DOE/RL-2014-48
Revision 0

Response Action Report for the 200-PW-1 Operable Unit Soil Vapor Extraction Remediation

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

U.S. DEPARTMENT OF ENERGY | Richland Operations Office

P.O. Box 550
Richland, Washington 99352

Approved for Public Release;
Further Dissemination Unlimited

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Title: *Response Action Report for the 200-PW-1 Operable Unit Soil Vapor Extraction Remediation*

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Executive Summary

The 200-PW-1 Operable Unit (OU) soil vapor extraction (SVE) systems are currently operating under a *Comprehensive Environmental Response, Compensation, and Liability Act of 1980*[1] Record of Decision (ROD) issued in 2011[2] by the U.S. Environmental Protection Agency (EPA), Washington State Department of Ecology (Ecology), and U.S. Department of Energy (DOE), hereafter referred to as the 200-PW-1 OU ROD. The 200-PW-1 OU ROD selected SVE as the final remedial action for carbon tetrachloride and methylene chloride cleanup in the vadose zone. The SVE systems had been operating as an interim remedy for carbon tetrachloride in the vadose zone since 1992 under an action memorandum.[3]

Because contaminant concentrations and SVE mass removal rates have declined and are currently minimal, it is appropriate to consider whether continued SVE system operation is warranted. This document provides an evaluation of the SVE remedy using the process outlined in PNNL-21843, hereafter referred to as the SVE Closure Guidance.[4] This guidance was developed by scientists and remediation experts at Pacific Northwest National Laboratory, the U.S. Army Corps of Engineers, and EPA to provide a technical basis for supporting the SVE system performance evaluation and remedy decisions. Based on the SVE Closure Guidance (PNNL-21843), the site-specific approach for assessing the 200-PW-1 OU SVE systems was provided in DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*.[5] DOE/RL-2014-18 received concurrence from EPA and DOE. The assessment approach includes evaluating and updating the conceptual site model (CSM), considering

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[1] *Comprehensive Environmental Response, Compensation, and Liability Act of 1980*, 42 USC 9601, et seq., Pub. L. 107-377, December 31, 2002. Available at: http://epw.senate.gov/cercla.pdf.

[2] EPA, Ecology and DOE, 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*, U.S. Environmental Protection Agency, U.S. Department of Energy, and Washington State Department of Ecology, Olympia, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093644.

[3] EPA and Ecology, 1992, *Action Memorandum: Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume*, U.S. Environmental Protection Agency and Washington State Department of Ecology, Olympia, Washington. Available at: http://pdw.hanford.gov/arpir/pdf.cfm?accession=D196088487.

[4] PNNL-21843, 2013, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0088374.

[5] DOE/RL-2014-18, 2014, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0082285H.

environmental impacts and regulatory context, and estimating the effects of remaining vadose zone contamination on groundwater quality. These elements feed into a decision logic process to determine an appropriate disposition for the 200-PW-1 OU SVE systems.

The carbon tetrachloride CSM was evaluated with respect to adequacy and completeness. The following key elements of the current conditions were identified:

- Current carbon tetrachloride concentrations in the vadose zone near the former carbon tetrachloride disposal sites are low and have been significantly decreased at most locations by one to four orders of magnitude from concentrations at the onset of SVE.
- Remedial investigation studies concluded that there are no sources outside of the three main disposal sites. Remaining carbon tetrachloride that can serve as a source for vapor-phase contaminant discharge is predominantly in the low-permeability Cold Creek unit (CCU) beneath the disposal sites. Of the three major disposal sites (216-Z-9, 216-Z-1A, and 216-Z-18), 216-Z-9 has the highest level of remaining contamination in the CCU.
- Vapor-phase carbon tetrachloride discharging from the CCU is at low levels and moves away from the CCU by diffusion when SVE is not operated. The vapor-phase contaminant discharge from the CCU has been significantly diminished by SVE and will continue to diminish by diffusive processes if SVE is terminated. Under the current contaminated conditions of relatively high carbon tetrachloride groundwater concentrations in the underlying 200-ZP-1 OU aquifer, mass transfer from the vadose zone into the groundwater would be inhibited.

The CSM for methylene chloride recognizes that methylene chloride was not a component of disposed waste, and it also accounts for current conditions. Any methylene chloride in the vadose zone is viewed as a dispersed remnant of historical conditions, when organic substrates and anaerobic conditions may have allowed microbial generation of methylene chloride from carbon tetrachloride (via chloroform as an intermediate compound). The lack of disposal and current absence of conditions suitable for microbial production mean that there is no continuing source of methylene chloride. The observation of low concentrations in the vadose zone (i.e., well below the cleanup goal in the 200-PW-1 OU ROD [EPA et al., 2011]), in conjunction with the lack of a continuing source and the biological attenuation mechanisms for methylene chloride,

indicate that methylene chloride is expected to diminish over time to even lower levels in the vadose zone. No groundwater impact from methylene chloride within the 200-PW-1 OU is expected in future years.

The CSM provides the qualitative and quantitative input needed to adequately describe contamination in the 200-PW-1 OU vadose zone. In particular, remaining contamination in the vadose zone at locations above, within, and below the CCU is well understood, with no data gaps, and the CSM provides an adequate framework for the subsequent assessment of both the environmental/regulatory context and the impact to groundwater.

As established in the 200-PW-1 OU ROD (EPA et al., 2011) and related documents, the environmental impact pathway, cumulative risk, and regulatory compliance context have been adequately determined and defined to support evaluation of the impact of vadose zone contamination on the groundwater concentrations and subsequent decisions regarding disposition of the 200-PW-1 OU SVE systems.

The carbon tetrachloride mass discharge from the vadose zone source at the 216-Z-9 site, which is the limiting case for the 200-PW-1 OU, is not currently impacting groundwater. Assuming no other contamination sources in the aquifer, the mass discharge from the vadose zone source is predicted to decline so that within about 40 years, the impact to carbon tetrachloride concentrations in the groundwater will be at or below the groundwater cleanup level of 3.4 µg/L specified in the 200-ZP-1 OU ROD.[6] During this time, the groundwater remedy (including institutional controls and monitoring) will be in place to prevent human health and environmental exposures to contaminated groundwater.

The site-specific SVE assessment, based on the CSM, the environmental impact pathway and regulatory context, and the evaluation of the impact of remaining vadose zone sources on groundwater concentrations, meets the steps outlined in the SVE Closure Guidance (PNNL-21843) and demonstrates that groundwater goals will not be exceeded. Thus, closure of the SVE remedy (i.e., permanently discontinuing SVE system

[6] EPA, Ecology and DOE, 2008, *Record of Decision, Hanford 200 Area, 200-ZP-1 Superfund Site, Benton County, Washington*, U.S. Environmental Protection Agency, U.S. Department of Energy, and Washington State Department of Ecology, Olympia, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=00098825.

operations) within the 200-PW-1 OU is appropriate. EPA concurrence with this report will initiate activities to terminate SVE operations and vadose zone monitoring.

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Terms

BRA	baseline risk assessment
CCU	Cold Creek unit
CERCLA	*Comprehensive Environmental Response, Compensation, and Liability Act of 1980*
CSM	conceptual site model
DNAPL	dense nonaqueous-phase liquid
DOE	U.S. Department of Energy
DOE-RL	DOE Richland Operation Office
Ecology	Washington State Department of Ecology
EE/CA	engineering evaluation/cost analysis
EPA	U.S. Environmental Protection Agency
FY	fiscal year
GAC	granular activated carbon
MCL	maximum contaminant level
MNA	monitored natural attenuation
NPL	National Priorities List (40 CFR 300, Appendix B)
OU	operable unit
P&T	pump and treat
PFP	Plutonium Finishing Plant
ppmv	parts per million by volume
RAO	remedial action objective
RI	remedial investigation
ROD	Record of Decision
SVE	soil vapor extraction
SVEET	Soil Vapor Extraction Endstate Tool
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*

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1 Introduction

This response action report documents completion of the remedial action for carbon tetrachloride and methylene chloride contamination in the vadose zone in the 200-PW-1 Operable Unit (OU) located at the Hanford Site. Remediation of carbon tetrachloride and methylene chloride contamination in the vadose zone in the 200-PW-1 OU was completed by the U.S. Department of Energy (DOE) under the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA). The carbon tetrachloride contamination resulted from liquid waste discharges to waste sites in the 200-PW-1 OU. Because methylene chloride was not a component of disposed waste, any methylene chloride contamination in the vadose zone is a potential degradation product of carbon tetrachloride (via chloroform as an intermediate compound). The remedial action for carbon tetrachloride was authorized in 1992 by the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology) by an action memorandum (EPA and Ecology, 1992, *Action Memorandum: Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume*). The remedial action for carbon tetrachloride and methylene chloride was authorized in 2011 by a Record of Decision (ROD) (EPA et al., 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and 200-PW-1, 200-PW-3 and 200-PW-6 Operable Units*) (hereafter referred to as 200-PW-1 OU ROD).

The remedy selected in 1992 for carbon tetrachloride contamination in the vadose zone was soil vapor extraction (SVE). The remedy selected in 2011 for carbon tetrachloride and methylene chloride contamination in the vadose zone was SVE. The SVE systems had been operating as an interim remedy for carbon tetrachloride in the vadose zone since 1992 in accordance with the expedited response action. Successful completion of the remedial action was confirmed by sampling data that demonstrate achievement of the remedial action objectives (RAOs) prescribed in the 200-PW-1 OU ROD.

This response action report has been prepared based on guidance provided in EPA 540-R-98-016, *Close Out Procedures for National Priorities List Sites*.

Completion of this remedial action will be used to provide the basis to change the status of the SVE component of the 200-PW-1 OU remedy in the ROD to “closed out” per the processes and definitions described in RL-TPA-90-0001, *Tri-Party Agreement Handbook Management Procedures*.

1.1 Site Description

The Hanford Site, located in southeastern Washington State and situated along the Columbia River, covers an area of approximately 1,518 km^2 (586 mi^2). From the early 1940s to about 1989, the Hanford Site mission included defense-related nuclear research and development and plutonium production. These activities created a wide variety of chemical and radioactive wastes. The Hanford Site mission is now focused on cleanup of those wastes and ultimate closure of the site.

During plutonium production, the Hanford Site was divided into production areas, including the 200 East Area and 200 West Area, which contained the major nuclear fuel processing, waste management, and disposal facilities. The historical designation for the 200 West Area is used in context throughout this response action report where appropriate. To achieve the environmental cleanup mission, the Hanford Site is now organized into three major components: River Corridor, Central Plateau, and tank farms/tank waste. The three waste sites in the 200-PW-1 OU that received liquid waste containing carbon tetrachloride are located in the Central Plateau Inner Area, which includes the 200 West Area waste sites noted in the following paragraph (Figure 1-1).

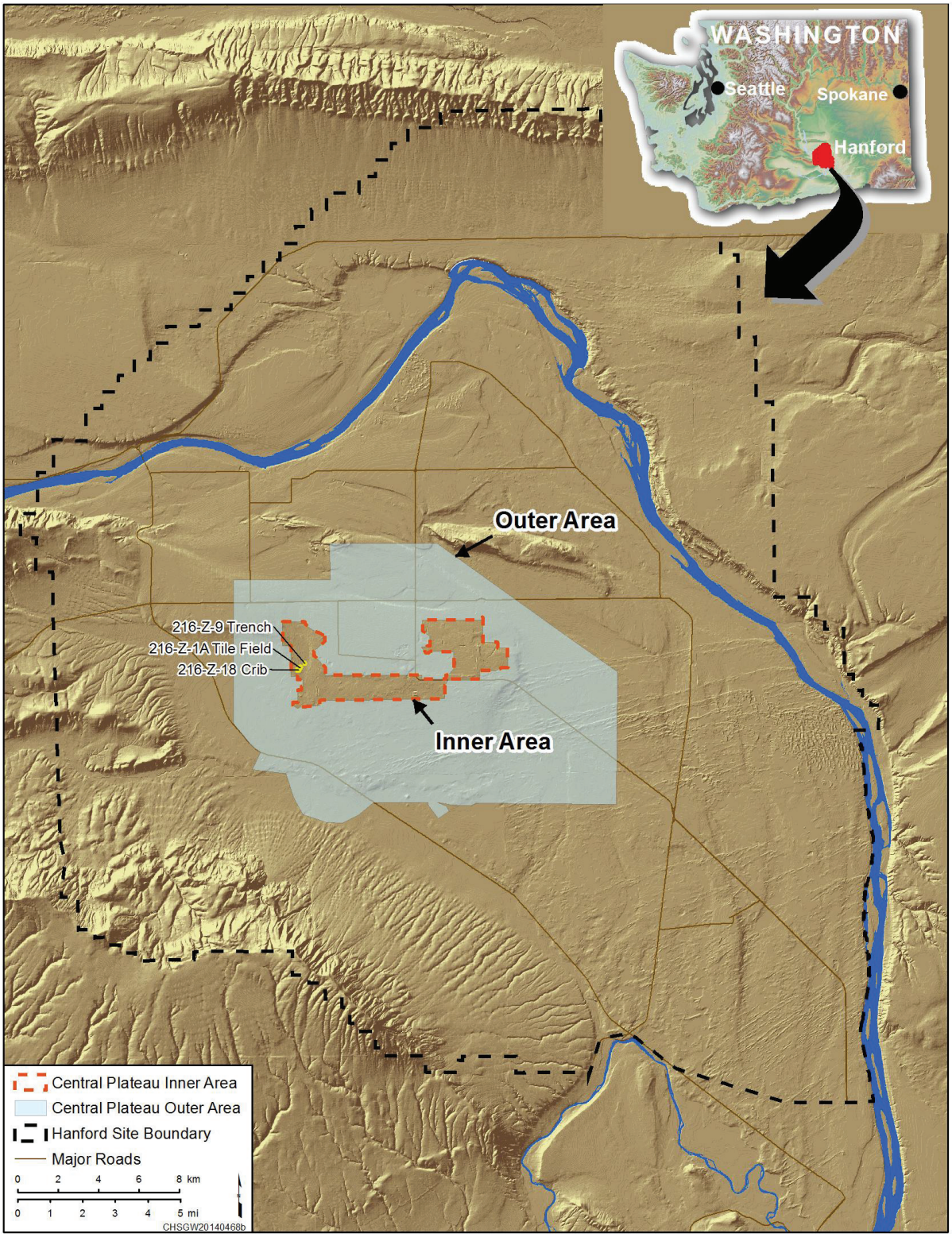


Figure 1-1. Location of the Three Waste Sites in the 200-PW-1 OU that Received Carbon Tetrachloride Discharges

At the Hanford Site, carbon tetrachloride was used in mixtures with other organics to recover plutonium in aqueous waste streams from the Plutonium Finishing Plant (PFP) in the 200 West Area. From 1955 to 1973, carbon tetrachloride contained in aqueous and organic liquid wastes was discharged primarily to three subsurface infiltration sites: 216-Z-9 Trench (1955 to 1962), 216-Z-1A Tile Field (1964 to 1969), and 216-Z-18 Crib (1969 to 1973). The liquid waste infiltrated into the ground, contaminating the underlying soil and groundwater. There was no known disposal of liquids containing methylene chloride, though methylene chloride is a potential degradation product of carbon tetrachloride (via chloroform as an intermediate compound).

1.2 Regulatory and Enforcement History

Beginning in 1986, Ecology and EPA began working with the DOE Richland Operation Office (DOE-RL) to develop a strategy to bring the Hanford Site into compliance with the *Resource Conservation and Recovery Act of 1976* and CERCLA. The regulatory agencies and DOE-RL developed a federal facility compliance agreement that set milestones for cleaning up hazardous waste sites and contaminated facilities under CERCLA authority and bringing operating facilities into compliance with the *Resource Conservation and Recovery Act of 1976*. As a result, Ecology et al., 1989, *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement), was signed by the three agencies in 1989. During this time frame, the Hanford Site was proposed for inclusion on 40 CFR 300, "National Oil and Hazardous Substances Pollution Contingency Plan," Appendix B, "National Priorities List," hereinafter called the NPL (53 FR 122, "National Priorities List for Uncontrolled Hazardous Waste Sites – Update 7"). EPA placed the four aggregate areas (100, 200, 300, and 1100 Areas) on the NPL (40 CFR 300, Appendix B) on November 3, 1989 (54 FR 191, "National Priorities List for Uncontrolled Hazardous Waste Sites – Final Rule 10/04/89"). The 200 Area NPL (40 CFR 300, Appendix B) site consists of the 200 West Area and 200 East Area, which contain waste management facilities and inactive irradiated fuel reprocessing facilities, and the 200 North Area, formerly used for interim storage and staging of irradiated fuel.

An interim action for removal of carbon tetrachloride from the 200-PW-1 OU vadose zone was approved in 1992 by the action memorandum (EPA and Ecology, 1992). Statutory authority for the removal action taken was in accordance with CERCLA; Executive Order 12580, *Superfund Implementation*; Tri-Party Agreement (Ecology et al., 1989); and 40 CFR 300. The action memorandum for the removal action selected SVE for removal of carbon tetrachloride from the 200-PW-1 OU vadose zone. SVE operations proceeded from February 1992 through October 2011 as an interim removal action (EPA and Ecology, 1992).

In 2011, the 200-PW-1 OU ROD (EPA et al., 2011) selected SVE as the final remedy for carbon tetrachloride and methylene chloride in the vadose zone. Statutory authority for the remedial action taken is in accordance with CERCLA, Tri-Party Agreement (Ecology et al., 1989), and 40 CFR 300. After October 2011, SVE operations proceeded as a remedial action (EPA et al., 2011).

Carbon tetrachloride mass removal rates for SVE systems in the 200-PW-1 OU have declined to the point where it became appropriate to assess SVE performance to support decisions regarding disposition of the 200-PW-1 OU SVE systems. PNNL-21843, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance* (hereafter referred to as the SVE Closure Guidance), published in 2013, describes an approach and general decision logic for assessing whether termination of SVE operations is justified and appropriate. Based on the SVE Closure Guidance (PNNL-21843), a site-specific path forward was prepared for assessing the 200-PW-1 OU SVE systems (DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*). DOE/RL-2014-18 received concurrence from EPA and DOE. As described in this response action report, the path forward process was followed

to perform and document the assessment, thereby providing justification for the closure of the SVE systems.

Site investigations, interim decisions, and removal/remedial activities associated with carbon tetrachloride and methylene chloride contamination in the 200-PW-1 OU vadose zone are described in Appendix A. Appendix A also provides a comprehensive list and discussion of activities, which is based on information presented in DOE/RL-2014-18.

1.3 Environmental Setting

The environmental setting of the Hanford Site, including the 200-PW-1 OU, is described in detail in PNNL-6415, *Hanford Site National Environmental Policy Act (NEPA) Characterization*. The waste sites that received liquids containing carbon tetrachloride were cribs, trenches, and tile fields that extended nominally 6 m (20 ft) below ground surface, mainly in backfill material. The vadose zone below the waste sites is comprised of higher permeability Hanford formation materials (about 34 m [112 ft] thick) and Ringold Formation materials (about 25 m [82 ft] thick above the water table), which are separated by the low-permeability Cold Creek unit (CCU) sediments (about 6 m [20 ft] thick). Soil vapor was extracted directly from the higher-permeability Hanford formation and Ringold Formation units. Contamination from the low-permeability unit slowly diffused into the higher permeability units and then was extracted.

2 200-PW-1 Operable Unit Soil Vapor Extraction Background

This chapter provides background information for the three waste sites that received liquid discharges containing carbon tetrachloride and a description of the SVE remedy. Additional details regarding the waste sites are available in the 200-PW-1 OU remedial investigation (RI) report (Chapter 1 of DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*, hereafter referred to as the 200-PW-1 OU RI report).

2.1 Carbon Tetrachloride Waste Sites Description and Background

Three waste sites in the 200-PW-1 OU received most of the carbon tetrachloride contained in liquids that were discharged to the ground. The waste sites are east and south of PFP in the 200 West Area (Figure 2-1).

The 216-Z-9 Trench is located about 213 m (700 ft) east of PFP and 152 m (500 ft) south of 19th Street (Figure 2-1). The 216-Z-9 Trench consists of a 6 m (20 ft) deep excavation with a 37 m by 27 m (120 ft by 90 ft) concrete cover. The walls of the trench slope inward and downward to the 18 m by 9 m (60 ft by 30 ft) floor space, which had a slight slope to the south. The underside of the concrete cover was paved with acid-resistant brick/tiles. The cover of the trench is supported by six concrete columns. From July 1955 through June 1962, the 216-Z-9 Trench received all solvent and aqueous wastes from the recovery of uranium and plutonium by extraction process that operated in PFP. Carbon tetrachloride in the liquid wastes discharged to the 216-Z-9 Trench was commingled with other organic, inorganic, and radioactive contaminants. SVE was initiated at the 216-Z-9 Trench in 1993 to remove the carbon tetrachloride from the vadose zone.

The 216-Z-1A Tile Field is located about 153 m (500 ft) south of PFP and immediately south of the 216-Z-1 and 216-Z-2 Cribs and adjacent to the 216-Z-3 Crib (Figure 2-1). The tile field piping consists of 20 cm (8 in.) diameter perforated vitrified clay pipe placed on a 1.5 m (5 ft) deep gravel bed, 4 m (14 ft) below ground surface. The tile field includes a 79 m (260 ft) long north-south trunk or main pipeline with seven pairs of 21 m (70 ft) long laterals spaced at 11 m (35 ft) intervals in a centered, herringbone pattern. The piping system was overlaid with 15 cm (6 in.) of cobbles and 1.5 m (5 ft) of sand and gravel. A sheet of 0.05 cm (0.02 in.) thick polyethylene and a 30 cm (1 ft) thick layer of sand and gravel were added in 1964. From June 1964 through March 1969, the 216-Z-1A Tile Field received liquid wastes from the Plutonium Reclamation Facility, which replaced the recovery of uranium and plutonium by extraction process in 1964, and the Waste Treatment Facility. Carbon tetrachloride in the liquid wastes discharged to the 216-Z-1A Tile Field was commingled with other organic, inorganic, and radioactive contaminants. SVE was initiated at the 216-Z-1A Tile Field in 1992 to remove carbon tetrachloride from the vadose zone. The SVE pilot test was conducted at the 216-Z-1A Tile Field in 1991.

The 216-Z-18 Crib is located about 300 m (1,000 ft) south of the PFP and 49 m (160 ft) southwest of the 216-Z-1A Tile Field (Figure 2-1). The 95 m by 79 m (312 ft by 259 ft) crib consists of five parallel, north-south-oriented trenches, each 63 m by 3 m (207 ft by 10 ft), ranging from 4.5 m to 5.5 m (15 ft by 18 ft) deep. A 91 m (299 ft) long, 7.6 cm (3 in.) diameter steel distribution pipe runs east-west, bisecting the trenches. Near the center of each trench, two perforated, fiberglass reinforced epoxy pipes exit each side of the distribution line. The distribution and trench piping lie on a 0.3 m (1 ft) thick bed of gravel. The pipes were buried under an additional 0.3 m (1 ft) of gravel, a membrane, and sand cover. The trenches were then backfilled to grade. The westernmost trench was never used. From April 1969 through May 1973, the 216-Z-18 Crib replaced the 216-Z-1A Tile Field to receive liquid wastes from the Plutonium Reclamation Facility and the Waste Treatment Facility. The carbon tetrachloride in the liquid

wastes discharged to the 216-Z-18 Crib was commingled with other organic, inorganic, and radioactive contaminants. SVE was initiated at the 216-Z-18 Crib in 1992 to remove carbon tetrachloride from the vadose zone.

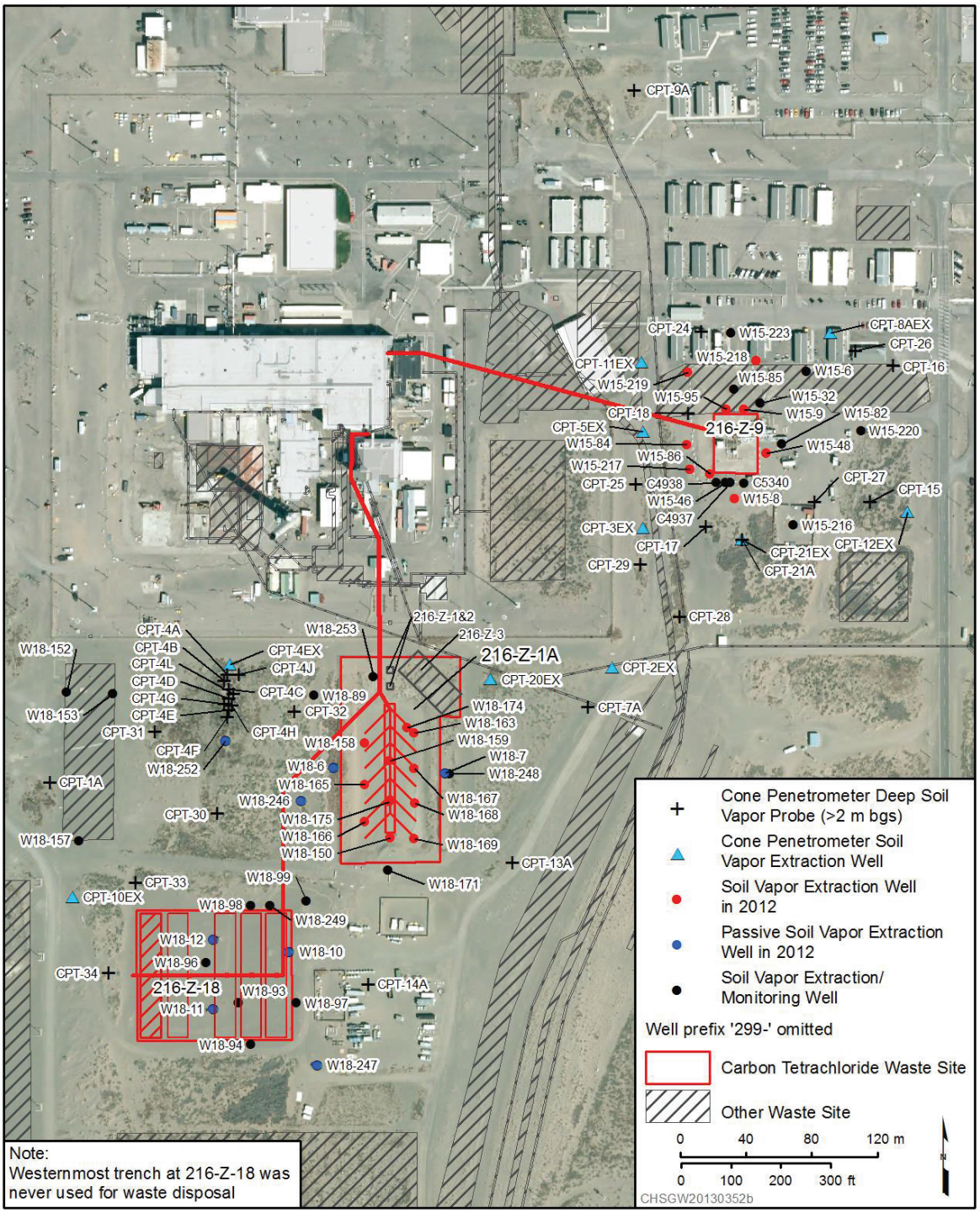


Figure 2-1. Location of Carbon Tetrachloride Waste Sites and SVE Wells, Monitoring Wells, and Deep Soil Vapor Probes

2.2 Description of the Remedy

This section summarizes the SVE response action requirements that are specified in the 200-PW-1 OU ROD (EPA et al., 2011).

2.2.1 Response Action Goals

The 200-PW-1 OU ROD (EPA et al., 2011) lists three specific RAOs, but only the one in Table 2-1 pertains to the SVE response action. This RAO is based on the anticipated future industrial land use for the 200-PW-1 OU, which is located in the Inner Area of Hanford Site Central Plateau.

Table 2-1. Cleanup Objectives for SVE Response Action

Response Action Objective*	
Response Action Objective	**Compliance Methods**
Control the sources of potential groundwater contamination to support the Central Plateau groundwater goal of protecting the beneficial uses of groundwater, including protecting the Columbia River from adverse impacts.	Achieved through implementation of soil vapor extraction for removal of carbon tetrachloride and methylene chloride from the vadose zone, with aboveground treatment of carbon tetrachloride and methylene chloride using granular activated carbon.

* Remedial action objective 3 from Section 8.0 of EPA et al., 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

The 200-PW-1 OU ROD lists final cleanup goals for carbon tetrachloride and methylene chloride soil vapor in the vadose zone (Table 2-2). Because this cleanup level was based on the objective of protecting groundwater, the ROD specified that soil vapor concentration cleanup levels "will be further refined and assessed to ensure they are protective of groundwater" and that cleanup is subject to WAC 173-340, "Model Toxics Control Act–Cleanup." The data and analyses presented in Chapter 5 of this response action report provide the refined consideration of vadose zone conditions that are protective of groundwater. The 200-PW-1 OU ROD also noted that, "As long as residual contamination remains above levels that allow for unrestricted use, institutional controls will be required."

Table 2-2. Carbon Tetrachloride and Methylene Chloride Final Cleanup Levels

Contaminant of Concern	Final Cleanup Level	Basis for Cleanup Level[b]	Risk at Cleanup Level
Carbon tetrachloride	100 ppmv[a]	Groundwater protection	Excess lifetime cancer risk = 1×10^{-5} [c]
Methylene chloride	50 ppmv[a]	Groundwater protection	

Note: Table is based on Table 35 in EPA et al., 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

a. Soil vapor concentrations will be further refined and assessed to ensure that they are protective of groundwater.

b. Cleanup levels are based on an industrial land-use scenario. When cleanup levels for ecological receptors or groundwater protection were lower than human health protection, the lower value was used as the final cleanup level.

c. The U.S. Department of Energy will clean up contaminants of concern for the 200-PW-1 Operable Unit subject to WAC 173-340, "Model Toxics Control Act–Cleanup" (carbon tetrachloride and methylene chloride), so the total excess lifetime cancer risk from carbon tetrachloride and methylene chloride does not exceed 1×10^{-5} at the conclusion of the remedy.

ppmv = parts per million by volume

2.2.2 Exposure and Land Use Assumptions

Ground surface exposure pathways for carbon tetrachloride contamination in the vadose zone were eliminated by a comprehensive risk assessment that was performed for the 216-Z-9 and 216-Z-1A waste sites, as documented in Appendix A of DOE/RL-2007-27, *Feasibility Study for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6 Operable Units*. This risk assessment thoroughly evaluated potential environmental pathways. The baseline risk assessment (BRA) stated that, under the anticipated industrial scenario and land use controls, industrial worker exposures for carbon tetrachloride would not occur via direct contact with contaminated soils. Based on air samples at the ground surface for the 216-Z-9 Trench (the most contaminated of the three waste sites) being below the permissible exposure limits of RCW 49.17, "Washington Industrial Safety and Health Act" (and well below a level of health significance for site workers), the BRA determined that the vapor inhalation exposure pathway did not represent a significant risk.

The remaining potential environmental pathway is exposure via groundwater (e.g., exposure through drinking, irrigation, and discharge to surface water). Based on the current conceptual site model (CSM) in Chapter 5 of this response action report, the remaining carbon tetrachloride contamination is primarily in the CCU sediments. Currently, diffusive transport of carbon tetrachloride in soil gas below the CCU is a potential pathway to the groundwater, where interphase mass transfer could result in a health risk to groundwater users.

2.2.3 Design Summary

SVE was selected as the response action for carbon tetrachloride in the action memorandum (EPA and Ecology, 1992) based on an initial screening of technologies in an engineering evaluation/cost analysis (EE/CA) (DOE/RL-91-32, *Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon Tetrachloride Plume*). Vapor extraction was identified as the preferred remedial technology based on the volatile organic contaminant, high permeability of the soil, high hydraulic conductivity of the soil, depth to groundwater, low soil moisture content, and low soil organic matter content (Table 2 in DOE/RL-91-32). Prior to preparing the EE/CA, a pilot test of SVE was performed at the 216-Z-1A Tile Field. The pilot test demonstrated that SVE was highly effective in recovering carbon tetrachloride from the soil.

SVE has been implemented at wells that are screened in the Hanford formation above the CCU, within the CCU, and/or in the Ringold Formation below the CCU and above the water table. The wells are distributed laterally within the well fields for the three carbon tetrachloride waste sites. The SVE systems extract simultaneously from multiple wells that are open above, within, and/or below the CCU layer. The operational strategy (e.g., number of SVE systems in operation and duration of operations) was modified based on changes in the rate of carbon tetrachloride removal with time. Methylene chloride also would have been removed during SVE operations. Details are provided in Appendix A of this document.

Use of SVE systems has successfully removed carbon tetrachloride and methylene chloride from the vadose zone to meet the RAO (Table 2-1) and cleanup levels (Table 2-2) specified in the 200-PW-1 OU ROD (EPA et al., 2011).

2.3 Record of Decision Amendments, Significant Differences, or Waivers

No ROD amendments, explanations of significant differences, or technical impracticability waivers were required for the SVE component of the 200-PW-1 OU removal action or remedial action.

3 Response Activity Summary

The SVE response action for carbon tetrachloride in the vadose zone at the 200-PW-1 OU carbon tetrachloride waste sites began in 1992. Soil vapor was extracted through wells screened or perforated in the vadose zone. Soil vapor extracted by the SVE systems was treated aboveground using granular activated carbon (GAC) contained in canisters. GAC adsorbs carbon tetrachloride from the vapor. The treated, clean soil vapor was then vented to the atmosphere. Used GAC was regenerated offsite. Between 1992 and 2012 (the last year that SVE was operated), SVE operations removed over 80,000 kg of carbon tetrachloride from the vadose zone (Figure 3-1). Methylene chloride also would have been removed during SVE operations.

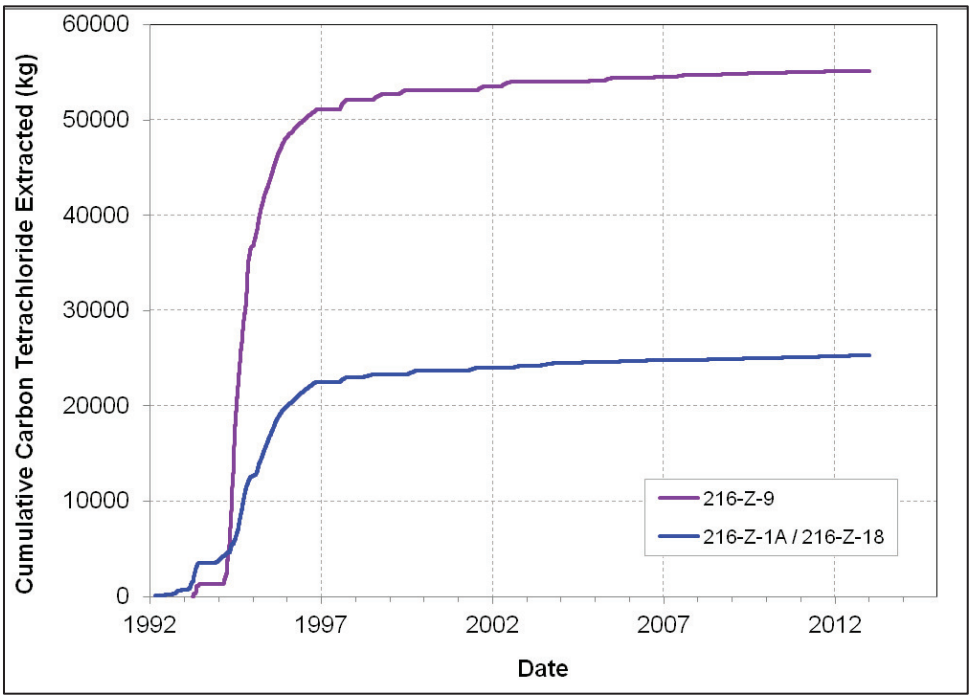


Figure 3-1. Mass of Carbon Tetrachloride Removed using SVE

3.1 Summary of Activities

Activities occurring iteratively during the response action included the following:

- Characterizing the lateral and vertical extent of carbon tetrachloride
- Drilling and constructing wells to provide vadose zone access
- Procuring, operating, and maintaining the SVE systems
- Regenerating GAC and disposing the knockout water
- Monitoring carbon tetrachloride concentrations and soil vapor flow rates at online wells
- Monitoring carbon tetrachloride concentrations at offline wells
- Demonstrating and testing innovative technologies
- Testing carbon tetrachloride source strength

A more detailed discussion of the remediation and investigation activities is provided in Table A-1 (Appendix A) of this report.

3.1.1 Verification Sampling

Carbon tetrachloride and methylene chloride rebound in soil vapor concentrations were measured at SVE wells and probes in 2013, 2014, and 2015. A low-flow (0.8 L/min [0.2 gal/min]) sampling pump was used to draw soil vapor samples from wells and probes into a 1 L (0.3 gal) Tedlar[1] bag for analysis using a Brüel & Kjær multi-gas analyzer or into a SUMMA[2] canister for laboratory analysis. Details are provided in the most recent sampling and analysis plan (DOE/RL-2014-20, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2015 Rebound Sampling*). Sampling results for 2013 are provided in SGW-54566, *Performance Evaluation Report for Soil Vapor Extraction Operations at the 200-PW-1 Operable Unit Carbon Tetrachloride Site, Calendar Year 2012*. Sampling results for 2014 and 2015 are provided in Appendix B of this report. All of the carbon tetrachloride concentrations, with the exception of samples from two soil vapor probes installed above the CCU, were found to be below the final cleanup level of 100 parts per million by volume (ppmv) specified in the 200-PW-1 OU ROD. All of the methylene chloride concentrations analyzed in the SUMMA canisters were found to be below the final cleanup level of 50 ppmv. Methylene chloride concentrations collected in Tedlar bags and analyzed using the Brüel & Kjær multi-gas analyzer were determined to be not usable for evaluating rebound because the data were significantly impacted by false-positive interference from another compound (Appendix B).

The refined assessment of soil vapor concentrations that are protective of groundwater, as required by the 200-PW-1 OU ROD, is provided in Chapter 5 of this response action report. The conclusion of this evaluation (Section 5.5) is that if SVE is terminated, there are no current or future impacts of vadose zone carbon tetrachloride or methylene chloride on groundwater that would result in concentrations in the groundwater above the groundwater cleanup level (3.4 µg/L) for carbon tetrachloride (EPA et al., 2008, *Record of Decision, Hanford 200 Area, 200-ZP-1 Superfund Site, Benton County, Washington*, hereinafter called the 200-ZP-1 OU ROD) or groundwater maximum contaminant level (MCL) (5 µg/L) for methylene chloride by the time this goal is required for the groundwater.

3.1.2 Statement of Protectiveness

As established in Chapter 5 of this response action report, the removal and remedial actions for carbon tetrachloride and methylene chloride in the vadose zone at the 200-PW-1 OU carbon tetrachloride waste sites have achieved the RAO applicable to the SVE remedy in the 200-PW-1 OU ROD.

[1] Tedlar® is a registered trademark of E.I. DuPont de Nemours and Company, Wilmington, Delaware.

[2] SUMMA® is a registered trademark of Summa Consulting, LLC, Solana Beach, California.

4 Chronology of Events

A timeline of SVE response action events for the 200-PW-1 OU is presented in Figure 4-1. Appendix A of this report provides a detailed discussion of activities, based on information provided in DOE/RL-2014-18.

The 2013 SVE Closure Guidance (PNNL-21843) is the basis for defining the site-specific evaluation and decision logic approach to determine when SVE operations for the 200-PW-1 OU can be terminated. The 2014 path forward document (DOE/RL-2014-18) established EPA and DOE concurrence with this approach. Chapter 5 of this response action report follows the defined path forward for the evaluation, providing justification for disposition of the SVE systems at the 200-PW-1 OU.

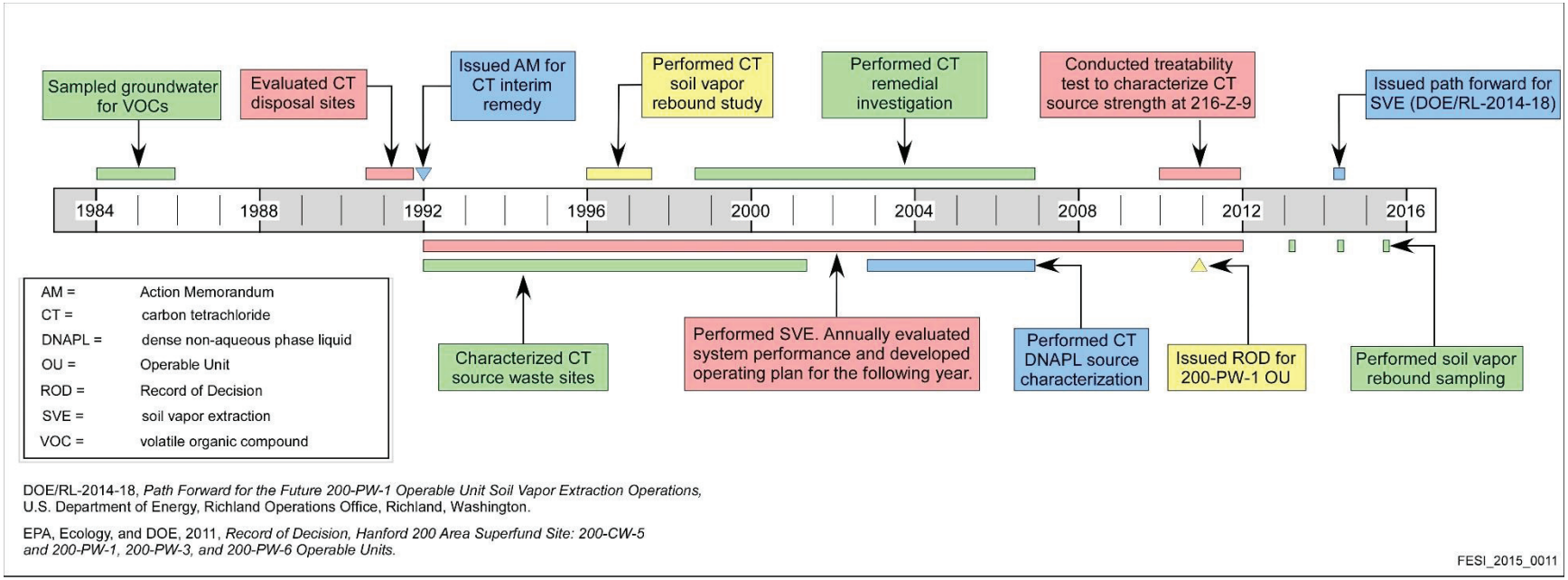


Figure 4-1. Timeline for Investigations and Remedial Activities for Carbon Tetrachloride and Methylene Chloride in the Vadose Zone at the 200-PW-1 OU

5 Endpoint Evaluation for the 200-PW-1 Operable Unit Soil Vapor Extraction System Operations

This chapter provides an evaluation of the SVE systems using the process outlined in the SVE Closure Guidance (PNNL-21843), which was developed in 2013 by scientists and remediation experts at Pacific Northwest National Laboratory, the U.S. Army Corps of Engineers, and EPA, to provide a technical basis for supporting the SVE system performance evaluation and remedy decisions. Based on the SVE Closure Guidance, the site-specific path forward was prepared to assess the 200-PW-1 OU SVE systems (DOE/RL-2014-18).

5.1 Soil Vapor Extraction System Closure Guidance

After an SVE system begins to show indications of diminishing contaminant removal rates, SVE performance needs to be evaluated to determine whether the system should be optimized, terminated, or transitioned to another technology to replace or augment SVE. The SVE Closure Guidance (PNNL-21843) specifically addresses the elements of this type of performance assessment, providing a stepwise process for gathering information and performing evaluations using a decision logic approach to support SVE endpoint decisions. Figure 5-1 summarizes the elements discussed in the SVE Closure Guidance, including an updated CSM, environmental impacts/regulatory context, and an estimate of the impact of remaining vadose zone contamination on the groundwater concentrations.

As part of determining the path forward approach (DOE/RL-2014-18), the general process outlined in Figure 5-1 was tailored specifically to the 200-PW-1 OU SVE systems. The resulting site-specific approach and decision logic (Figure 5-2) was used to facilitate assessment of the SVE systems to determine appropriate disposition. The assessment and decision process shown in Figure 5-2 involves four main steps:

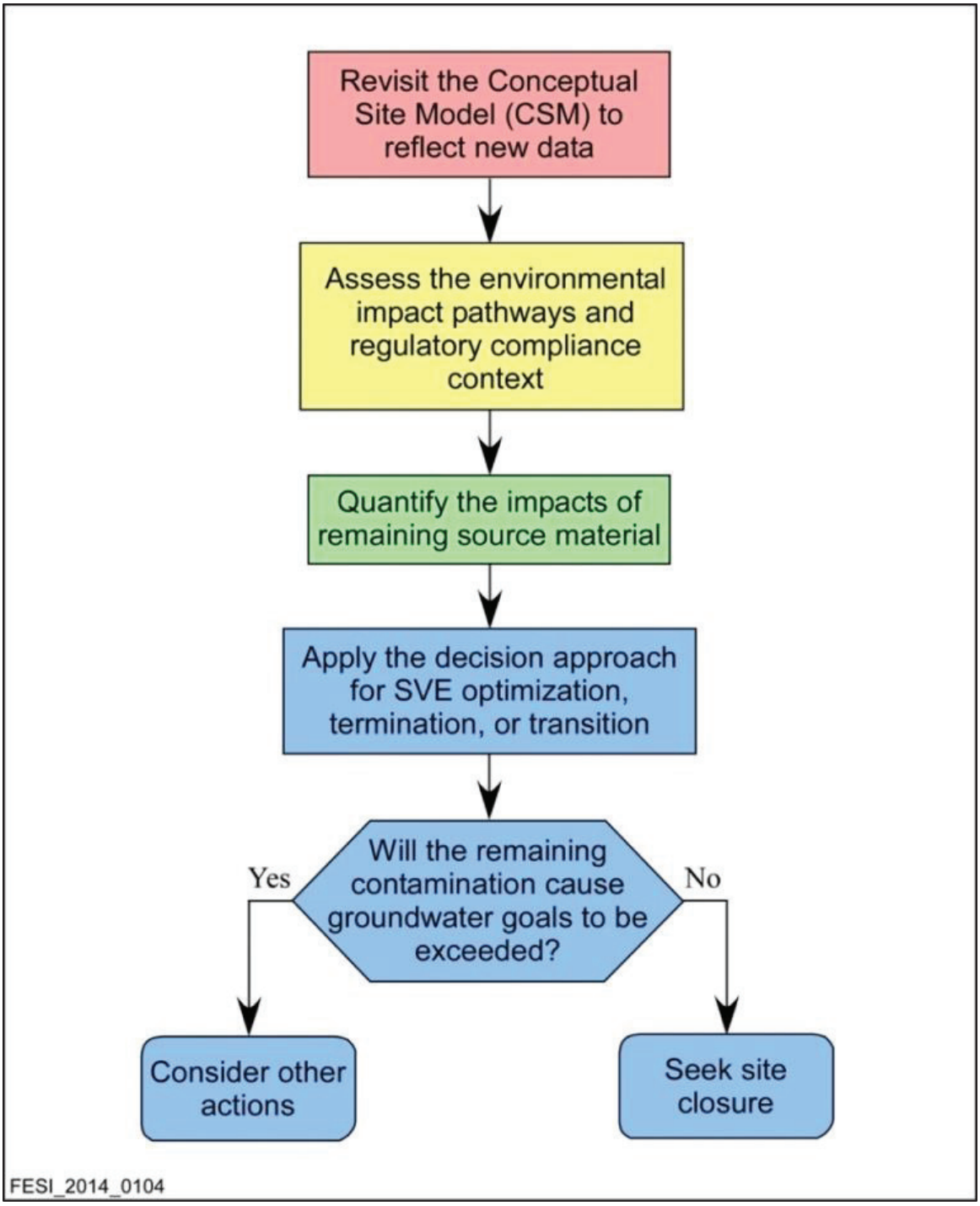
1. Revisit the CSM to incorporate new data and assess the adequacy of existing data. This step (discussed in Section 5.2) involves evaluating pertinent information, including carbon tetrachloride monitoring and operational data from 1992 through 2015. The CSM is updated to reflect current knowledge regarding the vadose zone contamination, contaminant migration, and subsurface characteristics. An updated CSM provides qualitative and quantitative input to SVE decisions.

2. Assess the environmental impact and regulatory compliance context. This step (discussed in Section 5.3) involves assessing whether the environmental pathways, cumulative risk, and RAOs are adequately defined, given the current (updated) CSM, to support decisions regarding the disposition of the SVE systems.

3. Quantify the environmental impact of remaining vadose zone contamination sources (discussed in Section 5.4). Specifically, estimate the impact of vadose zone contamination on contaminant concentrations in the groundwater of the underlying 200-ZP-1 OU.

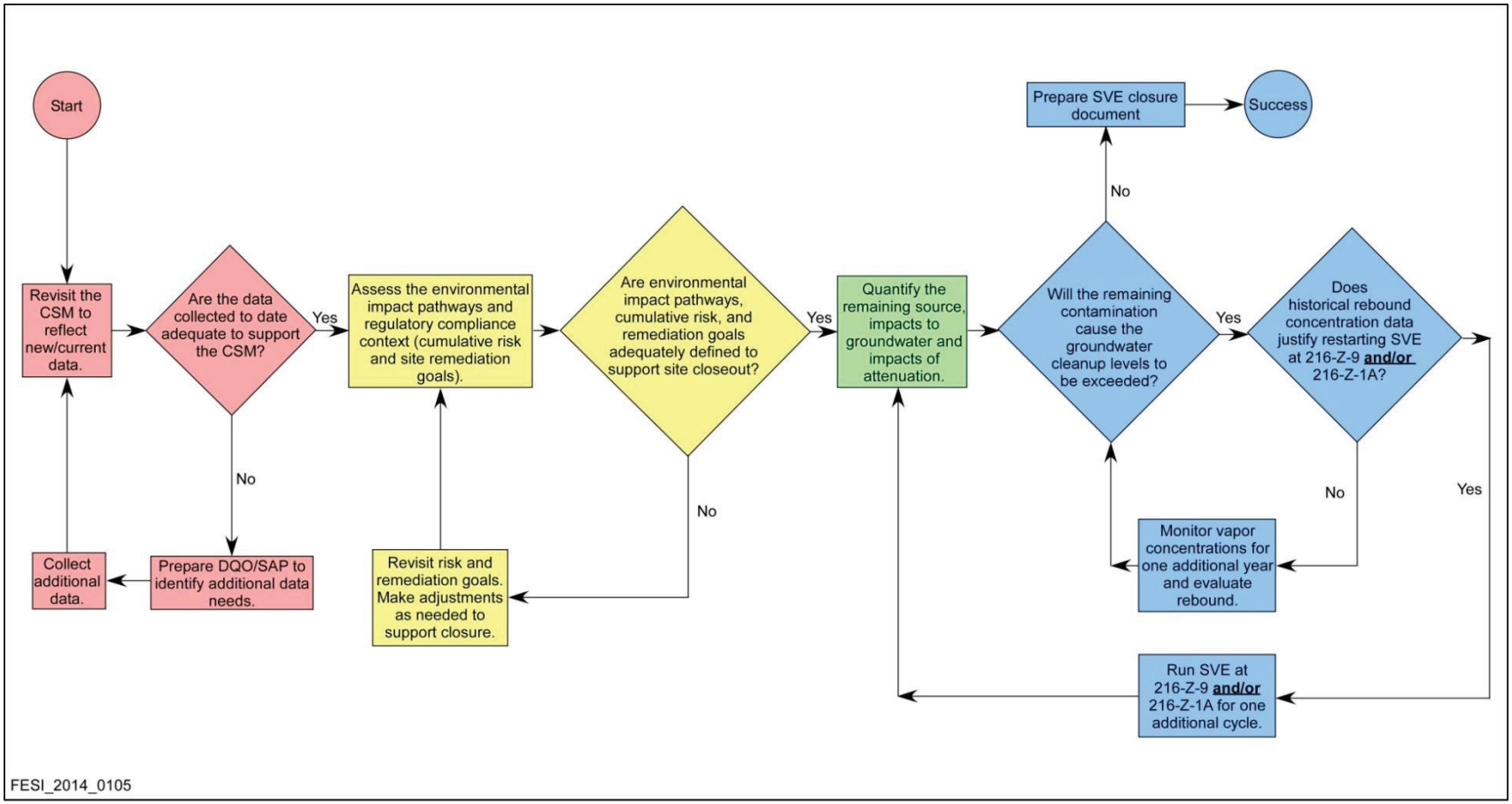
4. Apply the results of the previous three steps in a decision logic approach to determine the appropriate actions for disposition of the 200-PW-1 OU SVE systems (Section 5.5).

The decision logic approach shown in Figure 5-2 is summarized in the condensed flowchart shown in Figure 5-3. Similar condensed flowcharts (not labeled as figures) are displayed in subsequent sections within this chapter with highlighted boxes to indicate the elements that are under discussion (orange) or completed (green).



Source: DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*.

Figure 5-1. SVE Closure Guidance Assessment Approach to Support Decisions for SVE System Optimization, Transition, or Closure



Source: DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*.

Figure 5-2. Approach and Decision Logic for Assessment of SVE System Closure for the 200-PW-1 OU

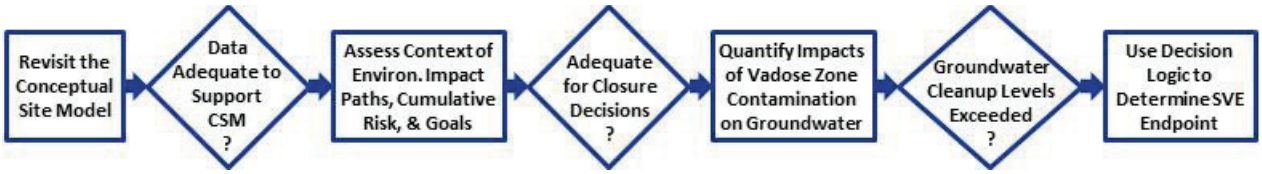
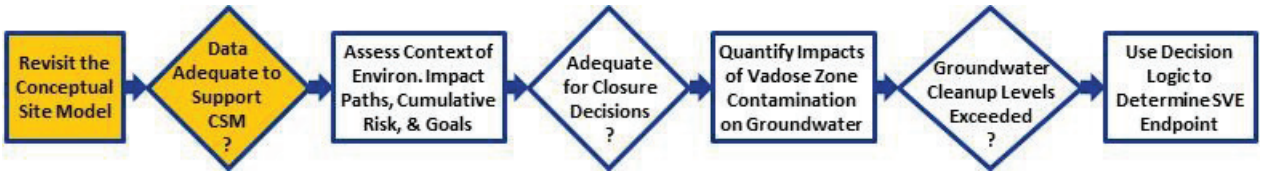


Figure 5-3. Condensed Flowchart for Approach and Decision Logic for Assessment of SVE System Closure for the 200-PW-1 OU CSM

5.2 Conceptual Site Model

The CSM provides a framework for describing the characteristics of the subsurface (e.g., geology, hydrology, and contaminant transport properties), the contamination (e.g., distribution and source strength), and the SVE system (e.g., operations and performance). When assessing SVE endpoint decisions, it is important to revisit the CSM to incorporate new data, reflect the current site conditions in the context of the SVE remediation conducted to date, and consider whether any data gaps exist. Extensive information about the 200-PW-1 OU has been collected over the course of site characterization and SVE operations (Chapter 4 and Appendix A in this report; DOE/RL-2014-18; DOE/RL-2006-51) and forms the basis for the CSM.

The CSM for disposed carbon tetrachloride is discussed in Section 5.2.1. Section 5.2.2 presents CSM information for methylene chloride. Conclusions with respect to the suitability of the CSM to support SVE decisions are presented in Section 5.2.3.



5.2.1 Carbon Tetrachloride Conceptual Site Model

The carbon tetrachloride CSM is summarized in Section 5.2.1.1, with key supporting information about contaminant distribution, the vadose zone source, SVE system performance, and other CSM aspects being presented in subsequent subsections. Appendix A, DOE/RL-2014-18, and DOE/RL-2006-51 provide additional details regarding site investigations.

5.2.1.1 Summary of the Conceptual Site Model

Carbon tetrachloride was disposed primarily at three waste sites (216-Z-9, 216-Z-1A, and 216-Z-18), where SVE has been applied to extract vapor-phase contaminants since 1992 using operational strategies and time frames commensurate with the degree of contamination at each site (Figure 5-4). Additionally, a small volume of carbon tetrachloride was discharged to the 216-Z-12 Crib. The waste sites were cribs, trenches, and tile fields that extended nominally 6 m (20 ft) below ground surface, mainly in backfill material. The material below the waste sites is comprised of higher permeability Hanford formation materials (about 34 m [112 ft] thick) and Ringold Formation materials (about 25 m [82 ft] thick above the water table), which are separated by low-permeability CCU sediments (about 6 m [20 ft] thick). Soil vapor was extracted directly from the higher permeability units. Contamination from the low-permeability unit slowly diffused into the higher permeability units and then was extracted.

In evaluating the current CSM, it is important to recognize that site conditions have changed over time. The site progressed through disposal, contaminant redistribution, continuous SVE, and cyclic SVE periods. As presented in the 200-PW-1 OU RI report (DOE/RL-2006-51), waste disposal and subsequent contaminant redistribution resulted in carbon tetrachloride contaminating the vadose zone and groundwater. Silt materials in the vadose zone, in particular the CCU, retained contamination during this time. Figure 5-5 depicts the progression of site conditions during the continuous and cyclic SVE operations, using the 216-Z-9 site as an example. At the onset of SVE in 1992, high concentrations of carbon tetrachloride were present in the vadose zone within high- and low-permeability regions. From 1992 to 1996, SVE systems operated nearly full-time throughout each year, removing approximately 73,000 kg (total) of carbon tetrachloride from the vadose zone during this period. Because only minor amounts of carbon tetrachloride were removed near 216-Z-12, it was determined not to be a continuing source area.

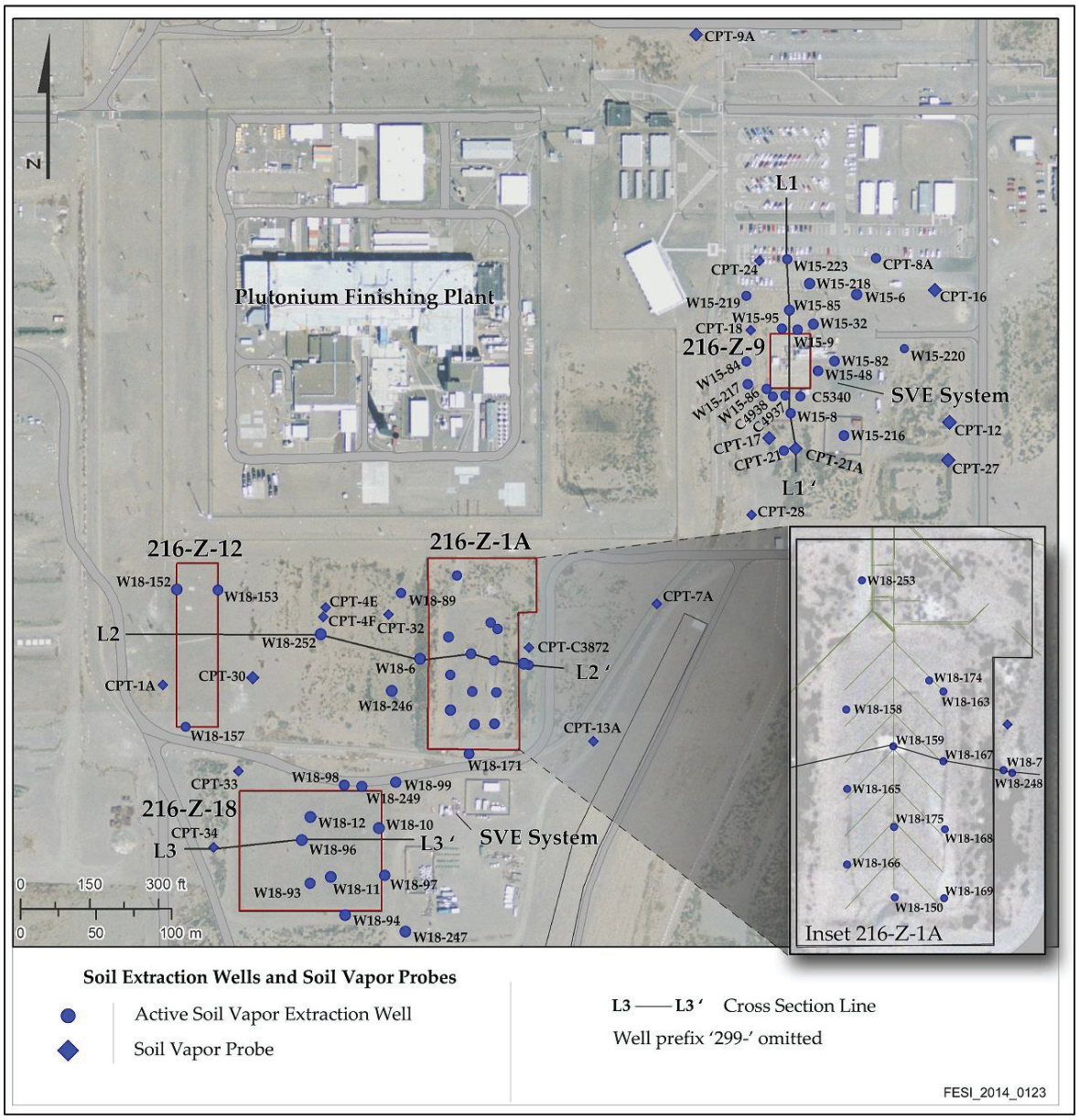


Figure 5-4. Carbon Tetrachloride Waste Sites and SVE Systems for the 200-PW-1 OU

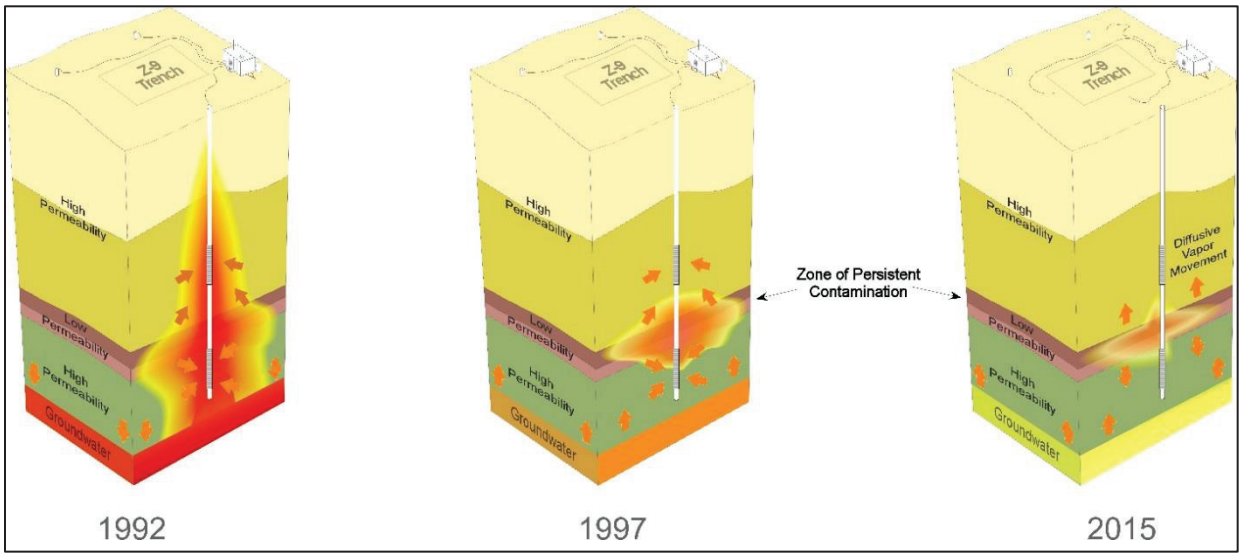


Figure 5-5. Evolution of the Magnitude and Extent of the Carbon Tetrachloride Contamination during Remediation Using SVE from 1992 to 2015

The SVE systems were shut down from November 1996 through July 1997 to conduct a rebound study (BHI-01105). The study indicated that carbon tetrachloride remaining in the vadose zone was located primarily within the finer grained CCU and recommended that the system be operated in a cyclic mode. Thus, by 1997, the vadose zone contamination had been significantly reduced in the high-permeability zones, and the remaining issue was high vapor-phase contamination discharging from the CCU.

Cyclic SVE operations continued from 1997 through the most recent active SVE operational cycle in 2012. During this time, performance monitoring has shown declining carbon tetrachloride concentrations in conjunction with declines in contaminant rebound during the quiescent portion of the operational cycle. These SVE cyclic operational data were recently analyzed, along with data from a targeted characterization effort at the 216-Z-9 site, as part of a treatability test (PNNL-21326, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*). This study indicated that the remaining carbon tetrachloride source was located in the CCU beneath the disposal site, and vapor-phase contaminant discharge from the source had been significantly diminished over time. These study results are consistent with the results of extensive investigations for the 200-PW-1 OU in the RI report (DOE/RL-2006-51), which indicate that no carbon tetrachloride sources exist other than beneath the three identified disposal sites. This progression of site conditions resulted in the current conditions depicted in Figure 5-5 and the following key elements of the current CSM:

- Current carbon tetrachloride concentrations in the vadose zone near the former disposal sites are low and have been significantly decreased at most locations by one to four orders of magnitude from concentrations at the onset of SVE (discussed in Section 5.2.1.2).

- RI studies (DOE/RL-2006-51) concluded that there are no sources outside of the three main disposal sites (Section 5.2.1.2). Remaining carbon tetrachloride that can serve as a source for vapor-phase contaminant discharge is predominantly in the CCU beneath the disposal sites, with 216-Z-9 having the highest level of remaining contamination in the CCU of the three major disposal sites (discussed in Section 5.2.1.3).

- Vapor-phase carbon tetrachloride discharging from the CCU is at low levels and moves away from the CCU by diffusion when SVE is not operating (discussed in Section 5.2.1.3). Vapor-phase contaminant discharge from the CCU has been significantly diminished by SVE and will continue to diminish by diffusive processes if SVE is terminated. The current vapor-phase contaminant discharge from the CCU at 216-Z-9 is too low to cause carbon tetrachloride to migrate from the vadose zone to the groundwater. That is, groundwater carbon tetrachloride concentrations beneath the disposal areas are currently high enough compared to the vadose zone concentrations that carbon tetrachloride transport from the CCU would remain in the vadose zone instead of moving into the groundwater.

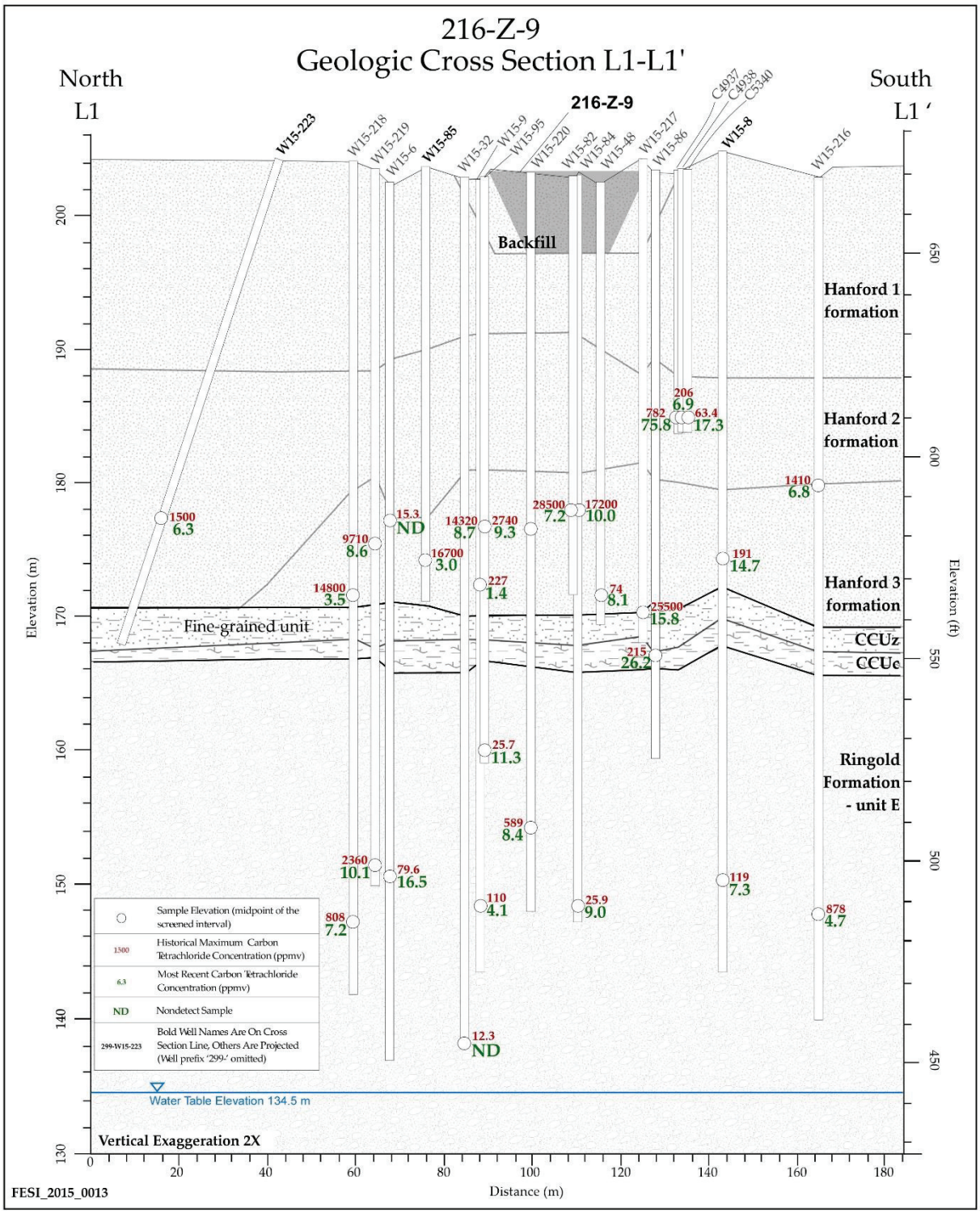
The potential environmental pathway for carbon tetrachloride is exposure via groundwater (Section 5.3.1). Because the CCU is the vadose zone source, groundwater would potentially be impacted by carbon tetrachloride concentrations emanating from the CCU to the vadose zone below the CCU. However, the groundwater is already contaminated with carbon tetrachloride, for which a separate and concurrent remedy (pump and treat [P&T] for 25 years, followed by monitored natural attenuation [MNA]) is ongoing. Attenuation mechanisms other than dispersion and dilution in the vadose zone are expected to be minor, and a conservative evaluation of the impacts of vadose zone carbon tetrachloride should not include these types of attenuation mechanisms.

5.2.1.2 Contaminant Distribution

The vadose zone consists of about 65 m (213 ft) of relatively permeable sand and gravel within the Hanford formation (about 34 m [112 ft] thick) and Ringold Formation (about 25 m [82 ft] thick above the water table), which are separated by the low-permeability CCU sediments (about 6 m [20 ft] thick). Figures 5-6 through 5-8 depict the stratigraphy for three cross sections (locations are shown in Figure 5-4). The 200-PW-1 OU RI report (DOE/RL-2006-51) provides additional discussion on the stratigraphy. The historical maximum carbon tetrachloride concentrations at the onset of SVE operations (1992) and the most recent maximum carbon tetrachloride concentrations during SVE operations (2012) are shown in these figures and demonstrate the significant reduction in concentration that has occurred due to SVE operations.

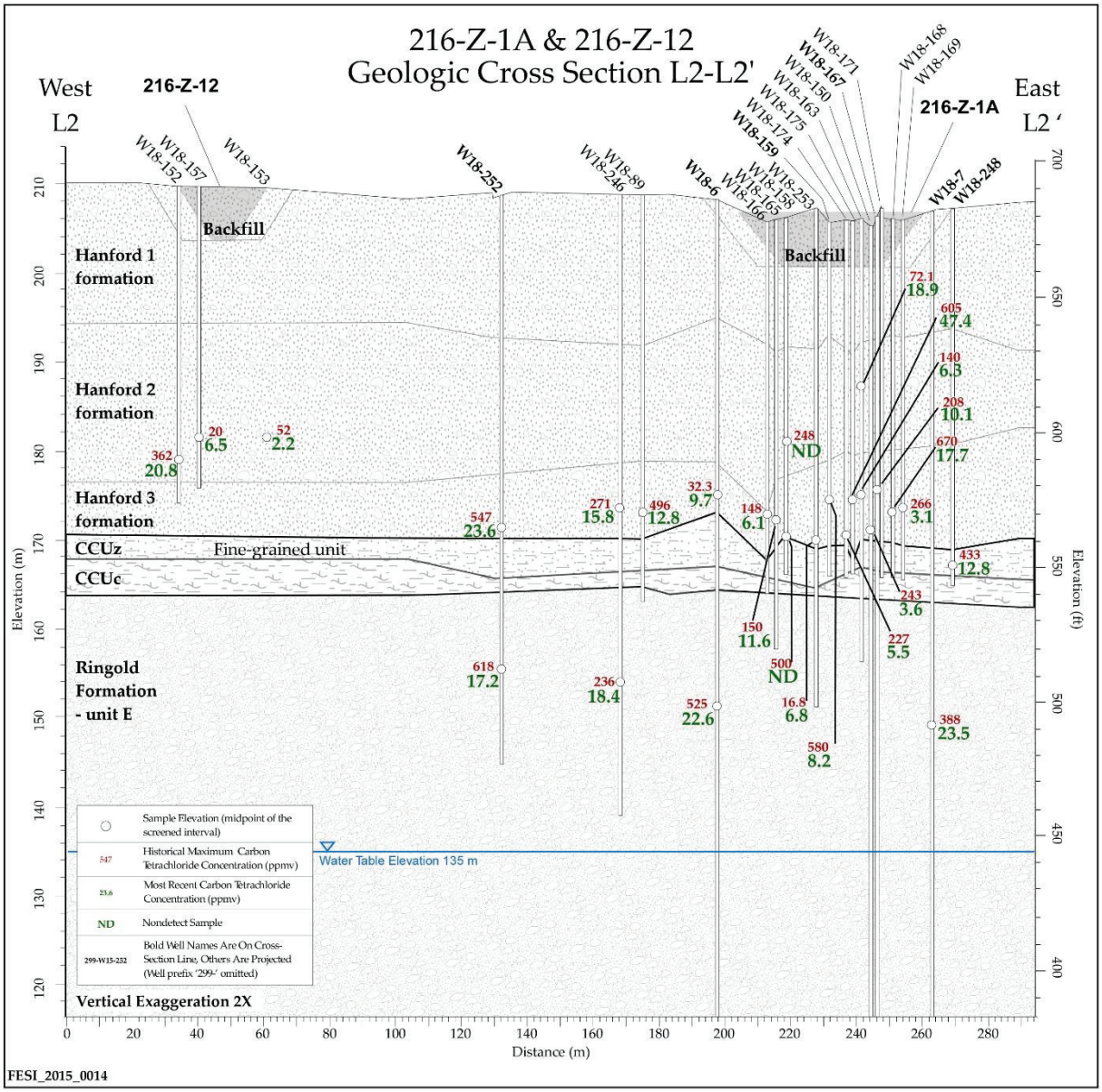
Extensive characterization (Figure 5-9) has taken place to determine the extent of carbon tetrachloride contamination and the vadose zone sources at the 200-PW-1 OU (see Appendix A for more detail). Passive soil gas surveys provided initial reconnaissance to guide soil vapor sampling in the RI for the 200-PW-1 OU (DOE/RL-2006-51). The RI soil vapor results for locations above, within, and below the CCU indicated that carbon tetrachloride was within or near the waste site footprints. Based on the soil vapor results, soil samples were collected to add to the characterization knowledge about carbon tetrachloride concentrations above, within, and below the CCU. No indications of an unknown carbon tetrachloride source were found.

A preliminary conceptual model included possible dense nonaqueous-phase liquid (DNAPL) carbon tetrachloride migration to the south along the top of the CCU beneath the 216-Z-9 disposal site (DOE/RL-2004-78, *Work Plan for Integrated Approach for Carbon Tetrachloride Source Term Location in the 200 West Area of the Hanford Site*). This preliminary conceptual model was developed during planning for the DNAPL investigation. Several lines of evidence have shown that there was no significant lateral migration of DNAPL along the top of the CCU and that this potential data gap has been closed out. The lines of evidence include 1) that the top of the CCU underneath the disposal sites lacks a southerly slope, 2) that RI data do not show indication of significant lateral DNAPL migration along the top of the CCU, 3) that numerical multi-phase modeling shows DNAPL primarily moves vertically downward through the CCU, and 4) that the remaining carbon tetrachloride source for the 216-Z-9 disposal site was investigated and found to be located in the CCU within an approximately 90 m by 90 m (295 ft by 295 ft) zone centered below 216-Z-9.



Note: The cross section location is shown in Figure 5-4.

Figure 5-6. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon Tetrachloride Concentrations (1993 to 2012) for 216-Z-9 Online Active SVE Wells



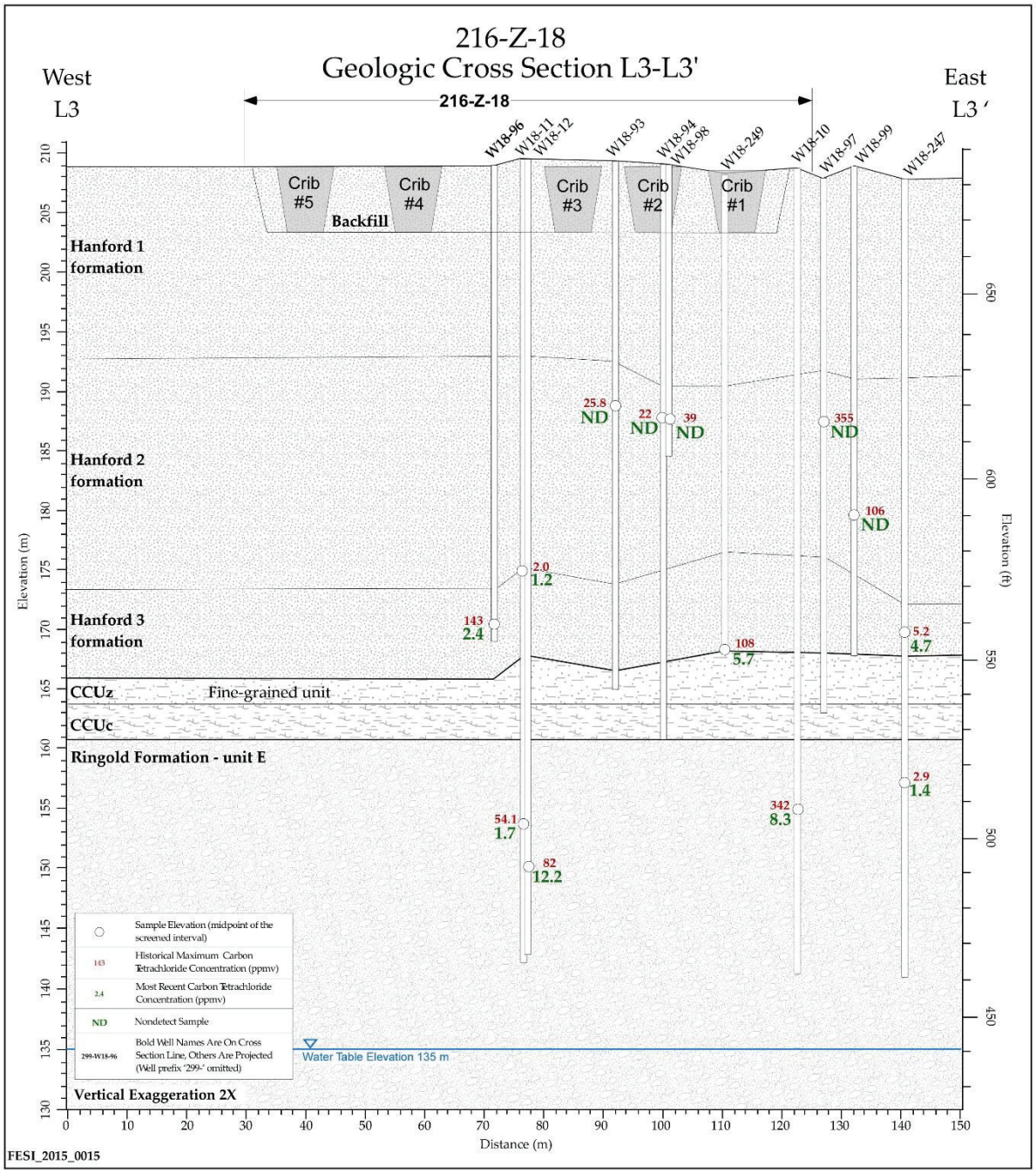
Note: The cross section location is shown in Figure 5-4.

Figure 5-7. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon Tetrachloride Concentrations (1992 to 2012) for 216-Z-1A/216-Z-12 Online Active SVE Wells

The current status of carbon tetrachloride is based on the most recent measurements (2012) at SVE extraction wells (Figures 5-6 through 5-8) and samples collected in 2014 and 2015 (Appendix B) from offline SVE wells and soil vapor probes (Figures 5-10 through 5-13). These data show that SVE operations over the past two decades have effectively diminished the magnitude and extent of carbon tetrachloride within the vadose zone. All measurements below the CCU and nearly all measurements above/within the CCU in 2014 and 2015 were below the 200-PW-1 OU ROD (EPA et al., 2011) cleanup level for carbon tetrachloride of 100 ppmv.

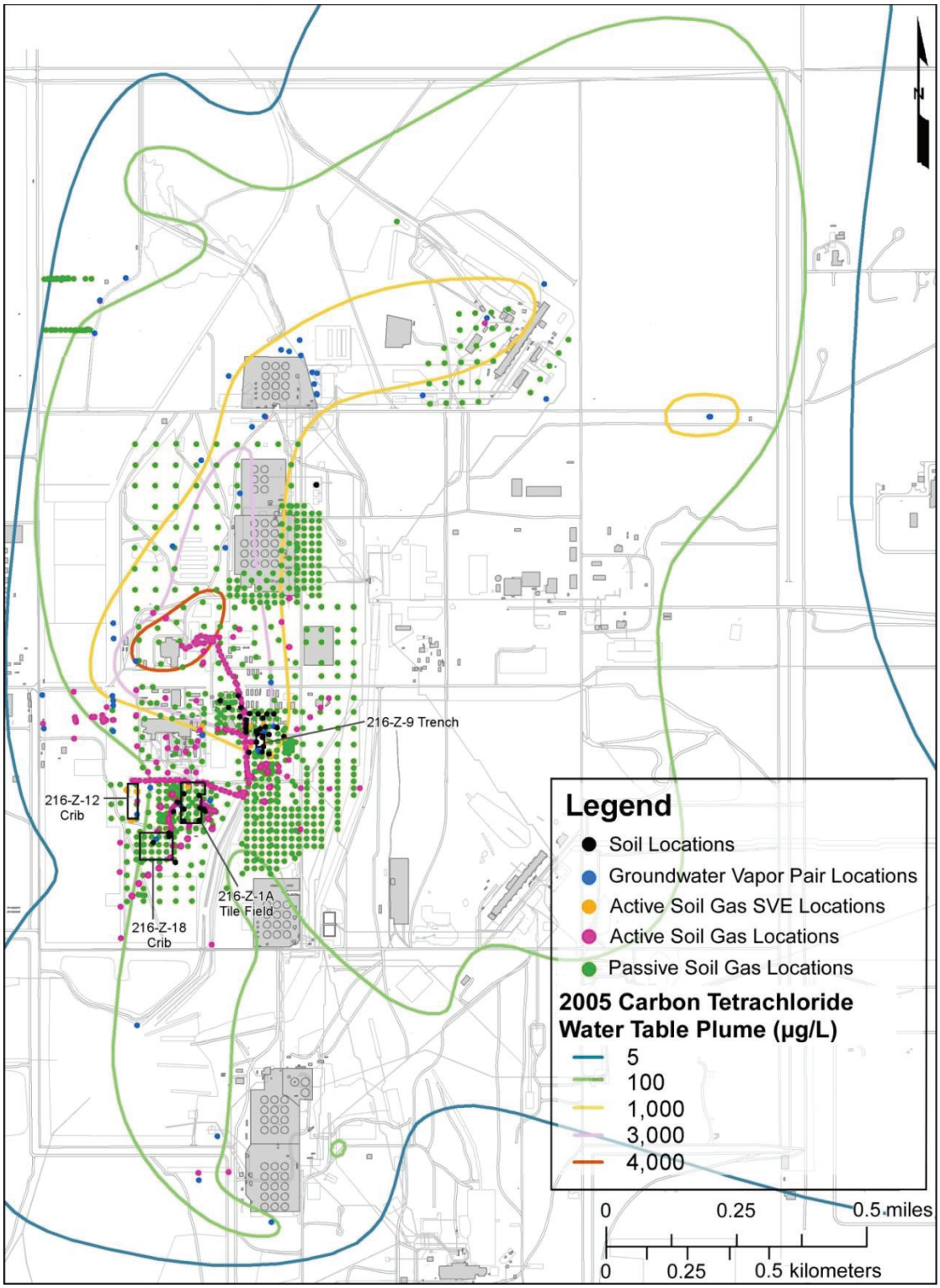
5.2.1.3 Vadose Zone Contaminant Source and Soil Vapor Extraction Performance

The 200-PW-1 OU RI investigations and modeling (DOE/RL-2006-51), and the subsequent characterization of the vadose zone (PNNL-21326), all indicate that the current residual carbon tetrachloride mass is located primarily within the CCU, with vapor diffusion of carbon tetrachloride out of the CCU currently resulting in relatively low soil vapor concentrations (generally below the 200-PW-1 OU ROD [EPA et al., 2011] cleanup level of 100 ppmv) both above and below the CCU.



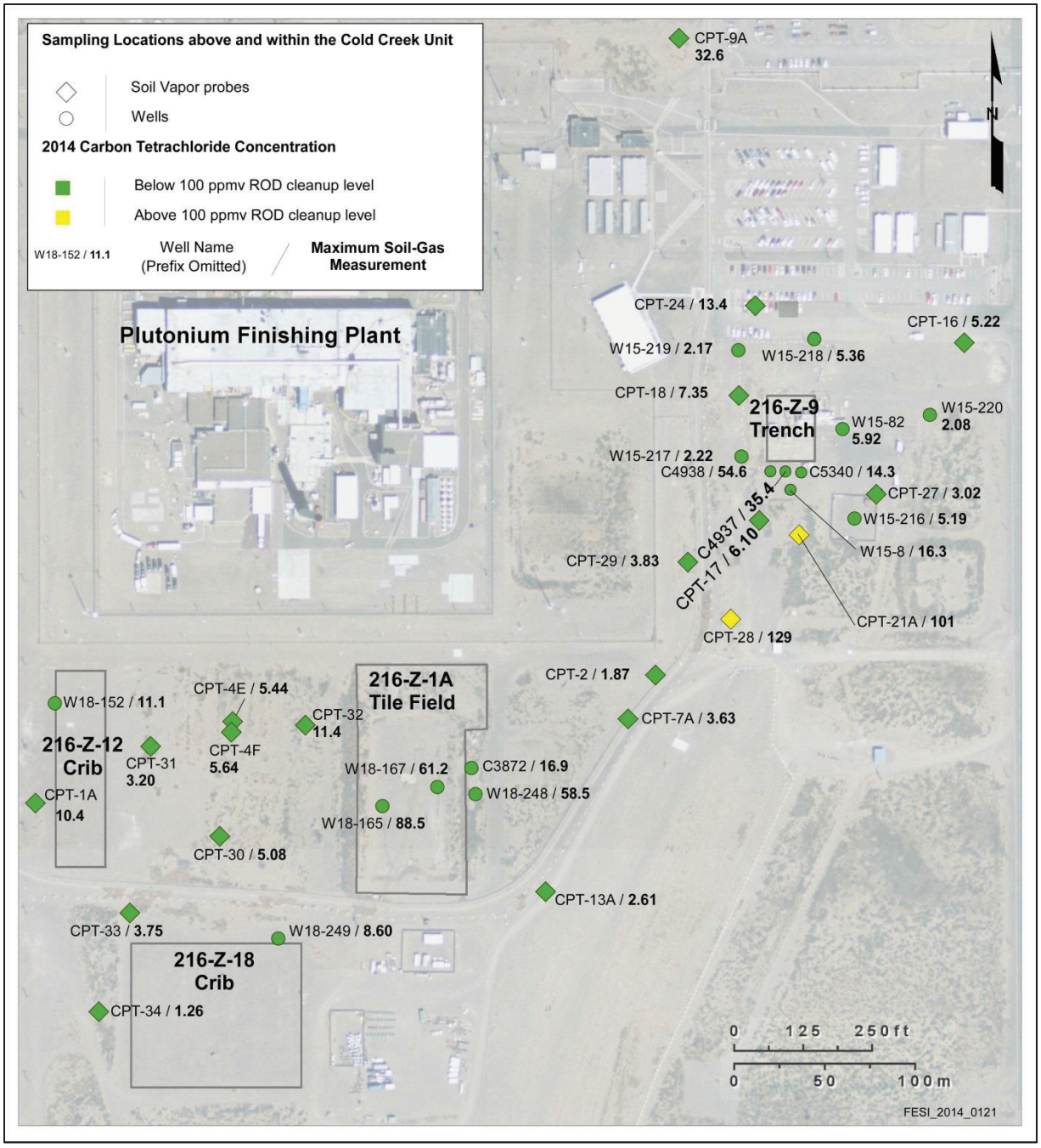
Note: The cross section location is shown in Figure 5-4.

Figure 5-8. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon Tetrachloride Concentrations (1992 to 2012) for 216-Z-18 Online Active SVE Wells



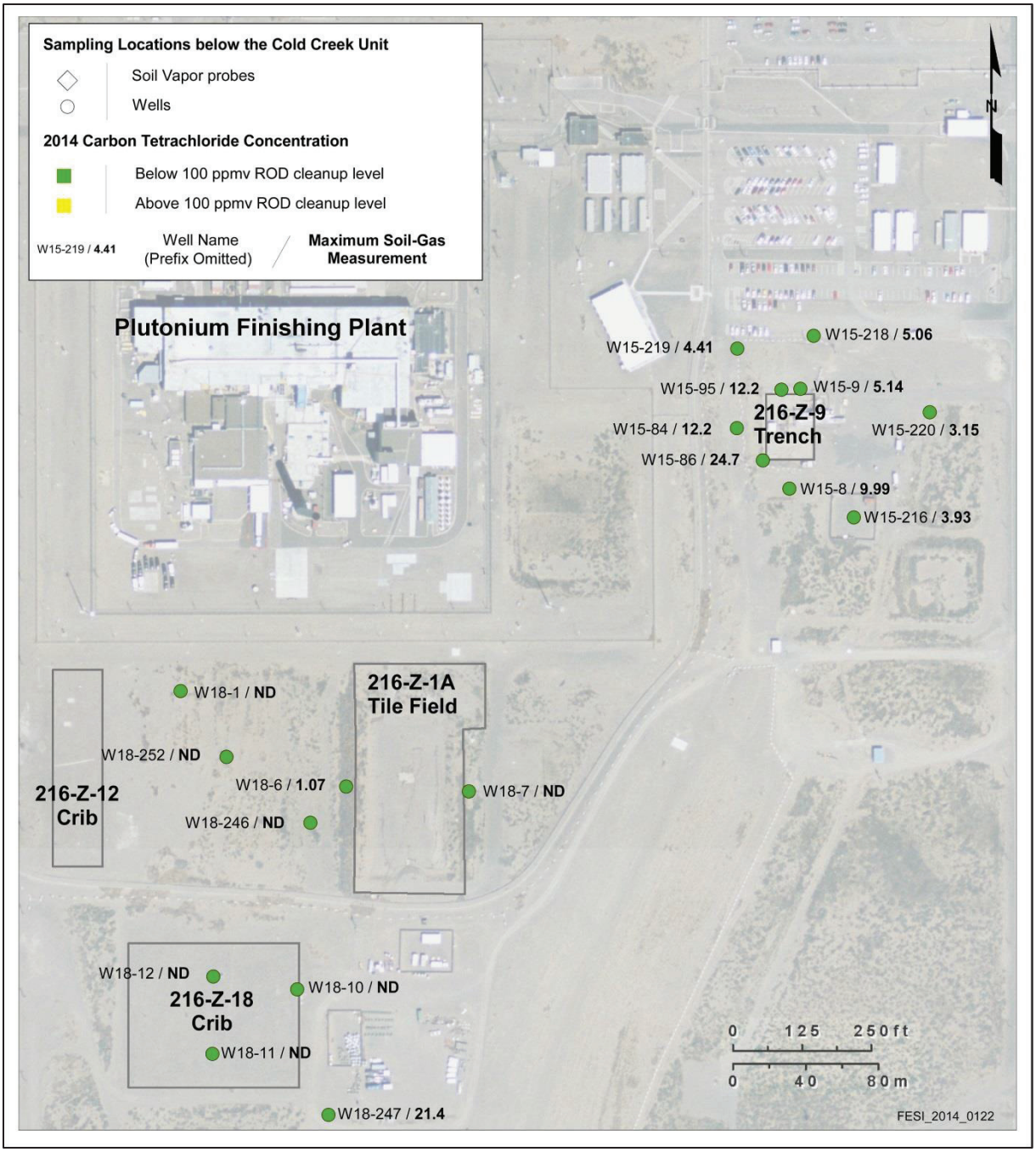
Source: Derived from Figure 3-20 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure 5-9. Carbon Tetrachloride Sampling Locations during the RI, Overlaid on the 2005 Groundwater Carbon Tetrachloride Plume Contours



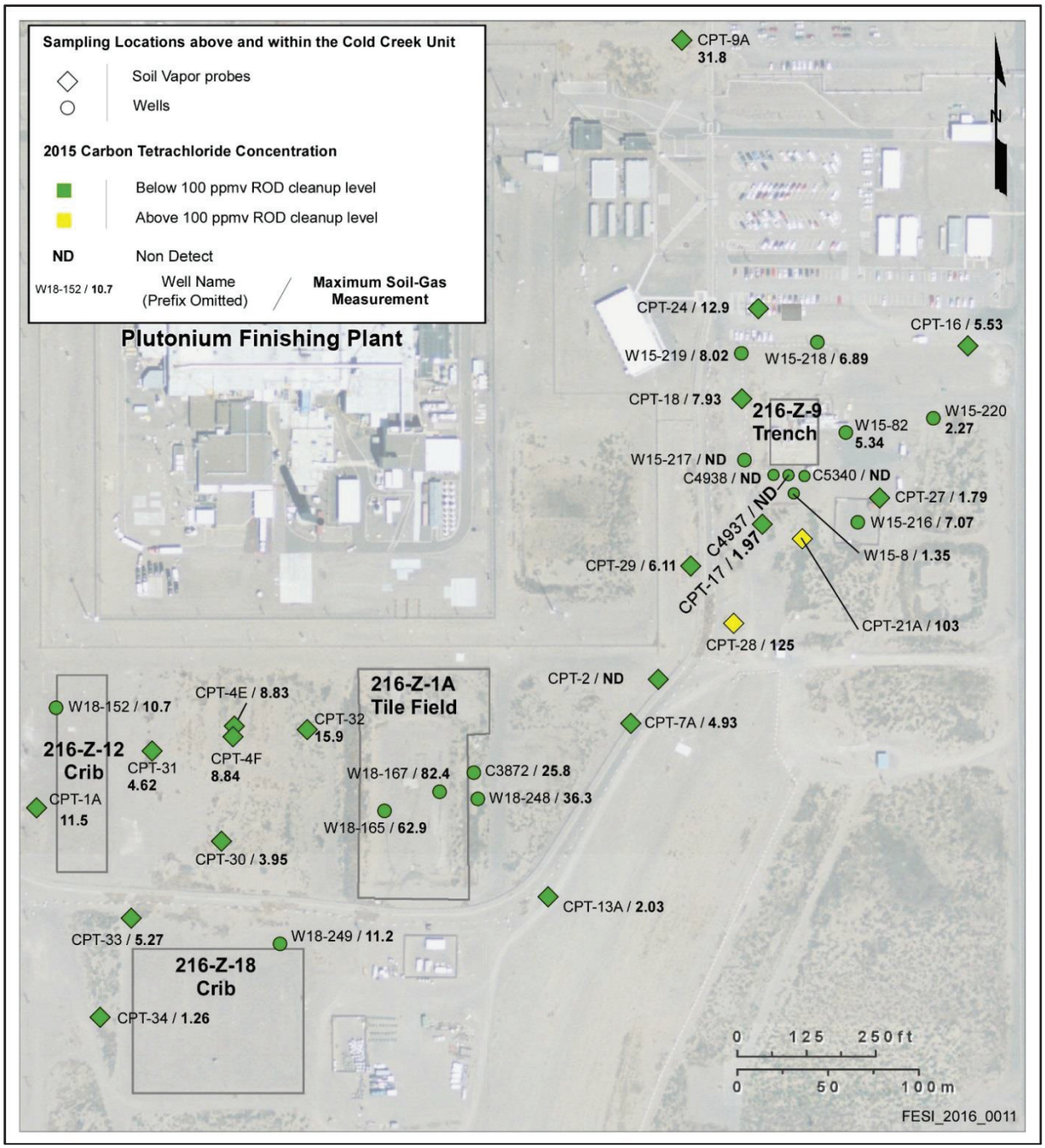
Note: Carbon tetrachloride concentrations were measured in the field using a Brüel & Kjær multi-gas analyzer.

Figure 5-10. Maximum Carbon Tetrachloride Concentrations (in ppmv) in Samples Collected in 2014 from Soil Vapor Probes and Offline Monitoring Wells Screened above and within the CCU



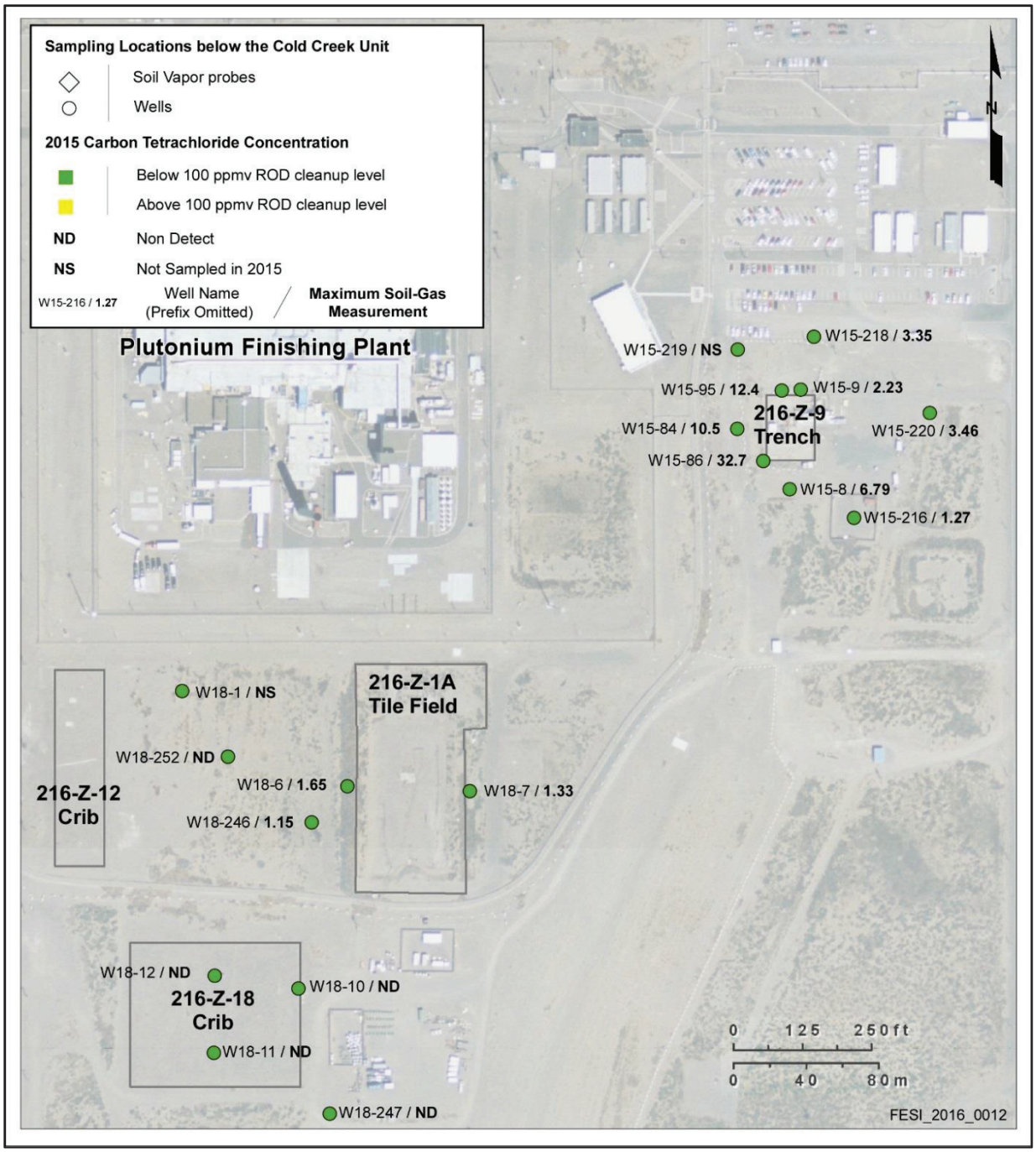
Note: Carbon tetrachloride concentrations were measured in the field using a Brüel & Kjær multi-gas analyzer. No soil vapor probes are located below the CCU.

Figure 5-11. Maximum Carbon Tetrachloride Concentrations (in ppmv) for Samples Collected in 2014 from Offline Monitoring Wells Screened below the CCU



Note: Carbon tetrachloride concentrations were measured in the field using a Brüel & Kjær multi-gas analyzer.

Figure 5-12. Maximum Carbon Tetrachloride Concentrations (in ppmv) in Samples Collected in 2015 from Soil Vapor Probes and Offline Monitoring Wells Screened above and within the CCU



Note: Carbon tetrachloride concentrations were measured in the field using a Brüel & Kjær multi-gas analyzer. No soil vapor probes are located below the CCU.

Figure 5-13. Maximum Carbon Tetrachloride Concentrations (in ppmv) for Samples Collected in 2015 from Offline Monitoring Wells Screened below the CCU

A detailed treatability test (PNNL-21326) was conducted to assess subsurface characterization methods and determine the vadose zone carbon tetrachloride source characteristics for the 216-Z-9 waste site. The overall carbon tetrachloride source mass discharge based on cyclic SVE operational data since 1997 and the evaluation method provided in Brusseau et al., 2010, "Analysis of Soil Vapor Extraction Data to Evaluate Mass-Transfer Constraints and Estimate Source-Zone Mass Flux," were used to assess

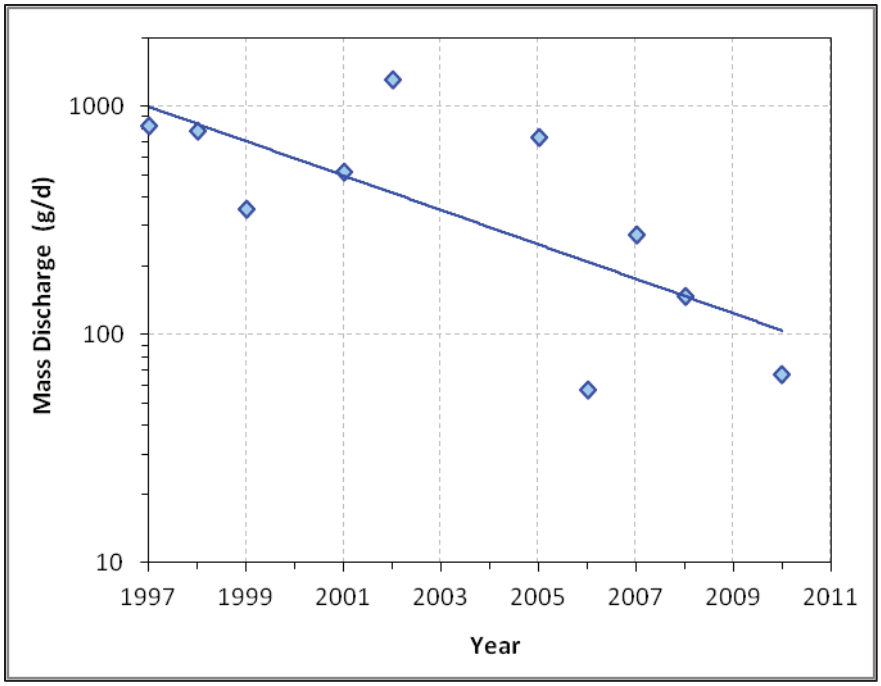
carbon tetrachloride source strength. Pneumatic responses and location-specific mass discharge (from single-well tests) were used to assess carbon tetrachloride distribution (extent and location). A distinct pattern in the carbon tetrachloride concentration and mass discharge data showed higher values near the CCU within a distinct lateral extent. The current lateral dimensions of the source zone for the 216-Z-9 waste site were estimated to be about 90 m by 90 m (295 ft by 295 ft). Remaining carbon tetrachloride source material was also verified to reside primarily in the CCU. The source mass discharge for the 216-Z-9 waste site has declined (Figure 5-14), as calculated over the period when SVE has been operated in a cyclic manner (operation followed by a period of no extraction to allow concentrations to rebound).

The same characterization testing as performed for the 216-Z-9 waste site in the treatability test (PNNL-21326) has not been conducted for the 216-Z-1A or 216-Z-18 sites. However, disposed DNAPL has a similar distribution in the subsurface at these sites (200-PW-1 OU RI report [DOE/RL-2006-51]). Until 1997, the SVE systems for the 200-PW-1 OU were operated continuously; thereafter, the operational strategy was changed to cycles of operation followed by periods without extraction. A plot of the cumulative mass of carbon tetrachloride removed over time (Figure 3-1) shows how the SVE systems removed significant quantities of mass early in the remediation, yet recent cycles of operation are contributing only small increments of extracted carbon tetrachloride mass. The diminished amount of mass extracted is also apparent from plots of the starting (i.e., initial value after a period without extraction) and ending (i.e., asymptotic) concentrations from an operational cycle, which are shown in Figure 5-15 for the 216-Z-9 SVE system and Figure 5-16 for the 216-Z-1A and 216-Z-18 SVE system. This lack of significant rebound indicates that the source mass discharge rate has significantly diminished, which is consistent with the source mass discharge values calculated for the 216-Z-9 waste site (Figure 5-14). These data also support the conclusion that, of the three major disposal sites, the 216-Z-9 site has the highest level of remaining contamination in the CCU.

5.2.1.4 Additional Conceptual Site Model Aspects

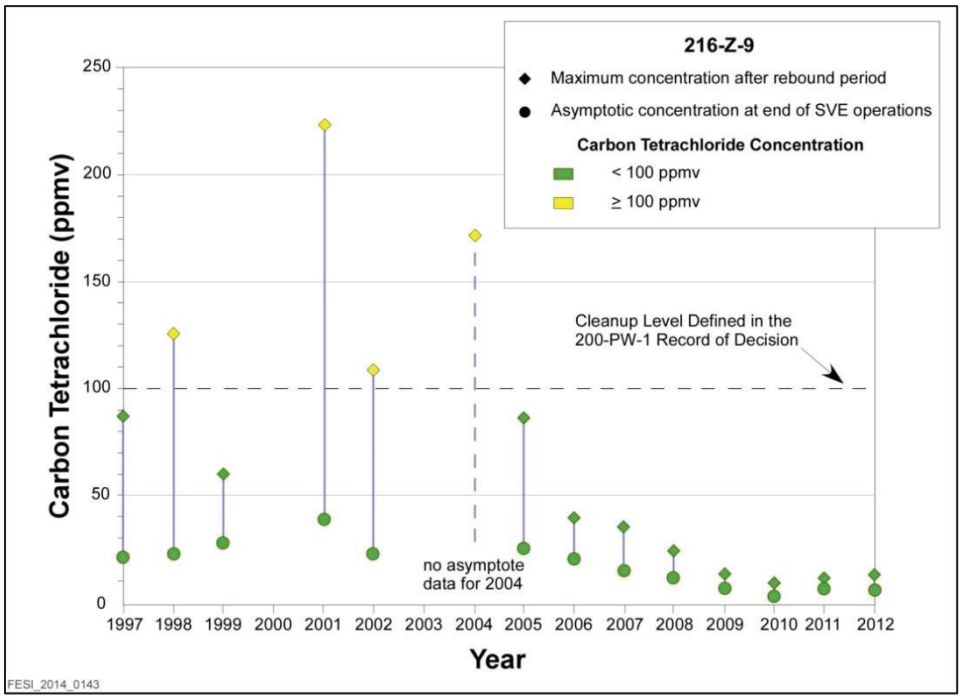
In addition to the subsurface characteristics, the source location/strength, and SVE system performance, the SVE Closure Guidance (PNNL-21843) describes several additional aspects to consider when revisiting the CSM. These additional aspects include attenuation processes, receptors, and complicating factors.

Transformation of carbon tetrachloride to other compounds can occur both abiotically and with microbial mediation (WSRC-STI-2006-00096, *Scenarios Evaluation Tool for Chlorinated Solvent MNA*). Abiotic hydrolysis of aqueous-phase carbon tetrachloride is known to occur regardless of reduction-oxidation conditions. However, the half-life for its transformation to carbon dioxide is about 41 years, so it is a slow process. Under anaerobic conditions, carbon tetrachloride can undergo microbially mediated reductive dechlorination, with chloroform being the primary transformation product. In the vadose zone, current conditions are such that oxygen is generally present (particularly when SVE is operating), so anaerobic reactions are unlikely. While these reactive attenuation processes have some potential to reduce the mass of carbon tetrachloride, they are either slow or of limited extent. Thus, for the purposes of the CSM and subsequent assessments, attenuation by transformation reactions will conservatively be neglected.



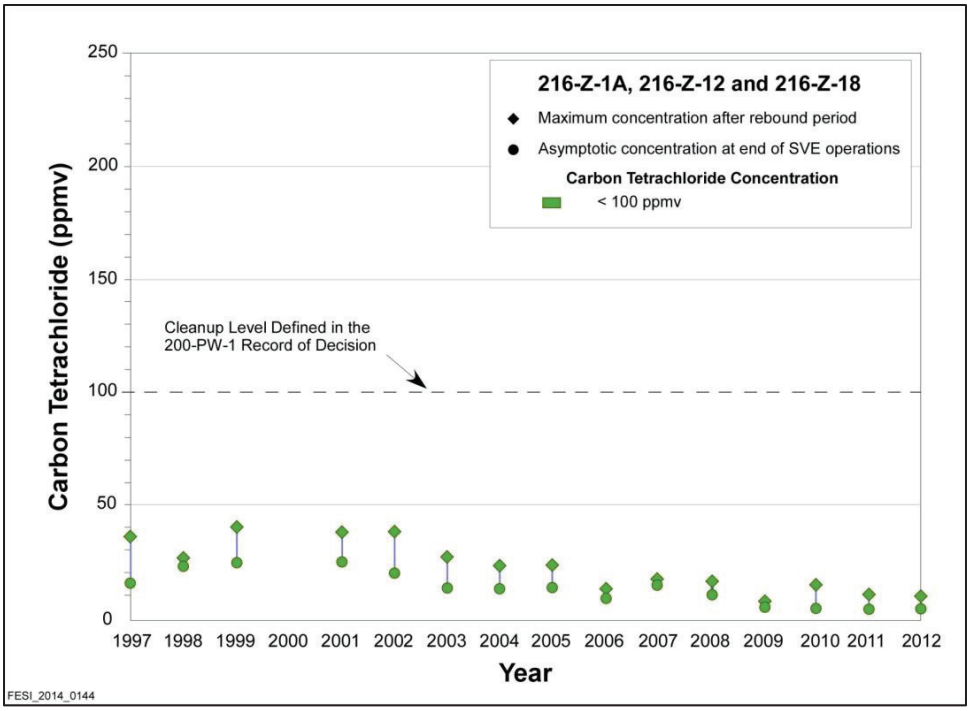
Source: Derived from PNNL-21326, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*.

Figure 5-14. Computed Source Mass Discharge for the 216-Z-9 Waste Site over Time (1997 to 2010)



Note: The tie lines between points indicate the connection between the starting and ending concentrations in a given operational cycle.

Figure 5-15. Rebound and Final Concentrations for Operational Cycles of the 216-Z-9 SVE System from 1997 to 2012



Note: The tie lines between points indicate the connection between the starting and ending concentrations in a given operational cycle.

Figure 5-16. Rebound and Final Concentrations for Operational Cycles of the 216-Z-1A/216-Z-18/216-Z-12 SVE System from 1997 to 2012

The one complicating factor relevant to vadose zone contamination is that groundwater is already contaminated with carbon tetrachloride, and the direction of contaminant mass transfer out of the groundwater into the vadose zone is possible, depending on the relative concentrations in these two zones. A separate and concurrent ongoing 200-ZP-1 OU groundwater remedy consists of using a P&T system for 25 years (through 2037) to extract carbon tetrachloride-contaminated groundwater and reduce concentrations to approximately 100 µg/L. The remedy then transitions to a 100-year period of MNA, during which time residual carbon tetrachloride in the groundwater is expected to decline sufficiently to meet the cleanup goal of 3.4 µg/L established in the 200-ZP-1 OU ROD (EPA et al., 2008). Carbon tetrachloride groundwater concentrations are an important part of the CSM because they need to be considered with respect to carbon tetrachloride movement. For example, current carbon tetrachloride concentrations in the groundwater are high with respect to vadose zone concentrations, and current carbon tetrachloride migration would be upward from the groundwater to the vadose zone.

5.2.2 Methylene Chloride Conceptual Site Model

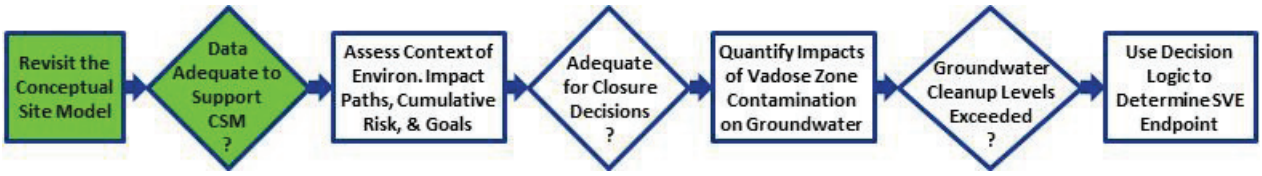
Methylene chloride was not a component of the disposed waste. Its presence in the subsurface would be due to anaerobic degradation of chloroform, which itself is an anaerobic degradation product of carbon tetrachloride (WSRC-STI-2006-00096). This type of reductive dechlorination process would take place only under highly anaerobic conditions with the presence of an organic substrate to drive the reactions. These conditions may have existed during (and for some time after) disposal, when the vadose zone moisture content was high (due to the presence of disposed water and organics such as lard oil). Over time, the potential for generating methylene chloride in the vadose zone would decrease as the organic material was degraded, the moisture content decreased, and the vadose zone transitioned to more aerobic conditions, especially with the onset of SVE. Under current conditions, methylene chloride is viewed as a dispersed remnant of these previous conditions, with no continuing source of methylene

chloride in the vadose zone. Methylene chloride can be biodegraded by anaerobic or aerobic direct metabolism mechanisms, which serve as attenuation processes that further reduce methylene chloride concentration over time in the vadose zone (WSRC-STI-2006-00096). The end product of such biological direct metabolism reactions is carbon dioxide.

The most recent methylene chloride concentrations measured at online active extraction wells in 2012 and offline monitoring wells and soil vapor probes in 2013 are less than the 50 ppmv cleanup level identified in the 200-PW-1 OU ROD (EPA et al., 2011) (Section A5 in Appendix A). Methylene chloride was not detected in laboratory analyses of soil vapor samples collected from offline monitoring wells and soil vapor probes in 2014 or 2015, with the exception of a detection in 2015 at a concentration of 0.00027 ppmv in well 299-W15-8 (31 m [103 ft] below ground surface) (Appendix B). Based on these low concentrations, current methylene chloride contamination in the vadose zone is minimal and well below the cleanup level. These observations, in conjunction with the lack of a continuing source and the biological attenuation mechanism for methylene chloride, indicate that methylene chloride concentrations are low, and are expected to stay low and diminish over time in the vadose zone.

5.2.3 Conclusions

The CSM information provides the qualitative and quantitative input needed to describe carbon tetrachloride and methylene chloride contamination in the 200-PW-1 OU vadose zone. The data are adequate to support a well-defined CSM. In particular, remaining contamination in the vadose zone at locations above, within, and below the CCU is well understood, with no data gaps. There are no unknown sources. This CSM provides an adequate framework for the subsequent assessment of the environmental and regulatory context and carbon tetrachloride and methylene chloride impacts on groundwater.



5.3 Environmental Pathways and Regulatory Compliance Context

Having reviewed/updated the CSM, the next step (per Section 5.1) is to assess the environmental impact pathway, cumulative risk, and regulatory compliance context. For most sites, these aspects are established early in the remediation process, but the situation may have changed over time as remediation progressed and new information was obtained. Thus, the updated CSM (Chapter 5.2) provides the framework to revisit these aspects and determine whether they are adequate to support SVE endpoint decisions.

5.3.1 Environmental Impact Pathways

The CSM describes the current extent of the vadose zone carbon tetrachloride contamination as being primarily in the fine-grained CCU sediments, with low concentrations (tens of ppmv) in the more permeable sediments above and below the CCU.

Ground surface exposure pathways for carbon tetrachloride in the vadose zone were eliminated by a comprehensive risk assessment performed for the 216-Z-9 and 216-Z-1A waste sites (Appendix A of DOE/RL-2007-27). This risk assessment thoroughly evaluated potential environmental pathways.

The BRA stated that, under the anticipated industrial scenario and land-use controls, industrial worker exposures to carbon tetrachloride would not occur via direct contact with contaminated soils. Also, based on air samples at the ground surface for 216-Z-9 (the most contaminated of the three waste sites) being below the permissible exposure limits of RCW 49.17 (and well below a level of health significance for site workers), the BRA determined that the vapor inhalation pathway was insignificant.

The remaining potential environmental exposure pathway is via contaminated groundwater (e.g., drinking, irrigation, and discharge to surface water) (Figure 5-17). Referring to the current CSM, the remaining carbon tetrachloride contamination is primarily in the CCU sediments. However, diffusive transport of carbon tetrachloride in soil gas below the CCU is a potential pathway to the groundwater, where interphase mass transfer could result in an impact to the groundwater quality, resulting in potential health risks to groundwater users (receptors). This pathway must be considered in the subsequent steps of the assessment and decision logic approach to support decisions regarding disposition of the SVE systems at the 200-PW-1 OU.

5.3.2 Cumulative Risk

Given the CSM framework and the existence of a single relevant environmental impact pathway (from vadose zone to groundwater to groundwater receptors), the applicable cumulative risk is potential human health and environmental risk due to carbon tetrachloride in groundwater via exposure to contaminated groundwater. This potential risk from groundwater exposure is assessed as part of the 200-ZP-1 OU groundwater remedy and is not directly applicable to vadose zone contamination. However, the groundwater cleanup objective of carbon tetrachloride concentrations at 3.4 µg/L or less (200-ZP-1 OU ROD [EPA et al., 2008]) is relevant input for assessing decisions regarding disposition of the SVE systems. Thus, the cumulative risk context is well defined and consists of risk assessment as part of the groundwater remedy and a groundwater carbon tetrachloride concentration cleanup goal of 3.4 µg/L.

5.3.3 Remediation Goals and Regulatory Setting

To support decisions regarding SVE endpoints, it is important to assess the remediation goal context to ensure that the goals have been defined and are appropriate for the site based on current knowledge.

Remediation goals were established in the 200-PW-1 OU ROD (EPA et al., 2011) based on an anticipated future land use as industrial (for DOE workers only) for at least 50 years, and as industrial (for DOE and non-DOE workers) thereafter. Only one RAO (RAO #3) applies to the carbon tetrachloride contamination in the vadose zone with the identified environmental impact pathway of groundwater exposure. RAO #1 applies to radiological contamination, and RAO #2 pertains to direct exposure to soil; thus, RAOs #1 and #2 are not applicable. RAO #3 from the 200-PW-1 OU ROD (EPA et al., 2011) is stated as follows: "Control the sources of potential groundwater contamination to support the Central Plateau groundwater goal of protecting the beneficial uses of groundwater, including protecting the Columbia River from adverse impacts."

The 200-PW-1 OU ROD (EPA et al., 2011) established a final cleanup level of 100 ppmv for carbon tetrachloride and 50 ppmv for methylene chloride in soil vapor to meet the intent of RAO #3 for the 200-PW-1 OU. Because this cleanup level was based on the objective of protecting groundwater, the ROD specified that soil vapor concentration cleanup levels "will be further refined and assessed to ensure they are protective of groundwater" and that cleanup is subject to WAC 173-340. The data and analyses present in the treatability test report (PNNL-21326) and in Section 5.4 provide the refined consideration of vadose zone conditions that are protective of groundwater. The 200-PW-1 OU ROD also noted that, "As long as residual contamination remains above levels that allow for unrestricted use, institutional controls will be required."

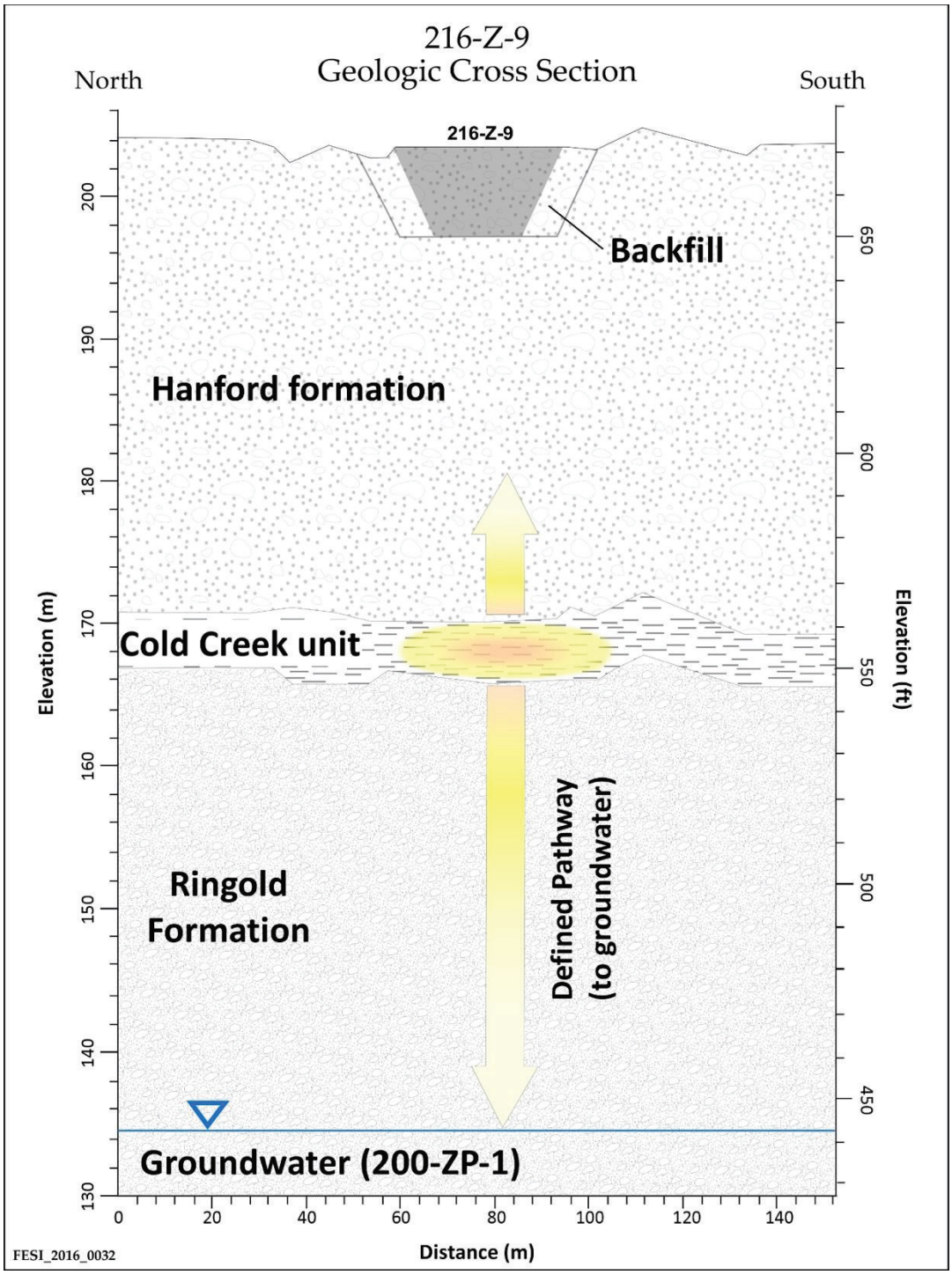
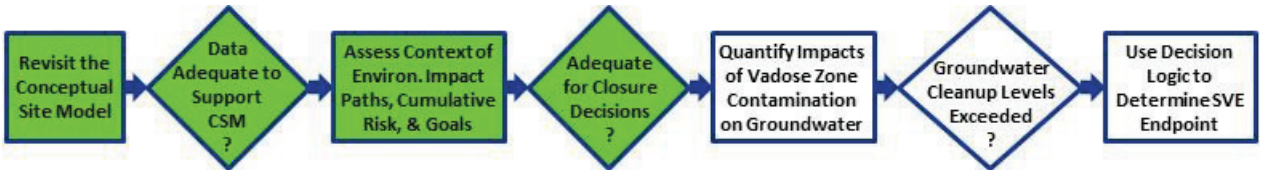


Figure 5-17. Potential Environmental Pathway from the Vadose Zone Source to Groundwater

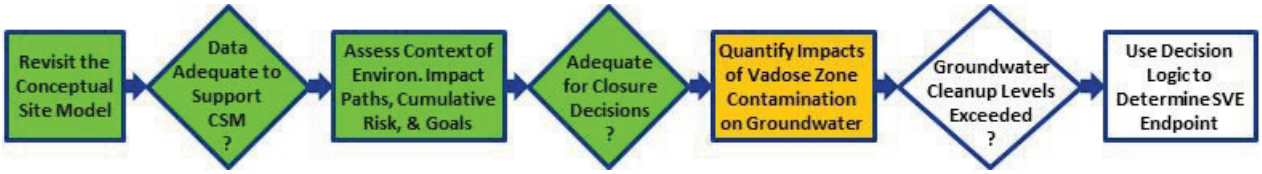
5.3.4 Conclusion for Environmental Pathways and Regulatory Compliance

The environmental pathway, cumulative risk, and regulatory compliance context have been adequately determined and defined to support an evaluation of the impact of vadose zone contamination on groundwater quality and subsequent decisions regarding disposition of the 200-PW-1 OU SVE systems.



5.4 Impacts of Remaining Source on Groundwater

An evaluation of the impact of the remaining vadose zone contamination within 200-PW-1 OU on the contaminant concentrations in the underlying aquifer (200-ZP-1 OU) is presented in this section. The evaluation for carbon tetrachloride contamination is presented in Section 5.4.1, followed by an evaluation for methylene chloride in Section 5.4.2.



5.4.1 Carbon Tetrachloride Impact on Groundwater

The approach for assessing the impact of carbon tetrachloride in the vadose zone on groundwater concentrations consists of four steps that are based largely on existing evaluations. This approach, based on the SVE Closure Guidance (PNNL-21843) and the site-specific treatability test (PNNL-21326), is a refined consideration of vadose zone conditions that are protective of groundwater, as specified in the 200-PW-1 OU ROD (EPA et al., 2011). The four steps are discussed in the following subsections:

- **Step 1:** For the three waste sites (216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib), calculate the relative impacts of vadose zone releases on groundwater concentrations using the calculation approach described in the SVE Closure Guidance (PNNL-21843).
- **Step 2:** Assess the current groundwater impact from the 216-Z-9 site based on the treatability test (PNNL-21326), which involved more detailed, site-specific contaminant transport analyses.
- **Step 3:** Compare the results from step 1 for the 216-Z-9 site to the results from the treatability test (step 2) in terms of impacts to groundwater.
- **Step 4:** Assess the future groundwater impact from the 216-Z-9 site based on the treatability test, with consideration of the ongoing remedy for the 200-ZP-1 OU and upward vapor diffusion from the groundwater.

5.4.1.1 Estimated Impact to Groundwater Based on the Soil Vapor Extraction Closure Guidance (Step 1)

Due to the effectiveness of SVE operations, carbon tetrachloride mass removal using SVE has declined over time, as discussed in Section 5.2. The SVE systems have reached a point of diminishing return with a low rate of diffusion-controlled mass discharge from the CCU. The SVE operations at the 216-Z-9 site have removed approximately 55,000 kg of contaminant mass compared to approximately 25,000 kg

removed by SVE operations at the combined 216-Z-1A/216-Z-18 site. This demonstrates that the 216-Z-9 site was the most contaminated of the 200-PW-1 OU carbon tetrachloride sites.

The Soil Vapor Extraction Endstate Tool (SVEET), documented in the SVE Closure Guidance (PNNL-21843), was used to estimate groundwater concentrations resulting from vadose zone sources at the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib (Table 5-1). The evaluation using SVEET was conducted in 2015 using 2014 data. Appendix C provides the SVEET calculation details. For the 216-Z-9 site, the vadose zone source strength was set to the maximum value of soil vapor measurements below the CCU collected during 2014. For the 216-Z-1A and 216-Z-18 sites, the maximum value of soil vapor measurements below the CCU collected during the period of 2012 to 2013 was used because all of the 2014 measurements below the CCU were below the detection limit. As expected from the source strengths, the 216-Z-9 site is estimated to have the most significant impact on groundwater. The impacts to groundwater from the 216-Z-1A and 216-Z-18 sites are estimated to be about 40 and 55 percent less than the estimated impact from the 216-Z-9 site. This indicates that the 216-Z-9 vadose zone contamination would be the limiting, worst-case scenario when considering termination of SVE operations.

SVEET results presented in Table 5-1 are conservative for two reasons:

- SVEET estimates the impact of vadose zone contamination on clean groundwater. Appendix D discusses the conditions for which mass transfer (e.g., via vapor diffusion) will be going either into the groundwater from the vadose zone or out of the groundwater into the vadose zone. Under the current contaminated conditions in the underlying 200-ZP-1 OU aquifer, mass transfer from the vadose zone into the groundwater would be inhibited.
- SVEET calculations assume that the vadose zone contaminant source remains constant over time. In reality, the source becomes depleted by diffusive mass transfer.

Table 5-1. Summary of SVEET Evaluation for the 216-Z-9, 216-Z-1A, and 216-Z-18 Waste Sites

Waste Site	216-Z-9	216-Z-1A	216-Z-18
Source gas concentration (ppmv)	24.7	13.9	9.65
Estimated groundwater concentration (µg/L)	27	17	12

ppmv = parts per million by volume

5.4.1.2 Predicted Impacts to Groundwater Using 216-Z-9 Treatability Test Results – Current Mass Discharges (Step 2)

A treatability test (PNNL-21326) was conducted at the 216-Z-9 site to evaluate methods for collecting characterization information to support refined assessment of SVE performance goals based on impact to groundwater. As part of the treatability test, the mass discharge of the source was calculated, the size of the vadose zone source was determined, and the impact of the source on groundwater concentrations was evaluated.

The treatability test applied the method of Brusseau et al. (2010) to estimate the vadose source discharge at 70 g/d in 2010, which was the last year of data to be analyzed. The treatability test also determined that the CCU is the primary remaining source of carbon tetrachloride in the vadose zone with areal extent approximately 90 m by 90 m (295 ft by 295 ft).

The modeling technique provided in Carroll et al., 2012, "Assessing performance and closure for soil vapor extraction: Integrating vapor discharge and impact to groundwater quality," was used to predict the groundwater impact from a 90 m by 90 m (295 ft by 295 ft) vadose zone source with varying mass release rates. For the 2010 measured source mass release rate of 70 g/d, the maximum groundwater concentration for carbon tetrachloride would be approximately 24 µg/L. As described in the treatability test report (PNNL-21326) and in Section 5.4.1.3, the source mass release rate and resulting groundwater carbon tetrachloride concentrations will continue to decline over time and reach a condition that meets the groundwater remediation goal (3.4 µg/L).

5.4.1.3 Comparison of the Soil Vapor Extraction Endstate Tool and the 216-Z-9 Treatability Test Report Results (Step 3)

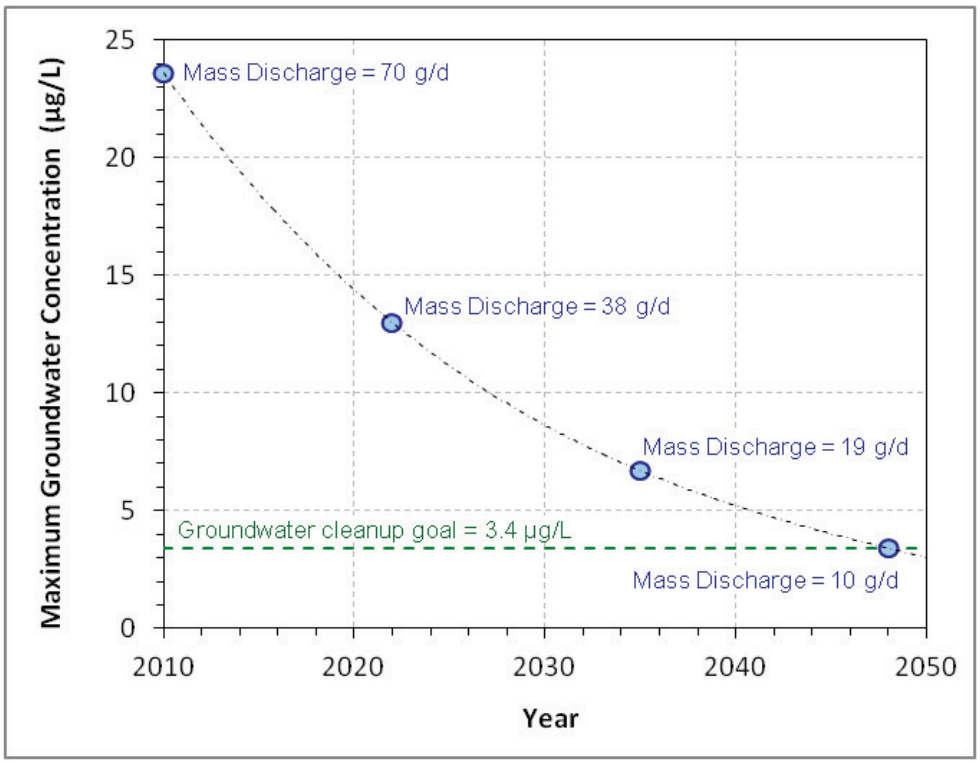
SVEET (PNNL-21843, the SVE Closure Guidance) and the treatability test (PNNL-21326) analyses were conducted for the 216-Z-9 site. SVEET estimates that the groundwater carbon tetrachloride concentration would be approximately 27 µg/L (based on soil vapor concentration of 24.7 ppmv at the source). This estimate is consistent with the 24 µg/L groundwater concentration calculated in the treatability test and corroborates the SVEET calculations. Thus, the relative comparisons of SVEET estimates in Section 5.4.1.1 for the three waste sites are appropriate. The SVEET results demonstrate that the 216-Z-9 site has the highest impact on groundwater. Because the treatability test uses a more detailed, site-specific analysis than SVEET, it provides a more accurate estimate of the groundwater carbon tetrachloride concentrations resulting from the 216-Z-9 vadose zone source. Therefore, it is appropriate to proceed with the evaluation of SVE impact to groundwater using the 216-Z-9 treatability test analyses.

5.4.1.4 Predicted Impacts to Groundwater Using 216-Z-9 Treatability Test Report Results – Future Mass Discharges (Step 4)

The mass discharge from the vadose zone source will continue to decrease after termination of SVE operations. During cyclic SVE operations, the higher permeability materials around the CCU source zone were periodically cleaned out, allowing vapor-phase contaminants to diffuse from the source zone into the clean zone. As described in the treatability test report (PNNL-21326), the source mass release rate will continue to decline over time due to diffusive mass transfer. Figure 5-18 shows how the maximum groundwater carbon tetrachloride concentrations decline over time based on the post-SVE decline in the source mass release rate described in the treatability test and summarized in this section. With termination of the SVE system, the vadose zone source at the 216-Z-9 site will be below levels of concern within 40 years.

Carroll et al. (2012) examined mass discharge rates for vadose sources comparable in size to the 216-Z-9 waste site. The study found that the post-SVE diffusion rate was about five times lower than the rate under cyclic SVE conditions (Appendix E). A source mass discharge rate of 70 g/d (i.e., the calculated mass discharge for the 216-Z-9 site in 2010 during SVE operations) is expected to decrease to 10 g/d about 40 years after termination of SVE operations (i.e., about 2050). The mass discharge value of 10 g/d is significant because it corresponds (Figure 5-18) to a predicted groundwater concentration below 3.4 µg/L, the carbon tetrachloride cleanup level specified for groundwater in the 200-ZP-1 OU ROD (EPA et al., 2008).

The P&T system for the 200-ZP-1 OU will be operated for 25 years (through 2037) to extract carbon tetrachloride contaminated groundwater and reduce concentrations to approximately 100 µg/L. In the 100 years following P&T operation, residual carbon tetrachloride in the groundwater is expected to decline during the MNA phase to meet the ultimate goal of 3.4 µg/L.



Source: Adapted from PNNL-21326, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*.

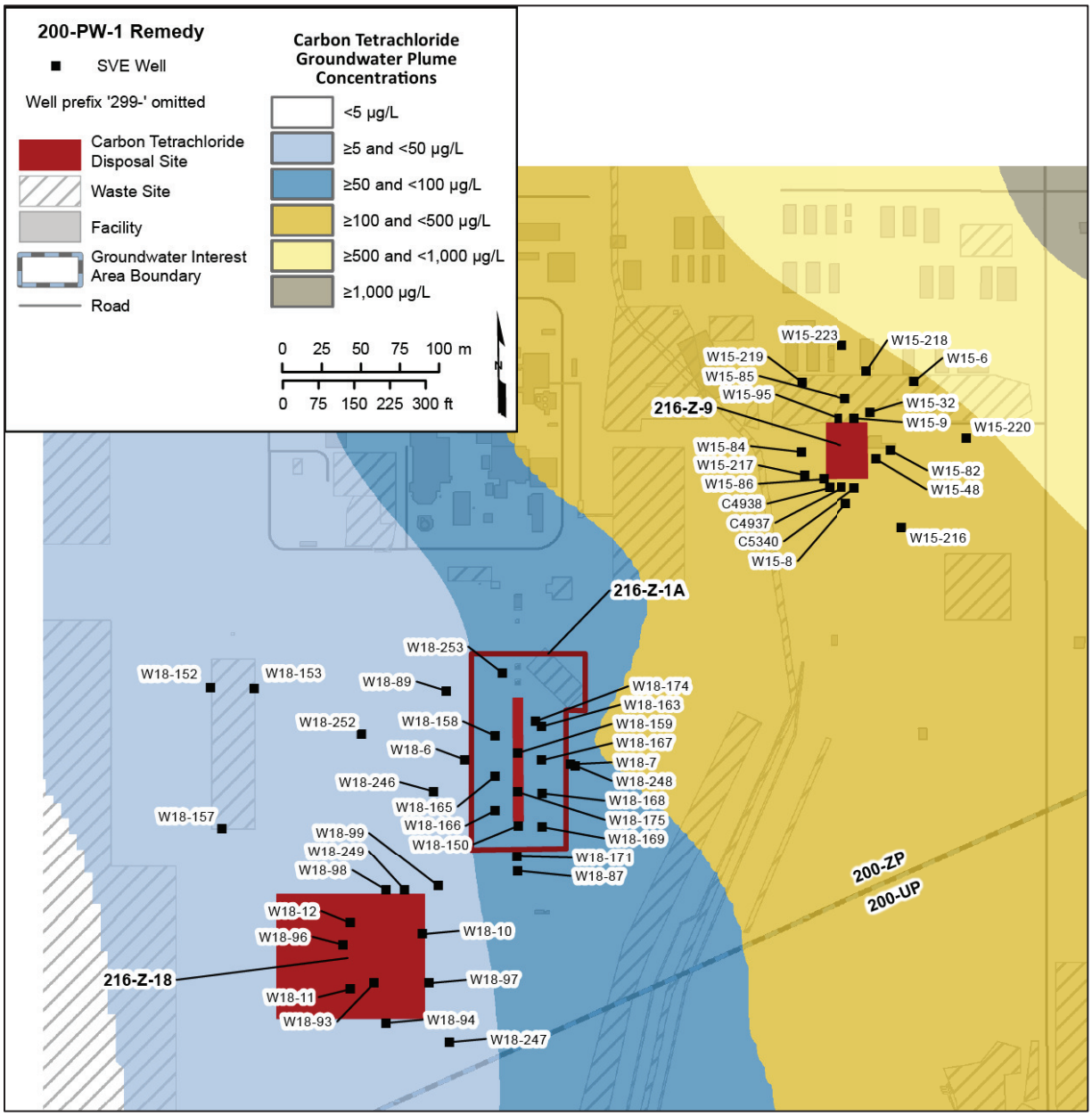
Note: Groundwater concentrations were predicted based on the contaminant source mass discharge shown in the figure. The estimated rate of decline in contaminant source mass discharge (PNNL-21326) was applied to define the time frame for groundwater concentration decrease.

Figure 5-18. Predicted Maximum Groundwater Carbon Tetrachloride Concentrations over Time for the 216-Z-9 Trench

Figure 5-19 shows the 2013 carbon tetrachloride concentrations in the groundwater below the 216-Z-9 site to be approximately 500 µg/L. These elevated groundwater concentrations preclude the migration of carbon tetrachloride vapor from the vadose zone into the groundwater due to Henry's law equilibrium calculations (Appendix D).

Thus, while groundwater concentrations remain relatively high (e.g., 10s to 100s of µg/L), residual carbon tetrachloride concentration in the vadose zone will not migrate downward and poses no additional risk to 200-ZP-1 OU groundwater. Within about 40 years, vadose zone contamination will have dissipated to approximately 10 g/d mass discharge and will pose no threat to clean groundwater. This time frame is well within the groundwater remedy timespan of 125 years.

As described in the treatability test report (PNNL-21326), the source mass release rate will continue to decline over time due to diffusive mass transfer. Figure 5-20 shows how the maximum groundwater carbon tetrachloride concentrations (contributed by soil vapor) decline over time, based on the post-SVE decline in the source mass release rate described in the treatability test. With termination of the SVE remedy, the groundwater carbon tetrachloride concentration resulting from the vadose zone source at the 216-Z-9 site will be below the groundwater target concentration of 3.4 µg/L within 40 years. In contrast, carbon tetrachloride concentrations in groundwater are not expected to drop below 3.4 µg/L for another 122 years.

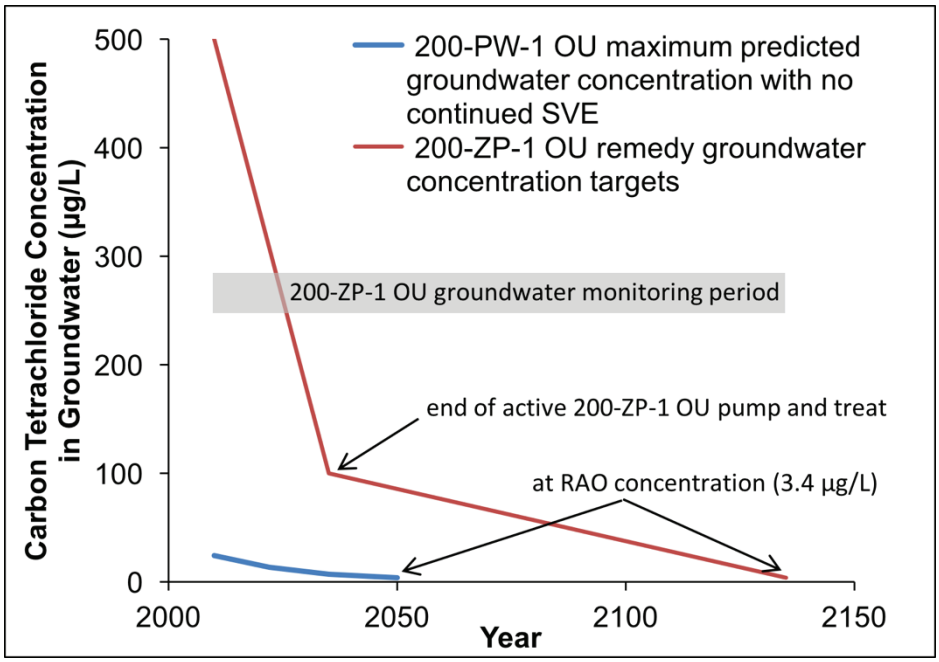


Source: Adapted from DOE/RL-2014-32, *Hanford Site Groundwater Monitoring Report for 2013*.

Figure 5-19. 2013 Carbon Tetrachloride Groundwater Concentrations Underlying the Carbon Tetrachloride Waste Sites

5.4.2 Methylene Chloride Impact on Groundwater

Methylene chloride concentrations in the vadose zone are below the 50 ppmv cleanup level specified in the 200-PW-1 OU ROD (EPA et al., 2011) (Section A5 [Appendix A] and Appendix B of this report).



Note: In this figure, 200-PW-1 represents the 200-PW-1 (vadose zone) OU impact, and 200-ZP-1 represents the 200-ZP-1 (groundwater) OU conditions.

Figure 5-20. Predicted Maximum Groundwater Carbon Tetrachloride Concentrations Over Time

To further investigate the potential impact of residual methylene chloride contamination in the vadose zone beneath the 216-Z-9 waste site, the Hanford Environmental Information System database was queried for groundwater sampling results in the underlying 200-ZP-1 OU aquifer. Groundwater wells that were queried are shown in Figure 5-21, and the results from the query are summarized as follows:

- Well 299-W15-46 has been continuously monitored since 2004 (including in 2014), with methylene chloride measurements below the detection limit (1 µg/L) since 2006.
- Well 299-W15-47 has been continuously monitored since 2004, with methylene chloride measurements below the detection limit (1 µg/L) since 2008. Sampling was discontinued after 2010 because the measurements did not exceed the MCL of 5 µg/L.
- Well 299-W15-6 has been continuously monitored since 1990, with methylene chloride measurements below the MCL (5 µg/L) since 2008. Only three measurements exceeded the detection limit (1 µg/L) since 2008 with measurements at or below 3 µg/L. Sampling was discontinued after 2011 because the measurements did not exceed the MCL.
- Wells 299-W15-32, 299-W15-38, and 299-W15-39 were continuously monitored since 1997, with methylene chloride measurements below the MCL since 2004. Sampling was discontinued after 2008 because the measurements did not exceed the MCL.

Thus, there appears to be no significant methylene chloride contamination beneath the 216-Z-9 waste site in the 200-ZP-1 OU aquifer. This is important because the Henry's Law constant would significantly favor partitioning of any methylene chloride contamination from the vadose zone to the groundwater.

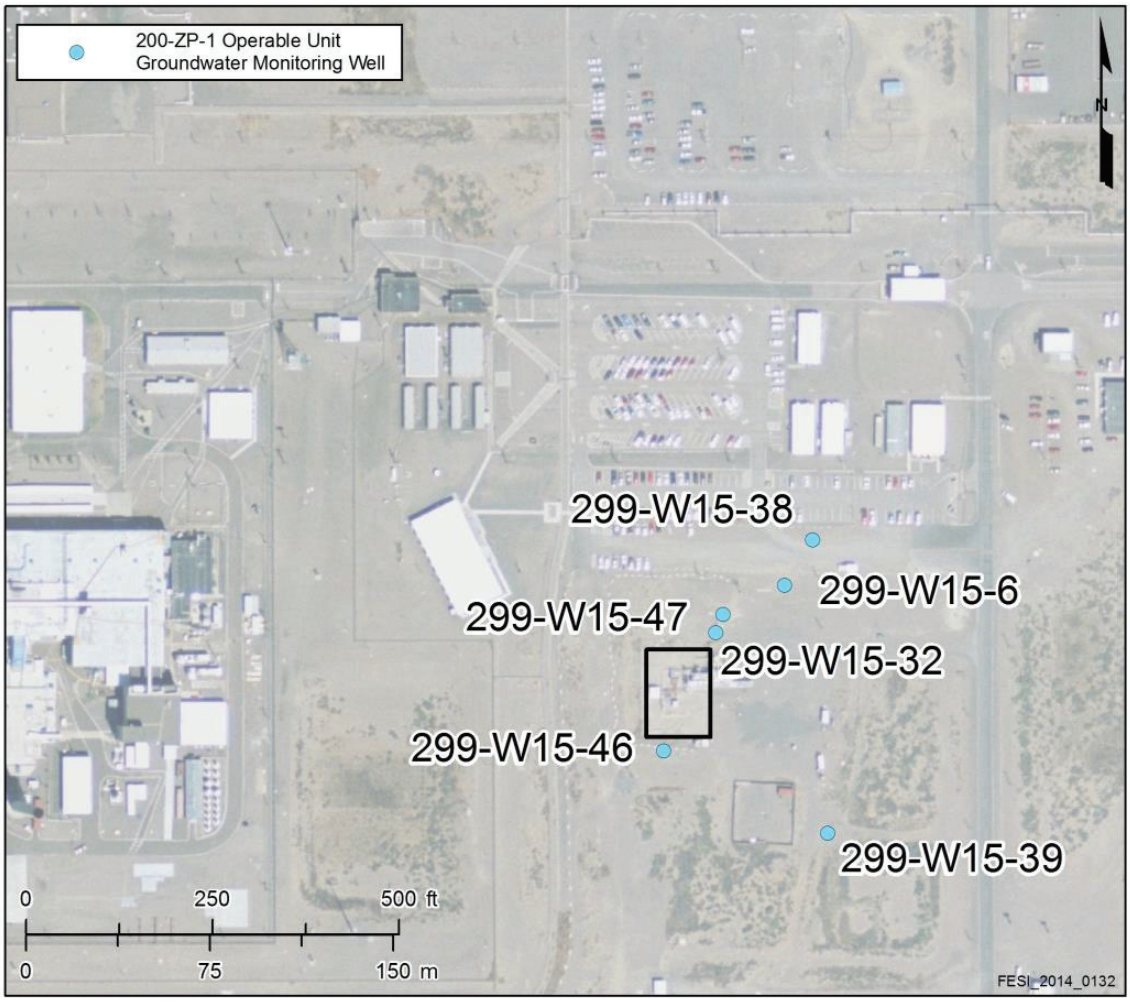


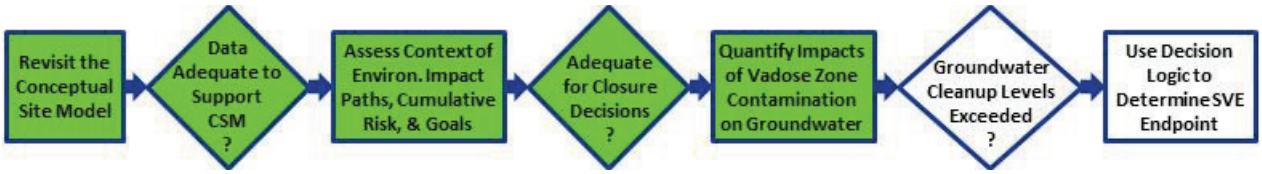
Figure 5-21. Groundwater Monitoring Wells for the 216-Z-9 Waste Site

These observations, in conjunction with the lack of a continuing source and the biological attenuation mechanism for methylene chloride discussed in the CSM (Section 5.2), indicate that methylene chloride contamination (1) is currently low in the vadose zone and expected to stay low and diminish over time, (2) is currently at concentrations below the MCL in the groundwater, and (3) does not have the potential to adversely affect groundwater in the underlying aquifer of the 200-ZP-1 OU.

5.4.3 Conclusions Regarding Remaining Source Impacts to Groundwater

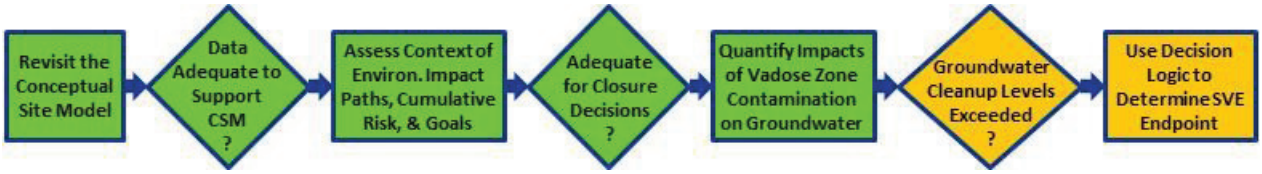
The carbon tetrachloride mass discharge from the vadose zone source at the 216-Z-9 site, which is the limiting case for the 200-PW-1 OU, is predicted to decline so that within approximately 40 years, the mass discharge would result in carbon tetrachloride concentrations in the groundwater at or below the groundwater cleanup level of 3.4 µg/L (200-ZP-1 OU ROD [EPA et al., 2008]), assuming no other contamination sources in the aquifer. During this time, the groundwater remedy, including institutional controls and monitoring, will be in place to eliminate exposures to contaminated groundwater.

No groundwater impact from methylene chloride contamination within the 200-PW-1 OU is expected in future years due to the current low concentrations (i.e., below the cleanup level in the vadose zone and below the MCL in the groundwater), lack of a continuing source, and attenuation that will continue to decrease concentrations.

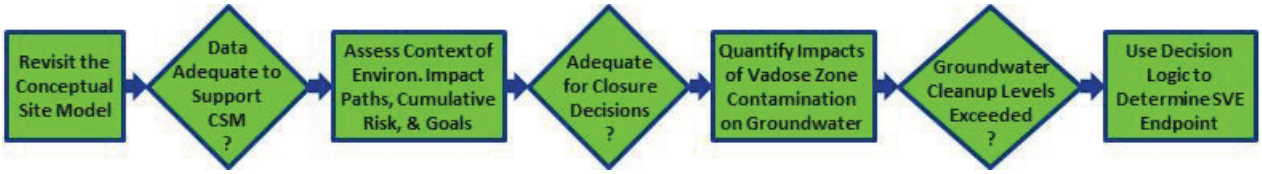


5.5 Decision Logic Assessment

The final step of the site-specific assessment approach is to combine the outcomes from the prior elements (Sections 5.2, 5.3, and 5.4) and apply the decision logic shown in Figure 5-2 to determine appropriate actions for disposition of the 200-PW-1 OU SVE systems.



The prior elements of the site-specific assessment approach have presented a CSM that is representative of current conditions and knowledge (with no data gaps), determined that the environmental impact pathway/regulatory context is appropriately defined, and evaluated the impact of remaining vadose zone sources on groundwater concentrations. These evaluations have determined that if SVE is terminated, there is no current or future impact of carbon tetrachloride or methylene chloride from the vadose zone on the groundwater that would result in concentrations in the groundwater above the cleanup level (3.4 µg/L) for carbon tetrachloride (200-ZP-1 OU ROD [EPA et al., 2008]) or MCL (5 µg/L) for methylene chloride by 2137, the time this goal is required for the groundwater (200-ZP-1 OU ROD [EPA et al., 2008]). This information, as presented in this document, meets the steps outlined in the SVE Closure Guidance (PNNL-21843) and demonstrates that residual vadose zone carbon tetrachloride and methylene chloride will not result in groundwater cleanup levels being exceeded. Thus, closure of the SVE remedy (i.e., permanently discontinuing operation of the SVE systems) for the 200-PW-1 OU is appropriate. EPA concurrence with this report will initiate activities to terminate SVE operations and vadose zone monitoring.



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6 Final Inspection and Certifications

Any final inspections, certifications, and/or institutional controls for the 200-PW-1 OU will be addressed through implementation of the 200-PW-1 OU ROD.

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7 Operations and Maintenance Activities

No ongoing operations, maintenance, or monitoring activities are needed for the SVE remedy.

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8 Summary of Project Costs

This chapter provides cost information for the SVE remedy addressed by this response action report.

The expense and capital costs for the 200-PW-1 OU SVE remedy are provided in Table 8-1 for fiscal year (FY) 2002 through FY 2015. Remedy costs for FY 1992 through FY 2001 are not available.

Between the 1991 pilot test and 2012 (the last year of SVE operations), 80,107 kg of carbon tetrachloride were removed from the vadose zone and 118.3 million m^3 of soil vapor were treated (SGW-54566, Table 2-1). For FY 2002 through FY 2012, the unit costs (sum of capital and expense costs divided by the amount of vapor treated) ranged from \$0.03/m^3 to \$0.69/m^3 (Table 8-2). The average unit cost during this time period was \$0.26/m^3.

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Table 8-1. 200-PW-1 OU SVE Costs from FY 2002 through FY 2015

	FY 2002	FY 2003	FY 2004	FY 2005	FY 2006	FY 2007	FY 2008	FY 2009	FY 2010	FY 2011	FY 2012	FY 2013	FY 2014	FY 2015	Total
Total expense costs (dollars)*	$89,700	$361,800	$349,300	$370,400	$601,600	$774,900	$707,000	$635,200	$951,600	$1,049,200	$613,400	$512,900	$760,600	$482,300	$8,259,900
Total capital costs (dollars)*	$0	$0	$0	$0	$0	$0	$815,600	$565,800	$0	$0	$0	$0	$0	$0	$1,381,400
Total costs (dollars)*	$89,700	$361,800	$349,300	$370,400	$601,600	$774,900	$1,522,600	$1,201,000	$951,600	$1,049,200	$613,400	$512,900	$760,600	$482,300	$9,641,300

* Costs are from Hanford Data Integrator database.

FY = fiscal year

Table 8-2. 200-PW-1 OU SVE Unit Costs from FY 2002 through FY 2012

	FY 2002	FY 2003	FY 2004	FY 2005	FY 2006	FY 2007	FY 2008	FY 2009	FY 2010	FY 2011	FY 2012	Total
Total costs (dollars)[a]	$89,700	$361,800	$349,300	$370,400	$601,600	$774,900	$1,522,600	$1,201,000	$951,600	$1,049,200	$613,400	$7,885,500
Volume of vapor recovered (cubic meters)[b]	2,662,000	2,637,000	1,868,000	1,797,000	1,862,000	2,227,000	2,198,000	2,493,000	5,356,000	3,718,000	3,044,000	29,862,000
Unit costs[c]	$0.03/m^3$	$0.14/m^3$	$0.19/m^3$	$0.21/m^3$	$0.32/m^3$	$0.35/m^3$	$0.69/m^3$	$0.48/m^3$	$0.18/m^3$	$0.28/m^3$	$0.20/m^3$	$0.26/m^3$

a. Costs are from Hanford Data Integrator database.

b. Volumes are from Table 2-1 in SGW-54566, *Performance Evaluation Report for Soil Vapor Extraction Operations at the 200-PW-1 Operable Unit Carbon Tetrachloride Site, Calendar Year 2012*.

c. Unit costs are total costs divided by volume of vapor recovered.

FY = fiscal year

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9 Observations and Lessons Learned

SVE was used from 1992 through 2012 to remove 80,107 kg of carbon tetrachloride from the vadose zone, mitigating additional groundwater contamination. Implementing this SVE remedy as a removal action in 1992 (20 years prior to the 2011 ROD) allowed an early response for protection of groundwater.

Over the course of the nearly 25-year-long SVE remedy, operational strategies were adjusted as carbon tetrachloride diminished. From 1992 to 1996, SVE systems operated nearly full-time throughout each year, removing about 73,000 kg (91 percent of the 1992 through 2012 total) of carbon tetrachloride from the vadose zone during these 5 years. The SVE systems were shut down from November 1996 through July 1997 to conduct a rebound study (BHI-01105). This study indicated that carbon tetrachloride remaining in the vadose zone was located primarily within the finer-grained CCU and recommended that the system be operated in a cyclic mode. The SVE systems operated in a cyclic mode from 1997 through 2012, removing about 7,000 kg (9 percent of the 1992 through 2012 total) during these 16 years. Performance monitoring showed declining carbon tetrachloride in conjunction with declines in contaminant rebound during the quiescent portion of the operational cycle.

An evaluation in 2010 concluded that operation of the SVE systems during the warm, dry summer months leads to as much as five times the mass of carbon tetrachloride retained in each granular activated carbon canister compared to operation in the cool, damp spring and fall months (SGW-48535, *Soil Vapor Extraction Extended Operation Evaluation*). Operating the systems during cooler months caused greater water condensation in the transfer lines, accelerated loading of water in the GAC canisters, and increased the risk of equipment damage due to moisture accumulation and freezing of system components.

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10 Contact Information

This chapter provides contact information for the DOE contractor, DOE, and agency representatives.

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A project manager for Ecology was not identified.

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Appendix A

Summary of Investigations and Remedial Activities

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Table

Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU A-2

Terms

B&K	Brüel & Kjær
CCU	Cold Creek unit
CPT	cone penetrometer
CSM	conceptual site model
CY	calendar year
DNAPL	dense nonaqueous-phase liquid
DOE	U.S. Department of Energy
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
OU	operable unit
PFP	Plutonium Finishing Plant
ppmv	parts per million by volume
RI	remedial investigation
ROD	Record of Decision
SVE	soil vapor extraction

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A1 Introduction

This appendix provides a summary of the carbon tetrachloride waste disposal history, site investigation activities, and remedial activities for the 200-PW-1 Operable Unit (OU), including results from two decades (1992 through 2012) of soil vapor extraction (SVE) operations.

A2 Chronology

The timeline of investigations and remedial activities for carbon tetrachloride in the 200-PW-1 OU is shown in Figure A-1. The corresponding activity summaries and document references are listed in Table A-1.

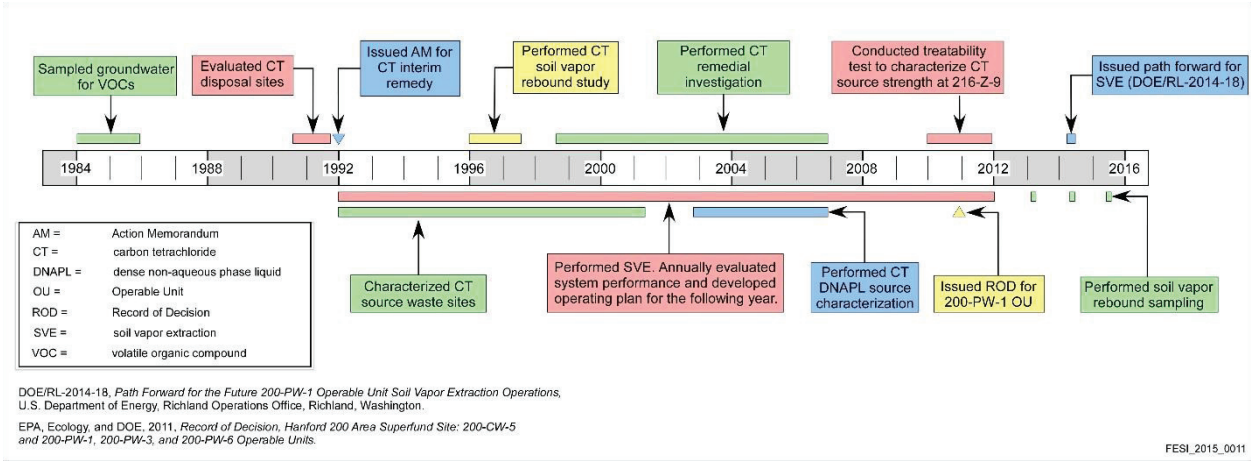


Figure A-1. Timeline for Investigations and Remedial Activities for Carbon Tetrachloride at the 200-PW-1 OU

A3 Investigation of Carbon Tetrachloride Sources at 200-PW-1 Operable Unit Waste Disposal Sites

Carbon tetrachloride was disposed to the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib from 1955 to 1973. An investigation regarding carbon tetrachloride distribution in the vadose zone in the vicinities of these three waste sites supported SVE implementation. At that time, carbon tetrachloride was present throughout the vadose zone. SVE was implemented in 1992 to remove carbon tetrachloride from the vadose zone associated with these three waste sites.

From 2003 to 2007, the 200-PW-1 OU remedial investigation (RI) (DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*) characterized the carbon tetrachloride distribution in the vadose zone in the vicinities of these three waste sites to support a final remedial decision. This investigation concluded that the highest carbon tetrachloride concentrations beneath the waste sites were located in fine-grained layers, particularly the Cold Creek unit (CCU). This comprehensive investigation did not identify any other carbon tetrachloride waste sites or sources.

Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU

Year	Project/Action	Description	Result/Recommendation	Key References
Mid-1980s	Initial groundwater sampling for volatile organic compounds	Discovery of a widespread carbon tetrachloride groundwater plume.	Initiated activities to evaluate removal of the carbon tetrachloride source in the vadose zone.	PNL-7396, 1990, *Hanford Site Ground-Water Surveillance for 1989*
1991–1992	Initial identification and site evaluation of carbon tetrachloride disposal sites and CSM	Conducted initial soil vapor sampling for carbon tetrachloride. Conducted pilot test of SVE system.	Proposed the use of SVE in the engineering evaluation/cost analysis as the preferred alternative.	DOE/RL-91-32, 1991, *Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon Tetrachloride Plume*
1992	Action memorandum for expedited response action proposal for 200 West Area carbon tetrachloride plume	EPA and Ecology approved DOE's proposal to conduct the 200 West Area carbon tetrachloride plume expedited response action as an interim remedy. DOE initiated the carbon tetrachloride soil vapor removal action at the three 200-PW-1 OU waste sites in the 200 West Area.	Selected SVE as the preferred technology. Authorized the operation of SVE systems at the 200-PW-1 OU carbon tetrachloride waste sites (216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib).	*Action Memorandum: Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume* (EPA et al., 1992)
1992–2001	Characterization of carbon tetrachloride source waste sites to support implementation of the interim action for the vadose zone	Drilled (or deepened) and characterized 15 SVE wells. Conducted active and passive soil gas surveys. Installed soil vapor probes and wells using a cone penetrometer.	Updated CSM for carbon tetrachloride in the vadose zone. Expanded number and location of wells available for use with SVE systems.	WHC-SD-EN-TI-063, 1992, *FY92 Site Characterization Status Report and Data Package for the Carbon Tetrachloride Site* WHC-SD-EN-TI-202, 1993, *FY93 Site Characterization Status Report and Data Package for the Carbon Tetrachloride Site* WHC-SD-EN-TI-248, 1994, *1994 Conceptual Model of the Carbon Tetrachloride Contamination in the 200 West Area at the Hanford Site* BHI-00105, 1995, *FY 1993 Wellfield Enhancement Status Report and Data Package for the 200 West Area Carbon Tetrachloride Expedited Response Action*

Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU

Year	Project/Action	Description	Result/Recommendation	Key References
1992–2012	Operation of SVE systems in the vicinities of the source waste sites Annual performance evaluation report of SVE system	Removed carbon tetrachloride from the vadose zone using active and passive SVE at the source waste sites. Reported SVE systems operating data and the effectiveness based on the existing remedial design.	Significantly reduced the concentration of carbon tetrachloride at the source sites. Removed over 80,000 kg of carbon tetrachloride between 1991 (pilot test) and 2012 (last year of SVE operation).	SGW-54566, 2013, *Performance Evaluation Report for Soil Vapor Extraction Operations at the 200-PW-1 Operable Unit Carbon Tetrachloride Site, Calendar Year 2012* (Note: This is the most recent annual report; Chapter 7 of this report lists all previous annual reports.)
1992–2014	SVE system monitoring and operation plan	Recommended operational and sampling strategies for the following calendar year.	Approved annual plan for operation of SVE systems at the 200-PW-1 OU carbon tetrachloride waste sites.	DOE/RL-2014-39, 2014, *Carbon Tetrachloride Soil Vapor Extraction System Operating and Monitoring Plan for CY 2015* (Note: This is the most recent monitoring and operating plan. Most previous annual plans were attachments to 200 Area project managers' meeting minutes.)
1996–1997	Carbon tetrachloride soil vapor rebound study	Evaluated the increase in carbon tetrachloride concentrations following temporary shutdown of the SVE systems.	Concluded the following: • Readily accessible mass has been removed. • The availability of additional carbon tetrachloride is limited due to the lower permeability zone (CCU). • 8-month suspended operation caused no additional degradation of groundwater quality. Recommendations included the following: • 4 to 8 weeks of operation followed by 8 to 16 weeks of nonoperation. • Monitor carbon tetrachloride soil vapor and groundwater quality. • Evaluate change in rebound rate and refine remedial action goals and objectives.	BHI-01105, 1997, *Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site, Fiscal Year 1997* BHI-01105-00-CN-01, 1997, *Change Notice: Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site*

Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU

Year	Project/Action	Description	Result/Recommendation	Key References
1999–2007	Carbon tetrachloride remedial investigation activities	Investigated carbon tetrachloride waste sites 216-Z-1A and 216-Z-9, including drilling and sampling two boreholes at 216-Z-9, to perform the following: • Characterize the nature and extent of the carbon tetrachloride contamination • Characterize the geology underlying the waste sites • Investigate the dispersed carbon tetrachloride plume that had migrated beyond the 200-PW-1 OU waste sites to determine the following: – Lateral extent of vadose zone carbon tetrachloride contamination overlying the carbon tetrachloride groundwater plume – Vertical extent of vadose zone carbon tetrachloride contamination from the ground surface to the water table Conducted numerical simulations of carbon tetrachloride disposal and migration at the 216-Z-9, 216-Z-1A, and 216-Z-18 sites.	Updated the conceptual models of carbon tetrachloride for 216-Z-9, 216-Z-1A, and the dispersed plume. Highest carbon tetrachloride concentrations in the vadose zone are generally located within about 75 to 150 m (246 to 492 ft) laterally from the source sites. Highest carbon tetrachloride concentrations beneath the waste sites are located in fine-grained layers. Found carbon tetrachloride DNAPL in soil sample within a silt layer above the CCU at 216-Z-9. No evidence of significant lateral migration of carbon tetrachloride along the top of the CCU. No evidence of downward migration from an undocumented source. At areas around the source sites, carbon tetrachloride concentrations up to about 10 to 12 ppmv were found at various locations in the vadose zone, but these concentrations are not considered to have significant impacts on groundwater. Sampling results at wells within the carbon tetrachloride groundwater hot spot areas indicated that the deep vadose zone soil vapor concentrations are not significant sources of groundwater contamination in these areas.	DOE/RL-2001-01, 2004, *Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit RI/FS Work Plan: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units* DOE/RL-2006-51, 2007, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*

Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU

Year	Project/Action	Description	Result/Recommendation	Key References
2003–2007	Carbon tetrachloride DNAPL source-term characterization	Investigated the presence, distribution, nature, extent, and mass of DNAPL in the vadose zone to support the remedial investigation. Developed conceptual model of the DNAPL in the vadose zone and unconfined aquifer.	Found carbon tetrachloride DNAPL in soil sample within silt layer above the CCU at 216-Z-9. Concluded that all significant remaining DNAPL was found in the fine-grained soils of the CCU and the overlying discontinuous silt lenses.	DOE/RL-2006-58, 2006, *Carbon Tetrachloride Dense Non-Aqueous Phase Liquid (DNAPL) Source Term Interim Characterization Report* DOE/RL-2007-22, 2007, *Carbon Tetrachloride Dense Non-Aqueous Phase Liquid (DNAPL) Source Term Interim Characterization Report Addendum*
2007–2011	200-PW-1 OU feasibility study	Presented the risk assessment and evaluated the remedial alternatives for 200-PW-1 OU waste sites.	Identified carbon tetrachloride and methylene chloride as contaminants of potential concern in soil. Identified the exposure pathway for carbon tetrachloride and methylene chloride as migration to groundwater.	DOE/RL-2007-27, *Feasibility Study for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6 Operable Units*
2010–2012	Treatability test for characterization of vadose zone carbon tetrachloride source strength using tomographic methods at the 216-Z-9 site	Conducted a test at the 216-Z-9 Trench to quantify the source mass of carbon tetrachloride and to estimate the size and location of the source. Used data to calculate the vapor-phase source strength (source mass discharge). The information was also used to support refinement of SVE performance goals based on impact to groundwater; also provided input to operational strategies for continued operation, closure, or transition to other remedies.	Concluded that the CCU is the primary remaining source of carbon tetrachloride in the vadose zone. Areal extent of the source zone at the 216-Z-9 waste site is approximately 90 m by 90 m (295 ft by 295 ft). Recommended three operational strategies: • Lengthen the SVE running time to minimize the built-up vapor. • Lengthen the shutdown time to provide additional time for rebound in vapor concentration. • Restart only at selected wells centralized around the diffusive mass discharge from the CCU contamination source.	DOE/RL-2010-79, 2010, *Treatability Test Plan for Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site* PNNL-21326, 2012, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*

Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU

Year	Project/Action	Description	Result/Recommendation	Key References
2011	Proposed Plan for the remediation of the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 OUs	Issued Proposed Plan for cleanup of vadose zone carbon tetrachloride contamination in the central portion of the Hanford Site.	Identified SVE for remediation of carbon tetrachloride in the vadose zone at the source sites as the common element to all alternatives. Stated that operation of the SVE system should continue until it is no longer necessary or is replaced by a component of a final action remedy.	DOE/RL-2009-117, 2011, *Proposed Plan for the Remediation of the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*
2011	Final Record of Decision for of the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 OUs	Selected SVE as the final remedial action to remove and treat carbon tetrachloride and methylene chloride contamination in the vadose zone at the contaminated source sites.	Established the final cleanup levels for soil vapor concentrations of carbon tetrachloride as 100 ppmv and for methylene chloride as 50 ppmv. Specified that the soil vapor concentrations will be further refined and assessed to ensure protectiveness of groundwater. Directed the continuing operation of the SVE until soil vapor levels no longer pose a threat to human health, environment, and groundwater.	EPA, Ecology, and DOE, 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*
2012	SVE system operational strategy	Provided the strategy to sample, modify, and operate the SVE systems.	Recommended the following: • Increase the rebound period. • Operate SVE from June to September at highest concentration area. • Operate SVE from August to September at wells located along the periphery of high-concentration area. • Evaluate biannual operational strategy if rebound continues to decline. • Collect data to evaluate rebound, individual well performance, and update source mass discharge.	SGW-53024, 2012, *200-PW-1 Operable Unit (OU) Soil Vapor Extraction (SVE) System Operational Strategy*

Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU

Year	Project/Action	Description	Result/Recommendation	Key References
2014	SVE system path forward plan	This document provided the following: • Overview of the 200-PW-1 OU regulatory status • Summary of the history of waste disposal, investigation activities, and remediation activities for the 200-PW-1 OU • Overview of SVE operations and performance over the past two decades	The approved recommendation was to use the SVE Closure Guidance (PNNL-21843) as the basis for determining when 200-PW-1 OU SVE operations can be terminated. A site-specific decision logic approach was proposed as the path forward for conducting the evaluation.	DOE/RL-2014-18, 2014, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*
2014	Soil vapor rebound sampling	Provided the quality assurance project plan and field sampling requirements for soil vapor rebound sampling at existing soil vapor sampling locations.	Approved the sampling and analysis plan for soil vapor sampling in 2014.	DOE/RL-2014-20, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2014 Rebound Sampling*
2015	Soil vapor rebound sampling	Provided the quality assurance project plan and field sampling requirements for soil vapor rebound sampling at existing soil vapor sampling locations.	Approved the sampling and analysis plan for soil vapor sampling in 2015.	DOE/RL-2014-20, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit Calendar Year 2015 Rebound Sampling*

Note: Complete reference citations are provided in Chapter A9.

CCU = Cold Creek unit
CSM = conceptual site model
DNAPL = dense nonaqueous-phase liquid
DOE = U.S. Department of Energy
Ecology = Washington State Department of Ecology
EPA = U.S. Environmental Protection Agency
OU = operable unit
ppmv = parts per million by volume
SVE = soil vapor extraction

A treatability test was conducted at the 216-Z-9 waste site in 2011 to assess subsurface characterization methods and to determine the vadose zone carbon tetrachloride source characteristics. The treatability test data indicated that most of the remaining carbon tetrachloride is located within the lower permeability CCU, from which the carbon tetrachloride is slowly diffusing. The treatability test results were used to assess the diminishing impact of the vadose zone source on the groundwater, providing a technical basis for evaluating potential termination of the SVE systems.

A3.1 Remediation and Characterization of Carbon Tetrachloride at 200-PW-1 Operable Unit Carbon Tetrachloride Waste Sites

At the Hanford Site, carbon tetrachloride was used in mixtures with other organics to recover plutonium in aqueous waste streams at the Plutonium Finishing Plant (PFP) in the 200 West Area. From 1955 to 1973, carbon tetrachloride contained in aqueous and organic liquid wastes was discharged primarily to three subsurface infiltration sites: 216-Z-9 Trench (1955 to 1962), 216-Z-1A Tile Field (1964 to 1969), and 216-Z-18 Crib (1969 to 1973). Additionally, a small volume of carbon tetrachloride was discharged to the 216-Z-12 Crib. Figure A-2 provides a map of carbon tetrachloride waste sites in the 200-PW-1 OU. The vadose zone below the waste sites is comprised of higher-permeability Hanford formation materials (about 34 m [112 ft] thick) and Ringold Formation material (about 25 m [82 ft] thick above the water table), which are separated by the low-permeability CCU sediments (about 6 m [20 ft] thick). Thus, as the liquid waste containing carbon tetrachloride infiltrated into the ground, these soils under the disposal sites became contaminated. In the mid-1980s, a widespread carbon tetrachloride plume was discovered in the underlying groundwater.

In 1992, the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology) issued an action memorandum (EPA and Ecology, 1992, *Action Memorandum: Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume*) to authorize an interim remedy for removal of carbon tetrachloride from the 200-PW-1 OU vadose zone using SVE systems. Between February 1992 and October 2011, the SVE systems were operated as an interim remedial action in accordance with the action memorandum. In October 2011, EPA, Ecology, and the U.S. Department of Energy (DOE) issued a Record of Decision (ROD) (EPA et al., 2011, *Record of Decision for the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*, hereafter referred to as the 200-PW-1 OU ROD). Between October 2011 and October 2015, the SVE systems were operated as a final remedial action in accordance with the 200-PW-1 OU ROD.

SVE was implemented at the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib in response to the action memorandum (EPA and Ecology, 1992). Site investigations were conducted in the area of the carbon tetrachloride source waste sites to support initial implementation of the SVE interim action. Active and passive soil gas surveys were conducted throughout the waste site areas to determine additional sources. Carbon tetrachloride was identified in the vicinity of the 216-Z-12 Crib based on soil gas surveys, and SVE was also initiated at that waste site.

Existing wells were perforated and new wells were drilled to enable extraction of soil vapor from the vadose zone above and below the CCU in the vicinities of the waste sites. Soil and soil vapor samples were collected from the new wells during drilling. A cone penetrometer (CPT) was used to collect depth-discrete soil vapor samples and to install soil vapor probes and wells (all at locations above the CCU) for monitoring and extraction. Based on soil and soil vapor samples collected in 1992 and 1993 to characterize the distribution of carbon tetrachloride in the vicinity of the waste sites and to support implementation of the interim remedy, carbon tetrachloride was found to be present throughout the vadose zone.

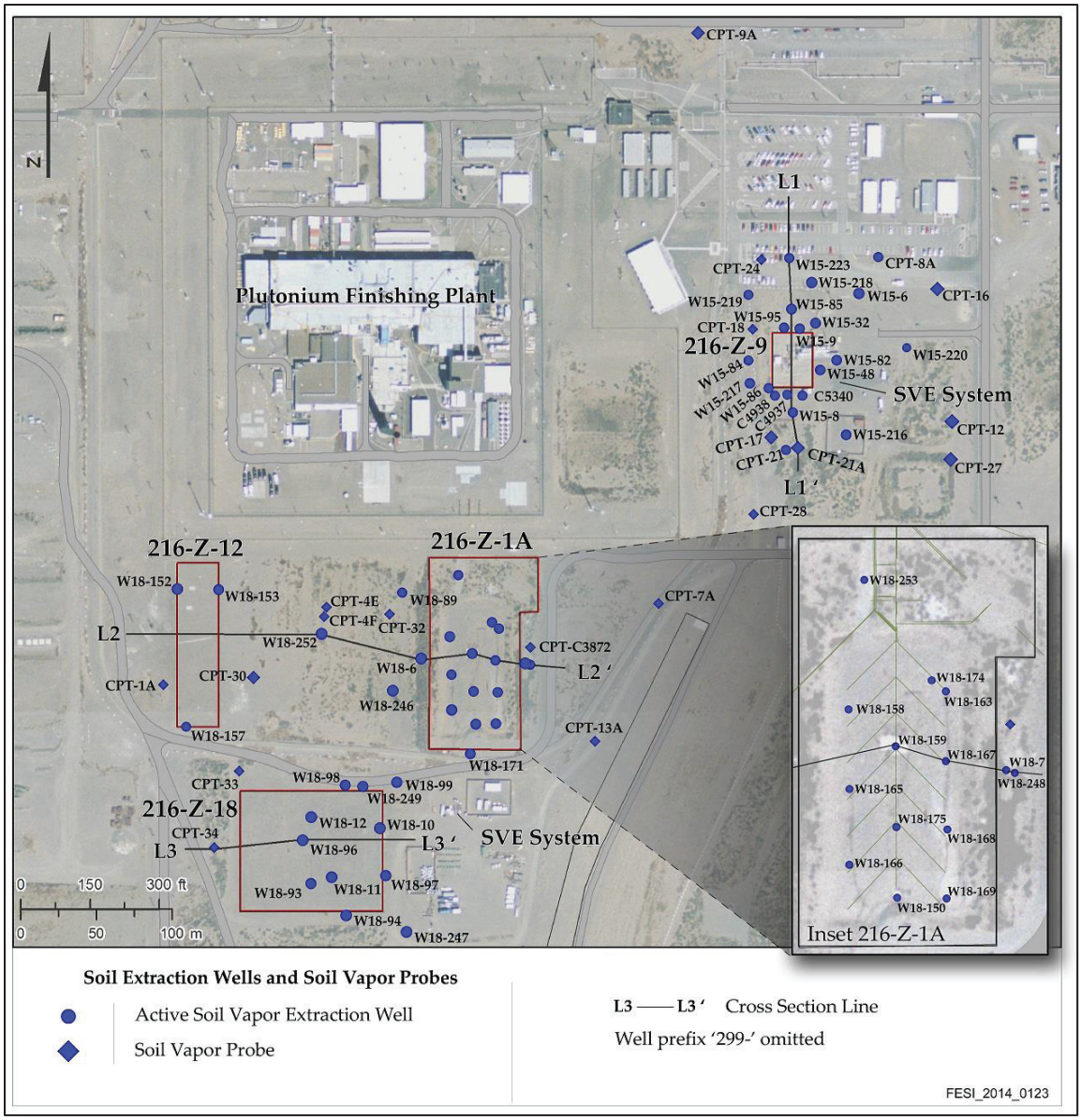


Figure A-2. Carbon Tetrachloride Waste Sites and SVE Systems for the 200-PW-1 OU

During the 200-PW-1 OU RI from 2003 to 2007 (DOE/RL-2006-51), investigations of the nature and extent of the carbon tetrachloride contamination were conducted at the 216-Z-9 and 216-Z-1A waste sites. Two characterization wells were drilled at the 216-Z-9 Trench between 2003 and 2006 and were sampled for soil and soil vapor. One vertical well (299-W15-46) was drilled to groundwater on the south side of the waste site, and one slant well (299-W15-48) was drilled to intersect the CCU under the waste site. One vertical characterization borehole (299-W18-253) was drilled within the 216-Z-1A Tile Field and sampled for soil and soil vapor.

The RI in the vicinities of the carbon tetrachloride waste sites included an investigation for any dense nonaqueous-phase liquid (DNAPL) vadose zone sources. The DNAPL investigation used a phased approach. Passive soil gas measurements of carbon tetrachloride were collected as a reconnaissance approach to focus the more intrusive soil gas and soil sampling using a CPT for subsurface access.

The RI concluded that the highest carbon tetrachloride concentrations beneath the waste sites were located in fine-grained layers, particularly within the CCU. Carbon tetrachloride DNAPL was identified in only two soil samples at the same depth within a silt lens above the CCU, adjacent to the south side of the 216-Z-9 Trench, indicating that remaining DNAPL is found only within the fine-grained sediments of the CCU or overlying silt lenses.

A3.2 Soil Vapor Extraction Performance

Between 1992 and 2012, SVE operations removed over 80,000 kg of carbon tetrachloride from the vadose zone (Figure A-3). In 2012 (the most recent year SVE was operated), 52 wells were available for SVE. Of the 52 wells, 13 wells have two open intervals, creating 65 intervals for vapor extraction. Wells completed with two screened or perforated intervals include an "L" or "U" at the end of the well name to designate either the "lower" or "upper" interval. Two intervals in a single well are isolated by a packer. The active SVE systems extract simultaneously from multiple wells that are open above, within, and/or below the CCU layer.

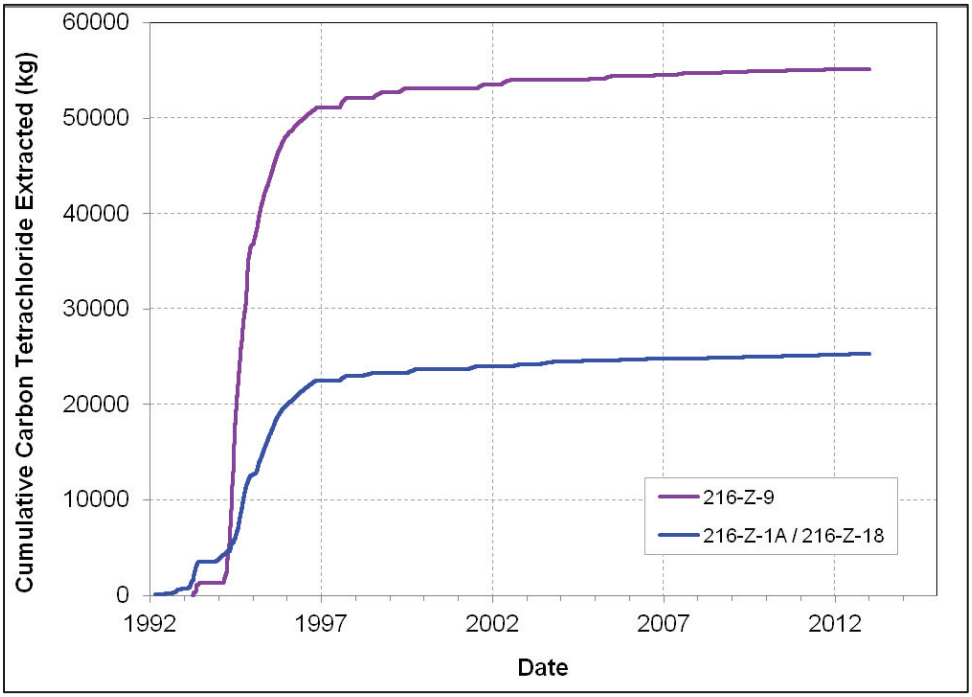


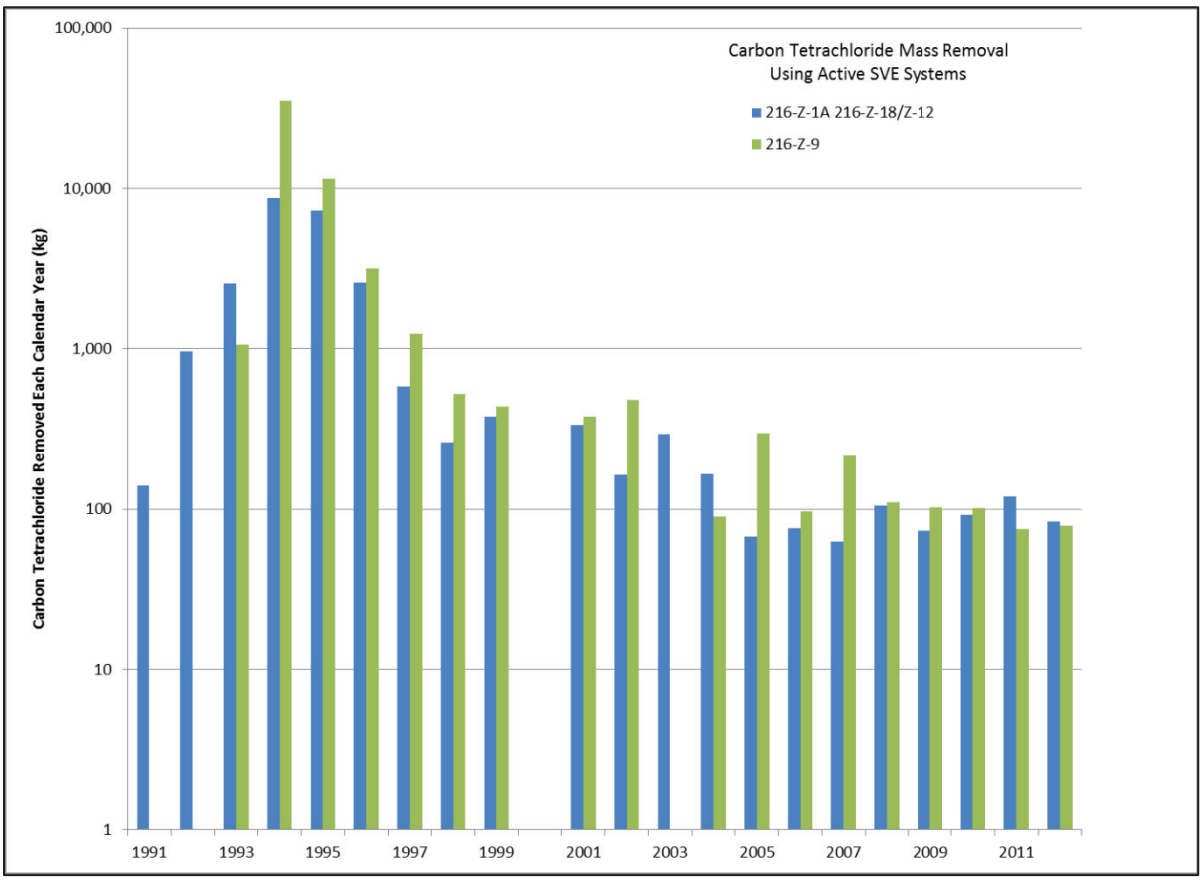
Figure A-3. Cumulative Carbon Tetrachloride Mass Removed from the 216-Z-9 and 216-Z-1A/216-Z-18 Waste Sites

Between 1992 and 1997, the strategy for SVE operations was to run throughout the year using up to three SVE systems with design capacities of 14.2, 28.3, and 42.5 m^3/min (500, 1,000, and 1,500 ft^3/min). The SVE systems were shut down from November 1996 through July 1997 for a rebound study to determine the increase in carbon tetrachloride vapor concentrations resulting from the temporary system shutdown (BHI-01105, *Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site, Fiscal Year 1997*). The study concluded that (1) in many areas, the readily accessible mass had been removed from the high-permeability zones; (2) the availability of additional carbon tetrachloride for capture is limited by diffusion from the lower permeability zones; and (3) the 8 months of suspended operation caused no additional degradation of groundwater quality. The study recommended that the SVE systems be operated in a cyclic mode (e.g., 4 to 8 weeks of active operation, followed by 8 to 16 weeks

of shutdown), soil vapor monitoring during future periods of nonoperation, and further evaluation of the rebound effect.

The operating strategy was modified based on the results of the rebound study and the declining rate of carbon tetrachloride removal during continuous extraction operations. Rather than operating all three SVE systems, only the 14.2 m^3/min (500 ft^3/min) system was used for carbon tetrachloride removal from 1998 through 2008. The system typically operated from April through September each year, alternating between the 216-Z-9 site and the 216-Z-1A/216-Z-18/216-Z-12 site (for approximately 3 months at each site). The system was maintained in standby mode from October through March each year to allow time for carbon tetrachloride vapor concentrations to rebound.

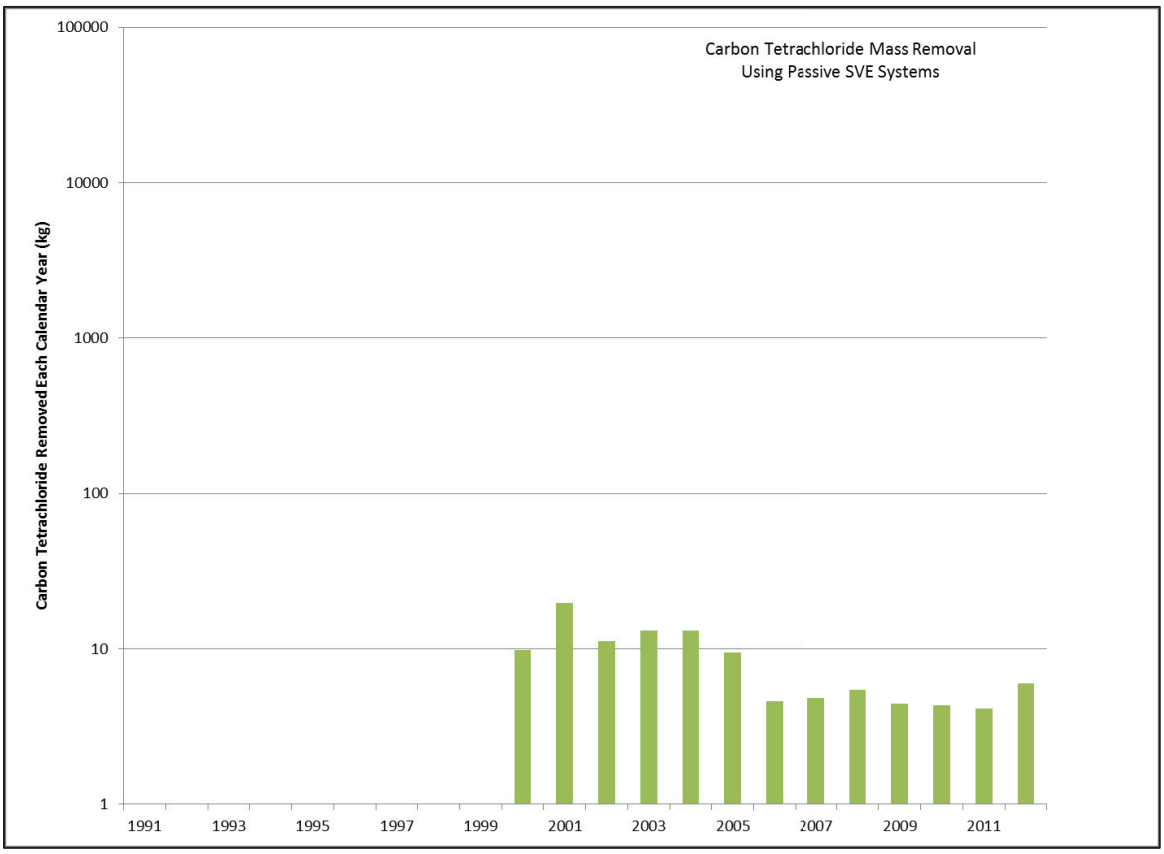
Two new SVE systems, each with a design capacity of 14.2 m^3/min (500 ft^3/min), were operated from 2009 through 2012. One system was operated at the 216-Z-1A/216-Z-18/216-Z-12 site, and one system at the 216-Z-9 site. Each system operated for 6 months in 2009, for 8 months in 2010, for 8 months in 2011, and for 6 months in 2012. The systems were not operated in 2013, 2014, or 2015 to allow carbon tetrachloride concentrations to rebound. Figure A-4 summarizes the mass removal history for the 216-Z-9 and 216-Z-1A/216-Z-18/216-Z-12 sites using active SVE systems.



Note: The logarithmic scale is provided on the Y-axis.

Figure A-4. Carbon Tetrachloride Mass Removal Using Active SVE, Depicting a Two-Order-of-Magnitude Decrease between the Early 1990s and Recent Times

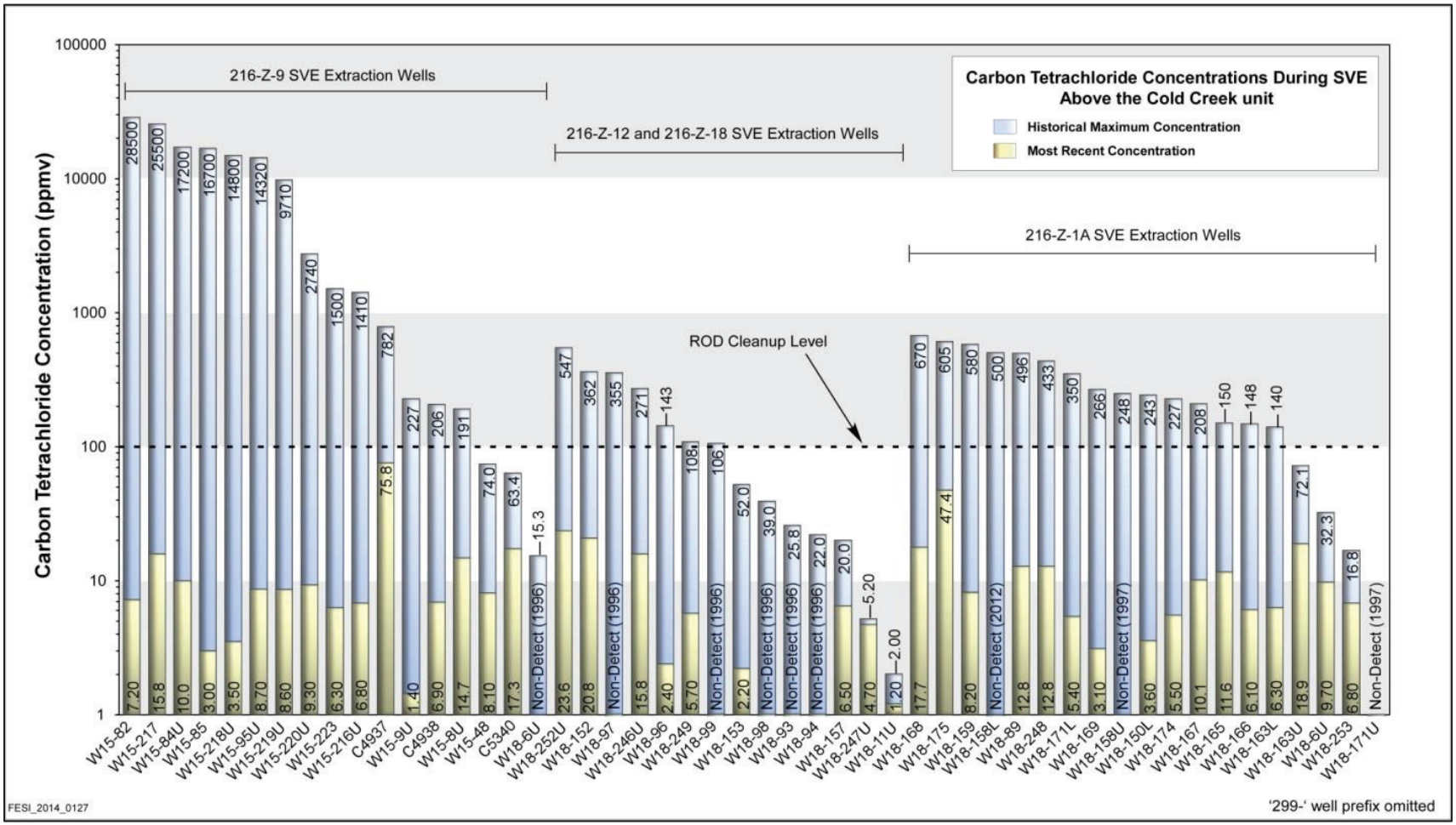
Eight wells were installed as passive SVE systems during 1999 at the 216-Z-1A and 216-Z-18 waste sites. The passive SVE systems use naturally occurring changes in barometric pressure to extract carbon tetrachloride vapor, a process also referred to as "barometric pumping." In general, falling atmospheric pressure causes subsurface vapor to move to the atmosphere through wells, while rising atmospheric pressure causes atmospheric air to move into the subsurface. Approximately 110 kg of carbon tetrachloride were removed using the passive SVE systems from 2000 through 2012; the annual mass removal ranged from 4 to 20 kg (Figure A-5). On March 18, 2013, EPA and DOE approved the termination of passive SVE operation based on the decline in carbon tetrachloride concentration at the passive wells to below the 200-PW-1 OU ROD cleanup level of 100 parts per million by volume (ppmv), and the cost per kilogram of carbon tetrachloride recovered, which was higher than using active SVE operations.



Note: The logarithmic scale is provided on the Y-axis.

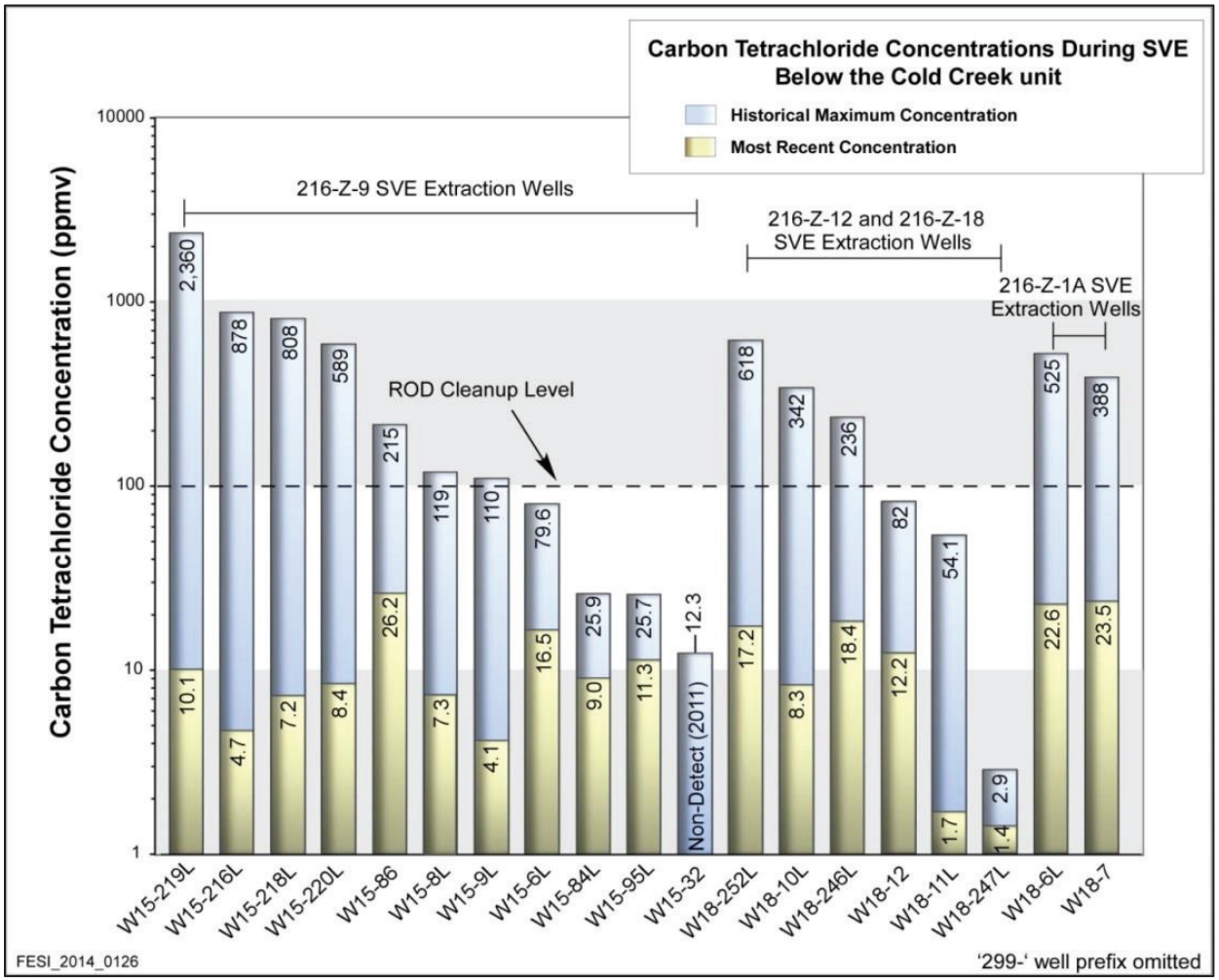
Figure A-5. Carbon Tetrachloride Mass Removal Using Passive SVE, Depicting an Order-of-Magnitude Less than the Active SVE Systems

Contaminant concentrations were measured at each online active extraction well during SVE operations. Figure A-6 depicts (on a logarithmic scale) the historical maximum and most recent carbon tetrachloride concentrations measured in online SVE wells with open (screened or perforated) intervals above the CCU from 1992 to 2012 (the most recent year of SVE operations). Figure A-7 depicts (on a logarithmic scale) the historical maximum and most recent carbon tetrachloride concentrations measured in online active SVE wells with open intervals below the CCU from 1992 through 2012. Concentrations have decreased by orders of magnitude since the initiation of SVE operations.



Note: The logarithmic scale is provided on the Y-axis.

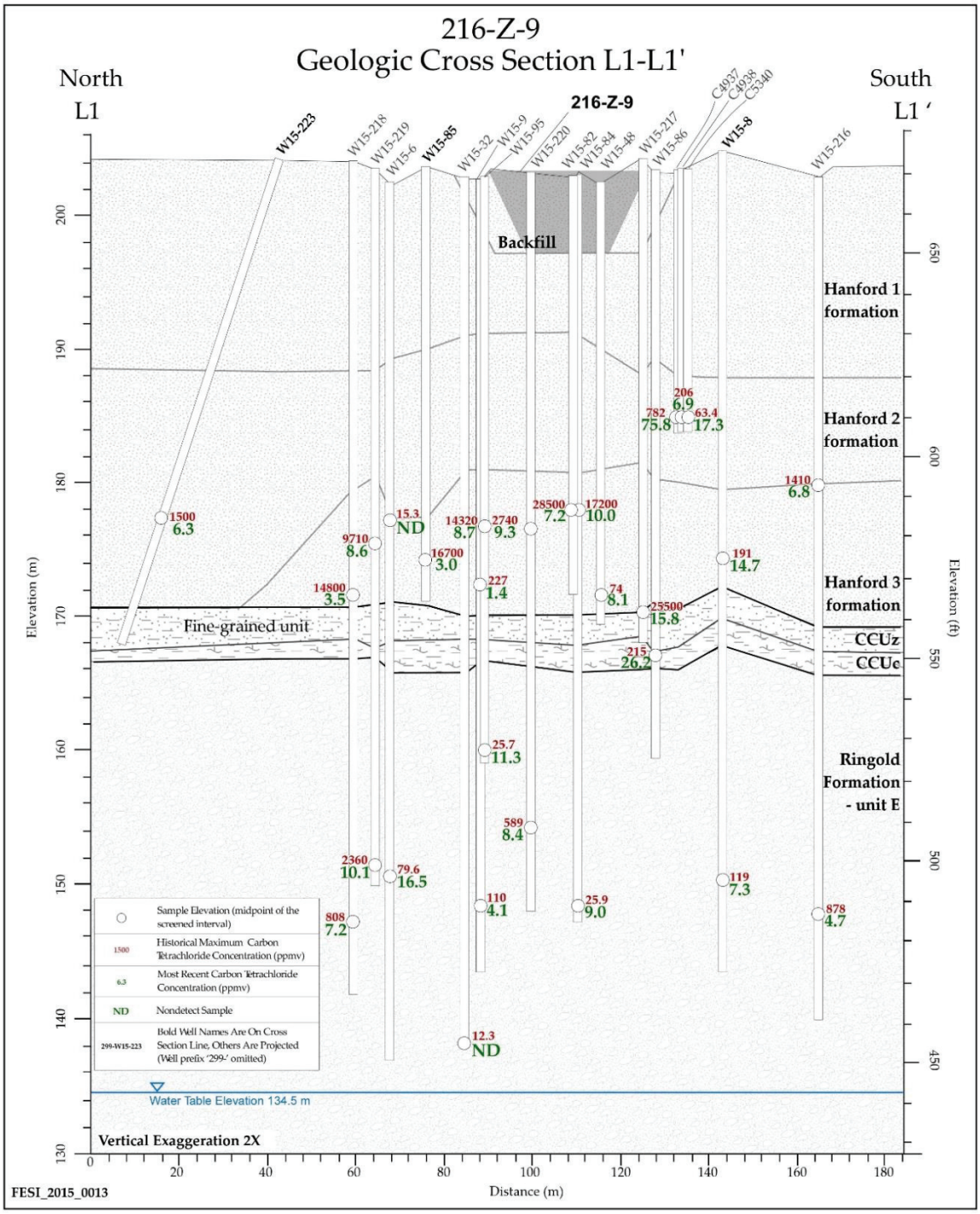
Figure A-6. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at Online Active SVE Wells with Screened Intervals above the CCU (1992 to 2012)



Note: The logarithmic scale is provided on the Y-axis.

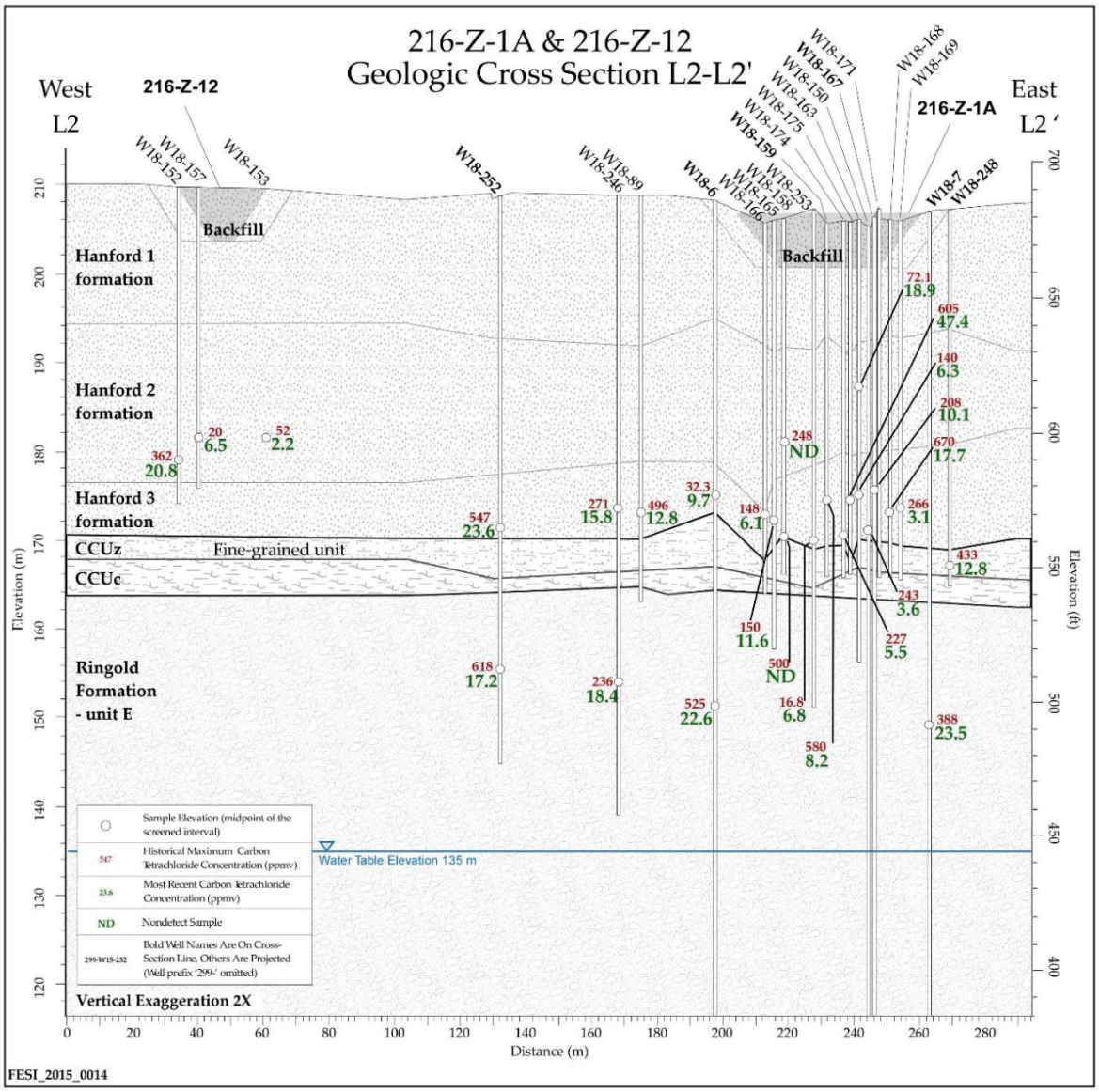
Figure A-7. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at Online Active SVE Wells with Screened Intervals below the CCU (1992 to 2012)

Figures A-8, A-9, and A-10 show cross-sectional representations of carbon tetrachloride at the 216-Z-9, 216-Z-1A/216-Z-12, and 216-Z-18 waste sites, respectively. The locations of the cross sections are shown in Figure A-2. The carbon tetrachloride values shown on these cross sections are the historical maximum and most recent concentrations, which are the same values as shown in Figures A-6 and A-7.



Note: The cross section location is shown in Figure A-2.

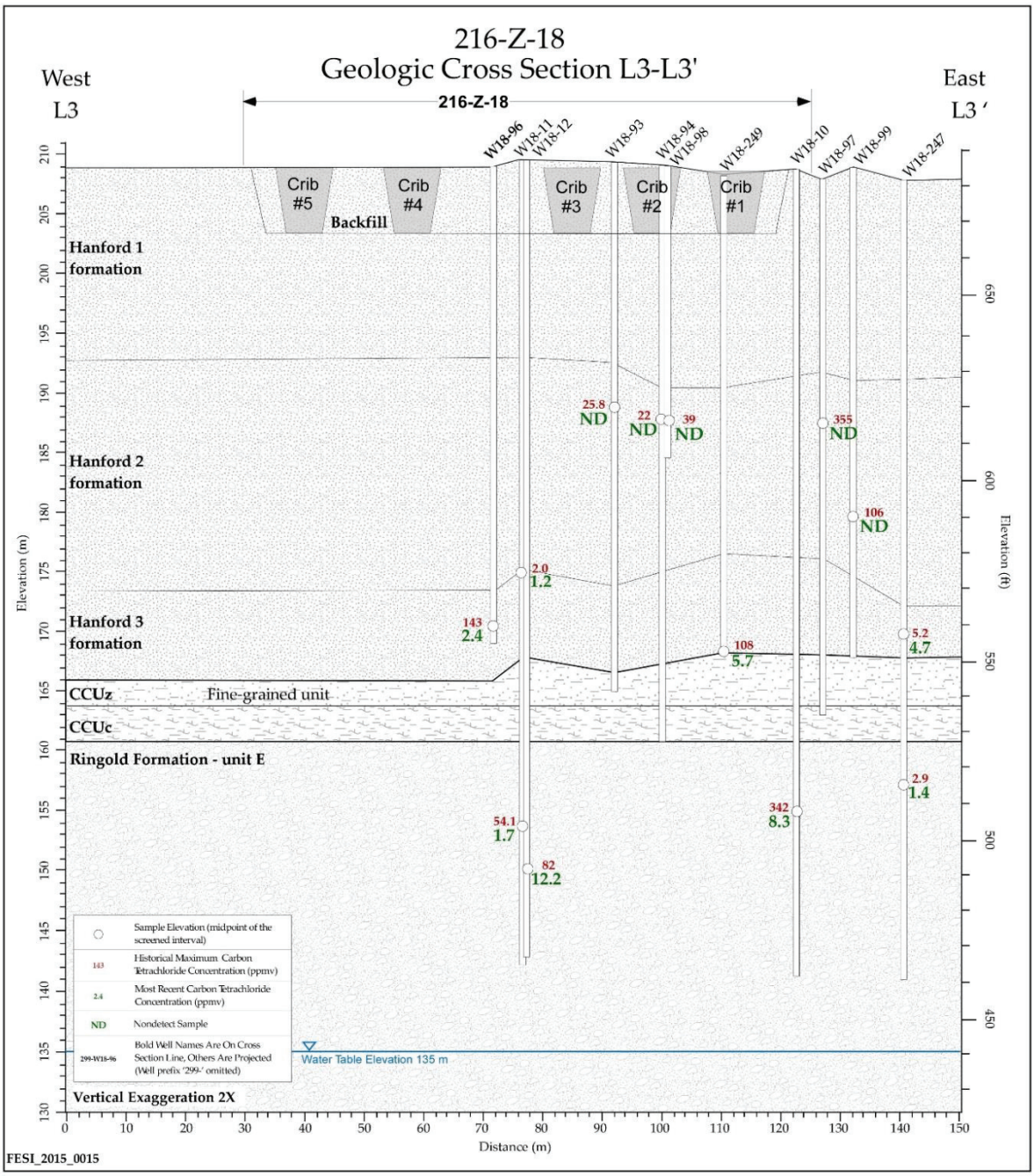
Figure A-8. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon Tetrachloride Concentrations (1993 to 2012) for 216-Z-9 Online Active SVE Wells



Note: The cross section location is shown in Figure A-2.

Figure A-9. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon Tetrachloride Concentrations (1992 to 2012) for 216-Z-1A/216-Z-12 Online Active SVE Wells

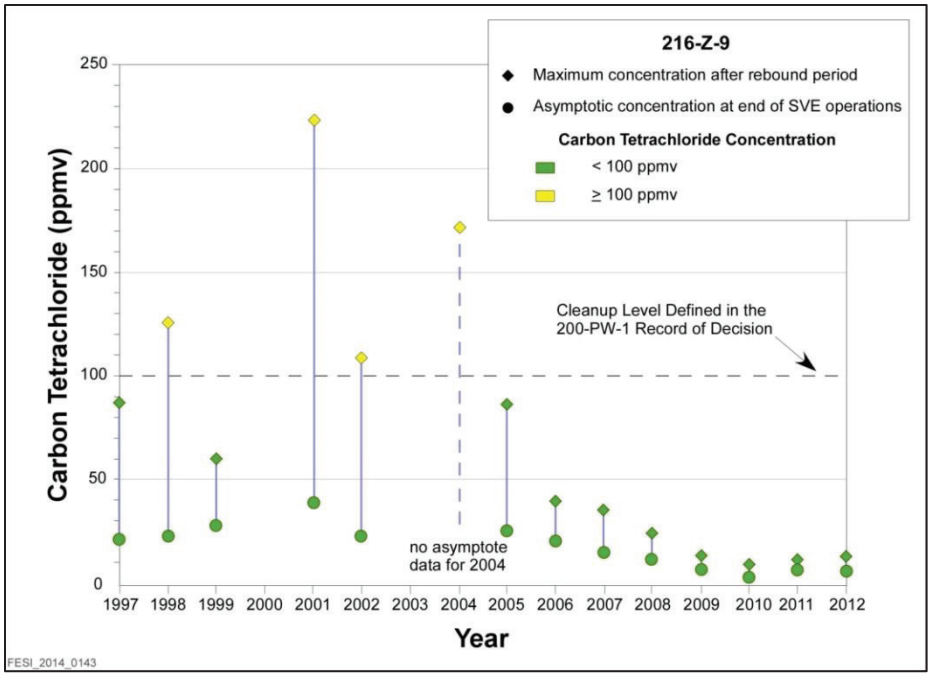
Carbon tetrachloride concentrations were also measured in the combined vapor stream entering each SVE treatment system (i.e., not from individual wells). Figure A-11 shows the initial maximum and final carbon tetrachloride concentrations at the 216-Z-9 SVE system during cyclic operations (1997 to 2012). Figure A-12 shows the initial maximum and final carbon tetrachloride concentrations at the combined 216-Z-1A/216-Z-18/216-Z-12 SVE system during cyclic operations. The maximum concentrations are typically observed at the beginning of each annual SVE operational cycle and represent the rebound in concentration during the quiescent period following the end of the previous operational cycle. The final concentrations are the average asymptotic concentrations measured at the end of the SVE operation cycle.



Note: The cross section location is shown in Figure A-2.

Figure A-10. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon Tetrachloride Concentrations (1993 to 2012) for 216-Z-18 Online Active SVE Wells

The maximum concentrations measured at the 216-Z-9 site were much higher than the maximum concentrations measured for the 216-Z-1A/216-Z-18/216-Z-12 sites from 1997 through 2008. Since 2009, the maximum and final concentrations at both sites have been similar. This convergence of the maximum values indicates the lack of significant rebound at either site.



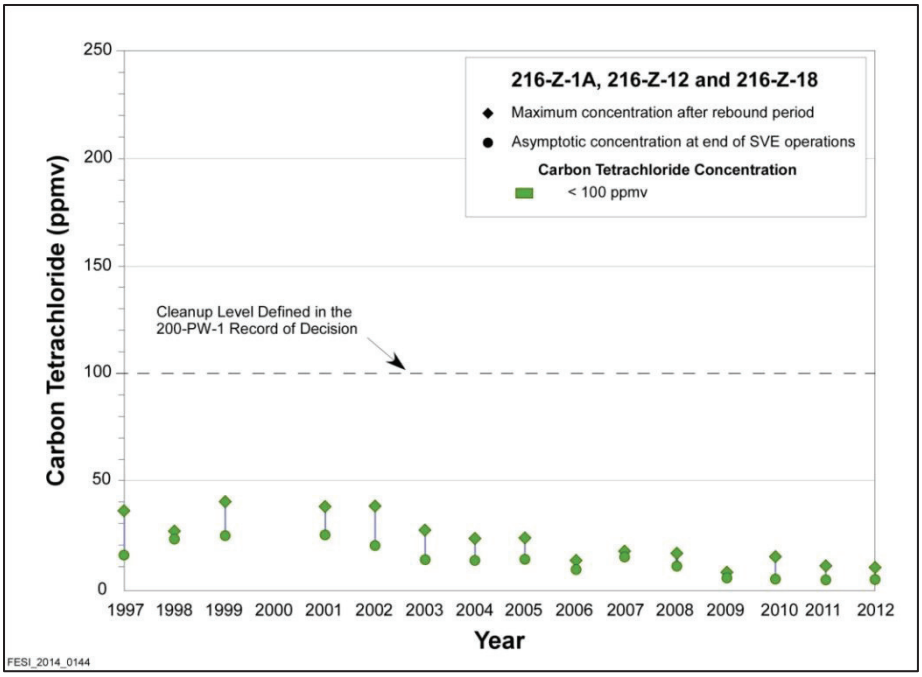
Note: The tie lines between points indicate the connection between starting and ending concentrations in a given operational cycle.

Figure A-11. Rebound and Final Concentrations for Operational Cycles of the 216-Z-9 SVE System, 1997 to 2012

In the earlier annual cycles, the maximum concentrations were significantly higher than the final concentrations at each site. Since 2005, both the maximum and the final concentrations during each operational cycle have declined. Figures A-11 and A-12 show that by 2009, the initial and final concentrations are nearly equal for the operational cycles at both sites. This indicates that the source mass discharge rate has significantly diminished.

Soil vapor concentrations were monitored at offline monitoring wells and soil vapor probes from November 1996 through March 2013 (at a monthly frequency) and in May and June 2014. Online active extraction wells may also be categorized as offline wells if the well was either taken offline or if the entire SVE system was offline. Figures A-13 and A-14 show the historical maximum and most recent (2014) carbon tetrachloride concentrations measured at these monitoring wells and soil vapor probes for the 216-Z-9 well field and the combined 216-Z-1A/216-Z-18/216-Z-12 well field, respectively. At some locations, soil vapor probes were installed by CPT at multiple depths for the same lateral location, although all depths were above the CCU. The corresponding depth is listed next to the soil vapor probe name (e.g., “CPT-21A [86 ft]” and “CPT-21A [65 ft]”) in Figures A-13 and A-14. The depth of the mid-point of the screened interval is listed next to the well name in these figures.

All of the most recent (2014) carbon tetrachloride concentrations, with the exception of “CPT-28 (87 ft)” and “CPT-21A (86 ft),” were found to be below the final cleanup level of 100 ppmv. The most recent carbon tetrachloride concentration in May 2014 at “CPT-28 (87 ft)” was 129 ppmv; the most recent carbon tetrachloride concentration in May 2014 at “CPT-21A (86 ft)” was 101 ppmv. The decline in carbon tetrachloride concentrations observed in online active wells (Figures A-6 and A-7) and in offline wells and probes (Figures A-13 and A-14) indicates that SVE operations have reduced carbon tetrachloride soil vapor concentrations at the carbon tetrachloride waste sites.



Note: The tie lines between points indicate the connection between starting and ending concentrations in a given operational cycle.

Figure A-12. Rebound and Final Concentrations for Operational Cycles of the 216-Z-1A/216-Z-18/216-Z-12 SVE System, 1997 to 2012

Figure A-15 shows the most recent (May to June 2014) carbon tetrachloride soil vapor sampling results from soil vapor probes and offline monitoring wells screened above/within the CCU. Figure A-16 shows sampling results for offline monitoring wells screened below the CCU. The values shown in Figures A-15 and A-16 are the maximum concentration detected using the Brüel & Kjær (B&K)[1] multi-gas analyzer. For CPT locations with soil vapor probes at multiple depths, the value shown is the maximum concentration based on samples from all depths at that location. All soil vapor concentrations were below 100 ppmv, with the exceptions of CPT-28 (87 ft) (129 ppmv) and CPT-21A (86 ft) (101 ppmv), as previously discussed. These probes are screened above the CCU and are located south of the 216-Z-9 waste site (Figure A-15).

After preparation and submittal in March 2015 of Draft A of DOE/RL-2014-48, *Endpoint Evaluation for the 200-PW-1 Operable Unit Soil Vapor Extraction Operations*, soil vapor concentrations were monitored at offline monitoring wells and soil vapor probes in June 2015. The rebound data for 2015 are very similar to the rebound data for 2014. The carbon tetrachloride concentrations were less than 100 ppmv in all of the SVE wells and in all but two of the soil vapor probes. These two probes are both above the CCU. The carbon tetrachloride concentrations in June 2015 at “CPT-28 (87 ft)” was 125 ppmv; the carbon tetrachloride concentration in June 2015 at “CPT-21A (86 ft)” was 103 ppmv.

[1] B&K is a trade name of Brüel & Kjær (Sound and Vibration Measurement A/S), Nærum, Denmark.

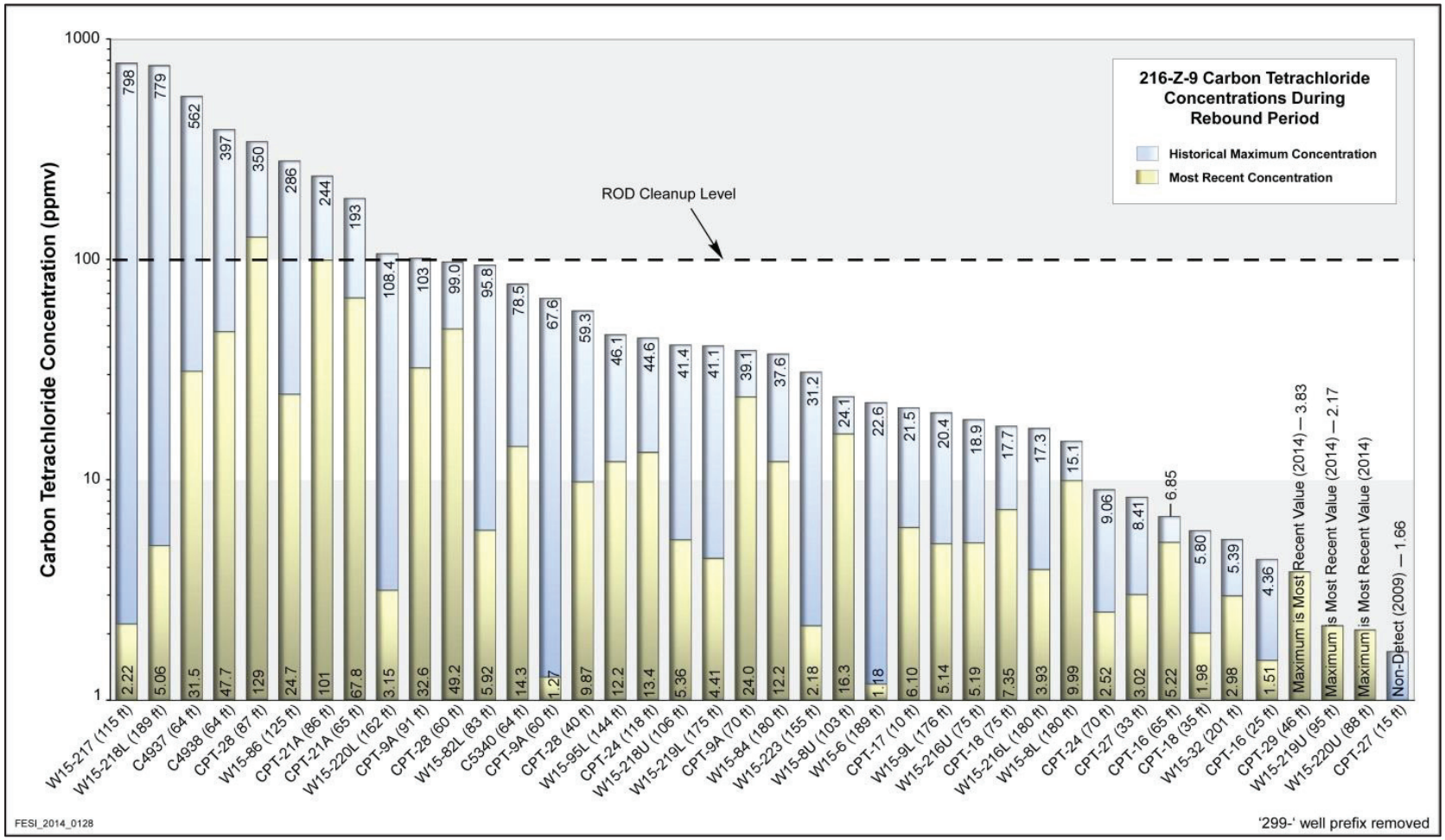


Figure A-13. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at Offline Monitoring Wells and Soil Vapor Probes at 216-Z-9 (1996 to 2014)

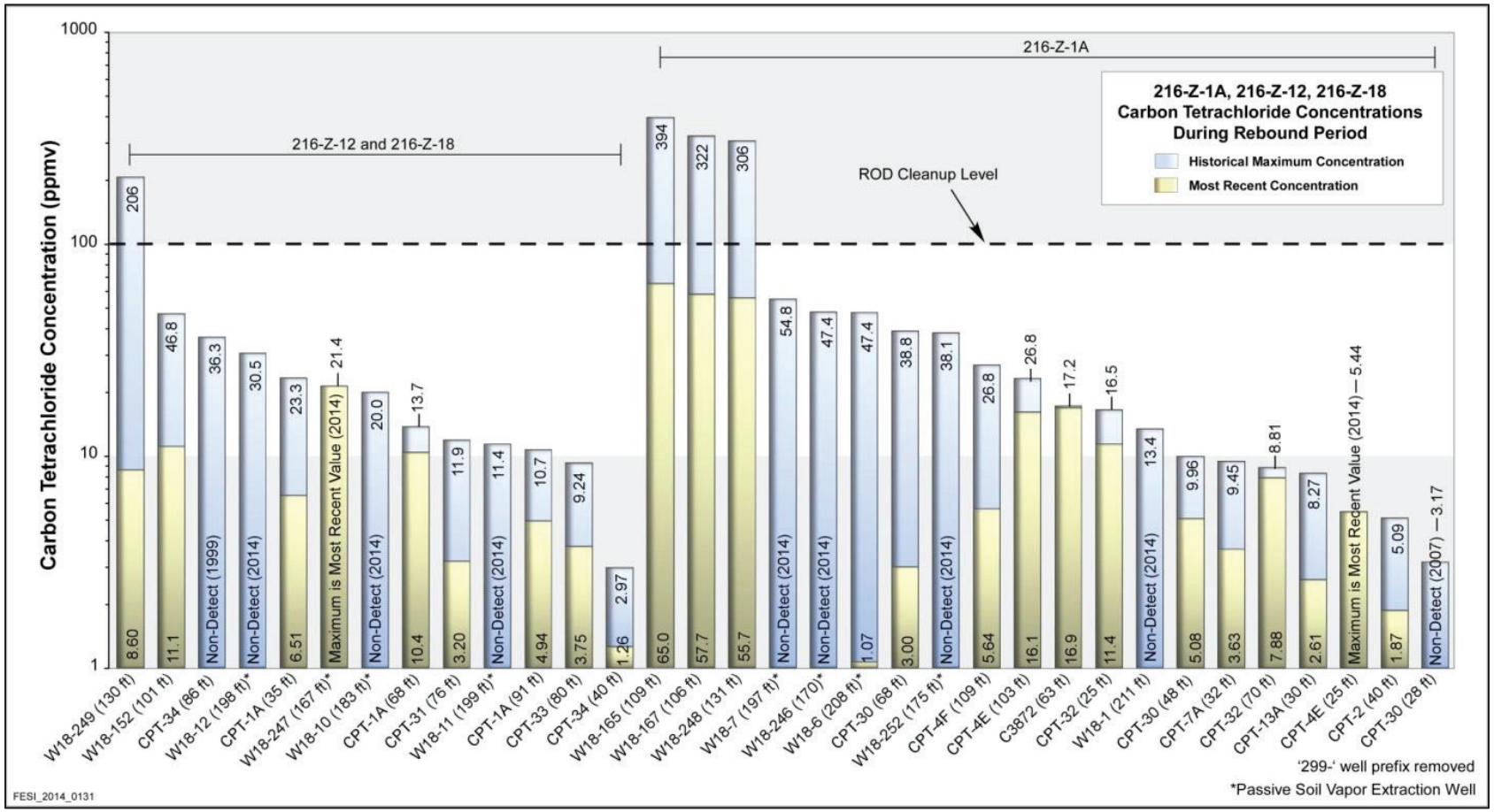
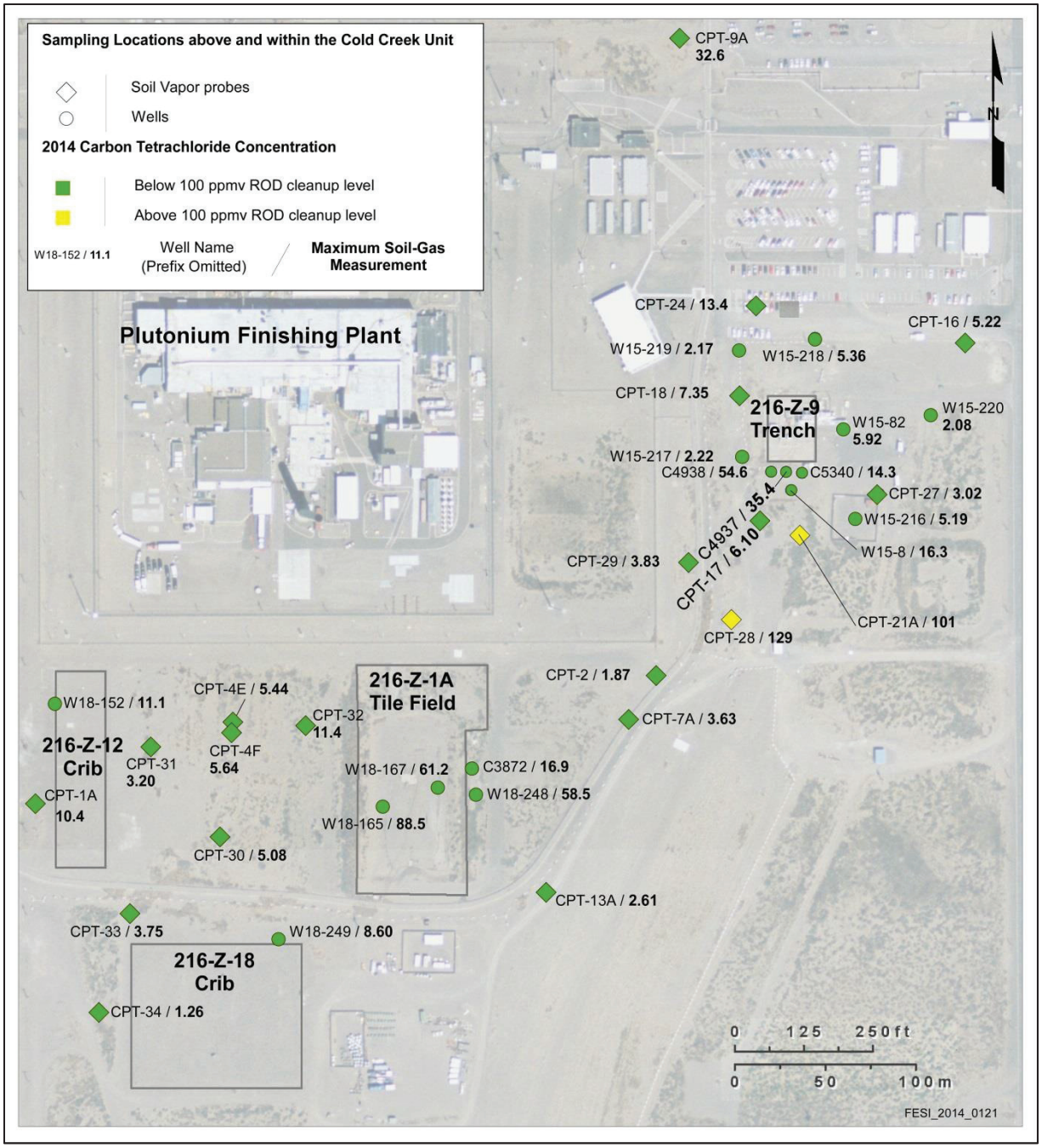


Figure A-14. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at Offline Monitoring Wells and Soil Vapor Probes at 216-Z-1A/216-Z-12/216-Z-18 (1996 to 2014)

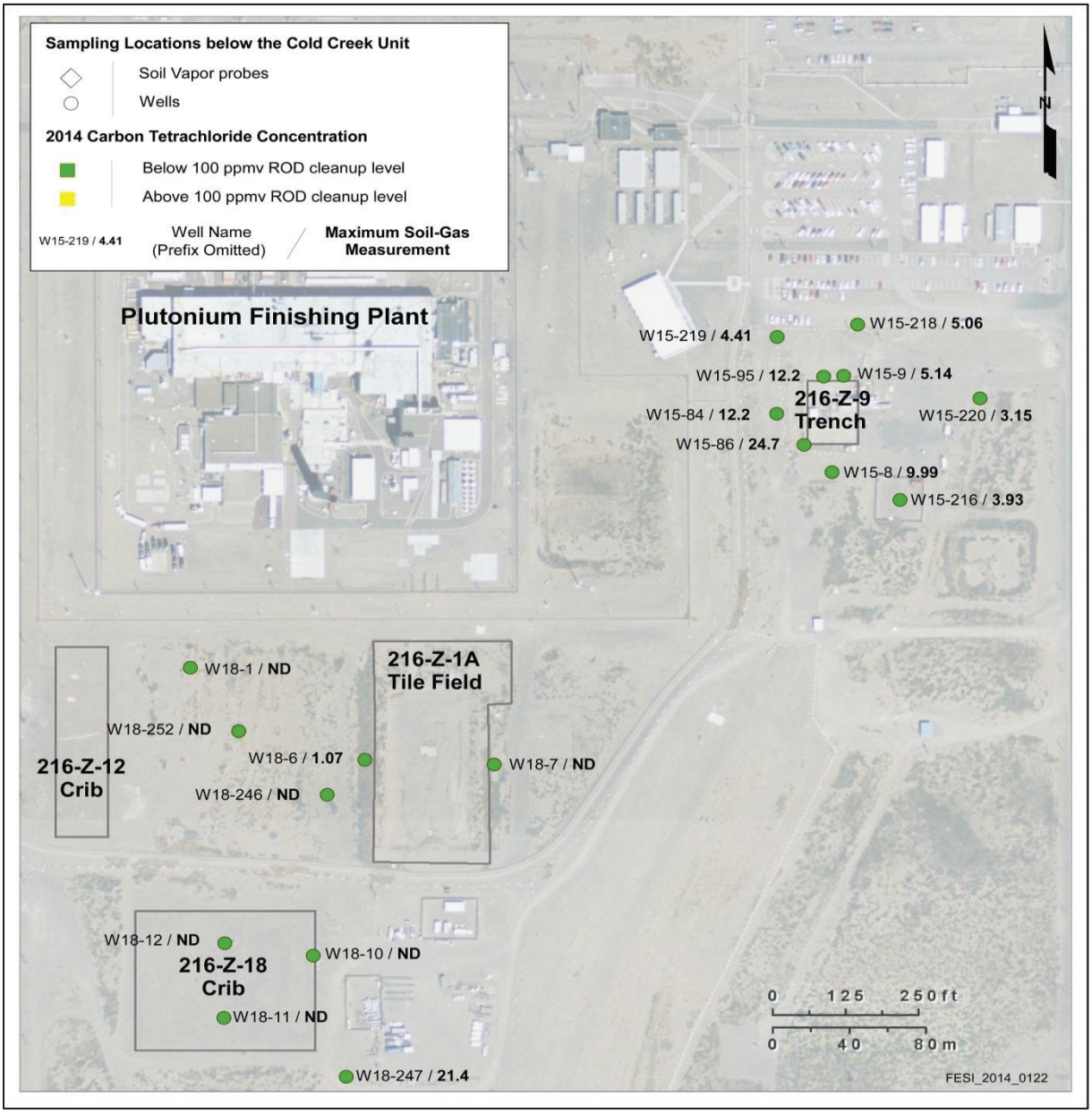


Note: Carbon tetrachloride concentrations were measured in the field using a B&K multi-gas analyzer.

Figure A-15. 2014 Carbon Tetrachloride Concentrations (in ppmv) for Samples Collected from Soil Vapor Probes and Offline Monitoring Wells Screened above and within the CCU

During 2011, a treatability test was conducted at the 216-Z-9 site to refine the understanding of the magnitude and spatial distribution of the remaining carbon tetrachloride in the vadose zone in accordance with DOE/RL-2010-79, *Treatability Test Plan for Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*. Test results were provided in PNNL-21326, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*. The treatability test data

indicated that most of the remaining carbon tetrachloride is located within the lower permeability CCU, from which the carbon tetrachloride is slowly diffusing. The treatability test provided information about the diminishing impact of the vadose zone source on the groundwater, providing a technical basis for evaluating potential termination of the SVE systems. The primary recommendation from this study with respect to SVE operations was to increase future rebound periods, allowing the carbon tetrachloride to reach a higher concentration before beginning the next operating cycle.



Note: Carbon tetrachloride concentrations were measured in the field using a B&K multi-gas analyzer. There are no soil vapor probes below the CCU.

Figure A-16. 2014 Carbon Tetrachloride Concentrations (in ppmv) for Samples Collected from Offline Monitoring Wells Screened below the CCU

Based on the recommendations provided in the treatability test report (PNNL-21326), DOE and EPA determined that the active SVE systems would not be operated or monitored during calendar year (CY) 2013 to allow for a longer rebound period (DOE/RL-2014-39, *Carbon Tetrachloride Soil Vapor Extraction System Operating and Monitoring Plan for CY 2015*). DOE and EPA agreed that the option of resuming active SVE operations in CY 2014 would be considered following an evaluation of the carbon tetrachloride rebound monitoring data collected during the spring of CY 2014. Rebound monitoring data were collected in May and June 2014 in accordance with DOE/RL-2014-20, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2014 Rebound Sampling* (Rev. 0). Based on the 2014 results (Figures A-15 and A-16), DOE and EPA agreed to extend the rebound period through CY 2014 with no SVE operations or monitoring. DOE and EPA agreed to consider resuming active SVE operations in CY 2015 based on carbon tetrachloride rebound monitoring data collected in the spring of CY 2015. Rebound monitoring data were collected in June 2015 in accordance with DOE/RL-2014-20, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit Calendar Year 2015 Rebound Sampling* (Rev. 1). Based on the 2015 soil vapor concentrations, which did not increase in 2015, EPA approved leaving the SVE systems offline for CY 2015.

A4 Investigation of Carbon Tetrachloride Sources beyond the 200-PW-1 Operable Unit Waste Disposal Sites

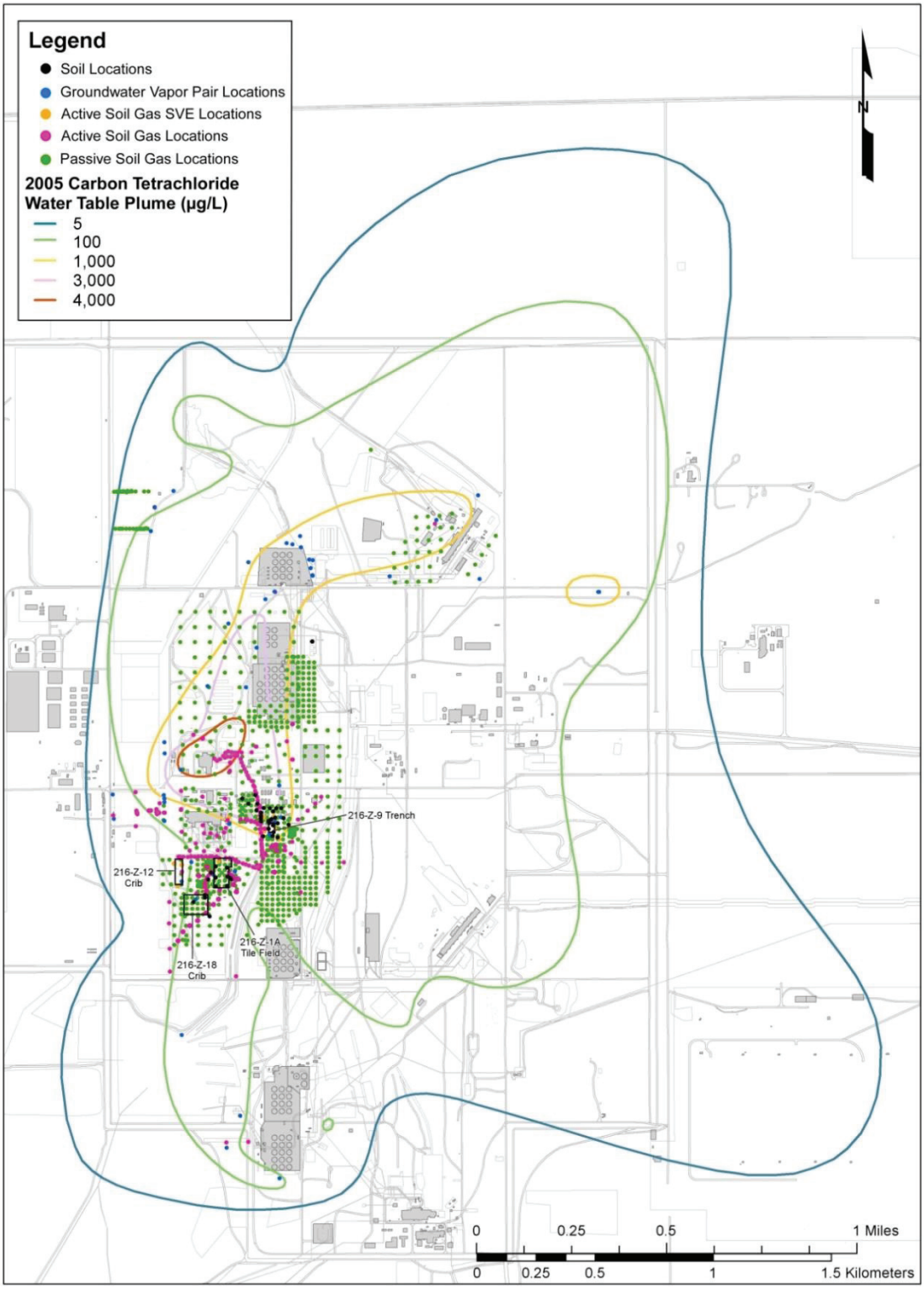
The 200-PW-1 OU RI (DOE/RL-2006-51) included investigations of the spatial extent (both lateral and vertical) of the dispersed carbon tetrachloride that had migrated beyond the boundaries of 200-PW-1 OU waste sites. Soil vapor, soil, and groundwater samples were collected in the area overlying the highest concentrations in the carbon tetrachloride groundwater plume. Vadose zone sampling was the most intense in the area overlying the highest groundwater concentrations.

The RI of the dispersed carbon tetrachloride contamination was conducted in two phases. The first phase of the investigation was based on systematic characterization of each of the potential mechanisms for release of carbon tetrachloride into the shallow vadose zone overlying the highest carbon tetrachloride groundwater concentrations. The second phase of the investigation was based on potential near-surface release sites and areas of elevated carbon tetrachloride concentrations in groundwater, including the intermediate and deep vadose zone overlying the entire carbon tetrachloride groundwater plume.

These extensive and comprehensive investigations conducted for the RI did not identify any carbon tetrachloride waste sites or sources other than the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib.

A4.1 Characterization Beyond the 200-PW-1 Operable Unit Carbon Tetrachloride Waste Sites

All of the sampling locations to characterize the carbon tetrachloride lateral and vertical extent during the RI (DOE/RL-2006-51) are shown in Figure A-17. The RI used passive soil gas surveys as a reconnaissance approach to focus more intrusive sampling. Passive soil gas collectors were placed within upper foot of the subsurface and retrieved 3 to 5 days later for analysis. Carbon tetrachloride in soil vapor that migrated past the collector was sorbed to absorbent material in the collector. The absorbent material was then analyzed in a laboratory for carbon tetrachloride. Because the CCU is relatively impermeable, the soil gas containing carbon tetrachloride detected by the passive soil gas collectors migrated from the vadose above the CCU.



Source: Derived from Figure 3-20 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-17. Carbon Tetrachloride Sampling Locations during the RI, Overlaid on the 2005 Groundwater Carbon Tetrachloride Plume Contours

Passive soil gas collectors were initially installed using coarse-grid spacing. Based on the results of the coarse-grid results, additional passive soil gas collectors were installed using a finer grid spacing to better define areas of elevated carbon tetrachloride detections.

All of the passive soil gas sampling locations are shown on Figure A-17 in green. These same sampling locations are shown in Figure A-18. In Figure A-18, the sampling location "dots" are color-coded based on sample concentration results. The density of sampling locations is higher in areas where passive soil gas collectors also were installed using a refined grid spacing.

The highest detections of carbon tetrachloride were found in passive soil gas collectors installed at the 216-Z-1A Tile Field and in an area northwest of the 216-Z-9 Trench. Intermediate-level detections were found in the vicinities of the 216-Z-1A Tile Field and 216-Z-9 Trench. These detections were used to focus the active soil vapor sampling, which was conducted using a CPT.

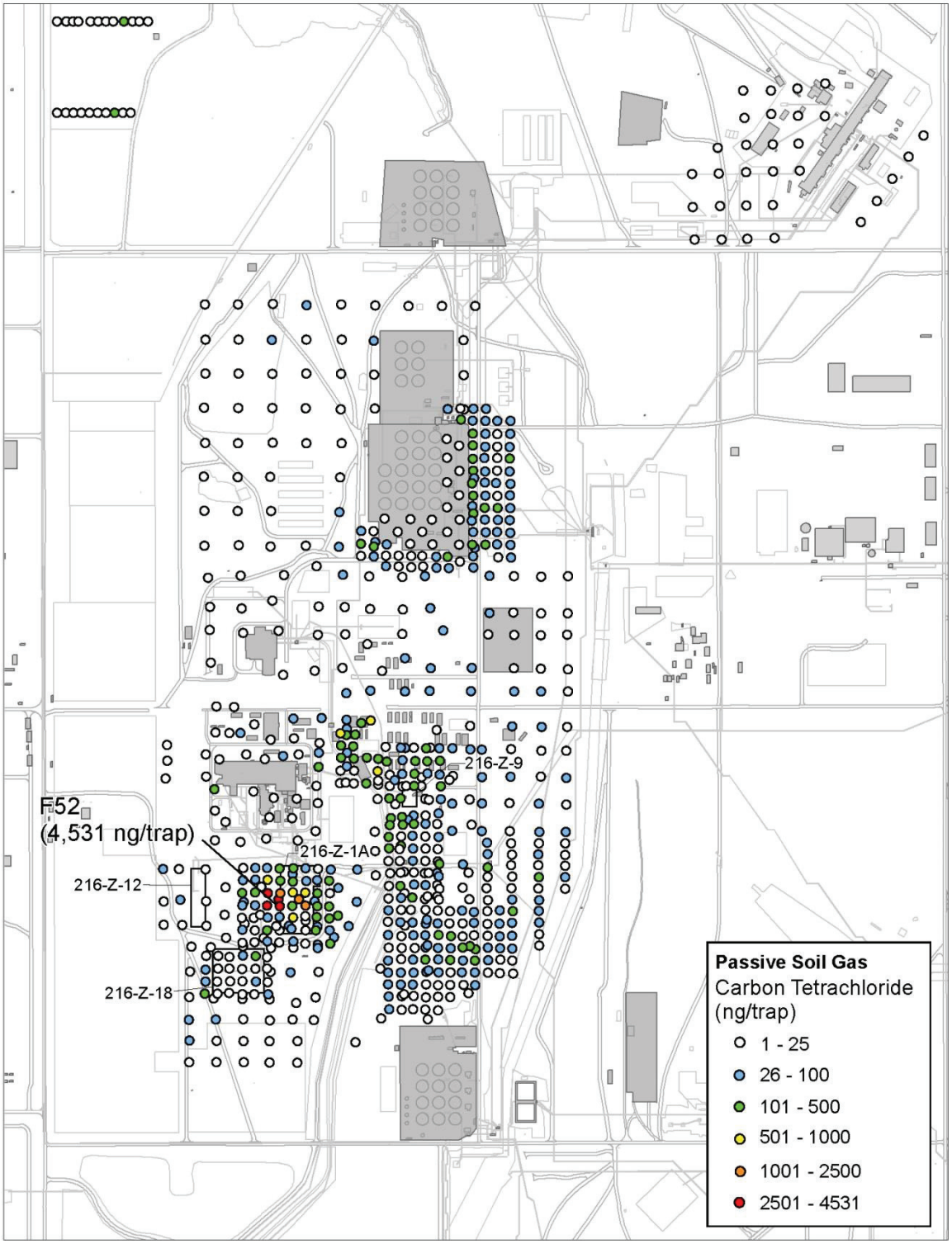
The active soil vapor sampling locations are shown in Figure A-17 in pink. Figure A-19 shows the results for the active soil vapor samples from locations above the CCU, where the "dots" are color-coded based on concentration. Active soil vapor sampling locations and results within the CCU are shown in Figure A-20; results for sampling locations below the CCU are shown in Figure A-21. Active soil vapor samples were collected in the areas of elevated carbon tetrachloride detections based on the passive soil gas measurements. The highest active soil gas carbon tetrachloride concentrations were in samples collected at the carbon tetrachloride waste sites.

The results of the active soil vapor sampling were used to focus collection of soil samples, which was accomplished using a CPT. The soil sampling locations are shown in Figure A-17 in black. Figure A-22 shows the results for soil samples from locations above the CCU, where the "dots" are color-coded based on concentration. Soil sampling locations and results within the CCU are shown in Figure A-23; results for sampling locations below the CCU are shown in Figure A-24. The highest carbon tetrachloride soil concentrations were in samples collected at the carbon tetrachloride waste sites.

Elevated hot spots of carbon tetrachloride concentrations in the groundwater were also used to focus the vadose zone investigation. At these locations, soil vapor samples were collected just above the water table in wells, and groundwater samples were collected at the water table in the same wells. The carbon tetrachloride concentrations in each groundwater/vapor sample pair were compared to evaluate whether the vadose zone was providing a source of contamination to the groundwater at that location. No additional vadose zone sources of carbon tetrachloride were identified at these groundwater locations. The groundwater/vapor pair sampling locations are shown in Figure A-17 in blue.

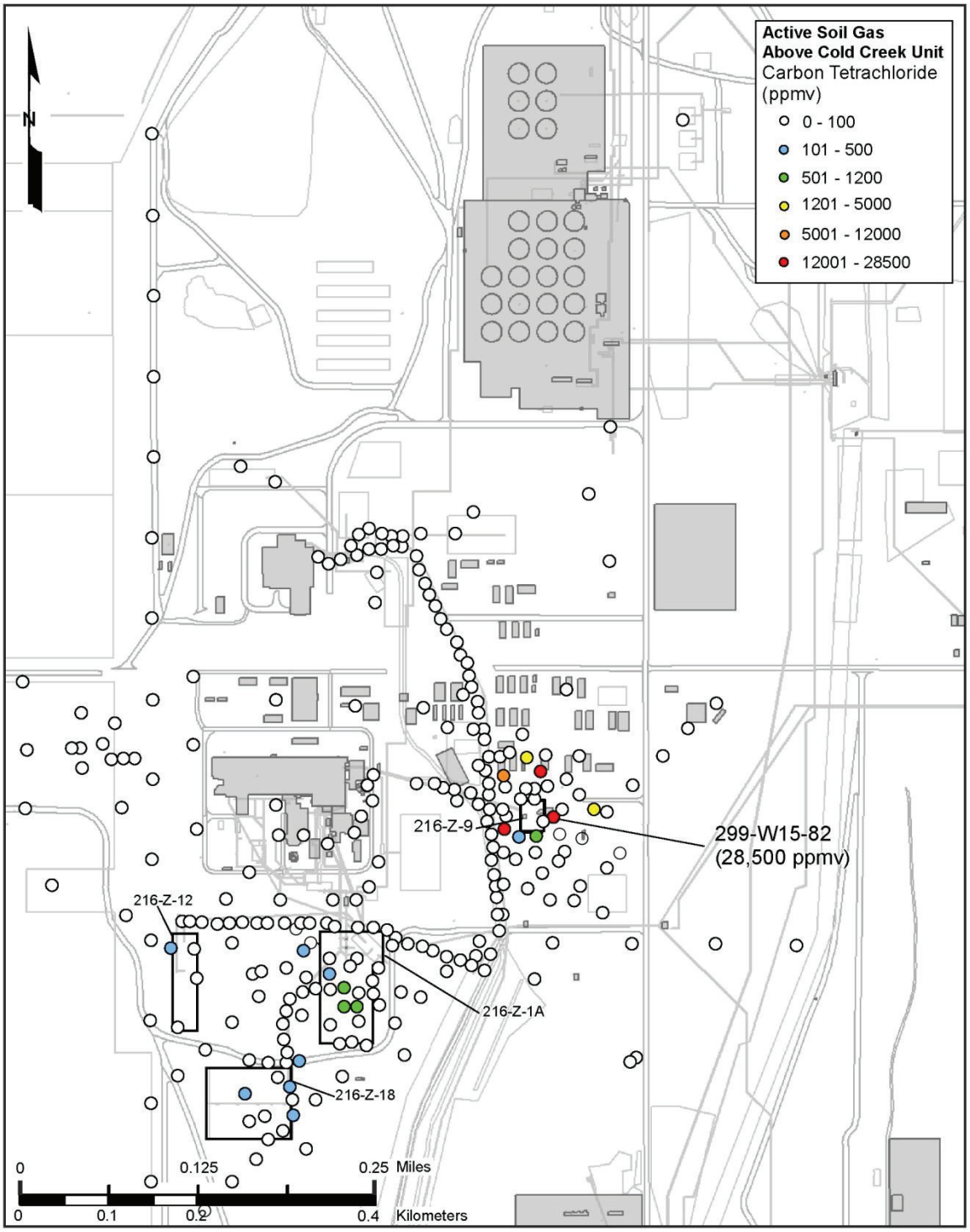
A4.2 Key Findings and Results of the Remedial Investigation

The 200-PW-1 OU RI (DOE/RL-2006-51) included investigations of the nature and extent of carbon tetrachloride contamination (including the presence of DNAPL) in the vicinities of the carbon tetrachloride waste sites and the lateral and vertical extent of the dispersed carbon tetrachloride that had migrated beyond the boundaries of 200-PW-1 OU waste sites.



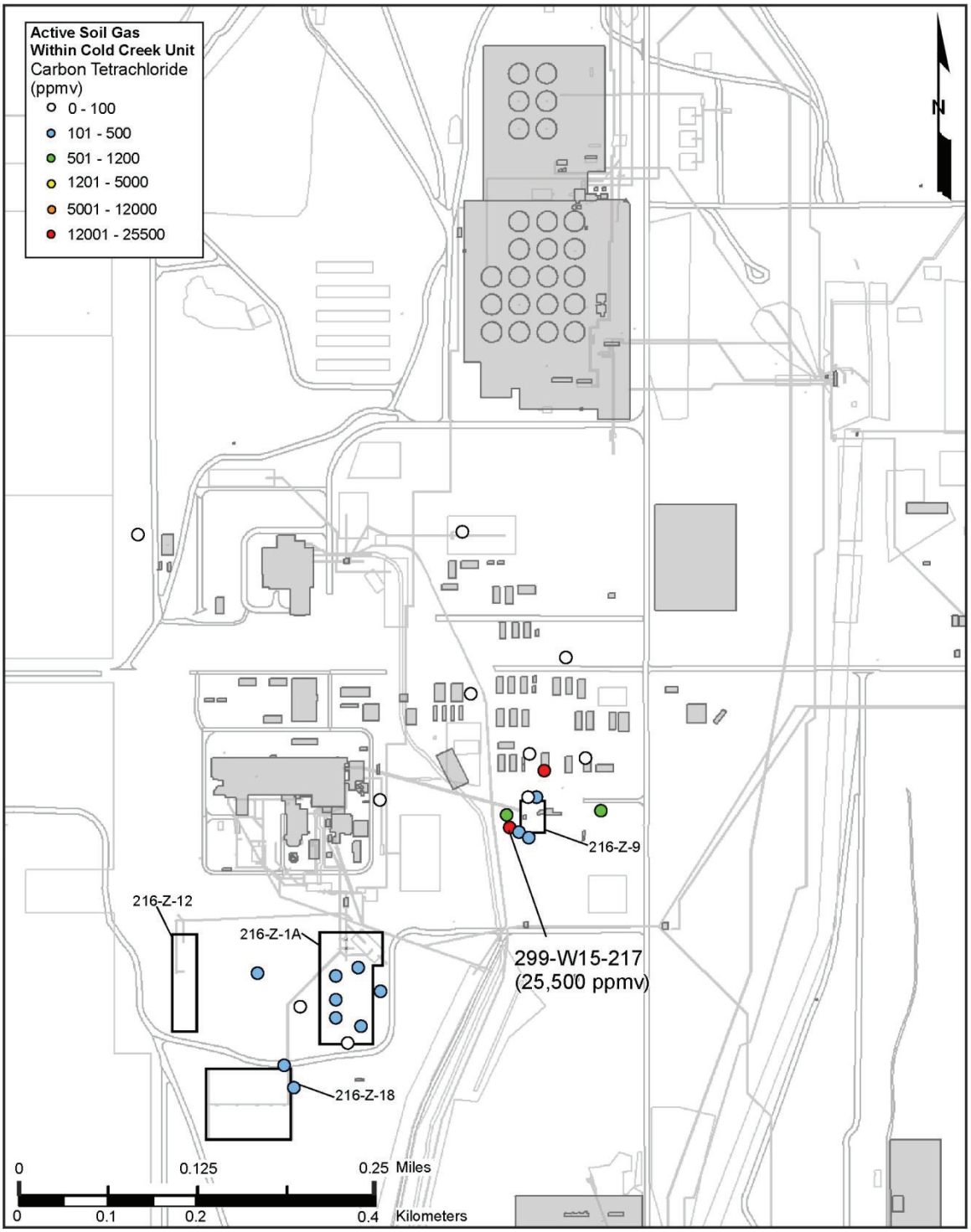
Source: Derived from Figure 3-21 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-18. Passive Soil Gas Vapor Sampling Results from the RI



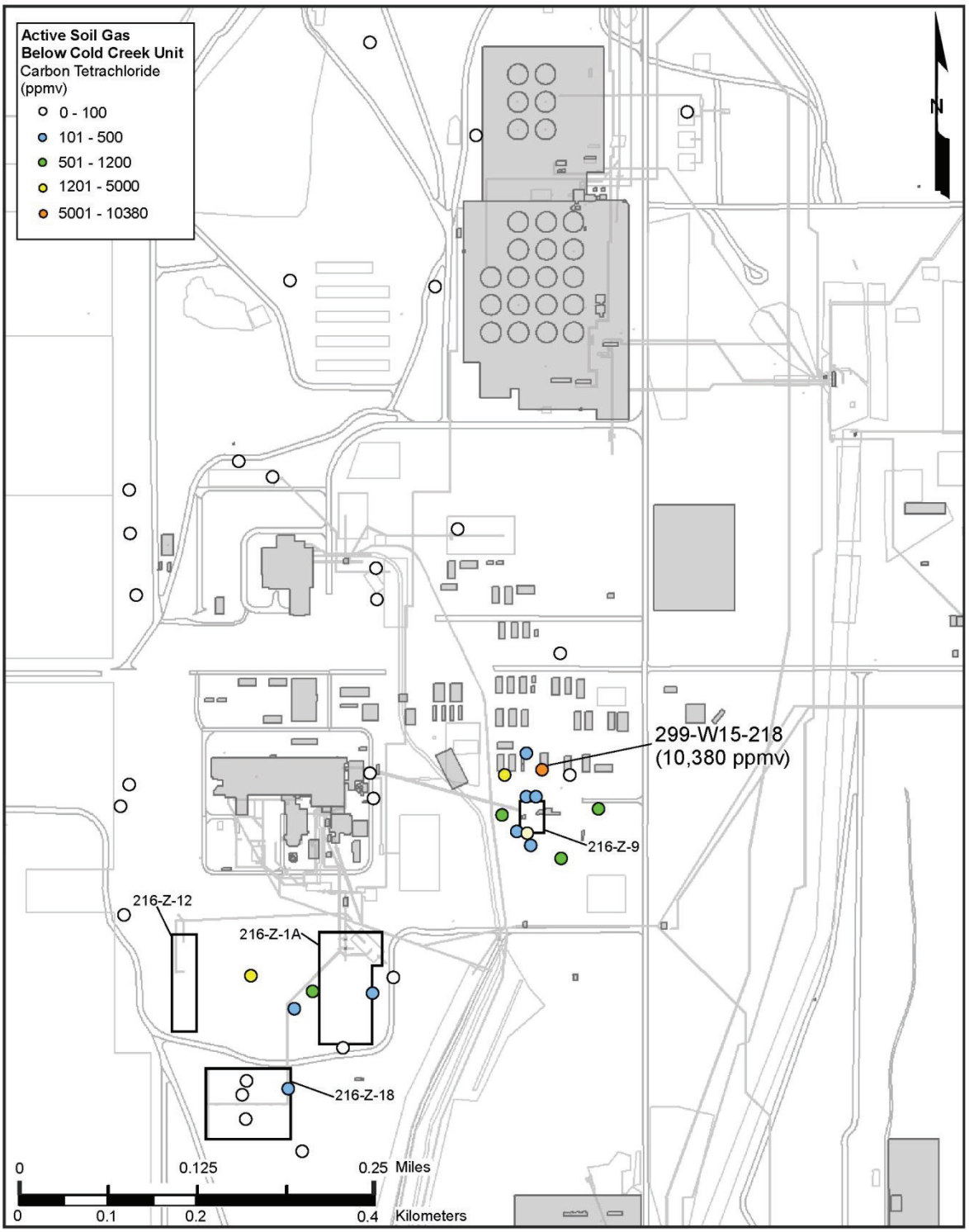
Source: Derived from Figure 3-23 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-19. Active Soil Vapor Sampling Results for Locations above the CCU from the RI



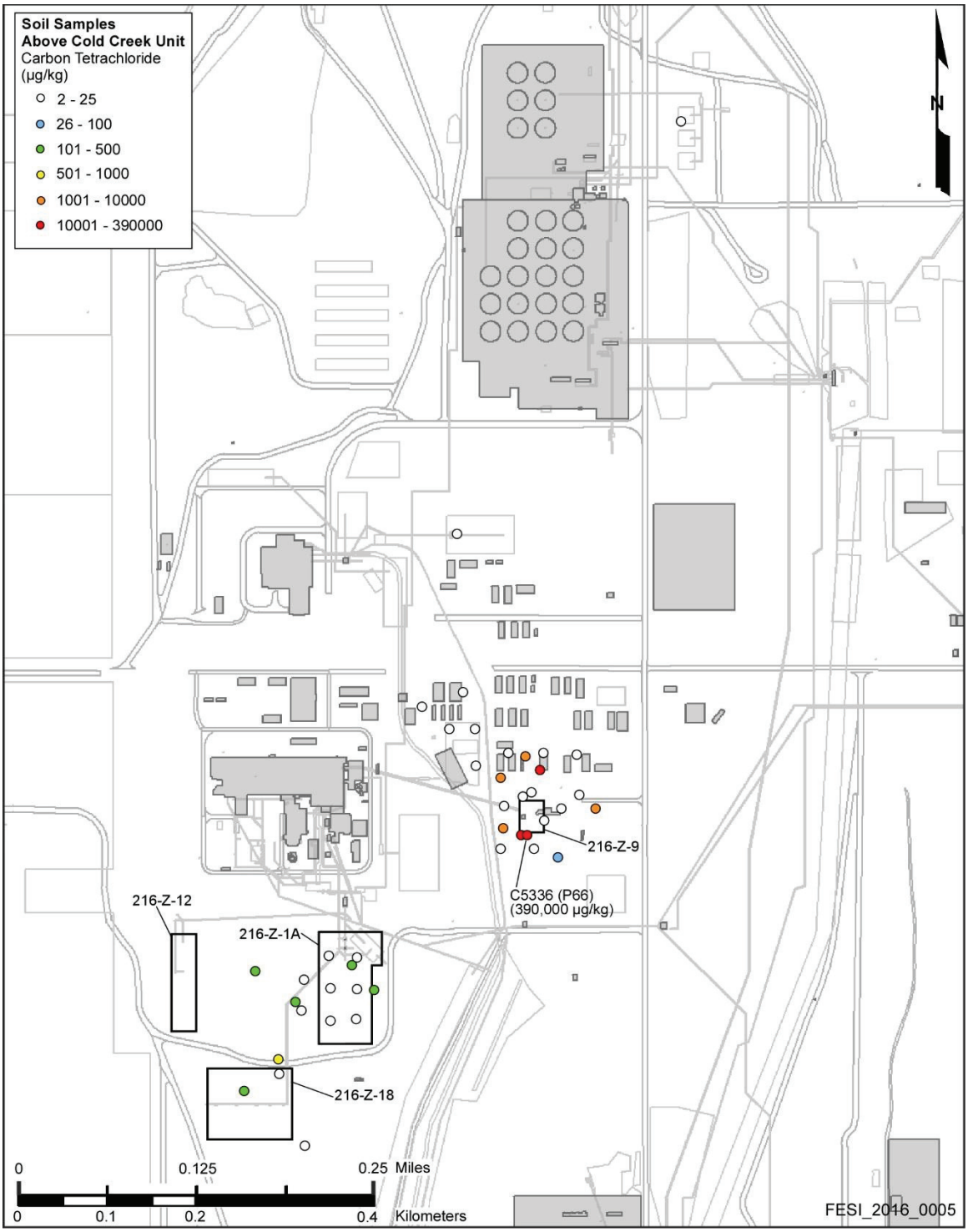
Source: Derived from Figure 3-25 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-20. Active Soil Vapor Sampling Results for Locations within the CCU from the RI



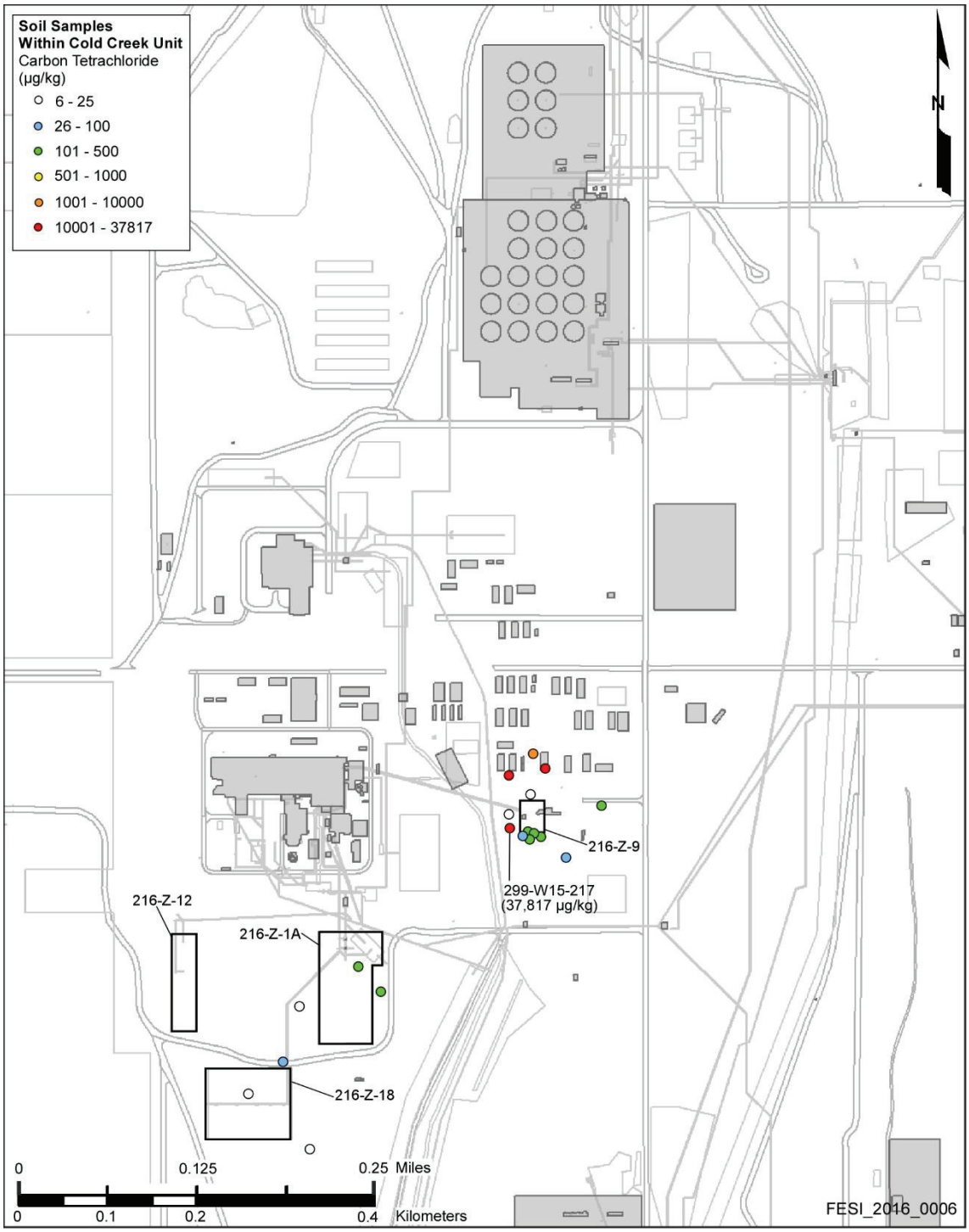
Source: Derived from Figure 3-27 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-21. Active Soil Vapor Sampling Results for Locations below the CCU from the RI



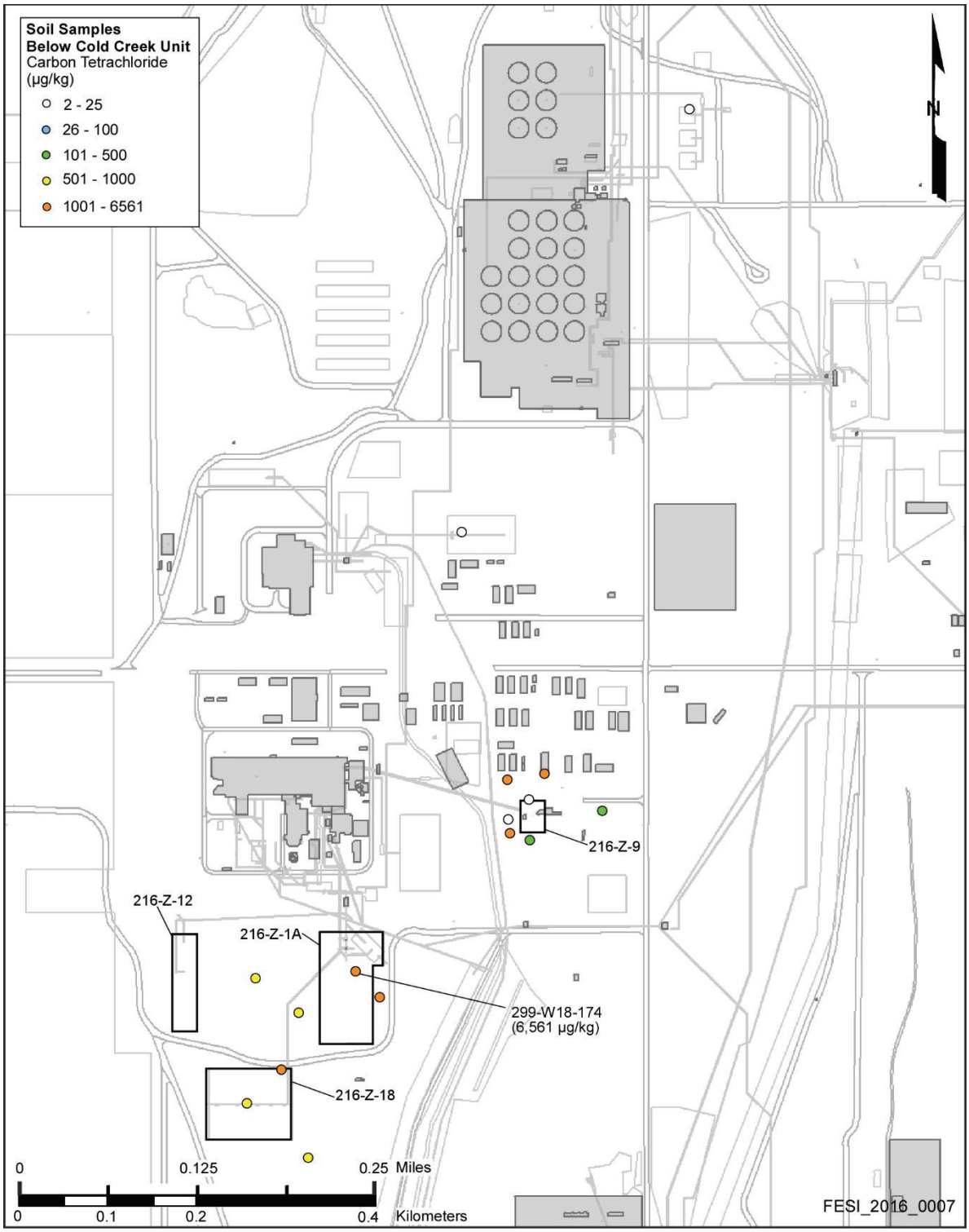
Source: Derived from Figure 3-29 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-22. Soil Sampling Results for Locations above the CCU from the RI



Source: Derived from Figure 3-30 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-23. Soil Sampling Results for Locations within the CCU from the RI



Source: Derived from Figure 3-31 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*.

Figure A-24. Soil Sampling Results for Locations below the CCU from the RI

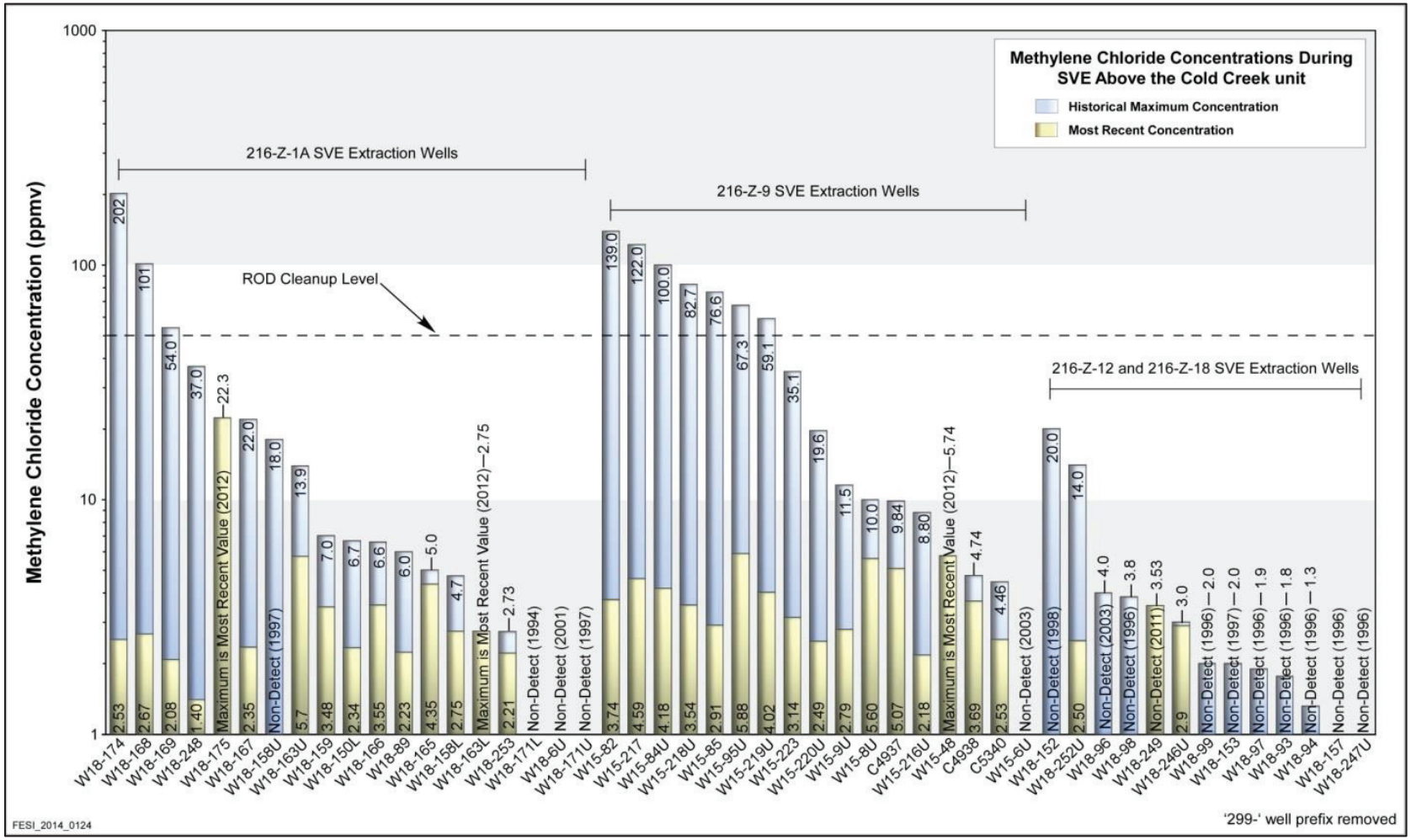
The following key findings and results are included in the RI report:

- The highest carbon tetrachloride concentrations in the vadose zone generally are located within about 75 to 150 m (246 to 492 ft) laterally from the source sites.
- The highest carbon tetrachloride concentrations are located in fine-grained layers, particularly within the CCU.
- No evidence was found to indicate significant lateral migration of carbon tetrachloride along the top of the CCU.
- There was no evidence of downward migration of carbon tetrachloride from an undocumented source.
- In areas away from the carbon tetrachloride waste sites, carbon tetrachloride soil vapor concentrations were less than 10 to 12 ppmv. These concentrations were not considered to have significant impact on groundwater quality. In particular, areas located south of the 216-Z-9 Trench (near the present location of CPT-28) and south of the 216-Z-9 Trench east of the 216-Z-20 Ditch showed no evidence of elevated carbon tetrachloride concentrations. Based on these investigations, it can be concluded that the area south of the 216-Z-9 Trench does not contain any undocumented contamination sources.
- Soil vapor and shallow groundwater sampling at wells within the groundwater hot spot areas indicated that carbon tetrachloride in the soil vapor phase beneath the CCU is not a significant source of groundwater contamination in these areas.
- An area of higher passive soil vapor detections was found northwest of the 216-Z-9 Trench near the entrance to PFP. Active soil vapor investigation of pipelines near the area did not identify any new sources in the shallow vadose zone. Active soil vapor sampling using a CPT detected the highest active soil vapor measurement (119 ppmv) at a depth of 31.1 m (102 ft), just above the CCU (CPT push P10A).
- Carbon tetrachloride DNAPL was found in one sample from borehole C5335 and one sample from well 299-W15-46. Both samples were obtained from a silt lens in the shallow vadose zone (19.8 m [65 ft] below ground surface) adjacent to the 216-Z-9 Trench.

Thus, extensive investigations conducted for the RI did not identify any carbon tetrachloride waste sites or sources other than the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib. In Figures A-19 through A-24, elevated carbon tetrachloride concentrations in active soil gas and soil samples were only seen in the vicinity of the 216-Z-9 Crib and the 216-Z-1A Tile Field. Furthermore, continuous soil vapor monitoring of the vadose zone during the years of SVE operation has not revealed any other undocumented sources. On this basis, no other carbon tetrachloride sources exist within the area overlying the carbon tetrachloride groundwater plume.

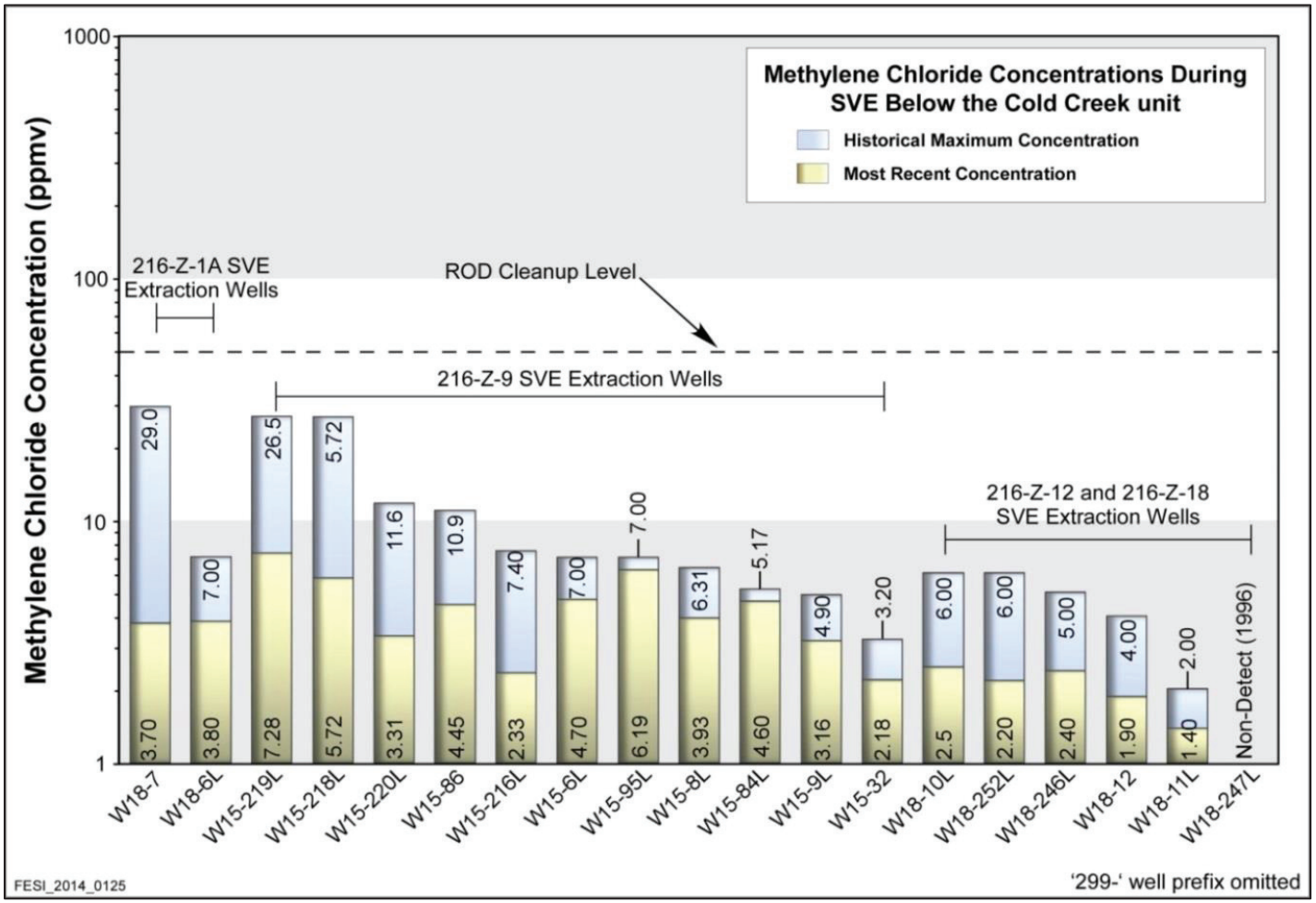
A5 Methylene Chloride at 200-PW-1 Operable Unit Waste Disposal Sites

Figure A-25 depicts (on a logarithmic scale) the historical maximum and most recent concentrations of methylene chloride measured in online active SVE extraction wells from 1993 to 2012 for open intervals above the CCU. Figure A-26 depicts (on a logarithmic scale) the historical maximum and most recent concentrations of methylene chloride measured in online SVE extraction wells from 1993 to 2012 for open intervals below the CCU. All methylene chloride concentrations in the online active extraction wells are below the 50 ppmv cleanup level specified in the 200-PW-1 OU ROD (EPA et al., 2011).



Note: The logarithmic scale is provided on the Y-axis.

Figure A-25. Historical Maximum and Most Recent Methylene Chloride Concentrations at Online SVE Wells with Screened Intervals above the CCU (1993 to 2012)



Note: The logarithmic scale is provided on the Y-axis.

Figure A-26. Historical Maximum and Most Recent Methylene Chloride Concentrations at Online SVE Wells with Screened Intervals below the CCU (1993 to 2012)

Figures A-27 and A-28 show the historical maximum and most recent methylene chloride concentrations measured at offline monitoring wells and soil vapor probes from 1996 (the first year of monitoring) and 2013 for the 216-Z-9 well field and the combined 216-Z-1A/ 216-Z-18/216-Z-12 well field, respectively. The most recent samples were collected in May and June 2014 and June 2015 (Appendix B). Samples were collected in Tedlar[2] bags for analysis using the B&K analyzer in the field. Samples were also collected at some locations in SUMMA[3] canisters for laboratory analysis. The methylene chloride results for samples collected in Tedlar bags and analyzed using the B&K analyzer were determined to be not usable (Appendix B). Therefore, these results were not used in Figures A-27 and A-28.

The methylene chloride results for 2014 and 2015 samples collected in SUMMA canisters and analyzed in the laboratory were all nondetect.

A6 Feasibility Study

Preparation of the feasibility study for the 200-PW-1 OU was initiated in 2007 (DOE/RL-2007-27, *Feasibility Study for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6 Operable Units*), and Rev. 0 was issued in 2011. The final contaminants of potential concern included carbon tetrachloride and methylene chloride, based on concentrations in soil and the fate and transport modeling that showed that the carbon tetrachloride and methylene chloride had the potential to migrate to groundwater

A7 Proposed Plan and Record of Decision

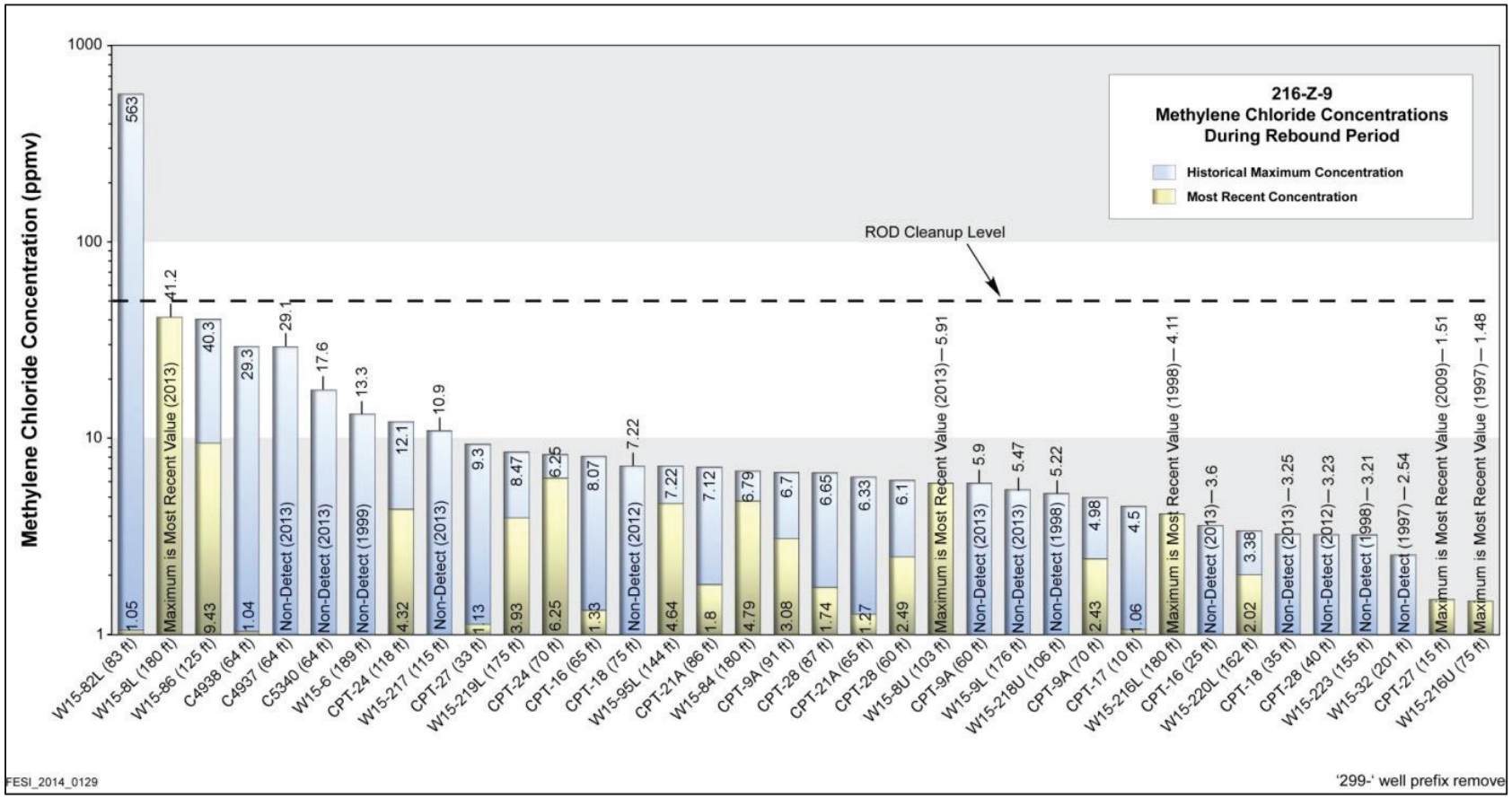
The proposed plan (DOE/RL-2009-117, *Proposed Plan for the Remediation of the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*), issued in 2011, recommended SVE as the remedial alternative for carbon tetrachloride at the three primary carbon tetrachloride waste sites: 216-Z-9, 216-Z-1A, and 216-Z-18. The proposed plan recommended that remediation using SVE continue under the expedited response action until it is no longer necessary or is replaced by a component of a final action remedy.

The 200-PW-1 OU ROD (EPA et al., 2011) selected SVE as the final remedial action for carbon tetrachloride and methylene chloride contamination at the three primary carbon tetrachloride waste sites that had received carbon tetrachloride waste liquids (216-Z-9, 216-Z-1A, 216-Z-18). The ROD specified that SVE will continue to be implemented in accordance with the expedited response action until the remedial design/remedial action work plan is approved. In accordance with the ROD, the remedial design/remedial action work plan is to be submitted to the EPA for review by September 30, 2015.

The 200-PW-1 OU ROD established cleanup levels as soil vapor concentrations for carbon tetrachloride (100 ppmv) and methylene chloride (50 ppmv) and indicated that the cleanup levels will be refined and assessed using the results of the treatability test to ensure protection of the groundwater.

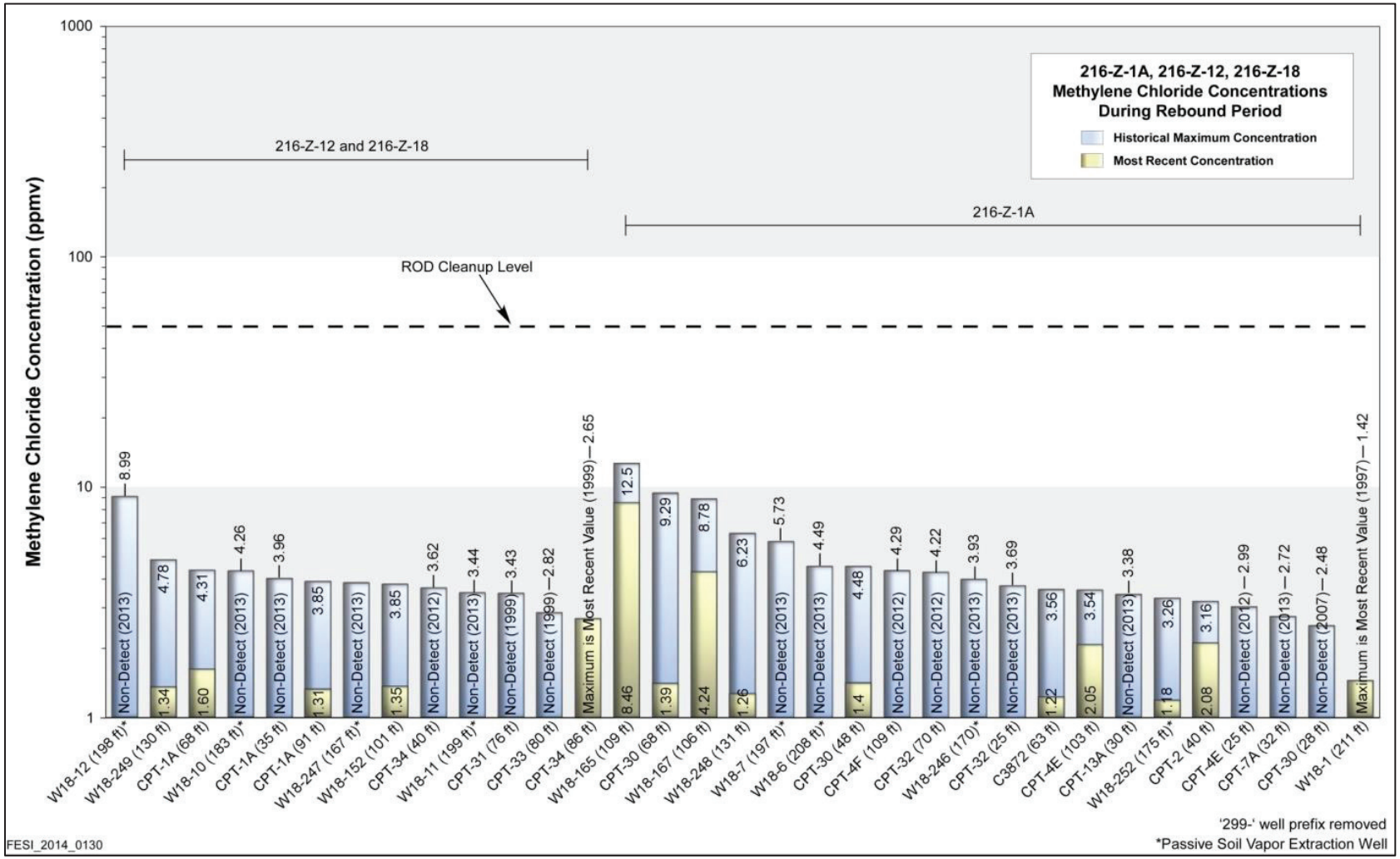
[2] Tedlar® is a registered trademark of E.I. DuPont de Nemours and Company, Wilmington, Delaware.

[3] SUMMA® is a registered trademark of Summa Consulting, LLC, Solana Beach, California.



Note: The logarithmic scale is provided on the Y-axis.

Figure A-27. Maximum Methylene Chloride Concentrations at Offline Monitoring Wells and Soil Vapor Probes at 216-Z-9 (1997 to 2013)



Note: The logarithmic scale is provided on the Y-axis.

Figure A-28. Maximum Methylene Chloride Concentrations at Offline Monitoring Wells and Soil Vapor Probes at 216-Z-1A/216-Z-18/216-Z-12 (1997 to 2013)

A8 Path Forward

In May 2014, DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*, was issued. The path forward document provided (1) an overview of the 200-PW-1 OU regulatory status; (2) a summary of the history of waste disposal, investigation activities, and remediation activities for the 200-PW-1 OU; and (3) an overview of SVE operations and performance over the past two decades. Recent guidance on evaluating the endpoint for SVE systems (PNNL-21843, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance*) was used as the basis for the 200-PW-1 OU path forward to determine when SVE operations for the 200-PW-1 OU can be terminated. The path forward uses site-specific evaluation and decision logic steps. EPA and DOE concurred with the path forward for evaluating transition of the 200-PW-1 OU SVE systems from the current cycle of active operations and monitoring to closure.

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Appendix B

200-PW-1 Operable Unit Calendar Year 2014 Rebound Study and Calendar Year 2015 Rebound Study – Soil Vapor Sampling Results

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Terms

B&K	Brüel & Kjær
bgs	below ground surface
CCU	Cold Creek unit
CPT	cone penetrometer
CY	calendar year
HEIS	Hanford Environmental Information System
OU	operable unit
ppmv	parts per million by volume
ROD	Record of Decision
SAP	sampling and analysis plan
SVE	soil vapor extraction

B1 Soil Vapor Rebound Sampling Results

This appendix provides the results of carbon tetrachloride and methylene chloride rebound sampling conducted in 2014 and 2015.

B1.1 2014 Results

Initial 2014 rebound sampling was conducted on May 14 and 15, 2014 in accordance with DOE/RL-2014-20, Rev. 0, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2014 Rebound Sampling*. The sampling and analysis methods identified in the sampling and analysis plan (SAP) for calendar year (CY) 2014 rebound sampling were consistent with methods used in previous years. Samples were collected at 64 soil vapor extraction (SVE) wells and soil vapor probes using new Tedlar[1] bags and were analyzed using a Brüel & Kjær (B&K)[2] analyzer in the field (Table B-1). Four split samples were collected in SUMMA[3] canisters for laboratory analysis, in accordance with the SAP.

Based on the initial results, confirmatory sampling was conducted on June 10, 2014 (Table B-1). During this event, samples were collected at 10 SVE wells and soil vapor probes in Tedlar bags for analysis using the B&K analyzer. Samples also were collected in SUMMA canisters at these same 10 locations for subsequent laboratory analysis.

B&K and laboratory analyses for carbon tetrachloride in samples collected during both sampling events were in agreement (Figure B-1). The cleanup level for carbon tetrachloride (100 parts per million by volume [ppmv]) in EPA et al., 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units* (hereafter referred to as the 200-PW-1 Operable Unit [OU] Record of Decision [ROD]), was exceeded at only two locations (two soil vapor probes screened above the Cold Creek unit [CCU]). Carbon tetrachloride also was detected in one field blank.

B&K and laboratory analyses for methylene chloride did not agree (Figure B-2). The B&K analyzer detected methylene chloride in every sample collected in a Tedlar bag, including the field blanks (Table B-1); however, laboratory analyses did not detect methylene chloride in any of the samples collected in SUMMA canisters. Another compound appears to be present in the Tedlar bag samples that is interfering with B&K analysis of methylene chloride; the source of this compound is likely the new Tedlar bags. The cleanup level for methylene chloride (50 ppmv) in the 200-PW-1 OU ROD (EPA et al., 2011) was not exceeded at any location sampled using a SUMMA canister; however, the cleanup level was exceeded at one SVE well screened below the CCU and sampled using a new Tedlar bag.

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[1] Tedlar is a registered trademark of E.I. DuPont de Nemours and Company, Wilmington, Delaware

[2] B&K is a trade name of Brüel & Kjær (Sound and Vibration Measurement A/S), Nærum, Denmark.

[3] SUMMA is a registered trademark of Summa Consulting, LLC, Solana Beach, California.

Table B-1. Analytical Results for Calendar Year 2014 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)				SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)					Comment
		05/14/2014 and 05/15/2014		06/10/2014		05/14/2014 and 05/15/2014		06/10/2014		HEIS Number	
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		
CPT-9A	18 (60)	1.27	5.38 B	—	—	—	—	—	—	—	—
CPT-9A	15 (50)	32.6	8.28 B	—	—	—	—	—	—	—	—
CPT-9A	64 (20)	24.0	8.25 B	—	—	—	—	—	—	—	—
CPT-29	14 (46)	3.83	5.29 B	—	—	—	—	—	—	—	—
CPT-2	12 (40)	1.87	6.68 B	—	—	—	—	—	—	—	—
CPT-7A	10 (32)	3.63 A	5.45 BA	—	—	5.13 D	0.0947 U	—	—	B2WJB2	—
CPT-C3872	19 (63)	16.9	9.22 B	—	—	—	—	—	—	—	—
299-W18-7	60 (197)	2 UA	6.44 BA	—	—	—	—	—	—	—	—
299-W18-248	40 (131)	58.5 A	8.12 BA	55.7 B	3.63 B	—	—	70.8 D	1.87 U	B2WWH9	—
299-W18-165	33 (109)	88.5 A	16.1 BA	65.0 B	13.6 B	—	—	68.1 D	1.72 U	B2WWJ0	—
299-W18-167	32 (106)	61.2	11.6 B	57.7 B	8.00 B	—	—	64.9 D	1.82 U	B2WWJ1	—
CPT-32	8 (25)	11.4	7.22 B	—	—	—	—	—	—	—	—
CPT-32	21 (70)	7.88	8.67 B	—	—	—	—	—	—	—	—
299-W18-6L	63 (208)	1.07	6.90 B	—	—	—	—	—	—	—	—
299-W18-246L	52 (170)	2 U	6.39 B	—	—	—	—	—	—	—	—
CPT-30	15 (48)	5.08	8.70 B	—	—	—	—	—	—	—	—
CPT-30	21 (68)	3.00	8.06 B	—	—	—	—	—	—	—	—
CPT-30	21 (68)	2.93	8.67 B	—	—	—	—	—	—	—	Duplicate
CPT-31	23 (76)	3.20	6.85 B	—	—	—	—	—	—	—	—
299-W18-252L	53 (175)	2 U	6.10 B	—	—	—	—	—	—	—	—
CPT-4F	33 (109)	5.64	7.36 B	—	—	—	—	—	—	—	—

Table B-1. Analytical Results for Calendar Year 2014 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)				SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)					Comment
		05/14/2014 and 05/15/2014		06/10/2014		05/14/2014 and 05/15/2014		06/10/2014		HEIS Number	
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		
CPT-4E	8 (25)	5.44	7.12 B	—	—	—	—	—	—	—	—
299-W18-1	64 (211)	2 U	6.14 B	—	—	—	—	—	—	—	—
299-W18-152	31 (101)	11.1	7.50 B	—	—	—	—	—	—	—	—
CPT-1A	11 (35)	6.51	7.14 B	—	—	—	—	—	—	—	—
CPT-1A	21 (68)	10.4 A	7.77 BA	—	—	—	—	—	—	—	—
CPT-1A	28 (91)	4.94 A	6.62 BA	—	—	1.69 D	0.0319 U	—	—	B2WJB3	—
CPT-33	24 (80)	3.75 A	7.79 BA	—	—	—	—	—	—	—	—
CPT-34	12 (40)	1.26 A	8.85 BA	—	—	—	—	—	—	—	—
299-W18-12	60 (198)	2 U	4.41 BA	—	—	—	—	—	—	—	—
299-W18-11L	61 (199)	2 U	4.54 BA	—	—	—	—	—	—	—	—
299-W18-10L	56 (183)	2 U	5.02 B	—	—	—	—	—	—	—	—
299-W18-249	40 (130)	8.60	6.70 BA	—	—	—	—	—	—	—	—
299-W18-247L	51 (167)	21.4 A	5.96 BA	—	—	—	—	—	—	—	—
299-W18-247L	51 (167)	20.1 A	6.54 BA	—	—	—	—	—	—	—	Duplicate
CPT-13A	9 (30)	2.61	5.16 B	—	—	—	—	—	—	—	—
CPT-28	12 (40)	—	—	9.87 B	3.29 B	—	—	—	—	—	—
CPT-28	18 (60)	48.6	4.71 B	49.2 B	3.89B	—	—	50.7 D	1.38 U	B2WWJ2	—
CPT-28	27 (87)	128 E	6.55 B	129 BE	5.52 B	—	—	125 D	4.17 U	B2WWJ3	—
CPT-17	3 (10)	6.10	5.47 B	—	—	—	—	—	—	—	—
299-W15-217	35 (114)	2.22	4.95 B	—	—	—	—	—	—	—	—
299-W15-84	55 (181)	12.2	7.98 B	—	—	—	—	—	—	—	—

Table B-1. Analytical Results for Calendar Year 2014 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)				SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)					Comment
		05/14/2014 and 05/15/2014		06/10/2014		05/14/2014 and 05/15/2014		06/10/2014		HEIS Number	
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		
CPT-18	11 (35)	1.98	5.60 B	—	—	—	—	—	—	—	—
CPT-18	23 (75)	7.35	8.06 B	—	—	—	—	—	—	—	—
299-W15-219U	29 (95)	2.17	5.76 B	—	—	3.15 D	0.0402 U	—	—	B2WJB4	—
299-W15-219	53 (175)	4.41	7.70 B	—	—	—	—	—	—	—	—
CPT-24	36 (118)	13.4	8.39 B	—	—	—	—	—	—	—	—
299-W15-218U	32 (106)	5.36	4.43 B	—	—	—	—	—	—	—	—
299-W15-218L	57 (188)	5.06	5.33 B	—	—	—	—	—	—	—	—
299-W15-86	38 (125)	24.7	8.74 B	—	—	—	—	—	—	—	—
299-W15-8U	31 (103)	16.3	16.4 B	—	—	—	—	—	—	—	—
299-W15-8U	31 (103)	16.2	16.2 B	—	—	—	—	—	—	—	Duplicate
299-W15-8L	55 (180)	7.00	38.5 B	9.99 B	78.1 B	—	—	7.59 D	0.182 U	B2WWJ4	—
C4938 (P69C)	20 (64)	54.6	31.0 B	47.7 B	27.7 B	—	—	47.7 D	1.2 U	B2WWJ5	—
C4937 (P66D)	20 (64)	35.4	36.2 B	31.5 B	28.9 B	—	—	29.9 D	0.761 U	B2WWJ6	—
C5340 (P68C)	20 (64)	14.3	23.8 B	—	—	—	—	—	—	—	—
CPT-21A	20 (65)	66.4	7.56 B	67.8 B	6.13 B	—	—	69.5 D	2.13 U	B2WWJ7	—
CPT-21A	26 (86)	98.8	7.06 B	101 BE	5.72 B	144 D	2.58 U	105 D	3.29 U	B2WJB5, B2WWJ8	—
299-W15-216U	23 (75)	5.19	3.42B	—	—	—	—	—	—	—	—
299-W15-216L	55 (179)	3.93	3.61 B	—	—	—	—	—	—	—	—
CPT-27	10 (33)	3.02	4.56 B	—	—	—	—	—	—	—	—
299-W15-82L	25 (83)	5.92	10.5 B	—	—	—	—	—	—	—	—

Table B-1. Analytical Results for Calendar Year 2014 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)				SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)				HEIS Number	Comment
		05/14/2014 and 05/15/2014		06/10/2014		05/14/2014 and 05/15/2014		06/10/2014			
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		
299-W15-9L	54 (176)	5.14	6.74 B	—	—	—	—	—	—	—	—
299-W15-95L	44 (144)	12.2	7.59 B	—	—	—	—	—	—	—	—
CPT-16	8 (25)	1.51	5.33 B	—	—	—	—	—	—	—	—
CPT-16	20 (65)	5.22	5.11 B	—	—	—	—	—	—	—	—
299-W15-220U	27 (88)	2.08	4.12 B	—	—	—	—	—	—	—	—
299-W15-220L	49 (162)	2.98	3.74 B	—	—	—	—	—	—	—	—
299-W15-220L	49 (162)	3.15	4.55 B	—	—	—	—	—	—	—	Duplicate
Field blank		2 U	5.06	—	—	—	—	—	—	—	—
Field blank		2 U	4.33	3.59	3.12	—	—	—	—	—	—

A = indicates an issue with the chain of custody that could affect data usability
B = analyte was detected in both associated quality control blank and sample
B&K = Brüel & Kjær
bgs = below ground surface
CPT = cone penetrometer
D = analyte was reported at a secondary dilution factor
E = concentration exceeds the calibration range of the analytical instrument
HEIS = Hanford Environmental Information System
ppmv = parts per million by volume
U = analyzed for but not detected

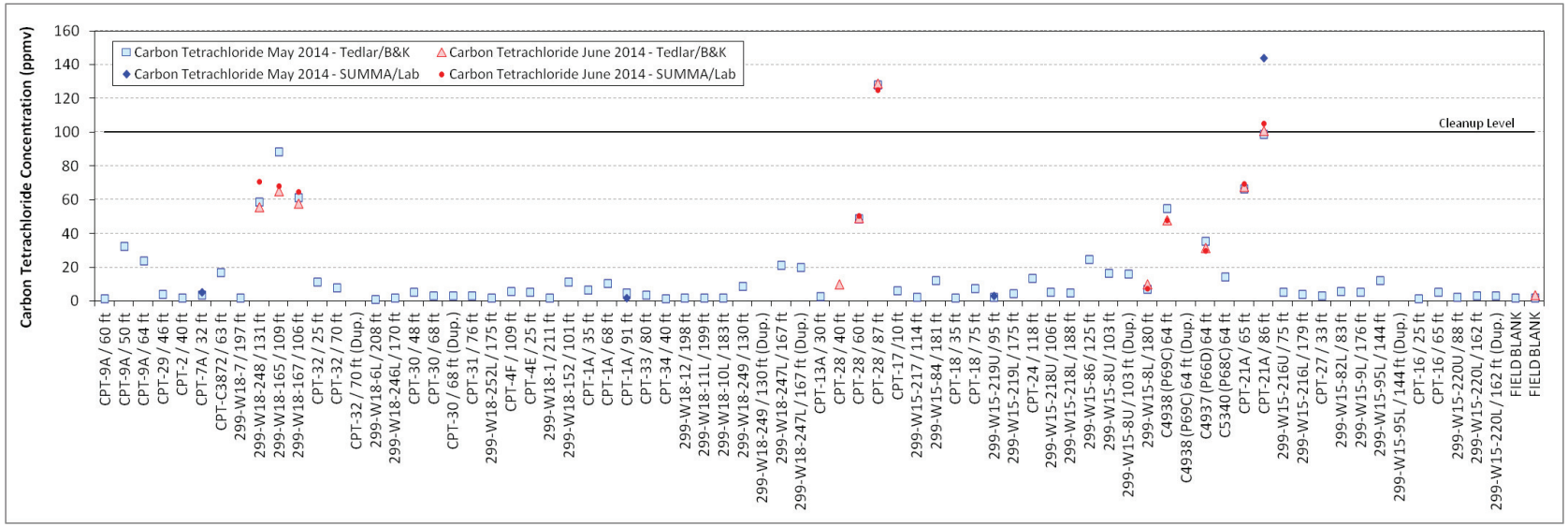

Figure B-1. Carbon Tetrachloride Concentrations Measured during 2014 Rebound Sampling for the 200-PW-1 OU

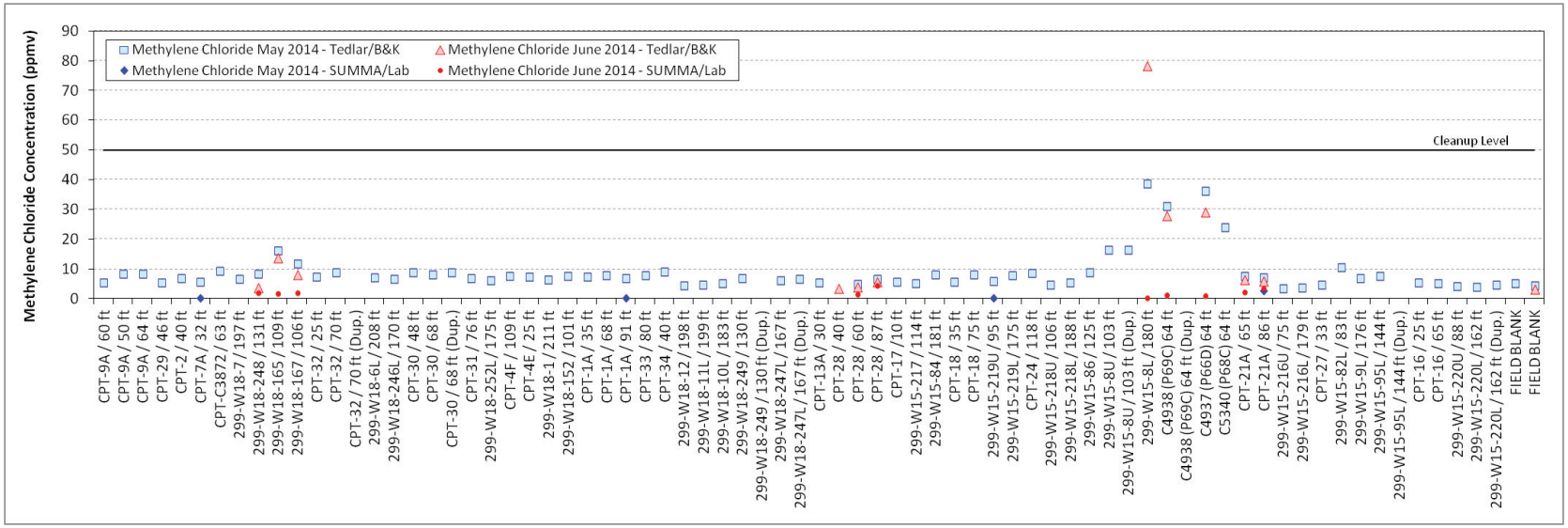

Figure B-2. Methylene Chloride Concentrations Measured during 2014 Rebound Sampling for the 200-PW-1 OU

B1.2 2015 Results

Rebound sampling was conducted on June 5 and 6, 2015 in accordance with DOE/RL-2014-20, Rev. 1, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit Calendar Year 2015 Rebound Sampling*. Methods identified in the SAP for CY 2015 rebound sampling were consistent with those used in previous years. Samples were collected at 64 SVE wells and soil vapor probes using new Tedlar bags and were analyzed using a B&K analyzer in the field (Table B-2). Six split samples were collected in SUMMA canisters for laboratory analysis in accordance with the SAP.

B&K and laboratory analyses for carbon tetrachloride in samples collected during both sampling events were in agreement (Figure B-3). The cleanup level for carbon tetrachloride (100 ppmv) in the 200-PW-1 OU ROD (EPA et al., 2011) was exceeded at only two locations (two soil vapor probes screened above the CCU).

B&K and laboratory analyses for methylene chloride did not agree (Figure B-4). The B&K analyzer detected methylene chloride in every sample collected in a Tedlar bag, including the field blanks (Table B-2). However, laboratory analyses did not detect methylene chloride in any of the samples collected in SUMMA canisters, with the exception of one detection (at a concentration of 0.00027 ppmv) in a well screened above the CCU. Prior to collecting the rebound samples on June 5 and 6, 2015, the new Tedlar bags were filled with zero air (20.9 percent oxygen, 79.1 percent nitrogen), which was then analyzed using the B&K multi-gas analyzer. Analysis of the zero air samples was conducted to mitigate the interference noted in the 2014 analyses of methylene chloride using B&K (Section B.1.1). Methylene chloride was detected in the zero air samples. In accordance with the SAP (DOE/RL-2014-20, Rev. 1), data from the zero air tests and soil vapor sampling operation were evaluated through the CH2M HILL Plateau Remediation Company Sample Management and Reporting group request for data review process. The request for data review process performed a comparison study between the zero air test results and soil vapor sampling results, which included the results of field blanks and method blanks to determine if the field sampling data were significantly impacted by false-positive interference or related complications. The request for data review investigation determined that data were significantly impacted by false-positive interference, and a laboratory data qualifier of “B” was associated with the results. The “B” qualifier indicates that the analyte was detected in both the associated quality control blank and the sample. Methylene chloride field data were determined to be suspect. The cleanup level for methylene chloride (50 ppmv) in the 200-PW-1 OU ROD (EPA et al., 2011) was not exceeded at any location sampled using a SUMMA canister.

B2 Conclusions

This chapter provides conclusions on which data sets are usable for evaluation of rebound.

B2.1 2014 Conclusions

Based on comparison of B&K and laboratory results, 2014 carbon tetrachloride concentrations in samples collected using Tedlar bags and analyzed using the B&K analyzer are usable for evaluating rebound. Based on comparison of B&K and laboratory results, 2014 methylene chloride concentrations in samples collected using Tedlar bags and analyzed using the B&K analyzer are not usable.

Table B-2. Analytical Results for Calendar Year 2015 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)		SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)			Comment
		06/05/2015 and 06/06/2015		06/05/2015 and 06/06/2015			
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	HEIS Number	
CPT-9A	18 (60)	4.08	5.15 BY	—	—	—	—
CPT-9A	15 (50)	31.8	7.31 BY	—	—	—	—
CPT-9A	20 (64)	23.5	6.93 BY	—	—	—	—
CPT-29	14 (46)	6.11	4.62 BY	—	—	—	—
CPT-2	12 (40)	1 U	4.67 BY	—	—	—	—
CPT-7A	10 (32)	4.93	4.74 BY	—	—	—	—
CPT-C3872	19 (63)	25.8	8.07 BY	—	—	—	—
299-W18-7	60 (197)	1.33	4.44 BY	0.00618 U	0.00013 U	B31CC2	—
299-W18-248	40 (131)	36.3	6.92 BY	—	—	—	—
299-W18-165	33 (109)	62.9	15.3 BY	42.1 D	1.56 U	B31CC3	—
299-W18-167	32 (106)	82.4	12.8 BY	—	—	—	—
CPT-32	8 (25)	15.9	5.58 BY	—	—	—	—
CPT-32	21 (70)	14.6	6.78 BY	—	—	—	—
CPT-32	21 (70)	14.5	6.53 BY	—	—	—	Duplicate
299-W18-6L	63 (208)	1.65	4.82 BY	—	—	—	—
299-W18-246L	52 (170)	1.15	4.48 BY	—	—	—	—
CPT-30	15 (48)	2.66	6.71 BY	—	—	—	—
CPT-30	21 (68)	3.95	6.30 BY	2.18 D	0.0013 U	B31CC4	—

Table B-2. Analytical Results for Calendar Year 2015 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)		SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)			Comment
		06/05/2015 and 06/06/2015		06/05/2015 and 06/06/2015		HEIS Number	
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		
CPT-31	23 (76)	4.62	6.12 BY	—	—	—	—
299-W18-252L	53 (175)	1 U	4.94 BY	—	—	—	—
CPT-4F	33 (109)	8.84	6.34 BY	—	—	—	—
CPT-4E	8 (25)	8.83	5.66 BY	—	—	—	—
299-W18-1	64 (211)	—	—	—	—	—	—
299-W18-152	31 (101)	10.7	6.42 BY	—	—	—	—
CPT-1A	11 (35)	5.86	6.06 BY	—	—	—	—
CPT-1A	21 (68)	9.39	6.51 BY	—	—	—	—
CPT-1A	28 (91)	11.5	6.29 BY	—	—	—	—
CPT-33	24 (80)	5.27	5.82 BY	—	—	—	—
CPT-34	12 (40)	1.26	5.84 BY	—	—	—	—
299-W18-12	60 (198)	1 U	3.52 BY	—	—	—	—
299-W18-11	61 (199)	1 U	4.10 BY	—	—	—	—
299-W18-10L	56 (183)	1 U	3.24 BY	—	—	—	—
299-W18-249	40 (130)	11.1	6.17 BY	—	—	—	—
299-W18-249	40 (130)	11.2	6.12 BY	—	—	—	Duplicate
299-W18-247L	51 (167)	1 U	3.70 BY	—	—	—	—
CPT-13A	9 (30)	2.03	4.40 BY	—	—	—	—

Table B-2. Analytical Results for Calendar Year 2015 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)		SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)			Comment
		06/05/2015 and 06/06/2015		06/05/2015 and 06/06/2015		HEIS Number	
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		
CPT-28	12 (40)	12.5	4.36 BY	—	—	—	—
CPT-28	27 (87)	125 E	7.70 BY	111 D	3.90 U	B31CC5	—
CPT-17	3 (10)	1.97	4.26 BY	—	—	—	—
299-W15-217	35 (114)	1 U	3.57 BY	—	—	—	—
299-W15-84	55 (181)	10.5	5.82 BY	—	—	—	—
CPT-18	11 (35)	1.08	4.06 BY	—	—	—	—
CPT-18	23 (75)	7.93	5.96 BY	—	—	—	—
299-W15-219U	29 (95)	8.02	6.36 BY	—	—	—	—
299-W15-219L	53 (175)	—	—	—	—	—	—
CPT-24	36 (118)	12.9	7.08 BY	—	—	—	—
299-W15-218U	32 (106)	6.89	6.19 BY	—	—	—	—
299-W15-218L	57 (188)	3.35	5.46 BY	—	—	—	—
299-W15-86	38 (125)	32.7	12.4 BY	—	—	—	—
299-W15-8U	31 (103)	1.35	4.01 BY	0.107	0.00027	B31CC6	—
299-W15-8L	55 (180)	6.79	58.9 BY	—	—	—	—
C4938 (P69C)	20 (64)	1 U	4.29 BY	—	—	—	—
C4938 (P69C)	20 (64)	1 U	3.81 BY	—	—	—	Duplicate
C4937 (P66D)	20 (64)	1 U	3.43 BY	—	—	—	—

Table B-2. Analytical Results for Calendar Year 2015 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)		SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)			Comment
		06/05/2015 and 06/06/2015		06/05/2015 and 06/06/2015		HEIS Number	
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		
C5340 (P68C)	20 (64)	1 U	4.01 BY	—	—	—	—
CPT-21A	20 (64)	69.3	7.15 BY	—	—		
CPT-21A	26 (86)	103 E	8.10 BY	128 D	3.08 U	B31CC7	—
299-W15-216U	23 (75)	7.07	3.92 BY	—	—	—	—
299-W15-216L	55 (179)	1.27	4.26 BY	—	—	—	—
CPT-27	10 (33)	1.79	3.98 BY	—	—	—	—
299-W15-82L	25 (83)	5.34	10.6 BY	—	—	—	—
299-W15-9L	54 (176)	2.23	3.64 BY	—	—	—	—
299-W15-95L	44 (144)	12.1	7.02 BY	—	—	—	—
299-W15-95L	44 (144)	12.4	6.50 BY	—	—	—	Duplicate
CPT-16	8 (25)	1.73	3.50 BY	—	—	—	—
CPT-16	20 (65)	5.35	3.65 BY	—	—	—	—
299-W15-220U	27 (88)	2.71	3.45 BY	—	—	—	—
299-W15-220L	49 (162)	3.46	4.82 BY	—	—	—	—
Field blank		1 U	3.92	—	—	—	—
Field blank		1 U	3.06	—	—	—	—

Table B-2. Analytical Results for Calendar Year 2015 Soil Vapor Rebound Samples

Sample Location	Depth (m [ft] bgs)	Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer)		SUMMA Canister Samples (Analyzed in Laboratory Using Gas Chromatography/Mass Spectrometry)			Comment
		06/05/2015 and 06/06/2015		06/05/2015 and 06/06/2015		HEIS Number	
		Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)	Carbon Tetrachloride (ppmv)	Methylene Chloride (ppmv)		

B = analyte was detected in both associated quality control blank and sample
B&K = Brüel & Kjær
bgs = below ground surface
CPT = cone penetrometer
D = analyte was reported at a secondary dilution factor
E = concentration exceeds the calibration range of the analytical instrument
HEIS = Hanford Environmental Information System
ppmv = parts per million by volume
U = analyzed for but not detected
Y = suspect result

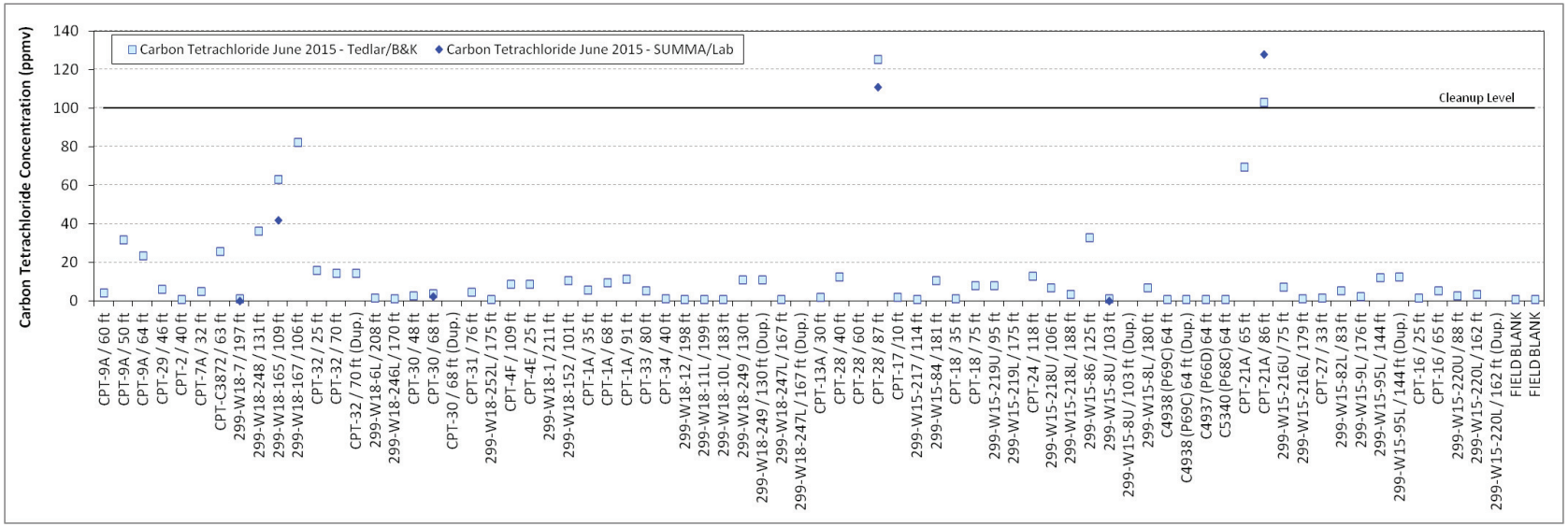

Figure B-3. Carbon Tetrachloride Concentrations Measured during 2015 Rebound Sampling for the 200-PW-1 OU

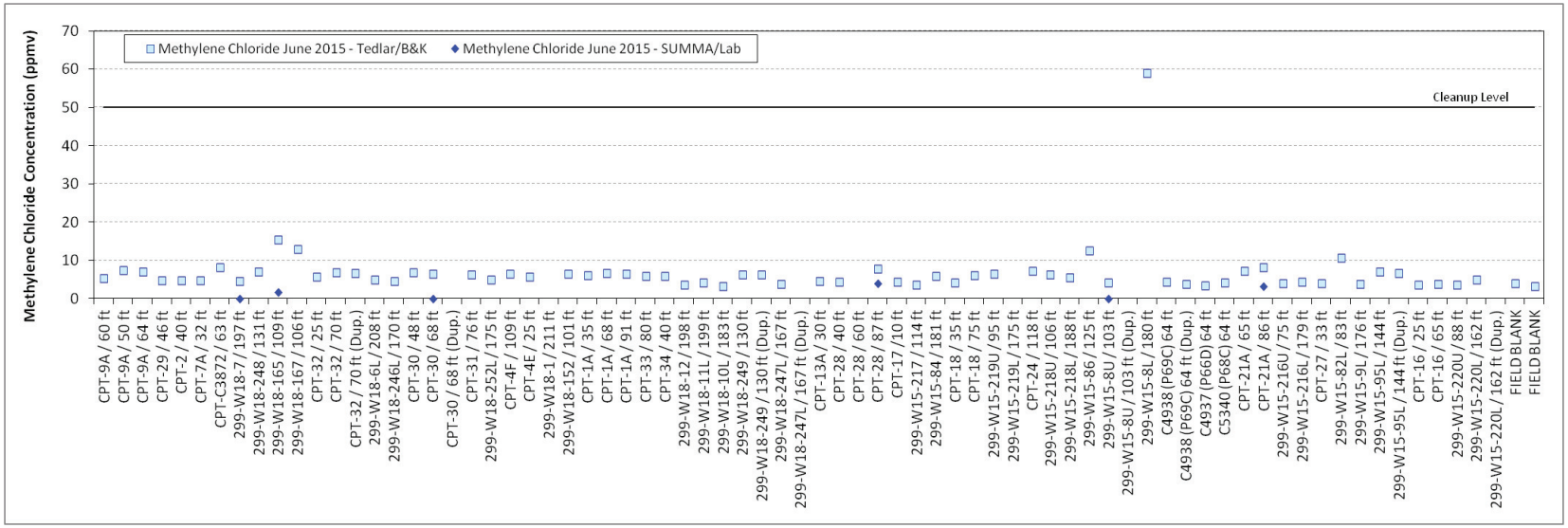

Figure B-4. Methylene Chloride Concentrations Measured during 2015 Rebound Sampling for the 200-PW-1 OU

B2.2 2015 Conclusions

Based on comparison of B&K and laboratory results, 2015 carbon tetrachloride concentrations in samples collected using Tedlar bags and analyzed using the B&K analyzer are usable for evaluating rebound. Based on comparison of B&K and laboratory results, 2015 methylene chloride concentrations in samples collected using Tedlar bags and analyzed using the B&K analyzer are not usable.

B3 References

DOE/RL-2014-20, 2014, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2014 Rebound Sampling*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1404210408.

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Appendix C

Soil Vapor Extraction Endstate Tool (SVEET) Calculations

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Terms

CCU	Cold Creek unit
OU	operable unit
ppmv	parts per million by volume
STOMP	Subsurface Transport Over Multiple Phases
SVE	soil vapor extraction
SVEET	Soil Vapor Extraction Endstate Tool

C1 Introduction

A procedure for calculating and estimating the groundwater contaminant concentration resulting from a vadose zone source, authored by Pacific Northwest National Laboratory, the U.S. Army Corps of Engineers, and the U.S. Environmental Protection Agency, is provided in PNNL-21843, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance* (hereafter referred to as SVE Closure Guidance). The procedure is based on a generalized conceptual model defined by key parameters describing the contaminant of interest, the location/extent of the vadose zone source, the source strength, vadose zone porous media properties, groundwater flow characteristics, and the magnitude of recharge (infiltration). For the calculation, 972 pre-modeled scenarios were simulated with the Subsurface Transport Over Multiple Phases (STOMP) code (PNNL-15782, *STOMP Subsurface Transport Over Multiple Phases, Version 4.0, User's Guide*) to obtain groundwater concentration results.

The pre-modeled scenarios represent combinations of parameter values for those parameters where the groundwater concentration results exhibit a nonlinear relationship with the parameter value. The STOMP simulation results are tabulated and the estimated impact to groundwater can be determined for site-specific combinations of parameters by interpolation between the relevant pre-modeled scenario results. The interpolated site-specific result is further scaled to account for parameters having a linear relationship with groundwater concentration (e.g., recharge or Henry's law constant).

The calculation procedure from the SVE Closure Guidance has been implemented in the Soil Vapor Extraction Endstate Tool (SVEET) software.[1] SVEET is a spreadsheet tool that allows users to easily enter data and calculate the estimated groundwater concentration for one or more scenarios conforming to the generalized conceptual model described in the SVE Closure Guidance (PNNL-21843).

C2 SVEET Predictions for the 216-Z-9, 216-Z-1A, and 216-Z-18 Waste Sites

SVEET was used in 2014 to estimate the groundwater concentrations resulting from vadose zone sources at the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib. Prior studies (e.g., PNNL-21326, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*) have determined that remaining vadose zone contamination is primarily located within the fine-grained Cold Creek unit (CCU), which is taken to be the source zone for the purposes of SVEET. Parameters for the generalized conceptual model, upon which SVEET is based (Figure C-1), were generally taken from the treatability test, although three aspects required additional consideration: definition of the source strength, location/thickness of the source, and the lateral extent of the source area. These three aspects are discussed below. The full set of SVEET inputs are listed in Table C-1 for these three waste sites.

[1] The software for the Soil Vapor Extraction Endstate Tool (SVEET) is available online at http://bioprocess.pnnl.gov/SVEET_Request.htm.

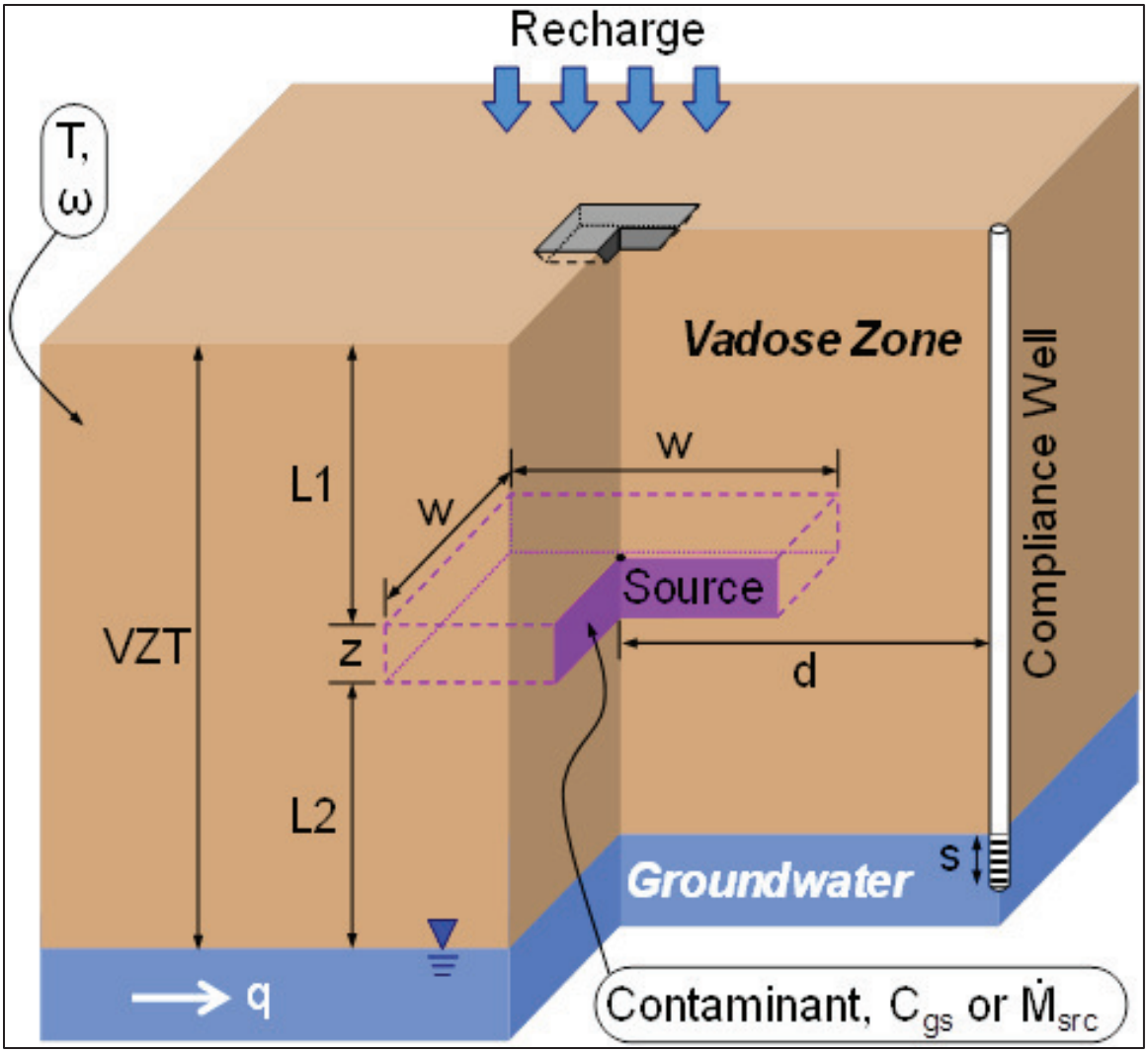

Figure C-1. Generalized Conceptual Model for SVEET

One aspect required for SVEET is a definition of the vadose zone source strength. Examination of soil vapor monitoring data demonstrated that the level of contamination above the CCU was greater than the contamination below the CCU at all sites, and that the contamination below the CCU at the 216-Z-1A and 216-Z-18 sites is lower than the contamination below the CCU at the 216-Z-9 site. Because the key factor for impact on groundwater concentrations is the contamination emanating from the CCU into the zone below the CCU, the determination of source strength focused on data from below the CCU. Of the samples collected at the 216-Z-9 site in 2014 (Appendix B), the highest concentration detected was 24.7 parts per million by volume (ppmv) at well 299-W15-86 on May 15, 2014. The 2014 measurements beneath the 216-Z-1A and 216-Z-18 sites were all below detection limits, except for an atypical result of 21.4 ppmv at well 299-W18-247L. Thus, the maximum result from the 2012–2013 time period was selected as a conservative soil gas concentration below the CCU at 216-Z-1A and 216-Z-18 for SVEET calculations. At the 216-Z-1A site, well 299-W18-246L had an average result of 13.9 ppmv on July 15, 2012. At the 216-Z-18 site, well 299-W18-247L had a result of 9.65 ppmv on May 20, 2012 (SGW-54566, *Performance Evaluation Report for Soil Vapor Extraction Operations at the 200-PW-1 Operable Unit Carbon Tetrachloride Site, Calendar Year 2012*).

Table C-1. Information on the 216-Z-9, 216-Z-1A, and 216-Z-18 Waste Sites Used as Input to SVEET

User Input Source/Transport Parameters	216-Z-9	216-Z-1A	216-Z-18	Data Source
Contaminant	Carbon tetrachloride	Carbon tetrachloride	Carbon tetrachloride	—
Temperature (°C)	16	16	16	PNNL-22062
Average moisture content (wt %)	6.5	6.5	6.5	PNNL-21326
Average recharge (cm/yr)	0.4	0.4	0.4	PNNL-21326
Vadose zone thickness (m)	60	60	60	Appendix A cross sections
Depth to top of source (m)	24	29	29	Appendix A cross sections
Source thickness (m)	6	6	6	Appendix A cross sections
Source width[a] (m)	90	90	90	PNNL-21326
Groundwater Darcy velocity (m/d)	0.00545	0.00545	0.00545	PNNL-21326
Distance to compliance well[b] (m)	25	25	25	—
Compliance well screen length (m)	10	10	10	PNNL-21326
Source strength input type	Gas concentration	Gas concentration	Gas concentration	—
Source gas concentration (ppmv)	24.7	13.9	9.65	2014 and 2012 soil vapor data

References: PNNL-12326, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*; PNNL-22062, *Abiotic Degradation Rates for Carbon Tetrachloride and Chloroform: Final Report*.

a. The SVEET software does not allow a source width value larger than 50 m (164 ft). However, for a source strength specified as a gas concentration, the results for several source widths ≤50 m (≤164 ft) can be linearly extrapolated to a source width of 90 m (295 ft), as discussed in the text.

b. A downgradient distance of 25 m (82 ft) to the compliance well was selected as the closest point to the source for these scenarios that is available in SVEET.

ppmv = parts per million by volume

SVEET = Soil Vapor Extraction Endstate Tool

A second aspect is the vertical position and thickness of the source zone. The vadose zone thickness of nominally 60 m (197 ft) can be represented in SVEET. However, SVEET constrains the source zone thickness to be between 10 and 50 percent of the vadose zone thickness, so the nominal 4 m (13 ft) thickness of the CCU source zone must be represented as 6 m (20 ft) thick. Because the thickness of the CCU source zone was adjusted, the distance between ground surface and the top of the source zone was also adjusted to maintain an accurate distance between the bottom of the CCU source and the groundwater. The distance between the source and the groundwater is a key aspect with respect to the influence of vadose contamination on concentrations in the groundwater. The distance from the bottom

of the CCU to groundwater is nominally 30 m (98 ft) at the 216-Z-9 site and 25 m (82 ft) at the 216-Z-1A/216-Z-18 sites.

The final aspect to consider is the size of the source area (i.e., lateral footprint). The size of the source area at the 216-Z-9 site was determined in the treatability test report (PNNL-21326) to be nominally 90 m by 90 m (295 ft by 295 ft). However, data are not available to calculate the source size in the same manner for the 216-Z-1A and 216-Z-18 sites; thus, the conservative approach was to use the same source dimensions for all three sites. This selection of the same source size for 216-Z-1A and 216-Z-18 as used for 216-Z-9 is conservative because when the source strength is defined by a given soil gas concentration, the impact to groundwater increases linearly as the size increases (i.e., there is more mass impacting the groundwater as the source size increases). Although the SVEET software tool does not allow for entry of a source size greater than a 50 m by 50 m (164 ft by 164 ft) area, it is straightforward to linearly extrapolate from key sizes (10, 20, 30, and 50 m [33, 66, 98, and 164 ft]) to the 90 m (295 ft) side length, as discussed below.

The SVEET tool estimates the impact of a vadose zone contaminant source on clean groundwater. This represents the most conservative situation because the driving force for mass transfer into the groundwater is the largest. If the groundwater already contains contamination, then the driving force for mass transfer to the groundwater is reduced. With groundwater concentrations above a certain level (which depends on the contaminant, temperature, and both aqueous and soil gas concentrations), mass transfer will be from the groundwater into the vadose zone soil gas. Appendix D discusses the conditions when mass transfer will occur into or out of the groundwater.

The SVEET inputs, calculated parameters, and outputs for each of the three waste sites, which each have four scenarios, are shown in Table C-2. The scenarios (for a given waste site) differ only in the size of the source width, applying the key values of 10, 20, 30, and 50 m (33, 66, 98, and 164 ft). Estimates of the groundwater concentrations resulting from the vadose zone source are obtained for the set of scenarios to allow extrapolation to the 90 m (295 ft) source width specified for the waste sites (Table C-1). When the source strength is defined in SVEET based on a soil gas concentration, the impact to groundwater concentrations increases linearly as the source size increases because more mass is impacting the groundwater as the source size increases. Figure C-2 shows the linear extrapolation of the results from the four scenarios to the 90 m (295 ft) source width size for all three waste sites for a 25 m downgradient distance from the center of the source area.

The SVEET estimates of the impacts of vadose zone source on groundwater (for the conditions specified in Table C-1) are listed in Table C-3. The predicted impacts of sources at the 216-Z-1A and 216-Z-18 waste sites (17 and 12 µg/L, respectively) are lower than the predicted impact for the 216-Z-9 source (27 µg/L). As would be expected from the source strengths, the 216-Z-9 site is estimated to have the most significant impact on groundwater concentrations. Thus, calculations based on the 216-Z-9 site, as the limiting case, would support soil vapor extraction (SVE) endpoint decisions for all three sites.

The SVEET results are conservative for two reasons:

- SVEET estimates the impact of vadose zone contamination on clean groundwater. Appendix D discusses the conditions for which mass transfer (e.g., via vapor diffusion) will be going either into the groundwater from the vadose zone or out of the groundwater into the vadose zone. Under the current contaminated conditions in the underlying 200-ZP-1 Operable Unit (OU) aquifer, mass transfer from the vadose zone into the groundwater would be inhibited.

- The SVEET calculations assume that the vadose zone contaminant source remains constant over time. In reality, the source becomes depleted by diffusive mass transfer. The constant source strength is conservative because it computes the maximum contribution of the vadose zone source to a groundwater contaminant plume.

Table C-2. SVEET Inputs, Calculated Parameters, and Results for Source Widths of 10, 20, 30, and 50 m at All Three Waste Sites

SVE Endstate Tool (SVEET) — Version 1.0.0

Described in: *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance* — 2012-Sep-24

User Input														
	Scenario Name:	—	Z-9	Z-9	Z-9	Z-9	Z-1A	Z-1A	Z-1A	Z-1A	Z-18	Z-18	Z-18	Z-18
	Contaminant:	—	CT	CT	CT	CT	CT	CT	CT	CT	CT	CT	CT	CT
T	Temperature:	[°C]	16	16	16	16	16	16	16	16	16	16	16	16
ω	Avg. Moisture Content:	[wt %]	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
R	Avg. Recharge:	[cm/yr]	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
VZT	Vadose Zone Thickness:	[m]	60	60	60	60	60	60	60	60	60	60	60	60
L1	Depth to Top of Source:	[m]	24	24	24	24	29	29	29	29	29	29	29	29
z	Source Thickness:	[m]	6	6	6	6	6	6	6	6	6	6	6	6
w (= l)	Source Width (= Length):	[m]	10	20	30	50	10	20	30	50	10	20	30	50
q	GW Darcy Velocity:	[m/day]	0.00545	0.00545	0.00545	0.00545	0.00545	0.00545	0.00545	0.00545	0.00545	0.00545	0.00545	0.00545
d	Distance to Compliance Well:	[m]	25	25	25	25	25	25	25	25	25	25	25	25
s	Compl. Well Screen Length:	[m]	10	10	10	10	10	10	10	10	10	10	10	10
	Source Strength Input Type:	—	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration	Gas Concentration
C_{gs}	Source Gas Concentration:	[ppmv]	24.7	24.7	24.7	24.7	13.9	13.9	13.9	13.9	9.65	9.65	9.65	9.65
$\dot{M}_{src}$	Source Mass Discharge:	[g/day]												
Calculated Input														
STR	Source Thickness Ratio*:	[--]	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
SA	Areal Footprint of Source*:	[m²]	100	400	900	2500	100	400	900	2500	100	400	900	2500
RSP	Relative Source Position*:	[--]	0.80	0.80	0.80	0.80	1.16	1.16	1.16	1.16	1.16	1.16	1.16	1.16
L2	Distance – Source to GW:	[m]	30.00	30.00	30.00	30.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
H	Henry's Law Constant**:	[--]	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761	0.761
Result – Estimated Groundwater Contaminant Concentration at Selected Compliance Well														
C_w	Final Groundwater Conc'n:	[µg/L]	6.2	8.9	11.7	16.6	4.1	5.8	7.5	10.3	2.8	4.1	5.2	7.2

		SVEET GW Conc'n Output (µg/L)				Extrapolated GW Conc'n (µg/L)
Site	**width (m):**	**10**	**20**	**30**	**50**	**90**
216-Z-9		6.2	8.9	11.7	16.6	27
216-Z-1A		4.1	5.8	7.5	10.3	17
216-Z-18		2.8	4.1	5.2	7.2	12

distance to compliance well = 25 m

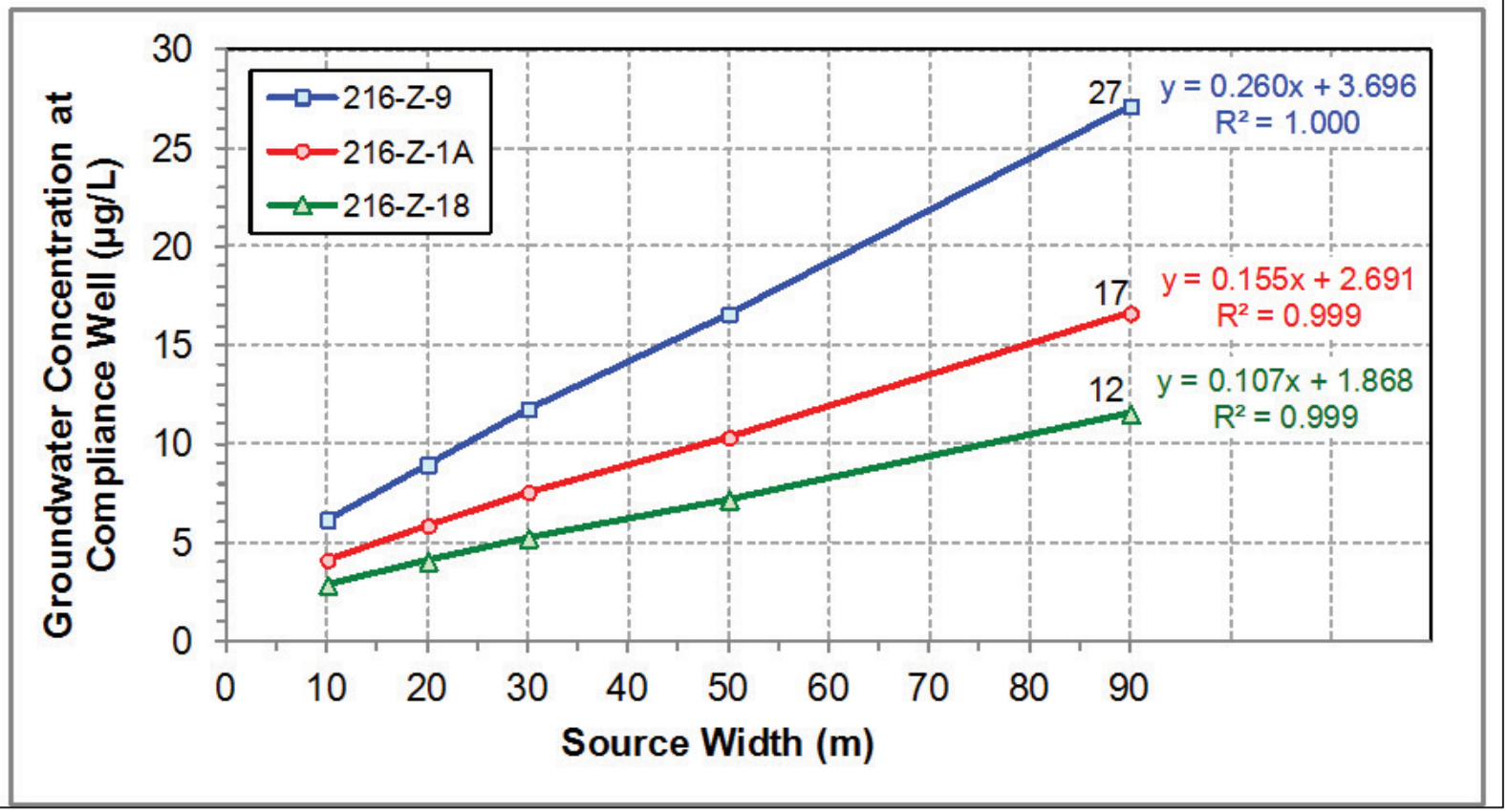

Figure C-2. SVEET Results Extrapolated to a Source Width of 90 m

Table C-3. SVEET Analysis Results for All Three Waste Sites (90 m Source Width, 25 m from Source Center)

Waste Site	216-Z-9	216-Z-1A	216-Z-18
Estimated groundwater concentration (µg/L)	27	17	12

C3 SVEET Versus Treatability Test Results

The SVEET spreadsheet tool is used to estimate concentrations of volatile contaminants in the groundwater resulting from a contaminant source in the vadose zone for a specified set of site and contaminant source properties. Because SVEET was designed for applications across a broad range of potential site conditions, generalizations were incorporated into the numerical simulations and provide the basis for the SVEET output. Thus, a site-specific numerical analysis (e.g., the treatability test [PNNL-21326]) will produce slightly different results compared to SVEET due to site-specific elements not available as inputs to SVEET and also due to differences in the numerical simulation grids. Although both approaches include the assumptions of clean groundwater and a constant source (making estimates of the impact to groundwater conservative, as previously discussed), there are some distinctions between the SVEET approach and the treatability test approach that can produce differing results.

As previously discussed, both SVEET and the treatability test analyses were conducted for the 216-Z-9 site. The SVEET estimated that the groundwater carbon tetrachloride concentration would be approximately 27 µg/L (based on soil vapor concentration of 24.7 ppmv at the source). This estimate is consistent with the 24 µg/L groundwater concentration calculated in the treatability test and corroborates the SVEET calculations. Thus, the relative comparisons between the SVEET estimates for the three waste sites (discussed in Section 5.4.1.1 in the main text and in Section C2 of this appendix) are appropriate.

The estimated concentrations of volatile contaminants in the groundwater from these two analyses are similar, although the results from the treatability test are lower. Contributing factors that account for the differences include the following:

- The treatability test analysis used the actual CCU thickness in the analysis (about 4 m [13 ft]), whereas the SVEET analysis was constrained to apply a CCU thickness of 6 m (19.7 ft) (10 percent of the total vadose zone thickness). Thus, the surface area of the source is larger in SVEET and results in a somewhat higher, more conservative estimate for the groundwater concentration.

- The treatability test analysis used a dimensionless Henry's law coefficient value of 0.813 (based on available literature). The SVEET tool incorporates a calculation method for the Henry's law coefficient as a function of temperature based on published vapor pressure and solubility data as functions of temperature (see Appendix D, Section D2). SVEET calculated the value of the dimensionless Henry's law coefficient to be 0.761, which is lower than the value used in the treatability test. A lower, dimensionless Henry's law coefficient will result in a higher and more conservative estimate for the groundwater concentration.

- The treatability test analysis incorporated a vadose zone moisture content distribution based on the variation in sediment properties at the site through multiple geological layers. In contrast, the SVEET analysis was constrained to use a single moisture content to represent the entire vadose zone. The moisture content impacts the vapor diffusion coefficients. Differences in magnitude and

distribution of moisture content result in relatively minor differences in the estimates for the groundwater concentration.

- The numerical grid for the pre-modeled scenarios that are the basis for SVEET calculations differs from the numerical grid that was used in the treatability test analysis because SVEET accommodates a broader range of potential site configurations. In addition, the SVEET results are based on linear interpolation of pre-modeled results to estimate the groundwater concentration. These differences in the numerical simulation grid and interpolation again result in relatively minor differences in the estimated groundwater concentrations.

Given the above factors, the SVEET groundwater concentration estimates are expected to be higher and more conservative than the results from the treatability test (PNNL-21326). The SVEET results provide an appropriate means to assess the relative impacts to groundwater at the 216-Z-9, 216-Z-1A, and 216-Z-18 waste sites. However, the site-specific analysis from the treatability test is a more accurate estimate of the groundwater carbon tetrachloride concentrations resulting from the 216-Z-9 vadose zone contaminant source.

The SVEET and treatability test assessments provided a basis for proceeding with the SVE evaluation based only on the 216-Z-9 site. The SVEET estimates for the 216-Z-9, 216-Z-1A, and 216-Z-18 sites have proven to be consistent with the treatability test results, and the 216-Z-9 waste site has been shown to represent the worst-case scenario (of the three sites) for potential impact to the groundwater. Furthermore, the detailed analysis used for the 216-Z-9 waste site in the treatability test provides a rigorous basis to support decisions for all three sites within the 200-PW-1 OU.

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Appendix D

Carbon Tetrachloride Mass Transfer from Vadose Zone to Groundwater

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D1 Introduction

At dilute aqueous concentrations, the equilibrium concentration of the solute in the gas phase above the water can be calculated using Henry's law. The functional relationship is shown in Equation D-1:

$$C_g = H \cdot C_w \qquad \textbf{(Equation D-1)}$$

where:

C_g = concentration in the gas phase (µg/L)

H = Henry's law constant (dimensionless)

C_w = concentration in the aqueous phase (µg/L)

Soil vapor concentrations in the vadose zone depend primarily on vapor diffusion, the nature of any vadose zone sources, and any advection (induced or natural). Given a subsurface temperature and an aqueous groundwater concentration of carbon tetrachloride, the relationship will determine the carbon tetrachloride soil vapor (or gas phase) concentration directly above the groundwater. Calculations were conducted for a range of groundwater concentrations to obtain a plot of the "equilibrium line" where gas and aqueous concentrations at the vadose zone/groundwater interface are in equilibrium, as described by Henry's law. The resultant plot of carbon tetrachloride gas concentrations versus water concentrations at the water table for a subsurface temperature of 16°C (60.8°F) is shown in Figure D-1. If the ratio of measured gas concentration to aqueous concentration at the water table interface is above the equilibrium line, then carbon tetrachloride will transfer into the aqueous phase from the gas phase. Conversely, a measured ratio falling below the equilibrium line means that carbon tetrachloride will transfer into the gas phase from the aqueous phase. A measured ratio falling upon the equilibrium line means that the concentrations at the gas/water interface are in equilibrium, with no net movement of carbon tetrachloride between the phases.

The slope of the equilibrium line is approximately 0.12 parts per million by volume (ppmv)/µg/L. When the groundwater concentration at the water table is 1,000 µg/L, for example, upward vapor migration to the vadose zone will occur whenever the soil vapor concentration above the water table is less than approximately 120 ppmv.

D2 Henry's Law and Temperature Relationship

The Henry's law constant is a function of the subsurface temperature and contaminant-specific, temperature-dependent property correlations. The Henry's law constant and its temperature dependence have been examined in a wide range of literature for contaminants of environmental interest (e.g., Staudinger and Roberts, 2001, "A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions;" Warneck, 2007, "A Review of Henry's Law Coefficients for Chlorine-Containing C_1 and C_2 Hydrocarbons;" Chen et al., 2012, "Henry's law constants of chlorinated solvents at elevated temperatures"). Brennan et al., 1998, "Comparison of Predictive Methods for Henrys Law Coefficients of Organic Chemicals," suggests that estimating the Henry's law constant as the ratio of the vapor pressure to the water solubility is the preferred approach for dilute aqueous contaminant concentrations (<0.02 mol fraction). Thus, a temperature dependent Henry's law constant can be found using temperature dependent vapor pressure and water solubility values.

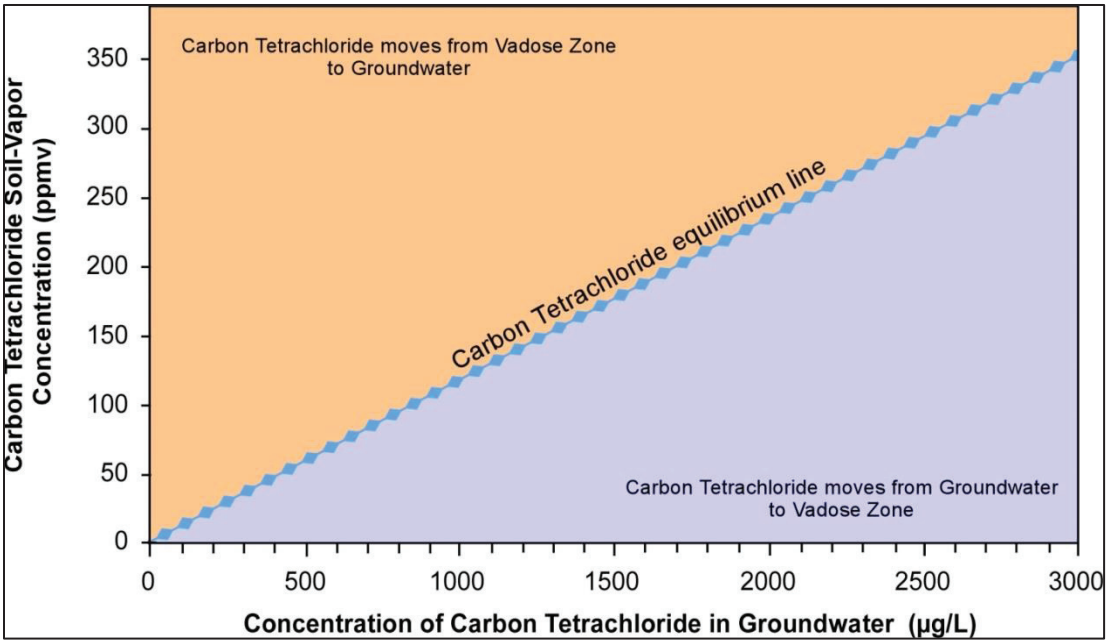

Figure D-1. Gas and Aqueous Phase Equilibrium Concentrations for Carbon Tetrachloride

The temperature-dependent vapor pressure correlation selected for use in this work is the Antoine correlation given in Equation D-2 (Yaws et al., 2009, *Yaws' Handbook of Antoine Coefficients for Vapor Pressure*). The correlation coefficients for calculating the vapor pressure of carbon tetrachloride with the Antoine correlation are listed in Table D-1.

$$Log_{10}(P_{vap}) = A - \frac{B}{T + C} \qquad \textbf{(Equation D-2)}$$

where:

T = temperature (°C)

P_{vap} = vapor pressure (mm Hg)

A, B, and C = contaminant-specific correlation coefficients

Table D-1. Correlation Coefficients for Vapor Pressure and Solubility for Carbon Tetrachloride

Contaminant Abbreviation	Contaminant	Molecular Weight (g/mol)	Correlation Coefficients for Vapor Pressure			Correlation Coefficients for Solubility			
			A	B	C	A	B	C	D
CT	Carbon tetrachloride	153.823	7.01144	1,278.54	232.888	9.7842 E-2	-1.4942 E-3	3.5854 E-5	2.2775 E-7

A polynomial correlation (Mackay et al., 2006, *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*) is used to obtain the temperature-dependent water solubility of a contaminant, as shown in Equation D-3. The correlation coefficients for calculating the solubility of carbon tetrachloride with Equation D-3 are listed in Table D-1.

$$x_p = A + B \cdot T + C \cdot T^2 + D \cdot T^3 \qquad \textbf{(Equation D-3)}$$

where:

x_p	=	mass fraction (wt %)
T	=	temperature (°C)
A, B, C, and D	=	tabulated contaminant-specific correlation coefficients

The mass fraction is converted to a mole fraction, x, in Equation D-4 by multiplying by the ratio of the molecular weight of water to the molecular weight of carbon tetrachloride. Molecular weights are calculated from the molecular formula and the atomic weights in IUPAC, 2016, *IUPAC Periodic Table of the Elements*.

$$x = \frac{x_p}{100} \cdot \frac{MW_w}{MW_{CT}} \qquad \textbf{(Equation D-4)}$$

where:

MW_{CT}	=	molecular weight of carbon tetrachloride (153.823 g/mol)
MW_w	=	molecular weight of water (18.01528 g/mol)
x	=	mole fraction
x_p	=	mass fraction (wt %)

The dimensionless Henry's law constant is calculated from the ratio of the vapor pressure to the mole fraction, with appropriate conversions from units of atm/mol fraction to units of concentration per concentration (i.e., dimensionless). Sander, 1999, "Modeling Atmospheric Chemistry: Interactions Between Gas-Phase Species and Liquid Cloud/Aerosol Particles," provides a discussion of different units commonly used for the Henry's law constant (where Sander's [1999] k_H^{cc} equates to $1/H$ used here). Equation D-5 shows the calculation for the unitless Henry's law constant. The standard density of water as a function of temperature is tabulated in "Standard Density of Water" (CRC, 2011, *CRC Handbook of Chemistry and Physics*). The gas constant value is calculated from the CODATA recommended value (Mohr et al., 2012, *CODATA Recommended Values of the Fundamental Physical Constants: 2010*).

$$H = \frac{P_{vap}}{x} \cdot \frac{MW_w}{\rho_w \cdot R_{gas} \cdot T} \cdot \frac{1\,L}{1000\,mL} \cdot \frac{1\,atm}{760\,mmHg} \qquad \textbf{(Equation D-5)}$$

where:

MW_w	=	molecular weight of water (18.01528 g/mol)
P_{vap}	=	vapor pressure
ρ_w	=	temperature-dependent density of water (g/mL)
R_{gas}	=	gas constant (0.08206 $L \cdot atm \cdot K^{-1} \cdot mol^{-1}$)
T	=	average subsurface temperature (K)
x	=	mole fraction

The gas phase concentration calculated with Equation D-1 is converted to a ppmv gas concentration using Equation D-6 (pressure is assumed to be atmospheric):

$$\hat{C}_g = C_g \cdot \frac{R_{gas} \cdot T}{MW_{CT}}$$

(Equation D-6)

where:

C_g = concentration in the gas phase (µg/L)

$\hat{C}_g$ = gas concentration of carbon tetrachloride (ppmv)

MW_{CT} = molecular weight of carbon tetrachloride (153.823 g/mol)

R_{gas} = gas constant (0.08206 $L \cdot atm \cdot K^{-1} \cdot mol^{-1}$)

T = average subsurface temperature (K)

Using a Hanford-specific subsurface temperature of 16°C (PNNL-22062, *Abiotic Degradation Rates for Carbon Tetrachloride and Chloroform: Final Report*) and an aqueous carbon tetrachloride concentration (C_w) of 100 µg/L, the following values are calculated:

P_{vap} = 74.89 mmHg		(from Equation D-2)
x_p = 0.0840 wt % →	x = 9.84E-05	(from Equations D-3 and D-4)
H = 0.7609		(from Equation D-5)
C_g = $H \cdot C_w$ = (0.7609)(100 µg/L) = 76.09 µg/L		(from Equation D-1)
$\hat{C}_g$ = 11.7 ppmv at the water table		(from Equation D-6)

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Appendix E

Degradation and Future Impacts of Vadose Zone Sources

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Figure E-1. Calculated Mass Discharge for the 216-Z-9 Site and Predicted Rate of Decline in Mass Discharge after Termination of SVE Operations E-2

Terms

MNA	monitored natural attenuation
OU	operable unit
SVE	soil vapor extraction

E1 Discussion

As noted in Appendix C, the Soil Vapor Extraction Endstate Tool and treatability test calculations (PNNL-21326, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*) assume that (1) the vadose zone source maintains a constant mass discharge over time, and (2) there is not a contaminant source in the groundwater. These are conservative assumptions with regard to estimating the impact of the vadose zone source on groundwater contaminant concentrations. However, the mass discharge from the vadose zone source is expected to continue decreasing after the termination of soil vapor extraction (SVE) operations, as shown in Carroll et al., 2012, "Assessing Performance and Closure for Soil Vapor Extraction: Integrating Vapor Discharge and Impact to Groundwater Quality." The underlying groundwater in the 200-ZP-1 Operable Unit (OU) already contains carbon tetrachloride contamination, which reduces the impact of vadose zone contamination on the groundwater. Therefore, the analyses based on the current mass discharge are overly conservative (high estimates). This appendix discusses the effects of a reduced mass discharge from the vadose zone source at the 216-Z-9 site and the existing carbon tetrachloride groundwater contamination with respect to the impact on future groundwater concentrations. Future impacts are evaluated in the context of the defined remedy (25 years of pump and treat, followed by 100 years of monitored natural attenuation [MNA]) for the underlying aquifer of the 200-ZP-1 OU.

The magnitude of mass discharge from the vadose zone source will continue to decrease after terminating SVE operations. During cyclic SVE operations, the higher permeability materials around the source zone were periodically "cleaned out" and vapor-phase contaminants diffused out of the source zone into this clean area. As demonstrated in the treatability test (PNNL-21326) by the series of measurements over time (re-created in Figure E-1), the source mass discharge declined over time, diminishing the source strength. Once SVE operations stop, contaminants will still both emanate from the CCU source zone and continue to diminish the source strength. However, the rate of the mass discharge decline will be slower because SVE operations will not be periodically cleaning out the higher permeability zones. The decline in source strength is controlled by diffusion of contaminants out of the source zone. The diffusion rate is governed by a constant related to the contaminant properties, subsurface conditions, and the concentration gradient (i.e., change in concentration over change in distance). When SVE is applied, the concentration gradient remains high between the source and the surrounding subsurface. Without SVE, less steep concentration gradients controlled by conditions between the source zone and the ground surface and by conditions between the source zone and the groundwater will be established in the vadose zone.

Carroll et al. (2012) examined the diffusion rate and associated source mass discharge under these two conditions (with and without SVE operating) and found that, for sources of the size found at the 216-Z-9 site, the post-SVE diffusion rate was about five times lower than the rate under cyclic SVE conditions. Thus, the source strength will continue to diminish at a rate about five times slower than the observed rate of diminishing source strength during SVE operations. Figure E-1 shows the data during SVE operations and the associated rate of source strength reduction. This figure also shows the projected rate after terminating SVE. In the treatability test, this type of evaluation was conducted, indicating that a source mass discharge starting at a value of 70 g/d (i.e., the calculated mass discharge for the 216-Z-9 site in 2010 during SVE operations) is expected to drop below 10 g/d about 40 years after terminating SVE operations (i.e., in about 2050). The decrease in source mass discharge to about 10 g/d is significant because that level of mass discharge is predicted to result in groundwater concentrations at or below 3.4 µg/L (see Figure 5-18 in the main text), which is the carbon tetrachloride cleanup level specified for the groundwater (post-MNA) in EPA et al., 2008, *Record of Decision, Hanford 200 Area, 200-ZP-1 Superfund Site, Benton County, Washington*.

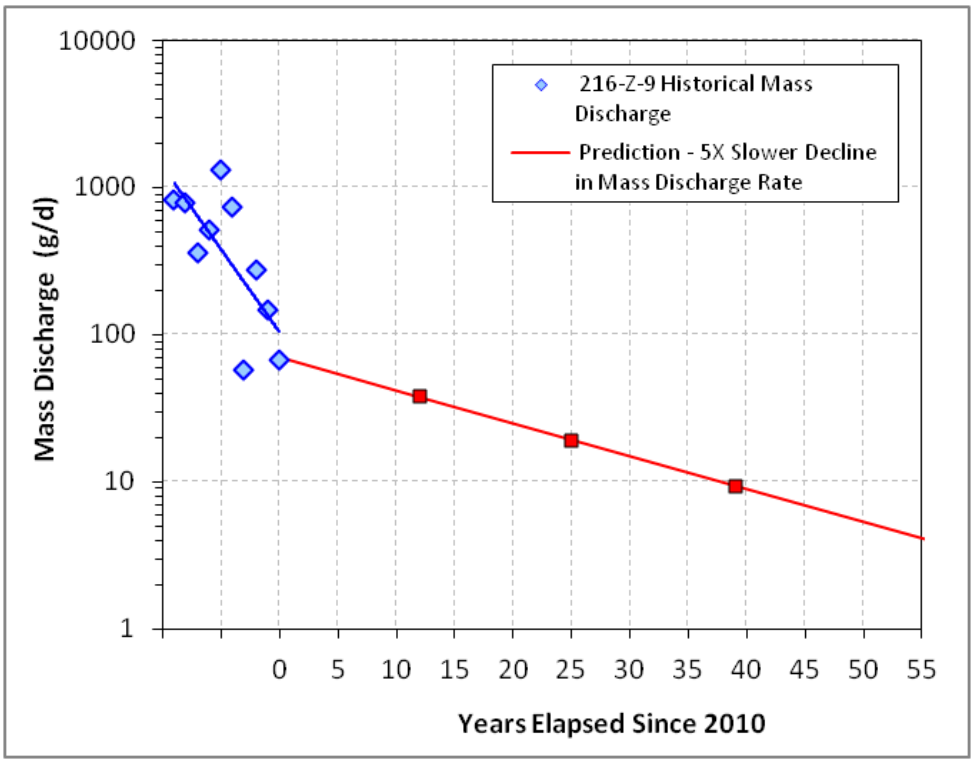

Figure E-1. Calculated Mass Discharge for the 216-Z-9 Site and Predicted Rate of Decline in Mass Discharge after Termination of SVE Operations

E2 References

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PNNL-21326, 2012, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1210310436.