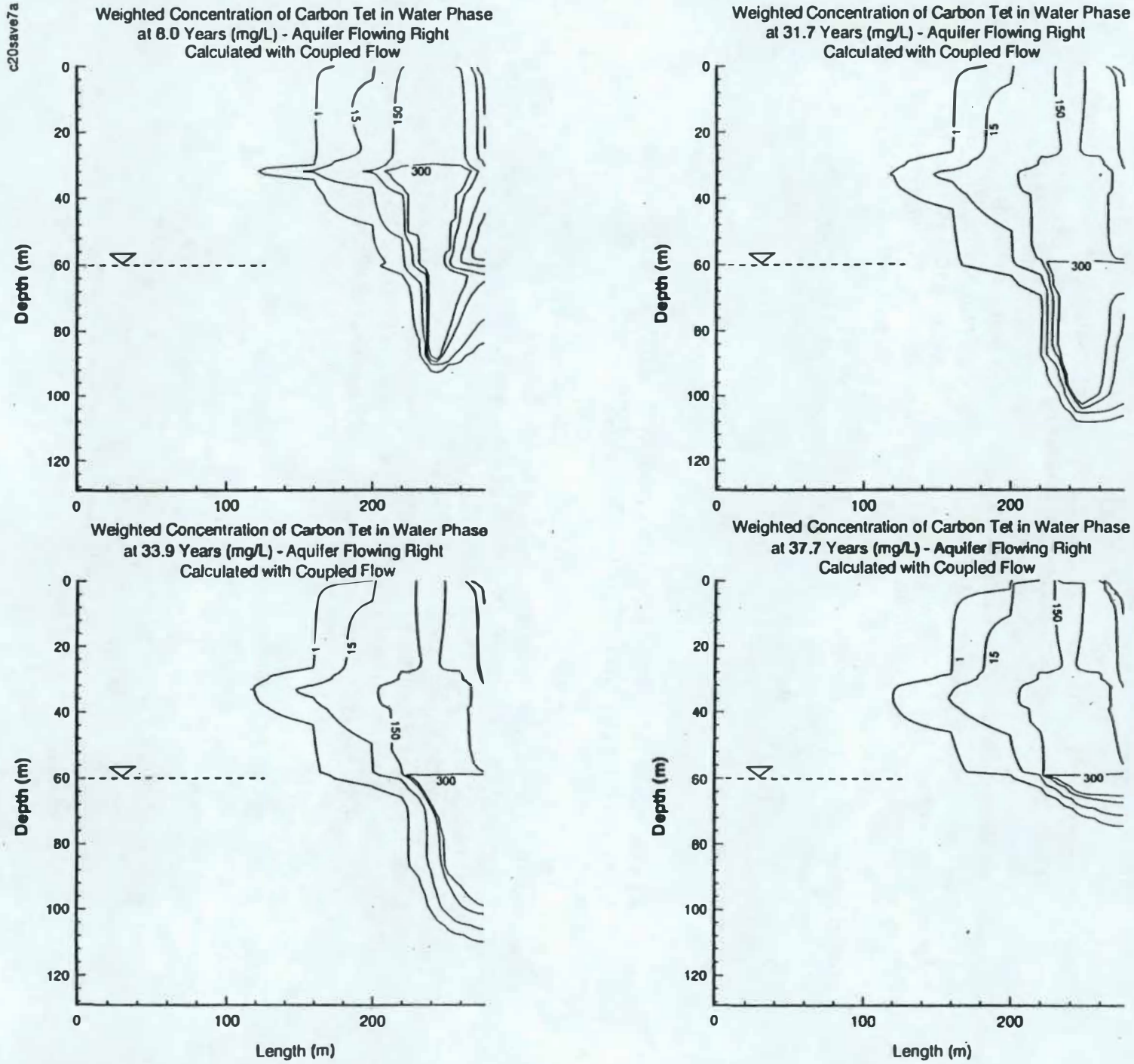

Figure 4-1. Case 1 Weighted Carbon Tetrachloride Concentrations in Water Phase.

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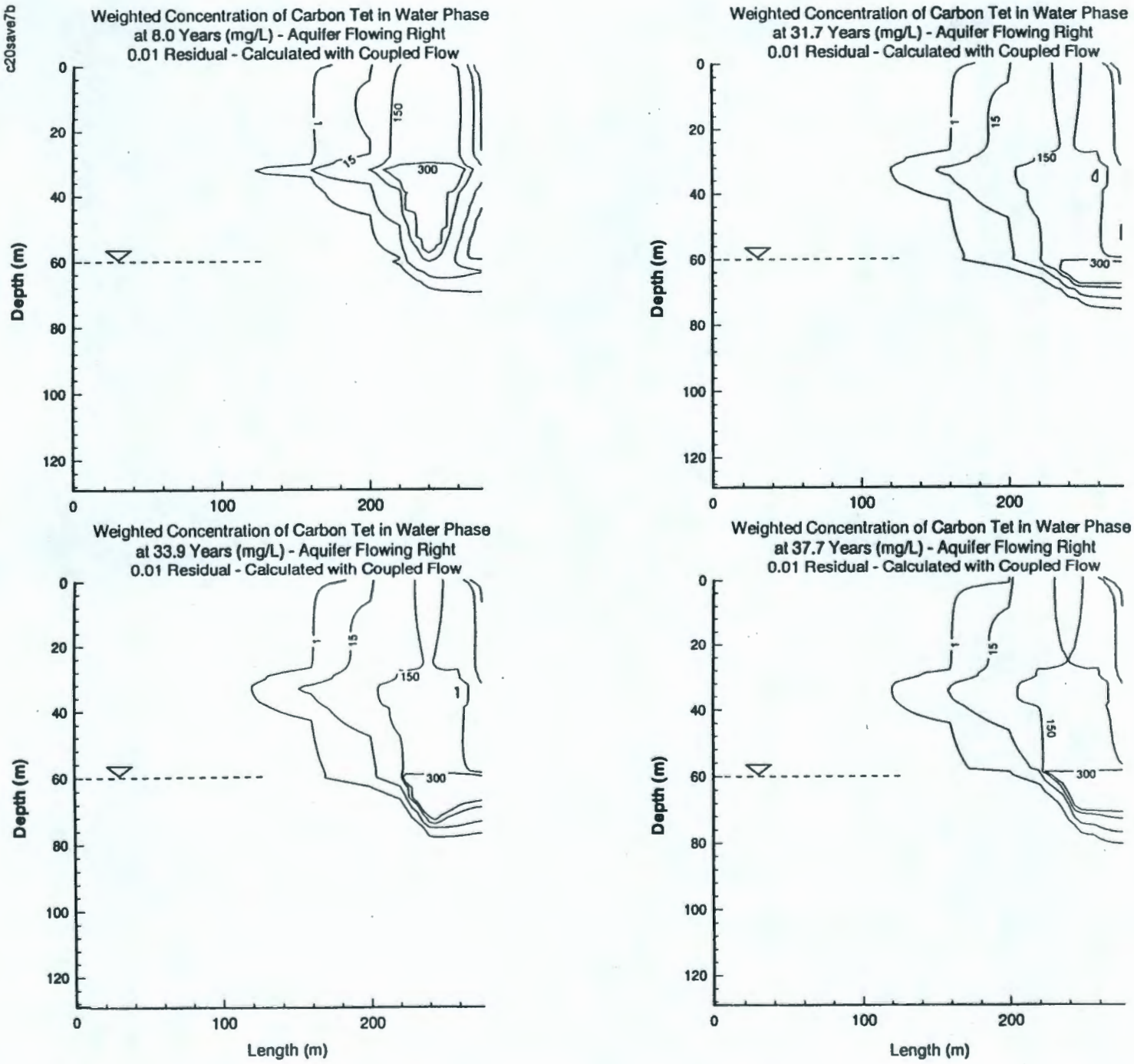

Figure 4-2. Case 2 Weighted Carbon Tetrachloride Concentrations in Water Phase.

4.3 EFFECTS OF GROUNDWATER FLOW WITH CARBON TETRACHLORIDE RESIDUAL SATURATION OF 0.01 - CASES 2 AND 3

The previous two cases showed that if the groundwater is flowing with a pore velocity as low as 1 m/yr, no CCl_4 mass reaches the bottom of the aquifer. Cases 2 and 3 show how this changes when the groundwater is not flowing. Clearly, the flowing groundwater in Case 2 has a large impact on the CCl_4 penetration depth in the aquifer. Figure 4-3 (Case 2 with flowing groundwater) shows that all of the CCl_4 is absorbed by the flowing water in the aquifer, whereas in Figure 4-4 (Case 3 with stagnant groundwater), the CCl_4 reaches the bottom of the aquifer and forms a CCl_4 pool. Hence, some liquid CCl_4 is expected to be found at the bottom of the aquifer if the groundwater is stagnant or moving at a velocity much smaller than 1 m/yr. The groundwater is not expected to be stagnant under the 216-Z-9 Trench; therefore, liquid CCl_4 is not expected to exist at the bottom of the aquifer in the 200 West Area at the Hanford Site. However, the analysis of these two cases using the compositional model is compared to the analysis using the independent flow model in Section 4.4.

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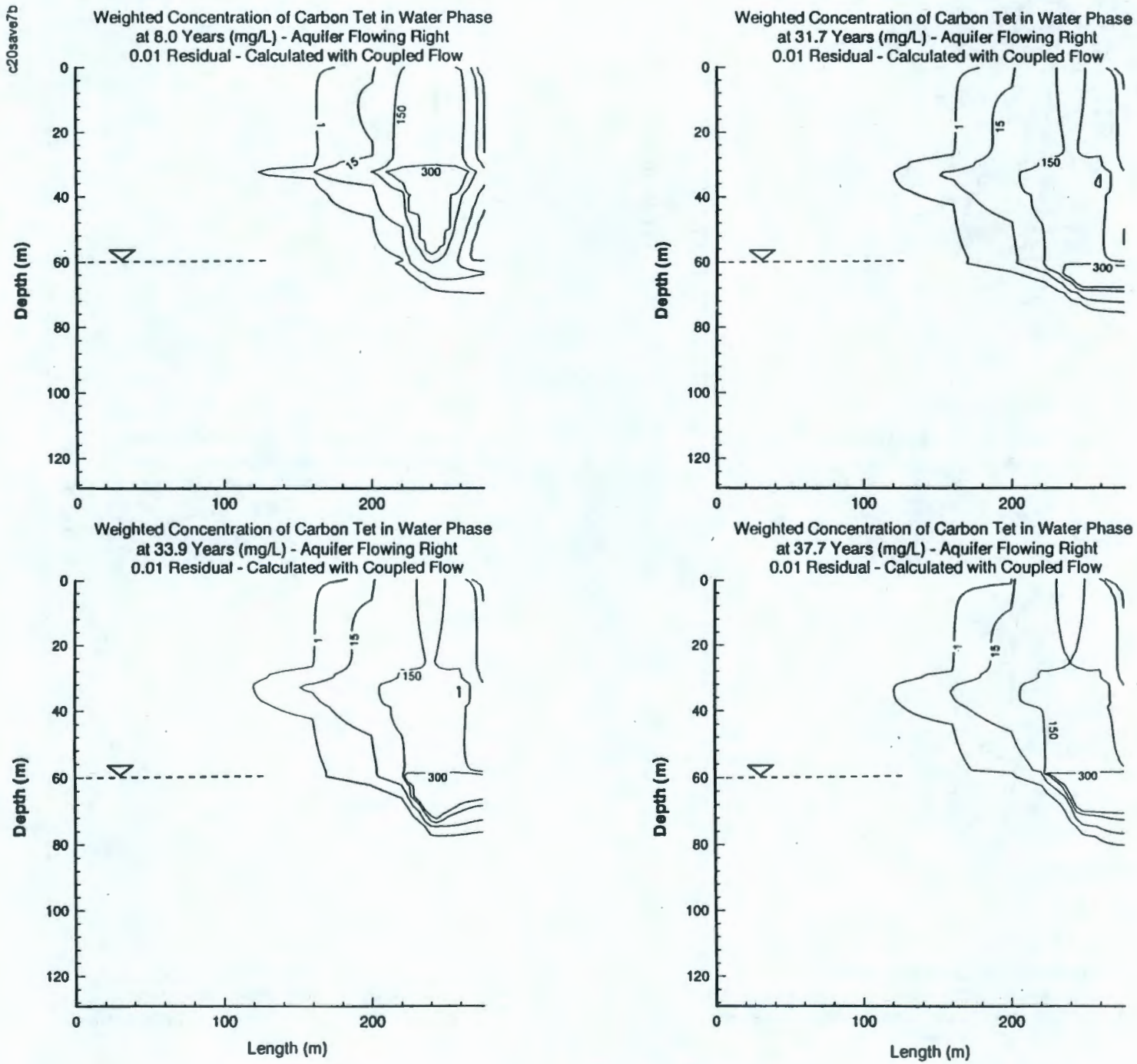

Figure 4-3. Case 2 Weighted Carbon Tetrachloride Concentrations in Water Phase.

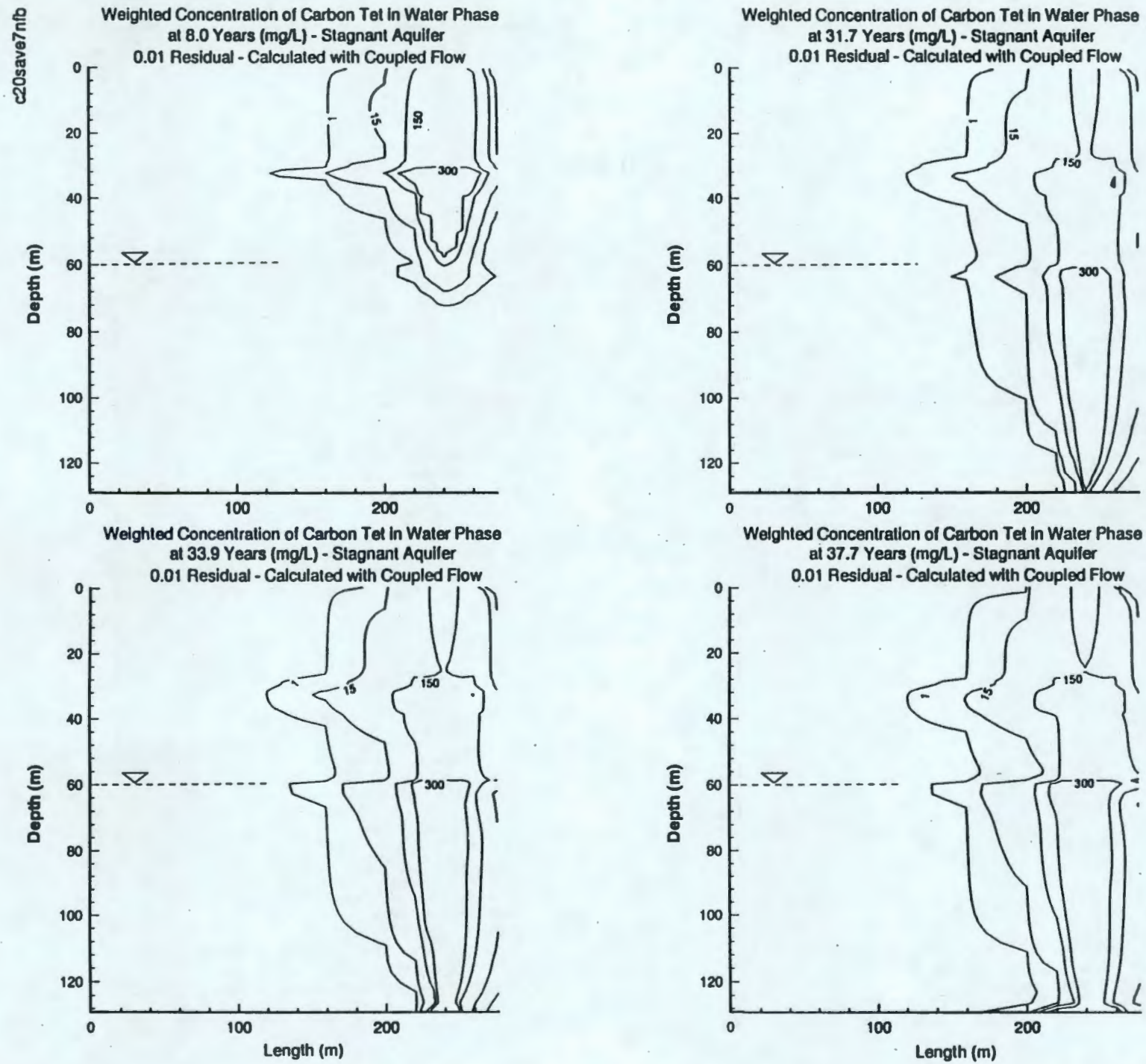

Figure 4-4. Case 3 Weighted Carbon Tetrachloride Concentrations in Water Phase.

4.4 EFFECTS OF NUMERICAL FLOW MODEL TYPE WITH FLOWING GROUNDWATER AND CARBON TETRACHLORIDE RESIDUAL SATURATION OF 0.01 - CASES 2 AND 5

When comparing the compositional flow model (flow and transport fully coupled) with the independent flow model (flow not dependent on transport), only the immiscible liquid CCl_4 saturations are shown and compared. Figure 4-5 (Case 2 with compositional model) clearly shows that no immiscible CCl_4 saturation exists in the flowing groundwater because all of the CCl_4 is absorbed by the water. Figure 4-6 (Case 5 with independent flow model), however, shows that the independent flow model calculates an immiscible saturation in the aquifer because the effects of the water absorption are not included in the CCl_4 flow velocities. The compositional model is expected to be more accurate and realistic than the independent flow model; therefore, the conclusion that there is no liquid CCl_4 ponding at the bottom of the aquifer (Section 4.3) is expected to be true.

Furthermore, it can be concluded from these cases (2 and 5) that use of the compositional model is mandatory if more accurate predictions of the flow and transport of CCl_4 in an aquifer are desired. However, for predictions of CCl_4 flow and transport in the vadose zone, either type of model may be sufficient because their saturation profiles are quite similar in the vadose zone, especially for the first 8 years. In other words, the water absorption of CCl_4 and volatilization of CCl_4 does not appear to affect the liquid CCl_4 flow in the vadose zone, but does in the saturated zone. This is due to the larger amounts of water available in the aquifer than in the vadose zone for absorbing the immiscible CCl_4.

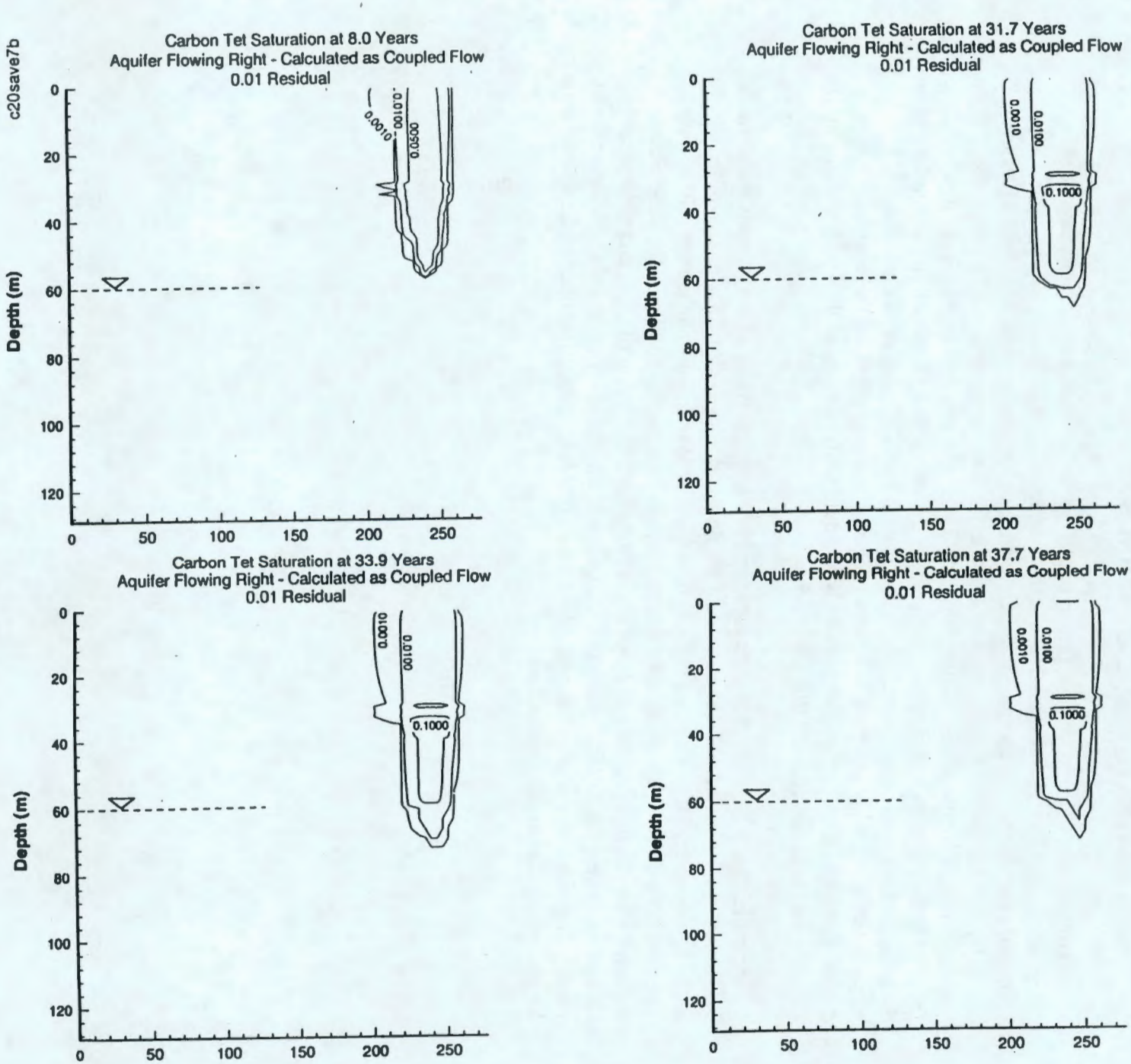

Figure 4-5. Case 2 Immiscible Liquid Carbon Tetrachloride Saturation.

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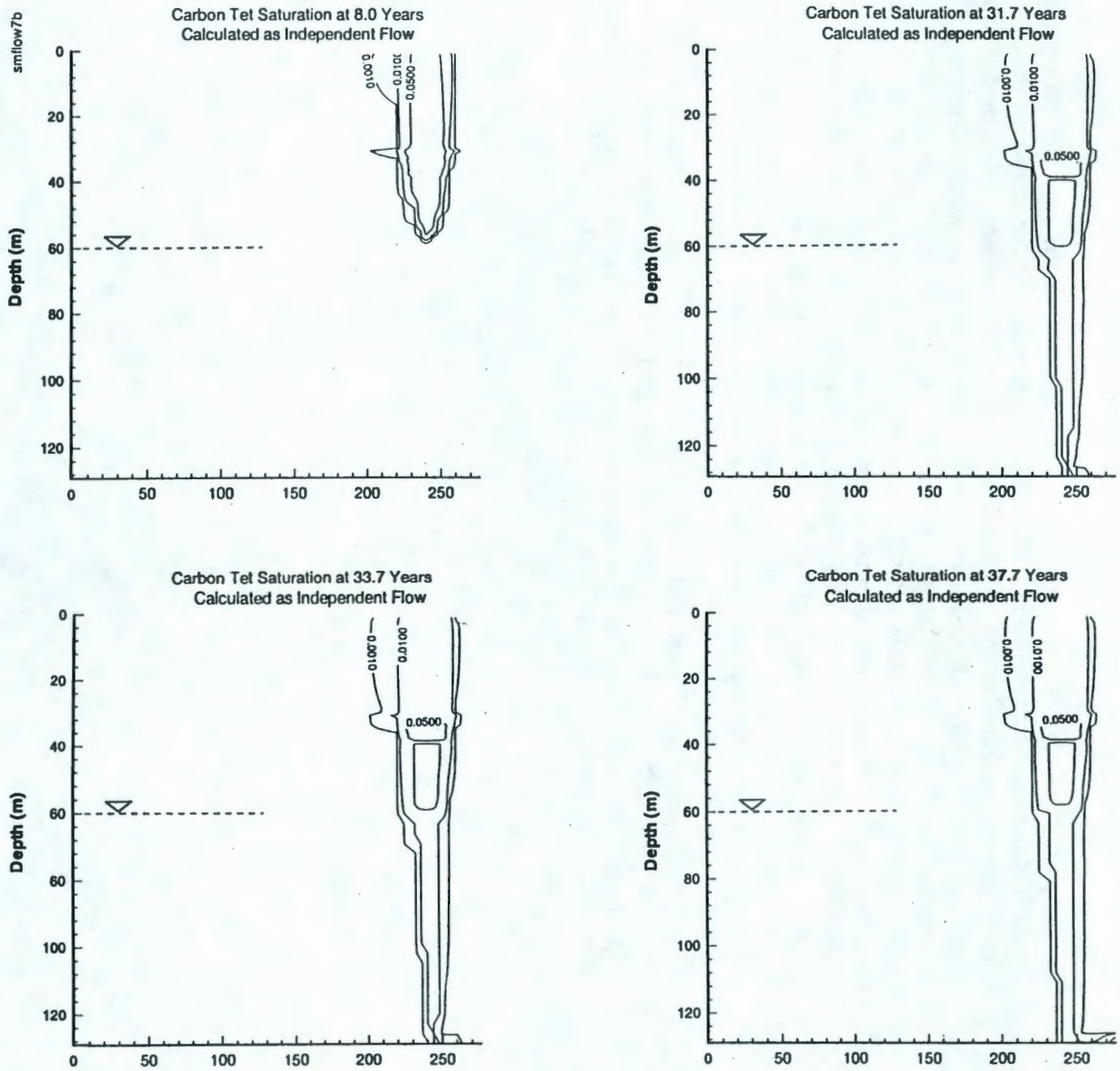

Figure 4-6. Case 5 Immiscible Liquid Carbon Tetrachloride Saturation.

4.5 EFFECTS OF NUMERICAL FLOW MODEL TYPE WITH FLOWING GROUNDWATER AND CARBON TETRACHLORIDE RESIDUAL SATURATION OF 0.0001 - CASES 1 AND 4

The compositional flow model shows higher CCl_4 concentrations in the aqueous (water) phase than the independent flow model for the flowing groundwater scenario as shown in Figure 4-7 (Case 1 with compositional model) and Figure 4-8 (Case 4 with independent flow model). This means that the compositional model allows more absorption of CCl_4 by water to take place. The reasons for this are not clear because the same solubility limit of 800 mg/L was used for both models. Apparently, the transport part of the independent flow model tends to keep more of the CCl_4 mass immiscible rather than allowing it to be absorbed. This difference needs more investigation as there could be an inconsistency in the computer codes or their input. The compositional model also shows higher CCl_4 concentrations in the air phase as shown in Figures 4-9 and 4-10. Again, these differences require additional investigation. It would be interesting to compare the concentrations in the air phase to actual field measurements.

Also, the time periods of 33.9 and 37.7 years in Figure 4-9 show the effects of the vapor extraction pump on the right boundary of the model domain. The concentration contours on the graph are pulled over to the right somewhat, indicating the presence of the pump that was turned on 32 years after the start of the simulation.

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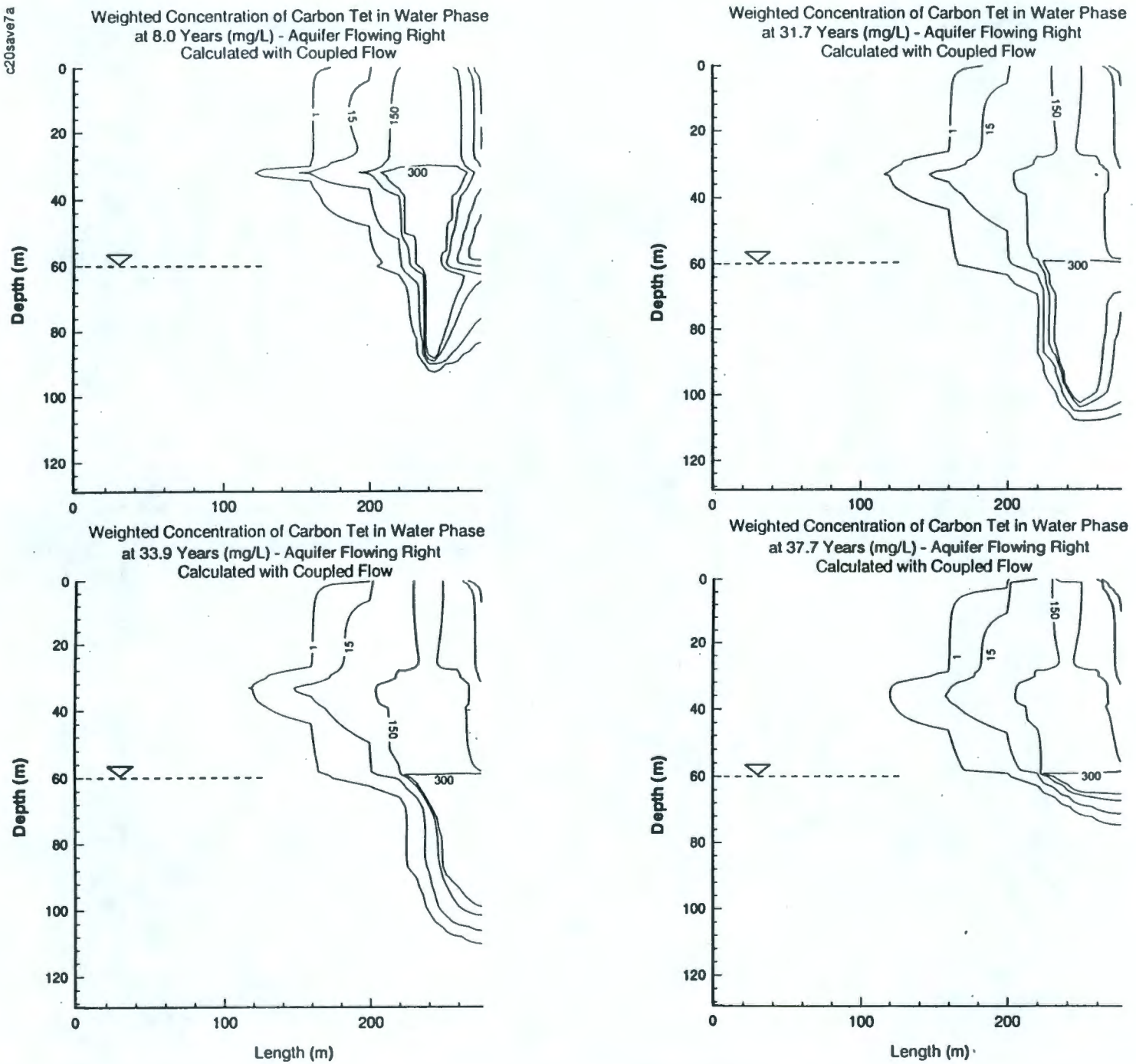

Figure 4-7. Case 1 Weighted Carbon Tetrachloride Concentration in Water Phase.

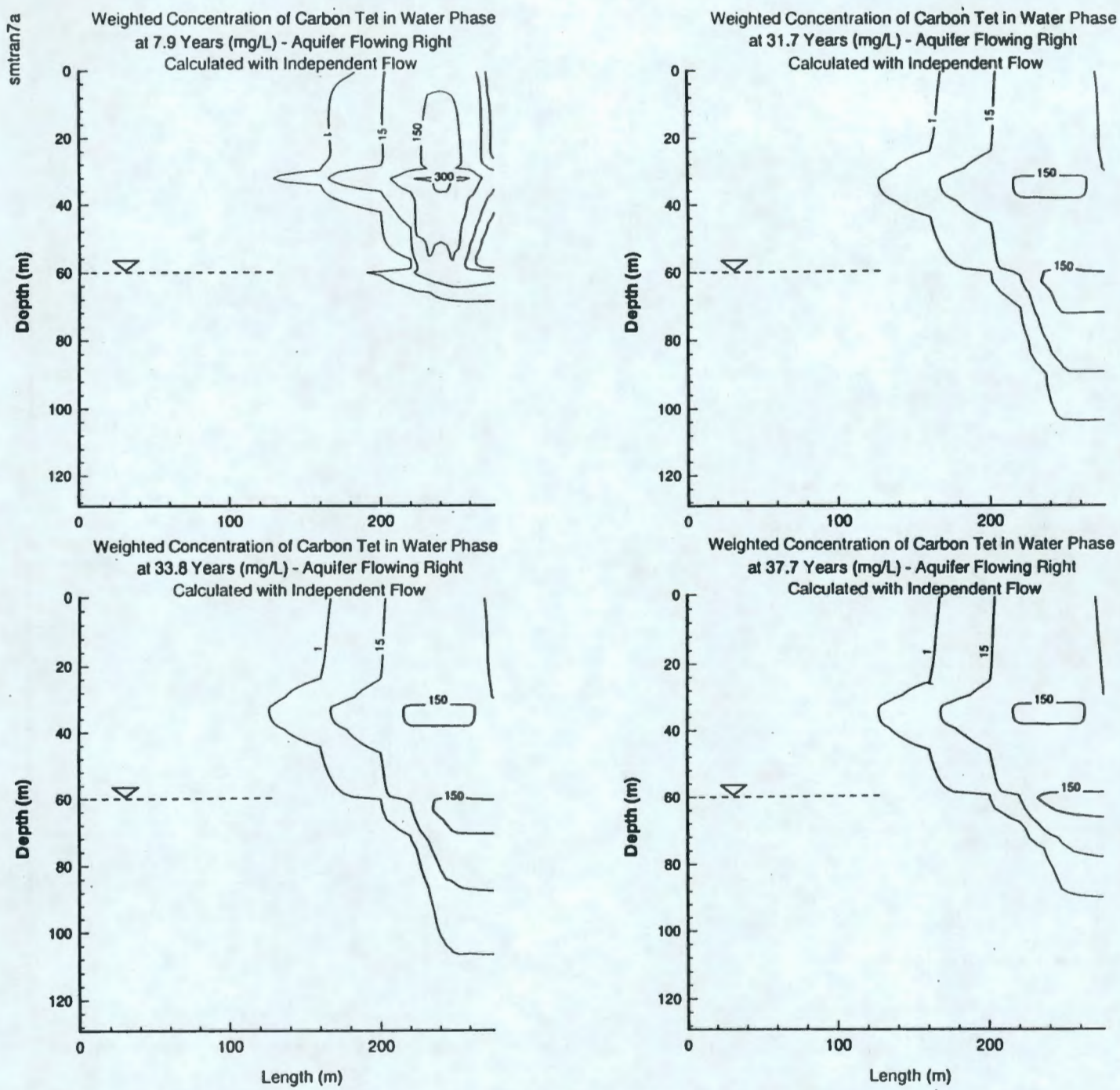

Figure 4-8. Case 4 Weighted Carbon Tetrachloride Concentration in Water Phase.

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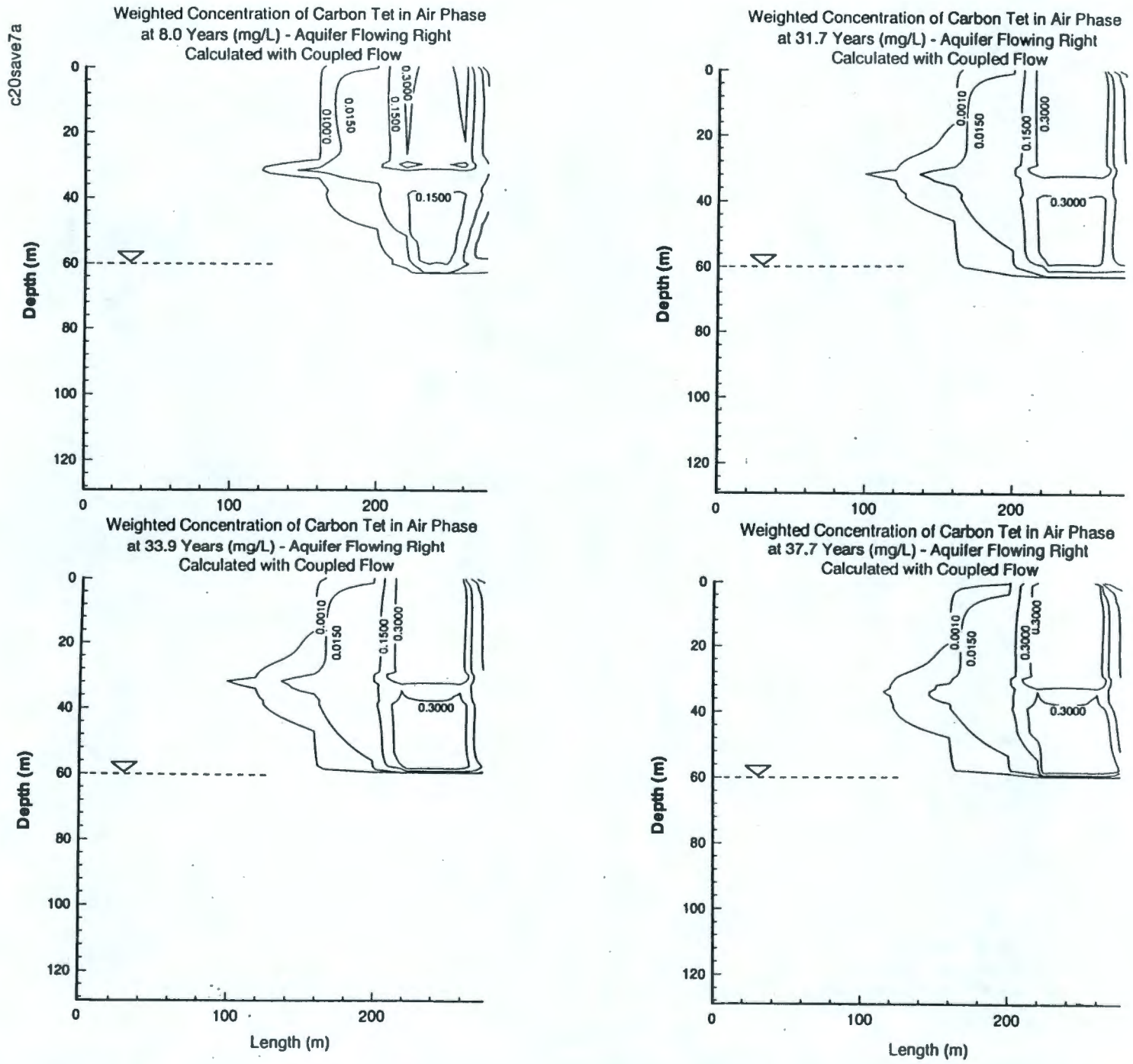

Figure 4-9. Case 1 Weighted Carbon Tetrachloride Concentration in Air Phase.

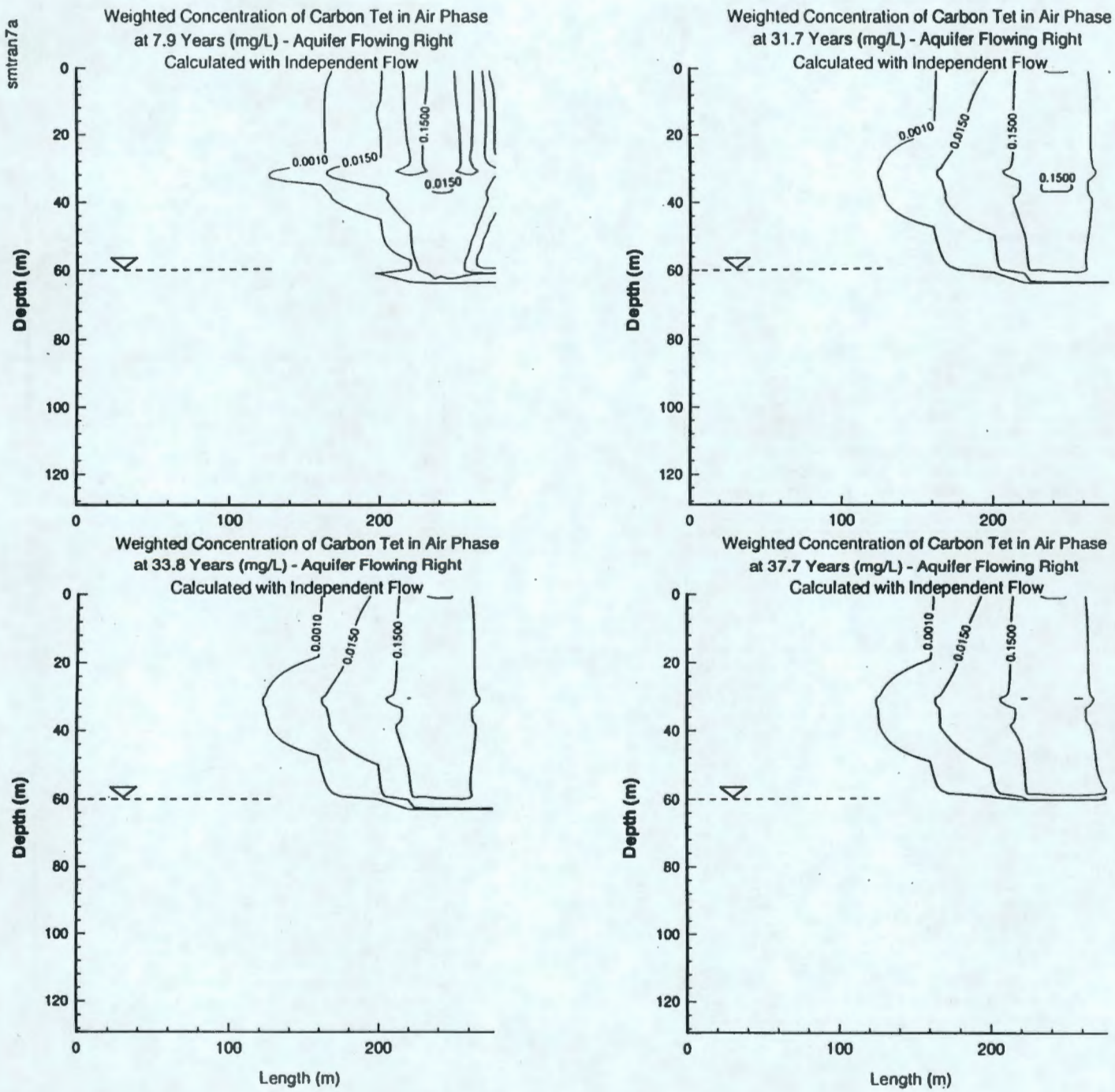

Figure 4-10. Case 4 Weighted Carbon Tetrachloride Concentration in Air Phase.

4.6 EFFECTS OF NUMERICAL FLOW MODEL TYPE WITH STAGNANT GROUNDWATER AND CARBON TETRACHLORIDE RESIDUAL SATURATION OF 0.01 - CASES 3 AND 6

Both the compositional and independent flow models produce very similar results when the groundwater is stagnant as shown in Figure 4-11 (Case 3 with compositional model) and Figure 4-12 (Case 6 with independent flow model). These results are in sharp contrast to Figures 4-5 and 4-6, which have flowing groundwater (see Section 4.4). With stagnant groundwater, only a very limited amount of CCl_4 liquid can be absorbed by the water. After the water becomes saturated with CCl_4, stagnant groundwater acts as a barrier to additional diffusion or adsorption of CCl_4. With flowing groundwater, more absorption capability is present due to additional uncontaminated water entering the contaminated area. Again, the groundwater under the 216-Z-9 Trench is flowing (faster than 1 m/yr); hence, CCl_4 ponding is not expected at the aquifer bottom.

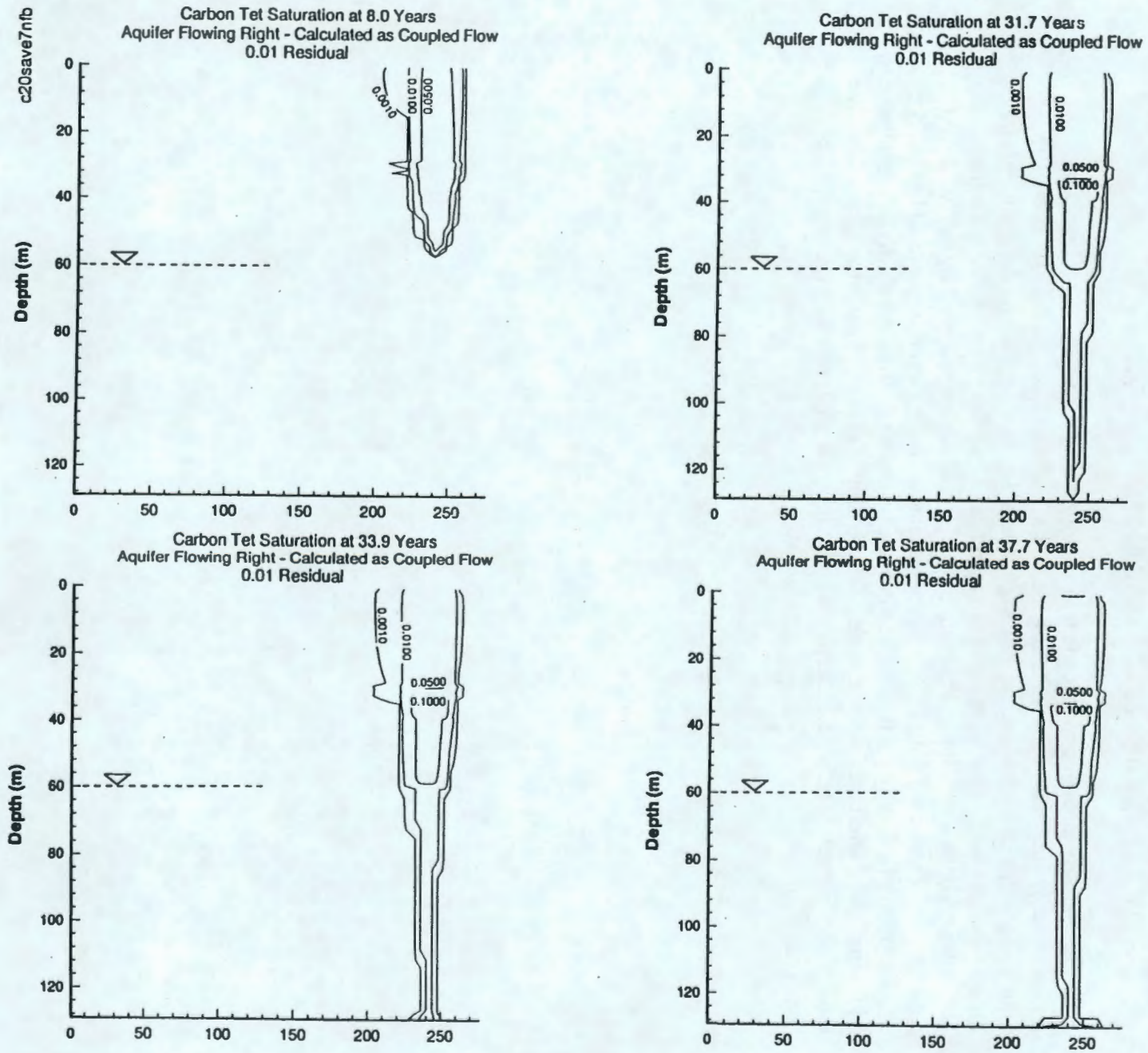

Figure 4-11. Case 3 Immiscible Liquid Carbon Tetrachloride Saturation.

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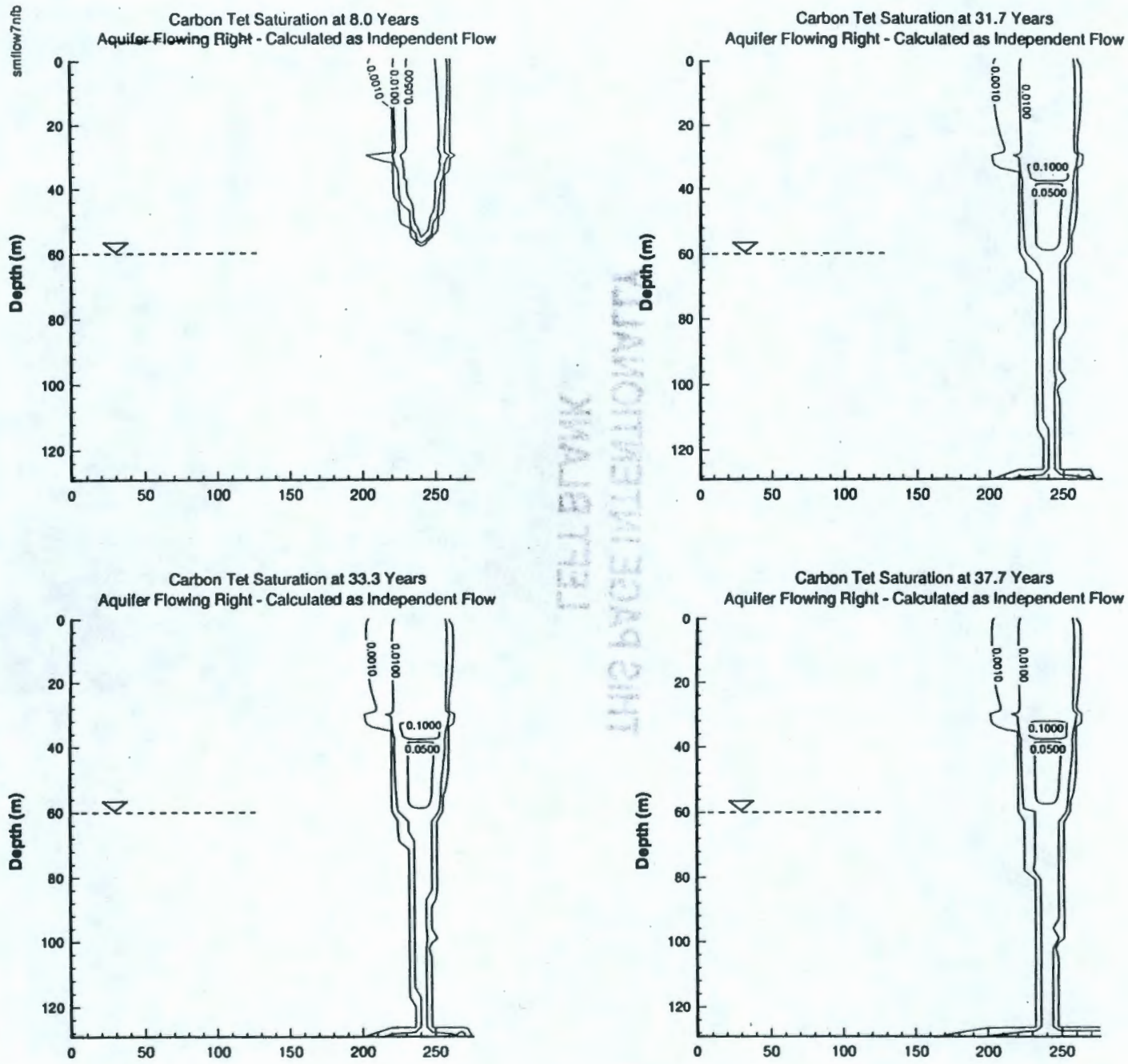

Figure 4-12. Case 6 Immiscible Liquid Carbon Tetrachloride Saturation.

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5.0 SUMMARY AND CONCLUSIONS

The main differences between the compositional and independent flow models are realized in the aquifer when the groundwater is flowing. There does not appear to be much difference in the model results in the vadose zone. In other words, the fully coupled compositional model produces numerical CCl_4 plumes in the vadose zone that are very similar (although concentrations are higher) to those produced by the independent flow model. This means that the effects of transport processes (mainly absorption with diffusion/dispersion and volatilization) on the vadose zone CCl_4 liquid flow are small; however, this is not the case for CCl_4 plumes in the groundwater. Also, the two types of models produce essentially the same numerical CCl_4 plumes when the groundwater is not flowing.

The CCl_4 residual saturation is a very important parameter as shown previously in Piepho et al. (1993). The importance of the CCl_4 residual saturation is shown again in the cumulative flux curves in Figures 5-1 and 5-2. In Figures 5-1 and 5-2, the cumulative CCl_4 mass flowing out of the north (right) aquifer boundary is shown by curves 2 and 3 where curve 3 indicates the mass flux in the top 10 m of the aquifer. Figure 5-1 shows the mass fluxes for Case 1, with residual saturation of 0.0001, and Figure 5-2 shows the mass fluxes for Case 2, with residual saturation of 0.01. Case 1 (Figure 5-1) has more CCl_4 mass entering the aquifer sooner. Also, not all of the mass is removed by the top 10 m of the aquifer as is the case with the small residual (0.01) as shown in Figure 5-2.

Figure 5-1 also indicates that about two-thirds of the CCl_4 mass is still in the vadose zone today, even with the most conservative bounding conditions of very small residual saturation and large source term. If the CCl_4 source term were smaller, an even larger percentage of the CCl_4 would still be in the vadose zone today. Also, if the CCl_4 residual saturation were higher (e.g., 0.01), approximately 80% to 90% of the CCl_4 would stay in the vadose zone (Figure 5-2). Although not varied in this report, the porosities of the soil formations are also expected to be very important as fluids will flow faster through smaller pore volumes because smaller pore volumes do not have as much retention space for the fluids as larger pore volumes. The porosities used in this report appear to be on the high side.

Figures 5-1 and 5-2 show that less than 0.5% of the CCl_4 is removed by the vapor extraction well that is placed 26 m north of the (right) edge of the trench. Because the model is only two-dimensional, mass is only removed at the south (left) side of the extraction well, which is placed on the north (right) boundary of the model domain. The extraction well is rectangular in the two-dimensional model, not round, and is located on a boundary. Hence, the front, back, and right sides of the two-dimensional extraction well have no flow. If the model were three-dimensional, mass would be removed at three or four sides of the extraction well. Hence, the extraction well may actually remove more of the CCl_4 mass in a three-dimensional model. Also, more mass could be removed if the vapor extraction well were placed closer to the trench and/or if an impermeable cover were placed around the well on the land surface. The cover would force the

Figure 5-1. Cumulative Mass Fluxes for Flowing Groundwater with Carbon Tetrachloride Residual Saturation of 0.0001 - Case 1.

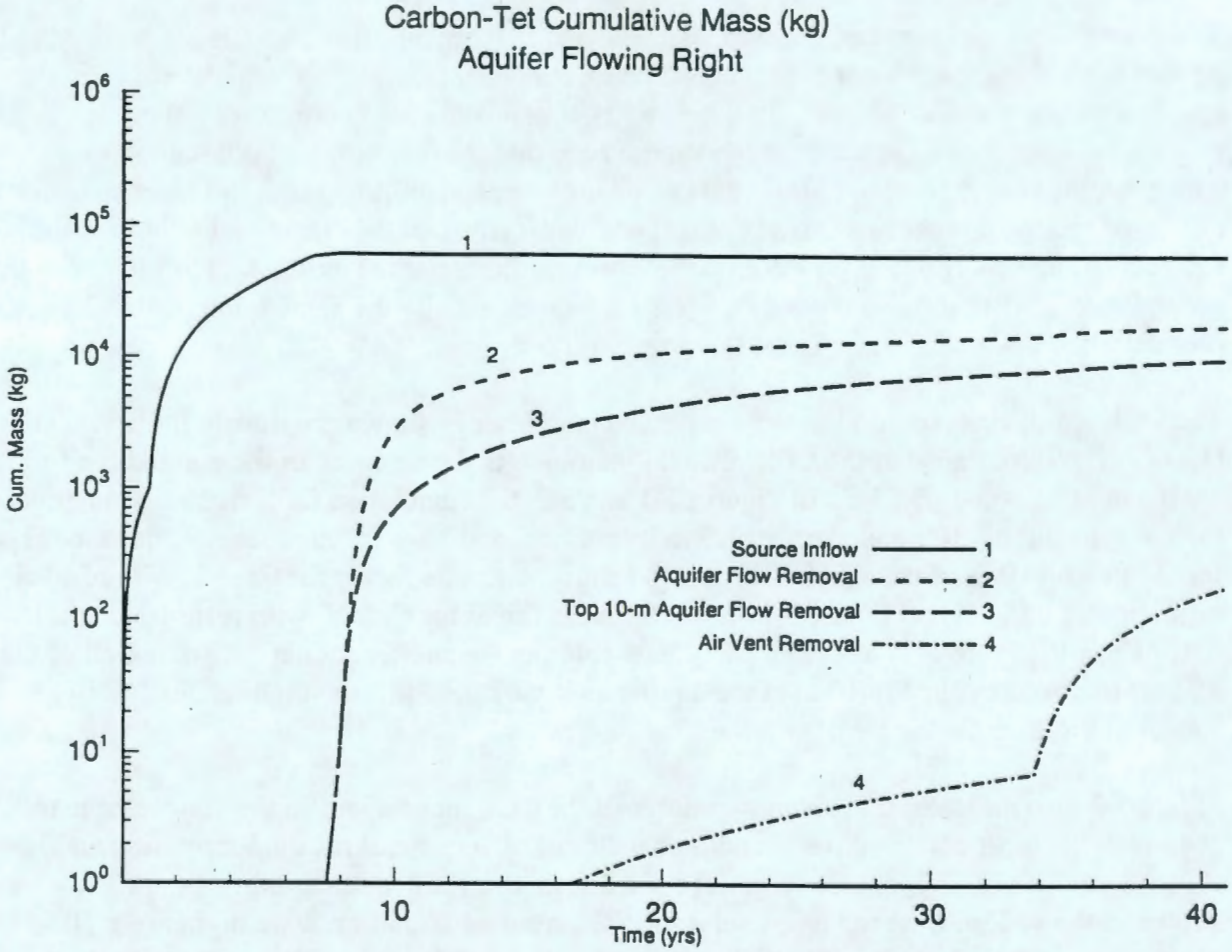
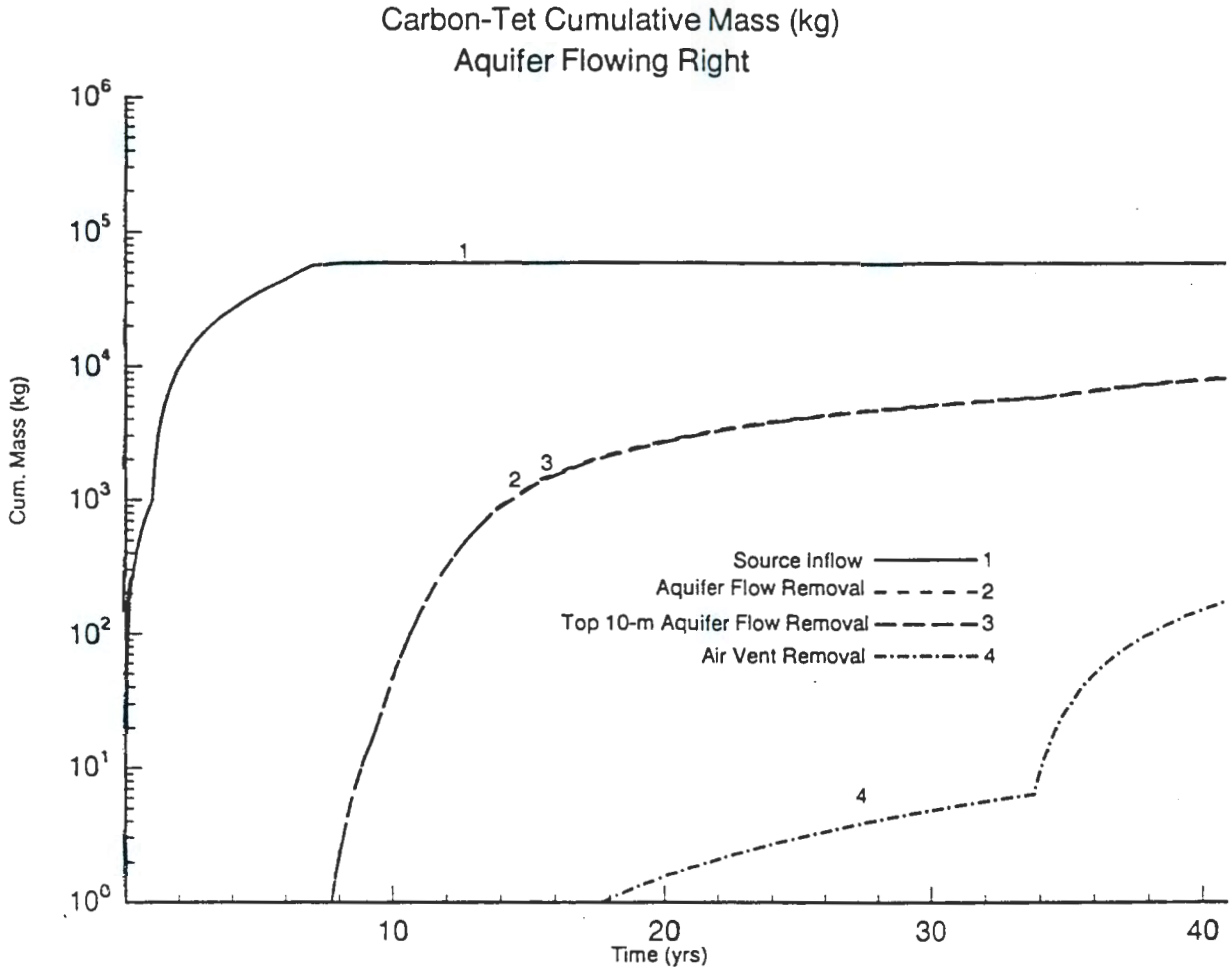


Figure 5-2. Cumulative Mass Fluxes for Flowing Groundwater with Carbon Tetrachloride Residual Saturation of 0.01 - Case 2.

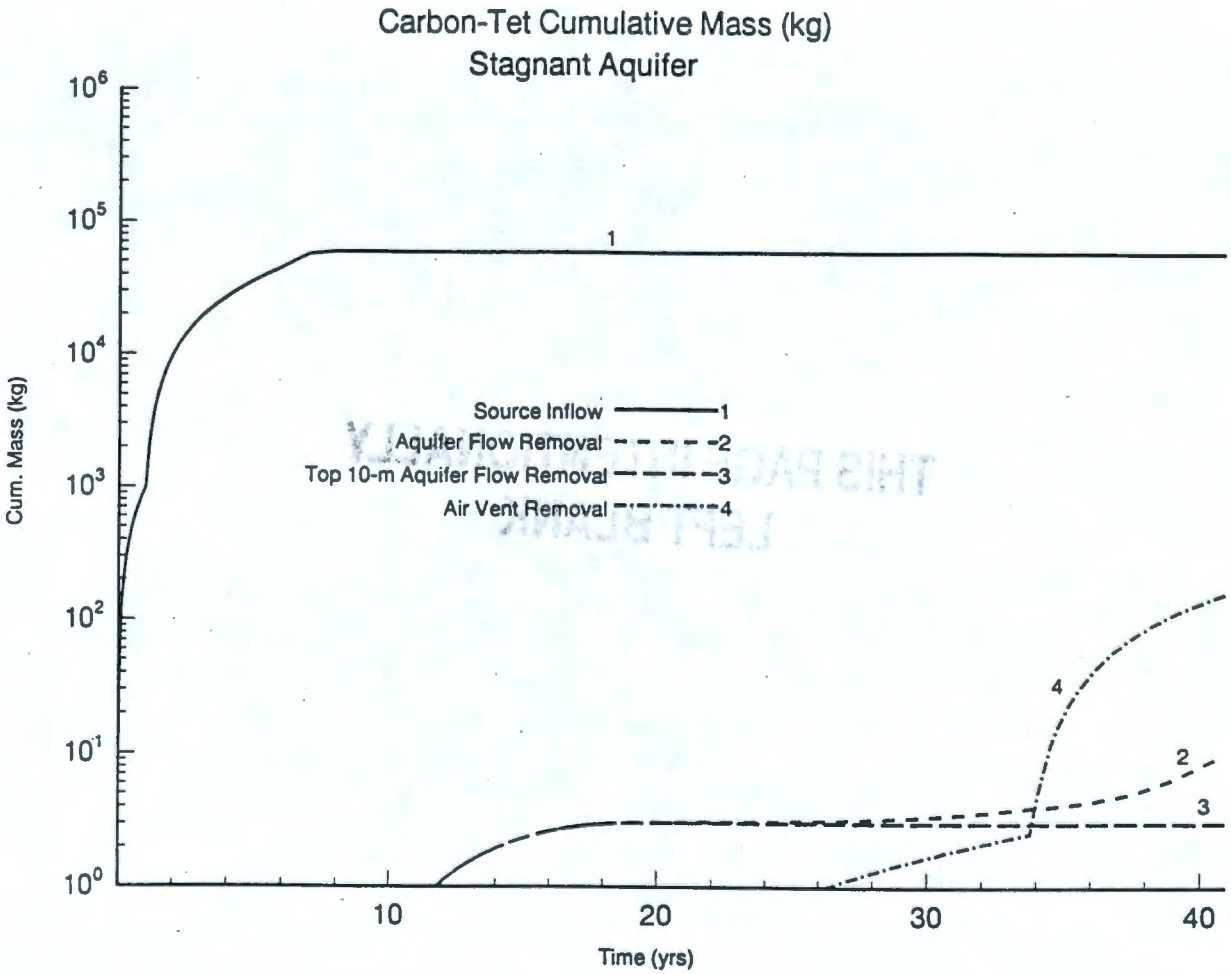


atmospheric air to infiltrate the soil farther away (horizontally) from the extraction well and help direct the CCl_4 vapor to the air vent.

Figure 5-3 shows that very little CCl_4 mass leaves the model domain if the groundwater is not flowing. The mass that does leave is due to diffusion as no flow is taking place. Also, the vapor extraction well is not quite as effective when the groundwater is not flowing. This is because flowing groundwater, carrying absorbed CCl_4, will tend to increase the CCl_4 vapor mass just above the water table due to Henry's Law. Hence, some of the CCl_4 vapor mass removed by the extraction well existed as a liquid that was absorbed and carried by the groundwater that flowed toward the extraction well.

The total CCl_4 mass in the two-dimensional model source term is about 5.5E4 kg as shown by curve 1 in all of the figures. The source term in the two-dimensional model is about one-ninth of the total source term (5.15E5 kg) for the entire 216-Z-9 Trench (see Table 2-1). This is because the two-dimensional model is 1 m wide in the third dimension, which is about one-ninth of the entire 9.1-m-wide trench. Hence, the numbers for CCl_4 mass for all of the curves in all of the figures should not be used as absolute numbers. If absolute numbers are desired for a reality check, all of the mass values in the figures need to be multiplied by 9.1. The numbers that are plotted can also be used directly for calculating percentages (e.g., <0.5% of CCl_4 mass is removed by the vapor extraction well, more than 66% of the CCl_4 mass is still in the vadose zone, etc.).

Figure 5-3. Cumulative Mass Fluxes for Stagnant Groundwater with Carbon Tetrachloride Residual Saturation of 0.01 - Case 3.



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