

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

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

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

 **CH2MHILL**
Plateau Remediation Company
P.O. Box 1600
Richland, Washington 99352

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

Date Published
March 2015

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

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

 **CH2MHILL**
Plateau Remediation Company
P.O. Box 1600
Richland, Washington 99352

APPROVED
By Ashley R Jenkins at 11:37 am, Mar 24, 2015

Release Approval _____ Date _____

**Approved for Public Release;
Further Dissemination Unlimited**

TRADEMARK DISCLAIMER

Reference herein to any specific commercial product, process, or service by tradename, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

This report has been reproduced from the best available copy.

Printed in the United States of America

1

Signature Sheet

Title DOE/RL-2014-48, *Endpoint Evaluation for the 200-PW-1 Operable Unit Soil Vapor Extraction System Operations*

M.W. Cline

U.S. Department of Energy, Richland Operations Office

Signature

Date

E. Laija

U.S. Environmental Protection Agency

Signature

Date

2

3

4

1

2

This page intentionally left blank.

Executive Summary

1 The 200-PW-1 Operable Unit (OU) soil vapor extraction (SVE) systems are currently
2 operating under a *Comprehensive Environmental Response, Compensation, and Liability*
3 *Act of 1980*¹ Record of Decision (ROD) issued in 2011² by the U.S. Environmental
4 Protection Agency (EPA), the Washington State Department of Ecology (Ecology), and
5 the U.S. Department of Energy (DOE) (hereafter referred to as the 200-PW-1 OU ROD).
6 The 200-PW-1 OU ROD selected SVE as the final remedial action for carbon
7 tetrachloride and methylene chloride cleanup in the vadose zone. The SVE systems had
8 been operating as an interim remedy since 1992 under the *Action Memorandum:*
9 *Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume.*³
10
11 Because contaminant concentrations and SVE mass removal rates have declined and are
12 currently low, it is appropriate to consider whether continued SVE system operation is
13 warranted. This document provides an evaluation of the SVE systems using the process
14 outlined in PNNL-21843, *Soil Vapor Extraction System Optimization, Transition, and*
15 *Closure Guidance* (hereafter referred to as SVE Closure Guidance).⁴ This guidance was
16 developed by scientists and remediation experts at Pacific Northwest National
17 Laboratory, the U.S. Army Corps of Engineers, and EPA to provide a technical basis for
18 supporting the SVE system performance evaluation and remedy decisions. Based on SVE
19 Closure Guidance (PNNL-21843), the site-specific DOE/RL-2014-18, *Path Forward For*
20 *Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*,⁵ was prepared for
21 assessing the 200-PW-1 OU SVE systems, which received concurrence from EPA and
22 DOE. The assessment approach includes evaluating and updating the conceptual site

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>.

1 model (CSM), considering environmental impacts and regulatory context, and estimating
2 the impact of remaining vadose zone contamination on the groundwater concentrations.
3 These elements feed into a decision logic process to determine an appropriate disposition
4 for the 200-PW-1 OU SVE systems.

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

- 7 • Current carbon tetrachloride concentrations in the vadose zone in the vicinity of the
8 former disposal sites are low and have been significantly decreased at most locations
9 by one to four orders of magnitude from concentrations at the onset of SVE.
- 10 • Remedial investigation studies concluded that there are no sources outside of the
11 three main disposal sites. Remaining carbon tetrachloride contamination that can
12 serve as a source for vapor-phase contaminant discharge is predominantly in the
13 fine-grained Cold Creek unit (CCU) beneath the disposal sites, with the 216-Z-9 site
14 having the highest level of remaining contamination in the CCU of the three major
15 disposal sites (216-Z-9, 216-Z-1A, and 216-Z-18).
- 16 • Vapor-phase carbon tetrachloride contamination discharging from the CCU is at low
17 levels and moves away from the CCU by diffusion when SVE is not operated.
18 The vapor-phase contaminant discharge from the CCU has been significantly
19 diminished by SVE and will continue to diminish by diffusive processes if SVE
20 is terminated. Under the current contaminated conditions in the underlying
21 200-ZP-1 OU aquifer with relatively high carbon tetrachloride concentrations in the
22 groundwater, mass transfer from the vadose zone into the groundwater would
23 be inhibited.

24 The CSM for methylene chloride recognizes that methylene chloride was not
25 a component of disposed waste and accounts for current conditions. Under current
26 conditions, any methylene chloride contamination in the vadose zone is viewed as
27 a dispersed remnant of historical conditions, when organic substrate and anaerobic
28 conditions may have allowed microbial generation of methylene chloride from carbon
29 tetrachloride (via chloroform as an intermediate compound). The lack of disposal and
30 current absence of conditions suitable for microbial production mean that there is no
31 continuing source of methylene chloride. The observation of low concentrations in the
32 vadose zone (i.e., well below the cleanup goal in the 200-PW-1 OU ROD [EPA et al.,

1 2011]), in conjunction with the lack of a continuing source and the biological attenuation
2 mechanism for methylene chloride, indicate that methylene chloride contamination is
3 expected to diminish over time to even lower levels in the vadose zone.

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

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

15 The carbon tetrachloride mass discharge from the vadose zone source at the 216-Z-9 site,
16 which is the limiting case for the 200-PW-1 OU, is not currently impacting groundwater
17 and is predicted to decline so that within about 40 years, the mass discharge would result
18 in carbon tetrachloride concentrations in the groundwater at or below the *Record of*
19 *Decision, Hanford 200 Area, 200-ZP-1 Superfund Site, Benton County, Washington,*
20 issued in 2008⁶ by EPA, Ecology, and DOE (hereafter referred to as the
21 200-ZP-1 OU ROD), groundwater cleanup level of 3.4 µg/L (assuming no other
22 contamination sources in the aquifer). During this time, the groundwater remedy
23 (including institutional controls and monitoring) will be in place to eliminate exposures to
24 contaminated groundwater.

25 No groundwater impact from methylene chloride contamination within the 200-PW-1 OU
26 is expected in future years because of the current low concentrations (i.e., below the
27 cleanup level in the vadose zone and below the maximum contaminant level in the

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>.

1 groundwater), lack of a continuing source, and attenuation that will continue to decrease
2 the concentrations.

3 The site-specific SVE assessment in this document provides a CSM that is representative
4 of current conditions and knowledge with no data gaps, determines that the
5 environmental impact pathway/regulatory context is appropriately defined, and evaluates
6 the impact of remaining vadose zone sources on groundwater concentrations. These
7 evaluations have determined that, if SVE is terminated, there is no current or future
8 impact of carbon tetrachloride or methylene chloride from the vadose zone on the
9 groundwater that would result in concentrations in the groundwater above the cleanup
10 level (3.4 µg/L for carbon tetrachloride [200-ZP-1 OU ROD]) by the time this goal is
11 required for the groundwater. This information, as presented in this document, meets the
12 steps outlined in SVE Closure Guidance (PNNL-21843) and demonstrates that
13 groundwater goals will not be exceeded. Thus, closure of the SVE remedy
14 (i.e., permanently discontinuing operation of the SVE systems) within the 200-PW-1
15 OU is recommended. EPA concurrence with this report will initiate activities to terminate
16 SVE operations and define any necessary continued monitoring.

Contents

1

2 **1 Introduction..... 1-1**

3 1.1 Brief Overview of Site History..... 1-1

4 **2 Soil Vapor Extraction System Closure Guidance 2-1**

5 **3 Conceptual Site Model..... 3-1**

6 3.1 Carbon Tetrachloride Conceptual Site Model..... 3-1

7 3.1.1 Summary of the Conceptual Site Model..... 3-1

8 3.1.2 Contaminant Distribution 3-4

9 3.1.3 Vadose Zone Contaminant Source and SVE Performance..... 3-4

10 3.1.4 Additional Conceptual Site Model Aspects..... 3-11

11 3.2 Methylene Chloride Conceptual Site Model 3-14

12 3.3 Conclusions 3-14

13 **4 Environmental Pathways and Regulatory Compliance Context 4-1**

14 4.1 Environmental Impact Pathways..... 4-1

15 4.2 Cumulative Risk 4-1

16 4.3 Remediation Goals and Regulatory Setting 4-2

17 4.4 Conclusion for Environmental Pathways and Regulatory Compliance 4-2

18 **5 Impacts of Remaining Source on Groundwater 5-1**

19 5.1 Carbon Tetrachloride Impact on Groundwater..... 5-1

20 5.1.1 Estimated Impact to Groundwater Based on the Soil Vapor Extraction

21 Closure Guidance (Step 1)..... 5-1

22 5.1.2 Predicted Impacts to Groundwater Using 216-Z-9 Treatability Test

23 Results – Current Mass Discharges (Step 2) 5-2

24 5.1.3 Comparison of the Soil Vapor Extraction Endstate Tool and the

25 216-Z-9 Treatability Test Report Results (Step 3) 5-3

26 5.1.4 Predicted Impacts to Groundwater Using 216-Z-9 Treatability Test

27 Report Results – Future Mass Discharges (Step 4) 5-3

28 5.2 Methylene Chloride Impact on Groundwater..... 5-4

29 5.3 Conclusions Regarding Remaining Source Impacts to Groundwater 5-6

30 **6 Decision Logic Assessment and Recommendations 6-1**

31 **7 References 7-1**

32

1 **Appendices**

2 **A Summary of Investigations and Remedial Activities A-i**

3 **B 200-PW-1 Operable Unit Calendar Year 2014 Rebound Study– Soil Vapor**

4 **Sampling Results B-i**

5 **C Soil Vapor Extraction Endstate Tool (SVEET) Calculations C-i**

6 **D Carbon Tetrachloride Mass Transfer from Vadose Zone to Groundwater D-i**

7 **E Degradation and Future Impacts of Vadose Zone Sources E-i**

8 **Figures**

9

10 Figure 1-1. Timeline for Investigations and Remedial Activities for Carbon

11 Tetrachloride in the Vadose Zone at the 200-PW-1 OU 1-3

12 Figure 2-1. SVE Closure Guidance Assessment Approach to Support Decisions for

13 SVE System Optimization, Transition, or Closure 2-1

14 Figure 2-2. Approach and Decision Logic for Assessment of SVE System Closure for

15 the 200-PW-1 OU 2-2

16 Figure 2-3. Condensed Flowchart for Approach and Decision Logic for Assessment

17 of SVE System Closure for the 200-PW-1 OU 2-3

18 Figure 3-1. Carbon Tetrachloride Waste Sites and SVE Systems for

19 the 200-PW-1 OU 3-2

20 Figure 3-2. Evolution of the Magnitude and Extent of the Carbon Tetrachloride

21 Contamination during Remediation Using SVE from 1992 to 2014 3-3

22 Figure 3-3. Cross-Sectional View of Site Stratigraphy with Historical Maximum and

23 Most Recent Carbon Tetrachloride Concentrations (1993 to 2012) for

24 216-Z-9 Online Active SVE Wells 3-5

25 Figure 3-4. Cross-Sectional View of Site Stratigraphy with Historical Maximum and

26 Most Recent Carbon Tetrachloride Concentrations (1992 to 2012) for

27 216-Z-1A/216-Z-12 Online Active SVE Wells 3-6

28 Figure 3-5. Cross-Sectional View of Site Stratigraphy with Historical Maximum and

29 Most Recent Carbon Tetrachloride Concentrations (1992 to 2012) for

30 216-Z-18 Online Active SVE Wells 3-7

31 Figure 3-6. Carbon Tetrachloride Sampling Locations during the Remedial

32 Investigation, Overlaid on the 2005 Groundwater Carbon Tetrachloride

33 Plume Contours 3-8

34 Figure 3-7. Maximum Carbon Tetrachloride Concentrations (ppmv) in Samples

35 Collected in 2014 from Soil Vapor Probes and Offline Monitoring Wells

36 Screened above and within the CCU 3-9

37 Figure 3-8. Maximum Carbon Tetrachloride Concentrations (ppmv) for Samples

38 Collected in 2014 from Offline Monitoring Wells Screened below

39 the CCU 3-10

40 Figure 3-9. Computed Source Mass Discharge for the 216-Z-9 Waste Site over Time

41 (1997 to 2010) 3-11

1 Figure 3-10. Cumulative Carbon Tetrachloride Mass Removed from the 216-Z-9 and
2 216-Z-1A/216-Z-18 Sites..... 3-12
3 Figure 3-11. Rebound and Final Concentrations for Operational Cycles of the
4 216-Z-9 SVE System from 1997 to 2012..... 3-12
5 Figure 3-12. Rebound and Final Concentrations for Operational Cycles of the
6 216-Z-1A/216-Z-18/216-Z-12 SVE System from 1997 to 2012 3-13
7 Figure 5-1. Predicted Maximum Groundwater Carbon Tetrachloride Concentrations
8 over Time for the 216-Z-9 Trench 5-4
9 Figure 5-2. 2013 Carbon Tetrachloride Groundwater Concentrations Underlying the
10 Carbon Tetrachloride Waste Sites..... 5-5
11 Figure 5-3. Groundwater Monitoring Wells for the 216-Z-9 Waste Site 5-6
12
13

Table

14 Table 5-1. Summary of SVEET Evaluation for the 216-Z-9, 216-Z-1A, and
15 216-Z-18 Waste Sites..... 5-2
16
17

1

2

This page intentionally left blank.

3

Terms

| | | |
|----|---------|---|
| 1 | | |
| 2 | B&K | Brüel & Kjær |
| 3 | CCU | Cold Creek unit |
| 4 | CSM | conceptual site model |
| 5 | CT | carbon tetrachloride |
| 6 | DOE | U.S. Department of Energy |
| 7 | DQO/SAP | data quality objective/sampling and analysis plan |
| 8 | Ecology | Washington State Department of Ecology |
| 9 | EPA | U.S. Environmental Protection Agency |
| 10 | GW | groundwater |
| 11 | MNA | monitored natural attenuation |
| 12 | ND | nondetect sample |
| 13 | OU | operable unit |
| 14 | P&T | pump-and-treat |
| 15 | ppmv | parts per million by volume |
| 16 | RAO | remedial action objective |
| 17 | RI | remedial investigation |
| 18 | ROD | record of decision |
| 19 | SVE | soil vapor extraction |
| 20 | SVEET | Soil Vapor Extraction Endstate Tool |
| 21 | VOC | volatile organic compound |
| 22 | VZ | vadoze zone |
| 23 | | |

1

2

This page intentionally left blank.

1 Introduction

Carbon tetrachloride mass removal rates for the soil vapor extraction (SVE) systems in the 200-PW-1 Operable Unit (OU) have declined to the point where it is appropriate to assess a transition from the current cycle of active operations to closure of the SVE systems. The recently published PNNL-21843, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance* (hereafter referred to as SVE Closure Guidance), describes an approach and general decision logic for assessing whether termination of SVE operations is justified and appropriate. Based on 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*). The objective of this current work is to follow the path forward process presented and to perform and document the assessment, thereby providing justification and recommendations for the future disposition of the SVE systems.

The SVE systems at the 200-PW-1 OU have been in operation as a *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) interim cleanup remedy since 1992 under the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology), 1992, *Action Memorandum: Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume*. The expedited response action was designed to mitigate further contamination of the 200-ZP-1 OU groundwater underneath the 200-PW-1 OU. The 200-PW-1 OU SVE systems have been operating since 2011 under 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 Record of Decision [ROD]). The 200-PW-1 OU ROD selected SVE as the final remedial action for carbon tetrachloride and methylene chloride; SVE will continue to be implemented in accordance with the expedited response action until the remedial design/remedial action work plan is approved.

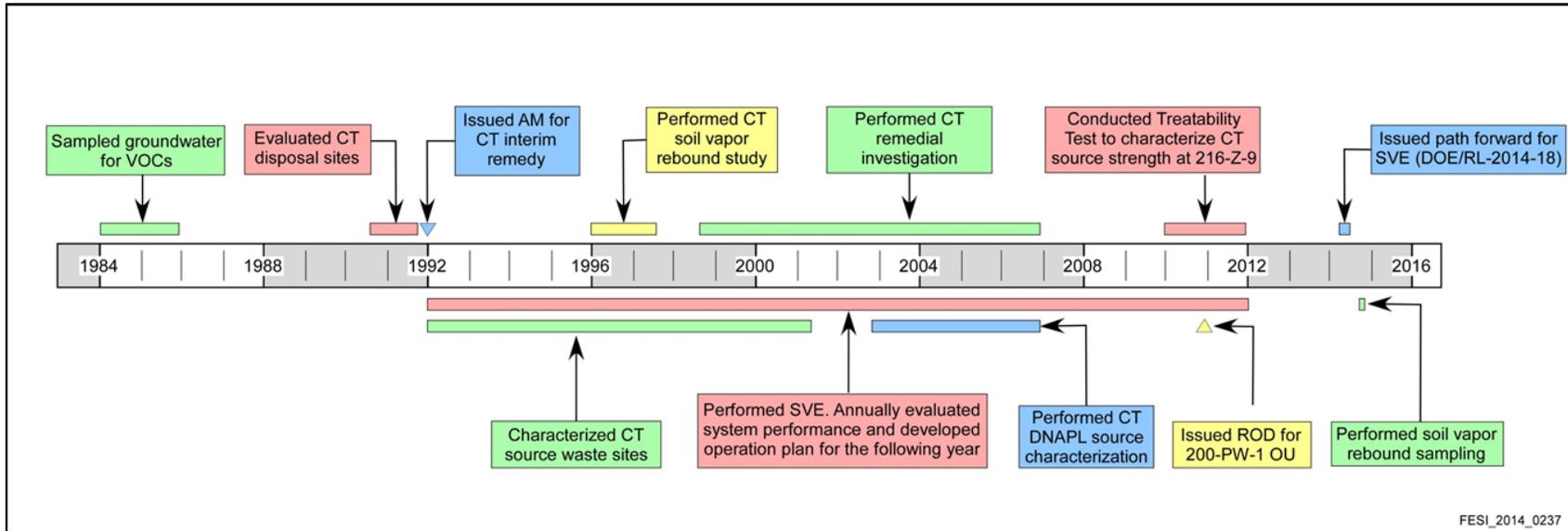
A brief overview of the history of activities for the 200-PW-1 OU is presented in Section 1.1 to provide background information for the subsequent assessment. The site-specific approach and decision logic for assessing whether termination of SVE operations is justified and appropriate is presented in Chapter 2. An updated conceptual site model (CSM) is described in Chapter 3 and is used as a framework for assessing the environmental impact pathways and regulatory compliance context (Chapter 4) and the impact of the remaining vadose zone contamination on the underlying 200-ZP-1 OU groundwater (Chapter 5). Chapter 6 assesses the decision logic and provides recommendations for the next actions for the 200-PW-1 OU SVE systems.

1.1 Brief Overview of Site History

A brief overview of the history of waste disposal, site investigation, remediation, and regulatory context for the 200-PW-1 OU is provided in the following discussion. Figure 1-1 provides a timeline of the activities. Appendix A provides a comprehensive list and discussion of activities, which is based on information presented in DOE/RL-2014-18.

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 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. The liquid waste infiltrated into the ground, contaminating the underlying soil and

- 1 groundwater. There was no known disposal of liquids containing methylene chloride, which is a potential
- 2 degradation product of carbon tetrachloride (via chloroform as an intermediate compound).



1 Documents cited: 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*.
 2
 3 DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*.

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

1 Following the discovery of carbon tetrachloride in the underlying groundwater in the mid-1980s,
2 an interim remedy for removal of carbon tetrachloride from the 200-PW-1 OU vadose zone using SVE
3 systems was approved in 1992 by the EPA and Ecology. SVE operations proceeded from February 1992
4 through October 2011 as an interim action (EPA and Ecology, 1992), and thereafter as a final remedy for
5 200-PW-1 OU vadose zone carbon tetrachloride and methylene chloride in accordance with the
6 associated 200-PW-1 OU ROD (EPA et al., 2011).

7 SVE was configured with two separate vadose-zone well fields: one for the 216-Z-9 waste site, and one
8 for the combined 216-Z-1A/216-Z-18/216-Z-12 sites. Multiple wells are used in each well field for
9 extraction, with wells distributed laterally and screened at intervals above, within, and/or below the
10 Cold Creek unit (CCU), which is a laterally extensive low-permeability layer in the vadose zone.
11 The operational strategy has shifted from the initial continuous operation (1992 to 1997) to cycles of
12 operation, followed by a period of inactivity to allow soil gas concentrations to rebound (1997 to present).
13 Between 1992 and 2012, over 80,000 kg of carbon tetrachloride was removed from the vadose zone.

14 The 200-PW-1 OU waste sites have been well characterized. Remedial investigations (RIs)
15 (e.g., DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich Process*
16 *Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6*
17 *Operable Units*, hereafter referred to as the 200-PW-1 OU RI report) and a treatability test (PNNL-21326,
18 *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using*
19 *Tomographic Methods at the 216-Z-9 Site*) have examined the geology beneath the waste sites and the
20 nature and extent of contamination in the vadose zone. The 200-PW-1 OU RI report (DOE/RL-2006-51)
21 included extensive characterization within the waste sites and across a broad portion of the 200 West Area
22 above the highest concentrations of the groundwater carbon tetrachloride plume. The 200-PW-1 OU RI
23 report (DOE/RL-2006-51) also compiled the results of previous investigations, including the rebound
24 study for the SVE systems (which was used to justify transition to a cyclic operational strategy) and
25 numerical modeling studies that supported the conceptual model presented in the 200-PW-1 OU RI report
26 (DOE/RL-2006-51). The treatability test characterized the location and extent of the remaining source
27 beneath the 216-Z-9 waste site and linked this information to an estimate of the impact of this vadose
28 zone source on groundwater contamination (PNNL-21326).

29 DOE/RL-2014-18 was prepared to summarize data and propose a path forward for the 200-PW-1 OU
30 SVE systems. This path forward document (1) provided an overview of the 200-PW-1 OU regulatory
31 status; (2) summarized the history of waste disposal, investigation activities, and remediation activities
32 for the 200-PW-1 OU; (3) provided an overview of SVE operations and performance over the past two
33 decades; and (4) proposed a method for evaluating the need for continuing SVE operations. The recent
34 SVE Closure Guidance (PNNL-21843) was used as the basis for defining the site-specific evaluation and
35 decision logic approach to determine when SVE operations for the 200-PW-1 OU can be terminated.
36 The path forward document established EPA and U.S. Department of Energy (DOE) concurrence with
37 this approach. The objective of this document is to follow the defined path forward for the evaluation,
38 providing justification and recommendations for disposition of the SVE systems at the 200-PW-1 OU.

1

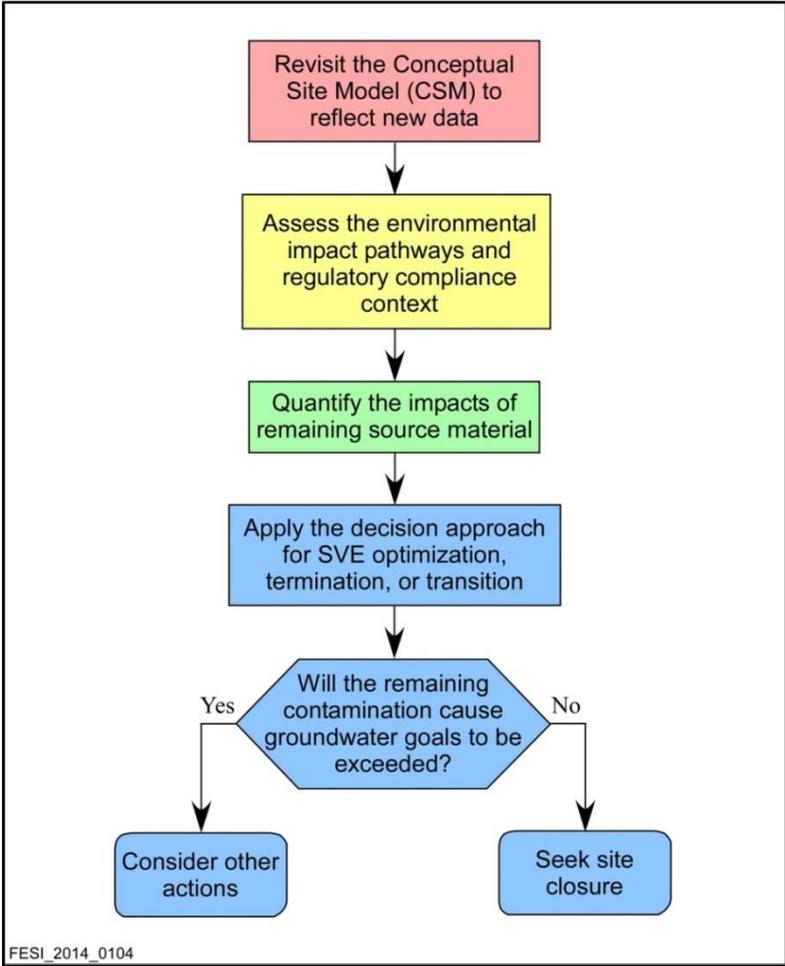
2

This page intentionally left blank.

3

2 Soil Vapor Extraction System Closure Guidance

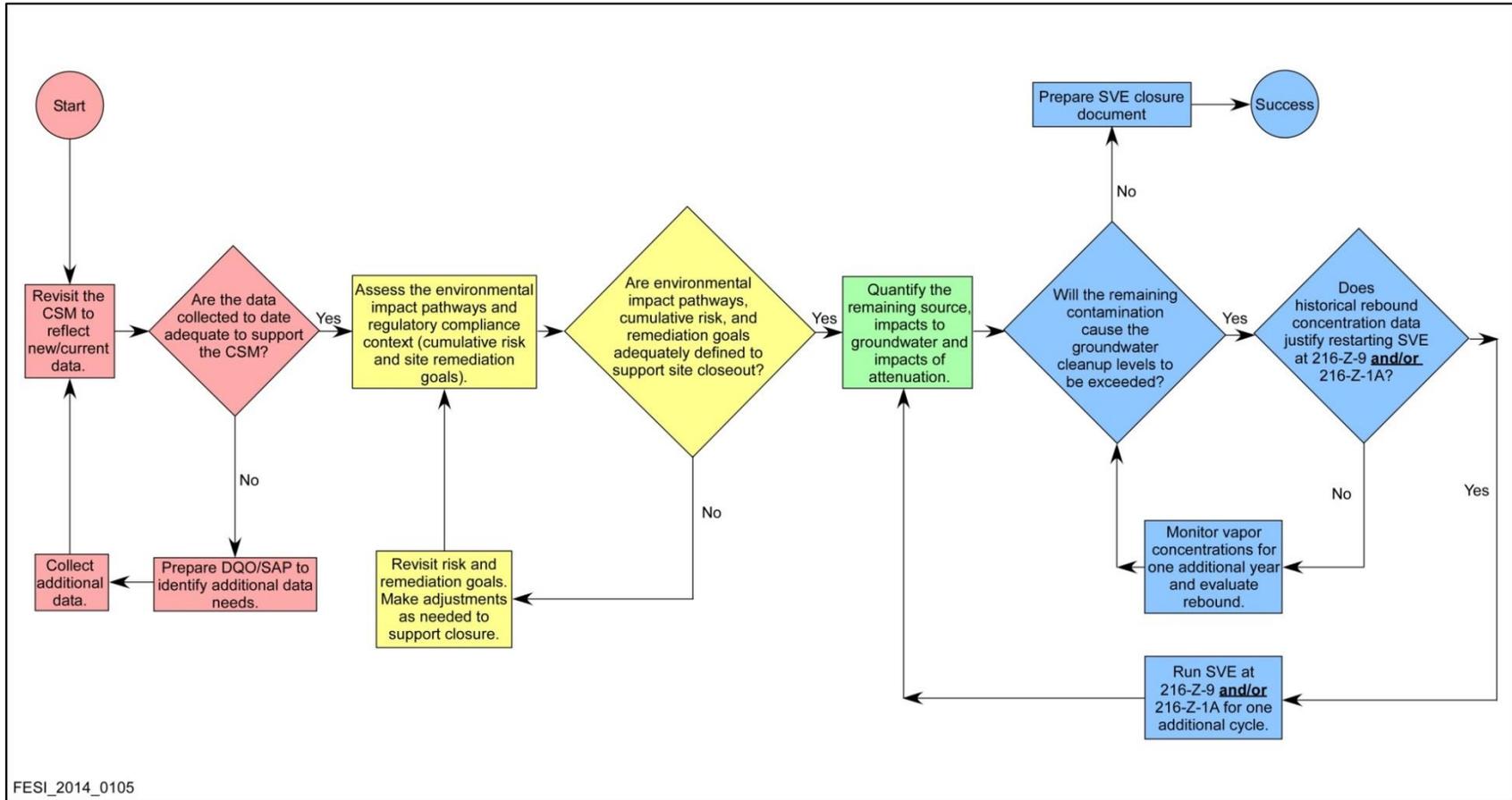
1
2 After an SVE system begins to show indications of diminishing contaminant removal rates, SVE
3 performance needs to be evaluated to determine whether the system should be optimized, terminated,
4 or transitioned to another technology to replace or augment SVE. SVE Closure Guidance (PNNL-21843)
5 specifically addresses the elements of this type of performance assessment, providing a stepwise process
6 for gathering information and performing evaluations to support SVE endpoint decisions. Figure 2-1
7 summarizes the elements discussed in SVE Closure Guidance (PNNL-21843). The elements of an
8 updated CSM, environmental impacts/regulatory context, and an estimate of the impact of remaining
9 vadose zone contamination on the groundwater concentrations all feed into a decision logic approach to
10 determine an appropriate SVE endpoint (optimization, transition, or closure) for the site.



11
12 Source: DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable*
13 *Unit Soil Vapor Extraction Operations.*

14 **Figure 2-1. SVE Closure Guidance Assessment Approach to Support Decisions**
15 **for SVE System Optimization, Transition, or Closure**

16 As part of determining the path forward approach (DOE/RL-2014-18), the general process outlined in
17 Figure 2-1 was tailored specifically to the 200-PW-1 OU SVE systems. The resulting site-specific
18 approach and decision logic (Figure 2-2) will be used to facilitate assessment of the SVE systems to
19 determine appropriate disposition.



FESI_2014_0105

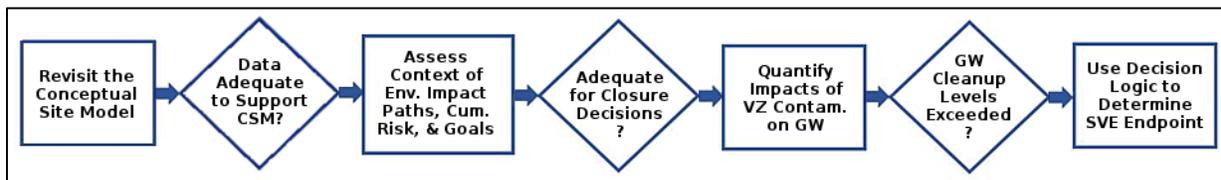
1
2 Source: DOE/RL-2014-18, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*.

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

1 The assessment and decision process shown in Figure 2-2 involves four main steps:

- 2 1. Revisit the CSM to incorporate new data and assess the adequacy of existing data. This step
3 (discussed in Chapter 3) involves evaluating pertinent information, including carbon tetrachloride
4 monitoring and operational data from 1992 through 2014. The CSM is updated to reflect current
5 knowledge regarding the vadose zone contamination, contaminant migration, and subsurface
6 characteristics. An updated CSM provides qualitative and quantitative input to SVE decisions.
- 7 2. Assess the environmental impact and regulatory compliance context. This step (discussed in
8 Chapter 4) involves assessing whether the environmental pathways, cumulative risk, and remedial
9 action objectives (RAOs) are adequately defined, given the current (updated) CSM, to support
10 decisions regarding the disposition of the SVE systems.
- 11 3. Quantify the environmental impact of remaining vadose zone contamination sources (discussed in
12 Chapter 5). Specifically, estimate the impact of vadose zone contamination on contaminant
13 concentrations in the groundwater of the underlying 200-ZP-1 OU.
- 14 4. Apply the results of the previous three steps in a decision logic approach to determine the appropriate
15 actions for disposition of the 200-PW-1 OU SVE systems (Chapter 6).

16 The decision logic approach shown in Figure 2-2 is summarized in the condensed flowchart shown in
17 Figure 2-3. This condensed flowchart is displayed in subsequent chapters with highlighted boxes to
18 indicate the elements that are under discussion (orange) or that are completed (green).



19
20 **Figure 2-3. Condensed Flowchart for Approach and Decision Logic**
21 **for Assessment of SVE System Closure for the 200-PW-1 OU**

1

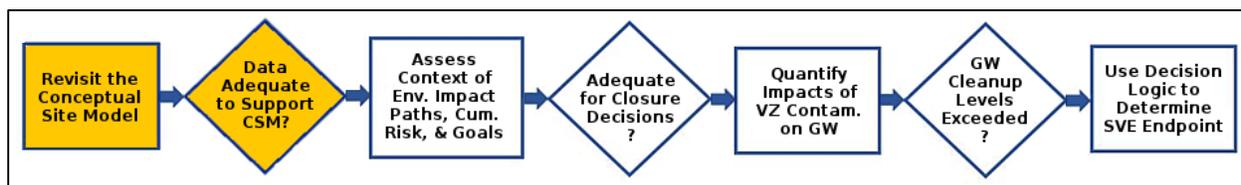
2

This page intentionally left blank.

3 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, source strength, etc.), and the SVE system (e.g., operations and performance). When assessing SVE endpoint decisions, it is important to revisit the CSM to (1) incorporate new data, (2) reflect the current site conditions in the context of the SVE remediation conducted to date, and (3) consider whether any data gaps exist. An extensive set of information about the 200-PW-1 OU has been collected over the course of site characterization and SVE operations (Section 1.1 and Appendix A) and forms the basis for the CSM.

The CSM for disposed carbon tetrachloride is discussed in Section 3.1. Section 3.2 presents CSM information for methylene chloride. Conclusions with respect to the suitability of the CSM to support SVE decisions are presented in Section 3.3.



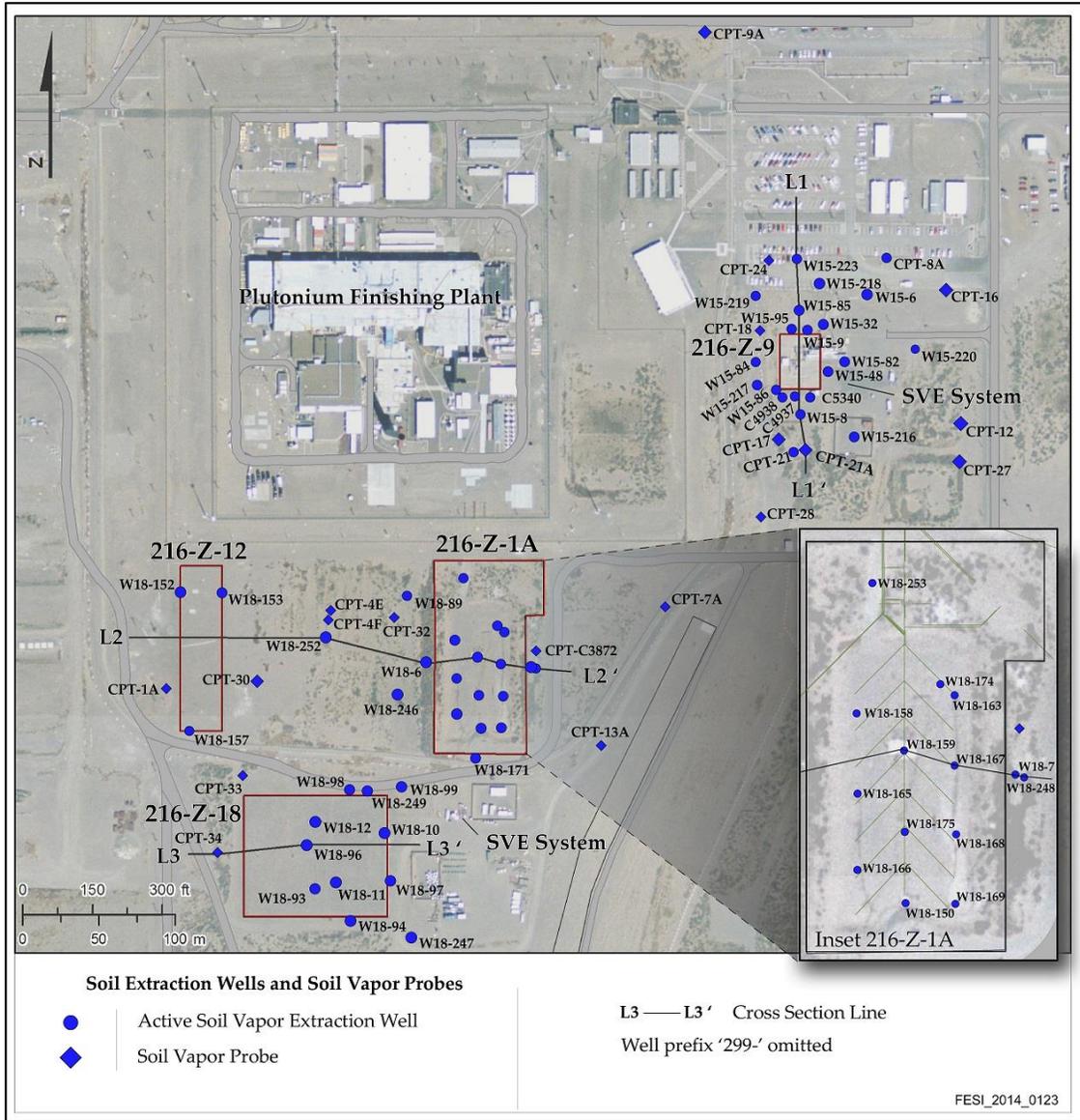
3.1 Carbon Tetrachloride Conceptual Site Model

The CSM is summarized in Section 3.1.1, with key supporting information presented in subsequent subsections. Appendix A and DOE/RL-2014-18 provide additional details regarding site investigations.

3.1.1 Summary of the Conceptual Site Model

Carbon tetrachloride was disposed at four waste sites (216-Z-9, 216-Z-1A, 216-Z-18, and 216-Z-12), 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 3-1). The waste sites were cribs/trenches/tile fields that extended nominally 6 m (20 ft) below ground surface, mainly in backfill material (about 4 m [13 ft] thick). The subsurface 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 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 has 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 contamination of the vadose zone and the groundwater. Silt materials in the vadose zone, in particular the CCU, retained contamination during this time. Figure 3-2 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 and within the CCU. From 1992 to 1996, the 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 the 216-Z-12 site, it was determined that it is not a continuing source area.



1

2

Figure 3-1. Carbon Tetrachloride Waste Sites and SVE Systems for the 200-PW-1 OU

3

The SVE systems were shut down from November 1996 through July 1997 to conduct a rebound study (BHI-01105, *Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site, Fiscal Year 1997*). The study indicated that the carbon tetrachloride contamination 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.

4

5

6

7

8

9

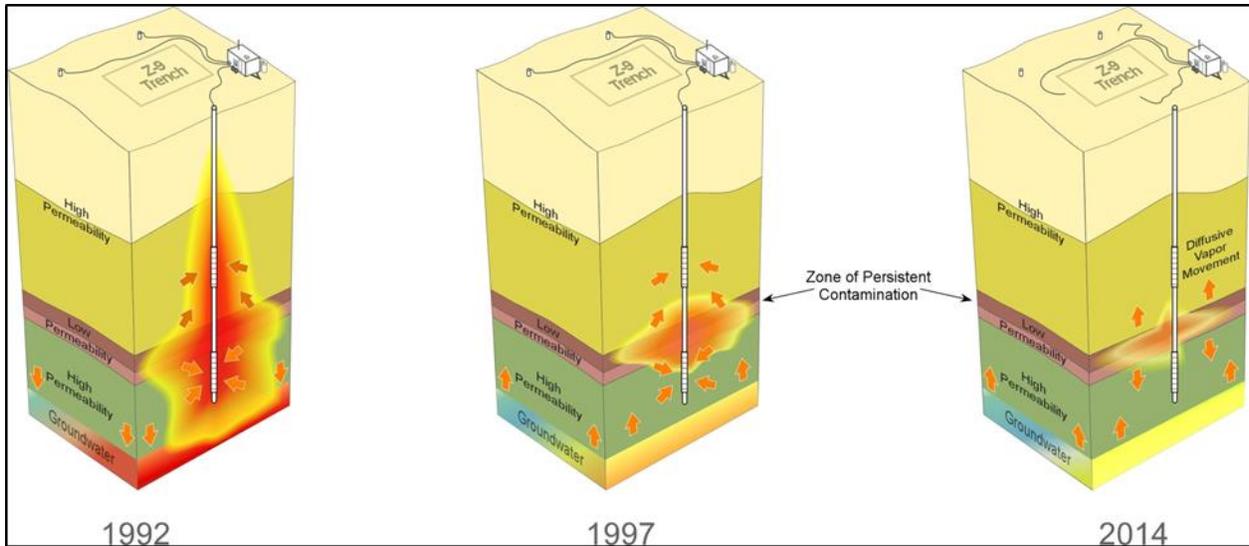


Figure 3-2. Evolution of the Magnitude and Extent of the Carbon Tetrachloride Contamination during Remediation Using SVE from 1992 to 2014

Cyclic SVE operations have continued since 1997 up through the most recent active SVE extraction 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 the treatability test (PNNL-21326). This study indicated that the remaining carbon tetrachloride source was located in the CCU beneath the disposal site, and that the 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 RI report (DOE/RL-2006-51) that indicate no carbon tetrachloride sources exist other than beneath the four identified disposal sites. This progression of site conditions leads to the current conditions depicted in Figure 3-2 and the following key elements of the current CSM:

- Current carbon tetrachloride concentrations in the vadose zone in the vicinity of 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 3.1.2)
- Remedial investigation studies concluded that there are no sources outside of the three main disposal sites (Section 3.1.2). Remaining carbon tetrachloride contamination that can serve as a source for vapor-phase contaminant discharge is predominantly in the CCU beneath the disposal sites, with the 216-Z-9 site having the highest level of remaining contamination in the CCU of the three major disposal sites (discussed in Section 3.1.3).
- Vapor-phase carbon tetrachloride contamination discharging from the CCU is at low levels and moves away from the CCU by diffusion when SVE is not operating (discussed in Section 3.1.3). 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. The current vapor-phase contaminant discharge from the CCU at the 216-Z-9 site 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 is upward into the vadose zone.

1 The receptor for the vadose zone carbon tetrachloride contamination is the groundwater (see Section 4.1).
2 Because the CCU is the vadose zone source, groundwater would potentially be impacted by
3 carbon tetrachloride concentrations emanating from the CCU to the vadose zone below the CCU.
4 The groundwater is already contaminated with carbon tetrachloride, for which a separate and concurrent
5 remedy (pump-and-treat [P&T] for 25 years, followed by monitored natural attenuation [MNA]) is
6 ongoing. Attenuation mechanisms other than dispersion and dilution in the vadose zone are expected to
7 be minor, and a conservative evaluation of the impacts of vadose zone carbon tetrachloride should not
8 include these types of attenuation mechanisms.

9 **3.1.2 Contaminant Distribution**

10 The contaminated vadose zone consists of approximately 65 m (213 ft) of relatively permeable sand and
11 gravel within the Hanford formation (about 34 m [1112 ft] thick) and Ringold Formation (about 25 m
12 [82 ft] thick above the water table), which are separated by the low-permeability CCU sediments (about
13 6 m [20 ft] thick). Figures 3-3 through 3-5 depict the stratigraphy for three cross sections (the locations
14 are shown in Figure 3-1). The 200-PW-1 OU RI report (DOE/RL-2006-51) provides additional discussion
15 on the stratigraphy. The historical maximum carbon tetrachloride concentrations at the onset of SVE
16 operations and the most recent maximum carbon tetrachloride concentrations during SVE operations are
17 shown in these figures and demonstrate the significant reduction in concentration that has occurred due to
18 SVE operations.

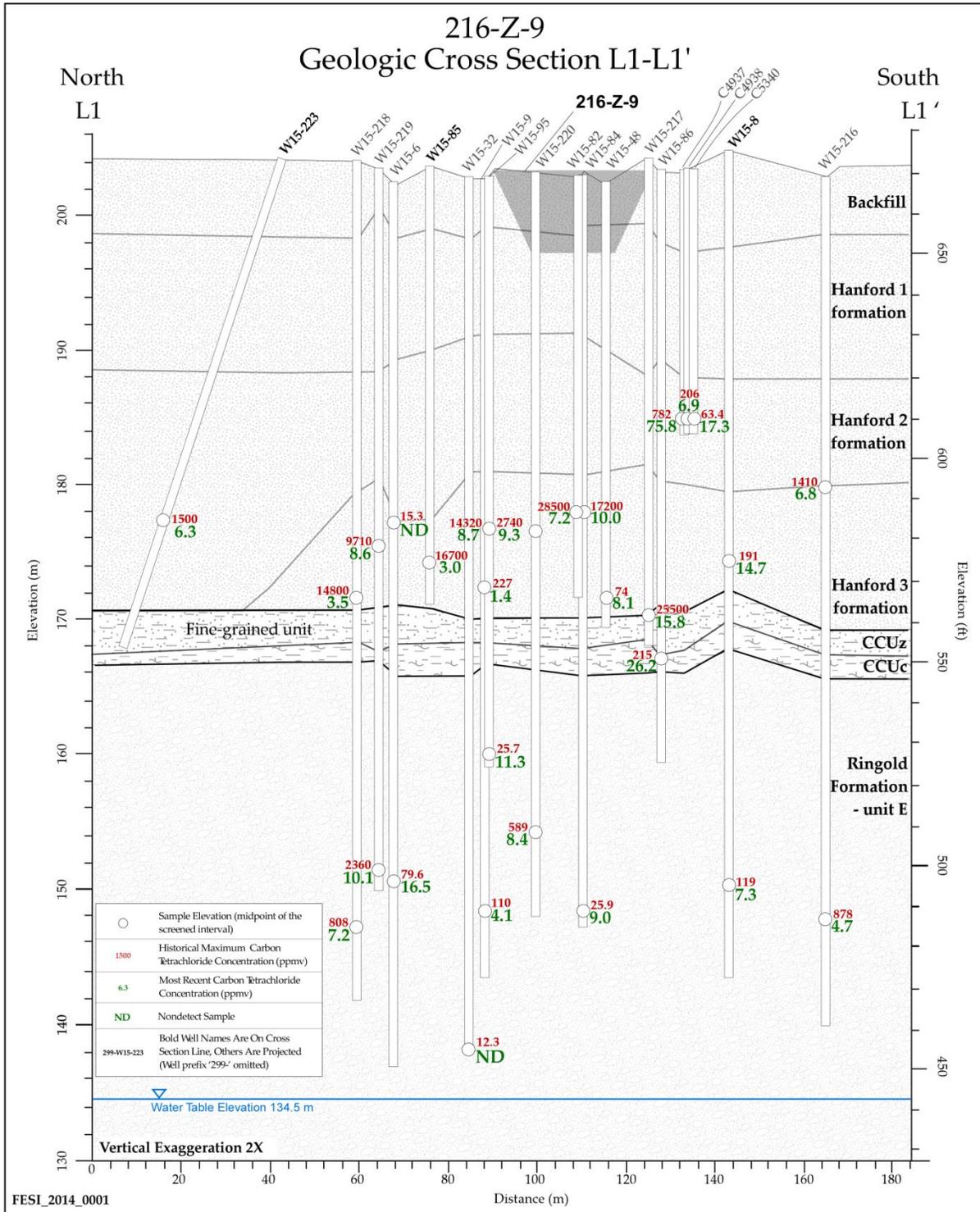
19 Extensive characterization (Figure 3-6) has taken place to determine the extent of carbon tetrachloride
20 contamination and the vadose zone sources at the 200-PW-1 OU (see Appendix A for more detail).
21 Passive soil gas surveys provided initial reconnaissance to guide soil vapor sampling in the 200-PW-1 OU
22 RI report (DOE/RL-2006-51). RI soil vapor results for locations above, within, and below the CCU,
23 respectively, indicated that carbon tetrachloride contamination was within or near the waste site
24 footprints. Based on the soil vapor results, soil samples were collected to add to the characterization
25 knowledge about carbon tetrachloride contamination above, within, and below the CCU. No indications
26 of an unknown carbon tetrachloride source were found.

27 The current status of carbon tetrachloride contamination is based on the most recent measurements at
28 SVE extraction wells (Figures 3-3 to 3-5) and samples collected in 2014 (Appendix B) from offline SVE
29 wells and soil vapor probes (Figures 3-7 and 3-8). This recent data shows that SVE operations over the
30 past two decades have effectively diminished the magnitude and extent of the carbon tetrachloride
31 contamination within the vadose zone. All measurements below the CCU and nearly all above/within
32 the CCU in 2014 were below the 200-PW-1 OU ROD (EPA et al., 2011) cleanup level of 100 parts per
33 million by volume (ppmv) for carbon tetrachloride.

34 **3.1.3 Vadose Zone Contaminant Source and SVE Performance**

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

1

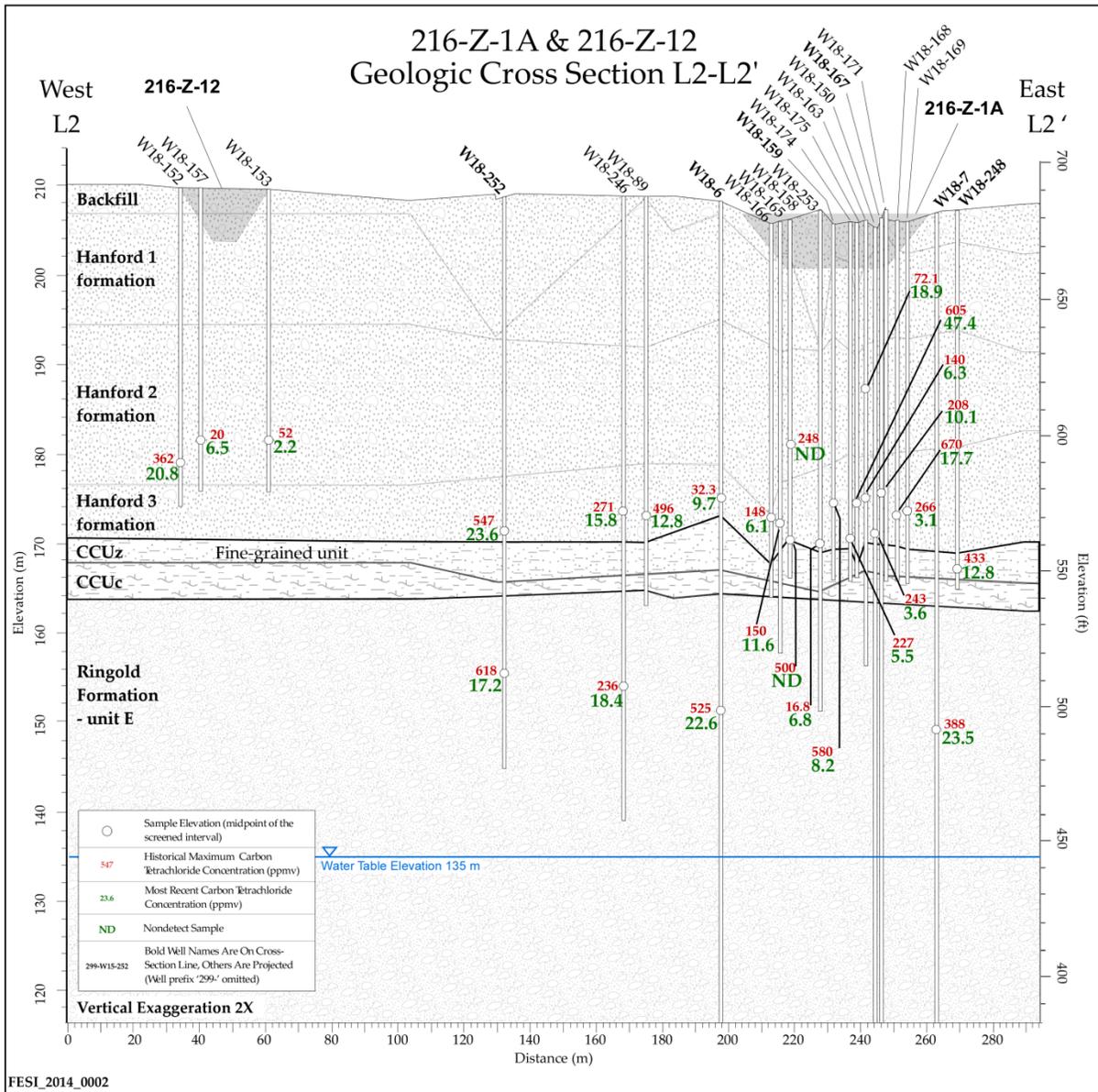


2
3
4
5

Note: The cross section location is shown in Figure 3-1.

Figure 3-3. 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

1

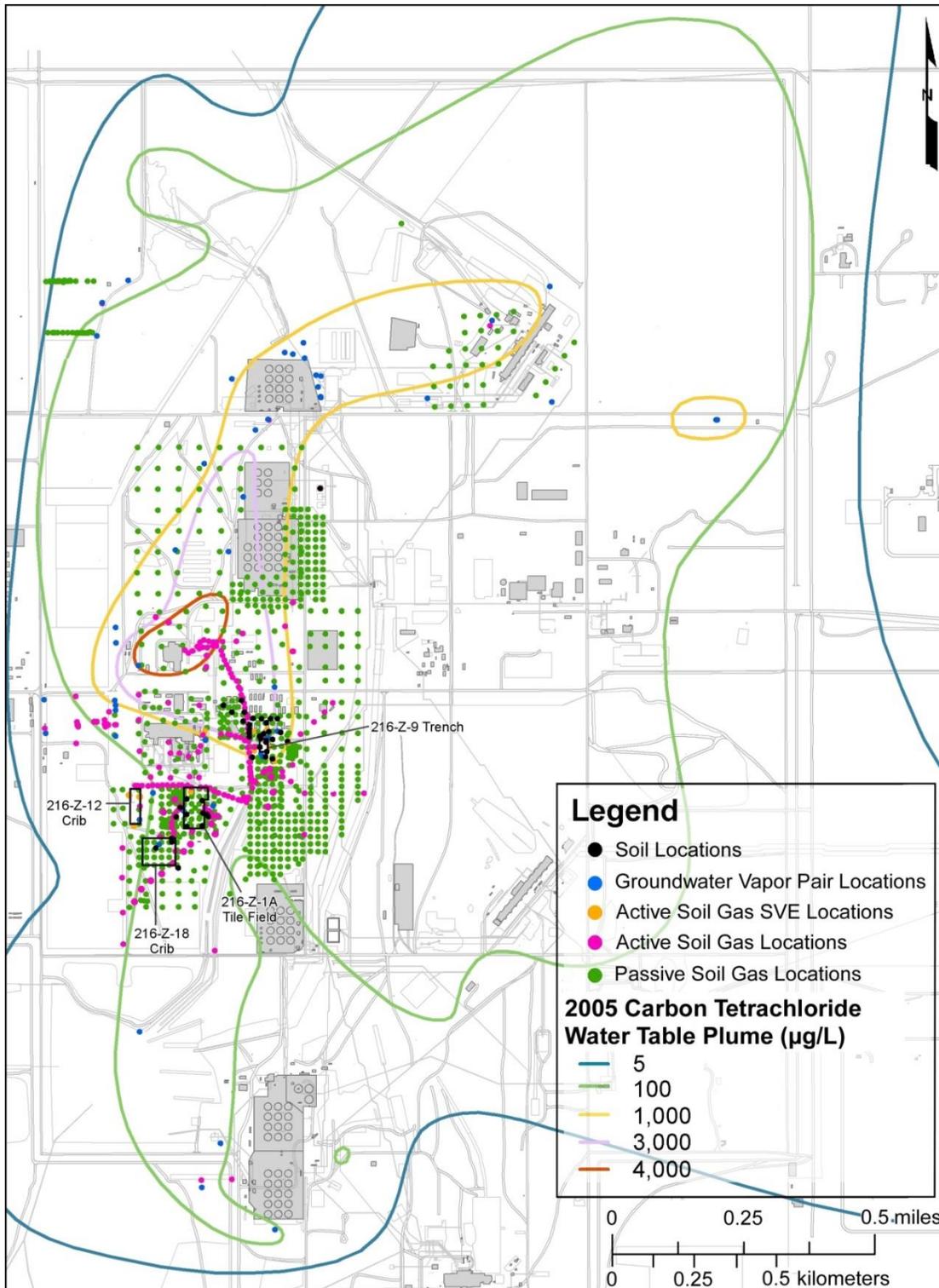


2
3

Note: The cross section location is shown in Figure 3-1.

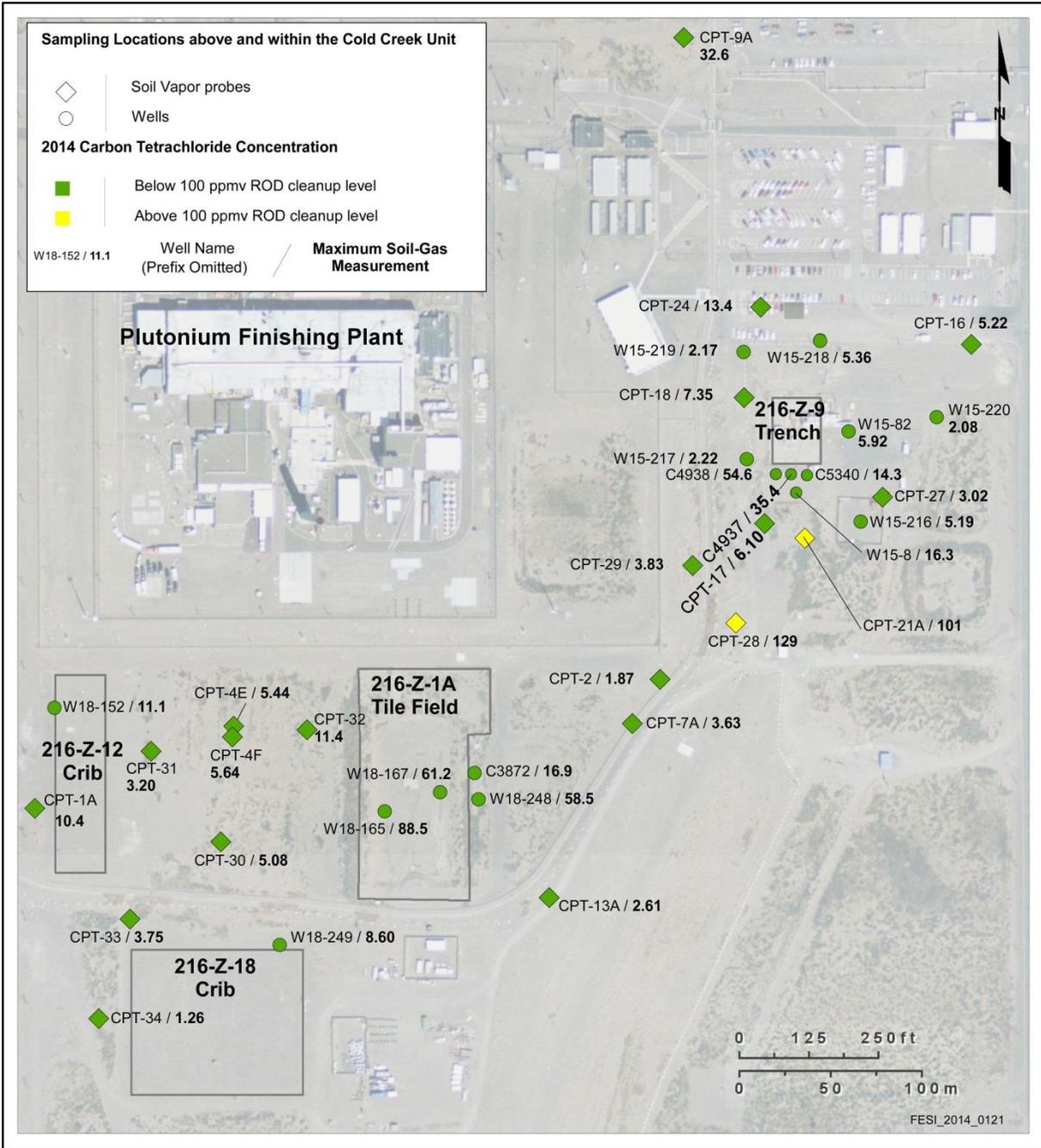
4 **Figure 3-4. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon**
5 **Tetrachloride Concentrations (1992 to 2012) for 216-Z-1A/216-Z-12 Online Active SVE Wells**

6 The detailed treatability test (PNNL-21326) was conducted to assess subsurface characterization methods
7 and to determine the vadose zone carbon tetrachloride source characteristics for the 216-Z-9 waste site.
8 The overall carbon tetrachloride source mass discharge based on cyclic SVE operational data since 1997
9 and the evaluation method provided in Brusseau et al., 2010, "Analysis of Soil Vapor Extraction Data to
10 Evaluate Mass-Transfer Constraints and Estimate Source-Zone Mass Flux," were used to assess carbon
11 tetrachloride source strength. Pneumatic responses and location-specific mass discharge (from single-well
12 tests) were used to assess carbon tetrachloride size and location. A distinct pattern in the carbon
13 tetrachloride concentration and mass discharge data showed higher values near the CCU within a distinct



1
2
3
4
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.*

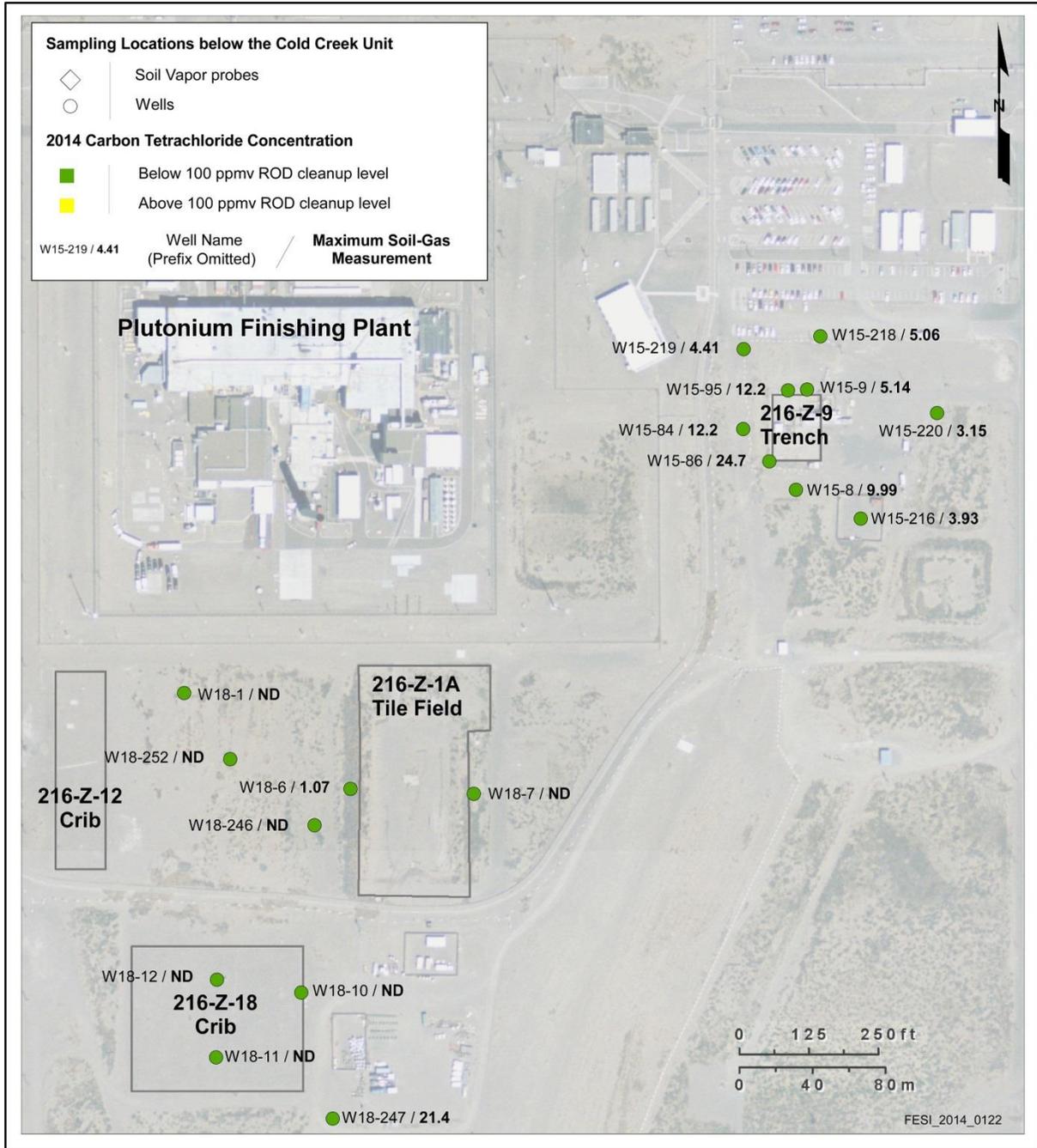
5
6
**Figure 3-6. Carbon Tetrachloride Sampling Locations during the Remedial Investigation,
Overlaid on the 2005 Groundwater Carbon Tetrachloride Plume Contours**



1
2 Note: Carbon tetrachloride concentrations were measured in the field using a B&K (a trade name of Brüel & Kjær [Sound and
3 Vibration Measurement A/S], Nærum, Denmark) multi-gas analyzer.

4 **Figure 3-7. Maximum Carbon Tetrachloride Concentrations (ppmv) in Samples Collected in 2014**
5 **from Soil Vapor Probes and Offline Monitoring Wells Screened above and within the CCU**

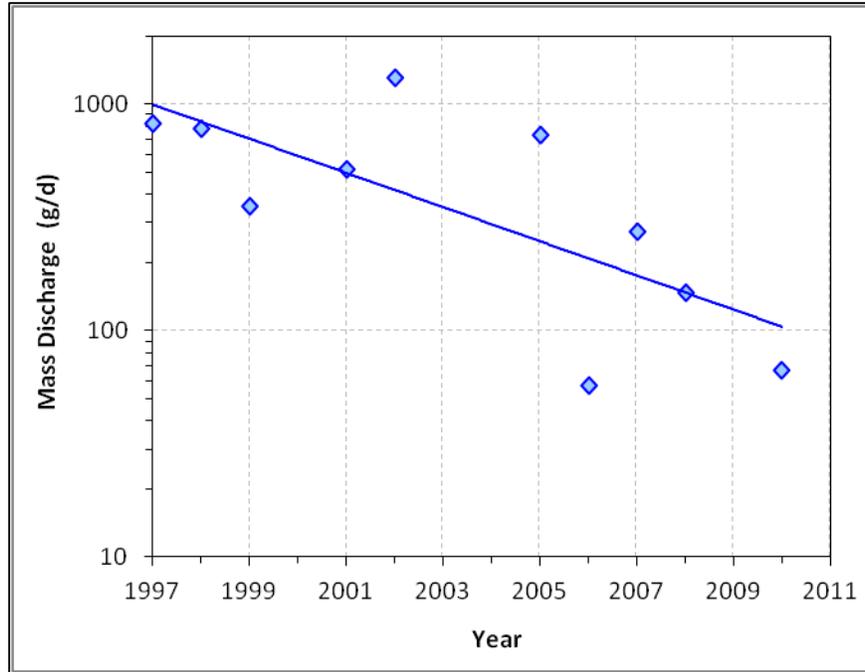
6



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

Figure 3-8. Maximum Carbon Tetrachloride Concentrations (ppmv) for Samples Collected in 2014 from Offline Monitoring Wells Screened below the CCU

1
2
3
4
5



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 3-9. Computed Source Mass Discharge for the 216-Z-9 Waste Site over Time (1997 to 2010)

1
2
3
4
5
6 The same characterization testing, as performed for the 216-Z-9 waste site in the treatability test
7 (PNNL-21326), has not been conducted for the 216-Z-1A or 216-Z-18 sites. However, disposed dense
8 nonaqueous phase liquid has a similar distribution in the subsurface at these sites (DOE/RL-2006-51,
9 200-PW-1 OU RI report). Until 1997, the SVE systems for the 200-PW-1 OU were operated continuously
10 and, thereafter, the operational strategy was changed to cycles of operation and no extraction. A plot of
11 the cumulative mass of carbon tetrachloride removed over time (Figure 3-10) shows how the SVE
12 systems removed significant quantities of mass early in the remediation, yet recent cycles of operation are
13 contributing only small increments of extracted carbon tetrachloride mass. The diminished amount of
14 mass extracted is also apparent from plots of the starting (i.e., initial value after a period without
15 extraction) and ending (i.e., asymptotic) concentrations from an operational cycle, which is shown in
16 Figure 3-11 for the 216-Z-9 SVE system and in Figure 3-12 for the SVE system encompassing the
17 216-Z-1A and 216-Z-18 waste sites. This lack of significant rebound indicates that the source mass
18 discharge rate has significantly diminished, which is consistent with the source mass discharge values
19 calculated for the 216-Z-9 waste site (Figure 3-9). These data also support the conclusion that, out of the
20 three major disposal sites, the 216-Z-9 site has the highest level of remaining contamination in the CCU.

21 **3.1.4 Additional Conceptual Site Model Aspects**

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

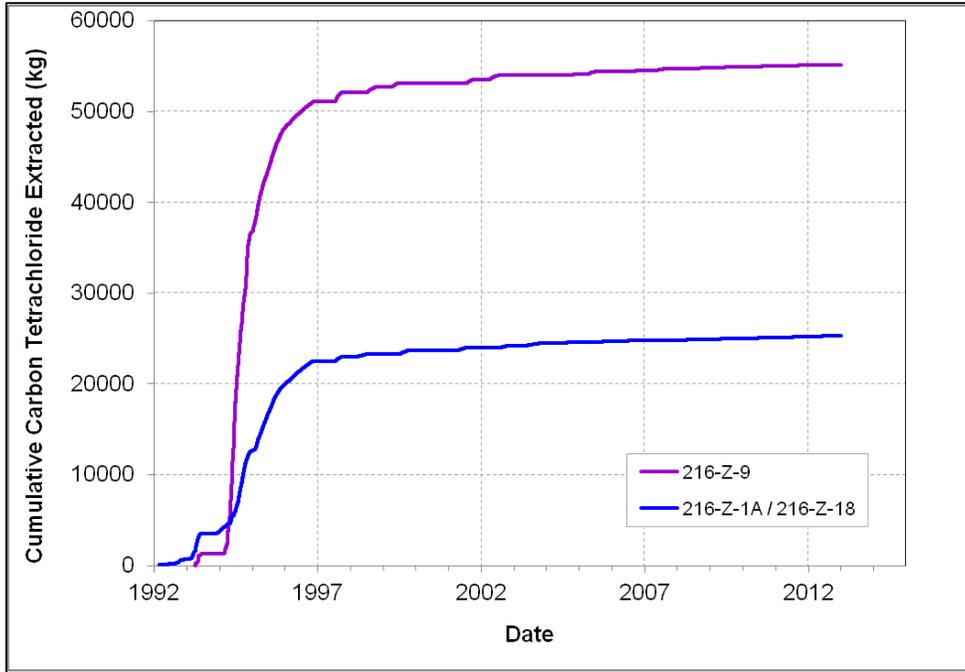
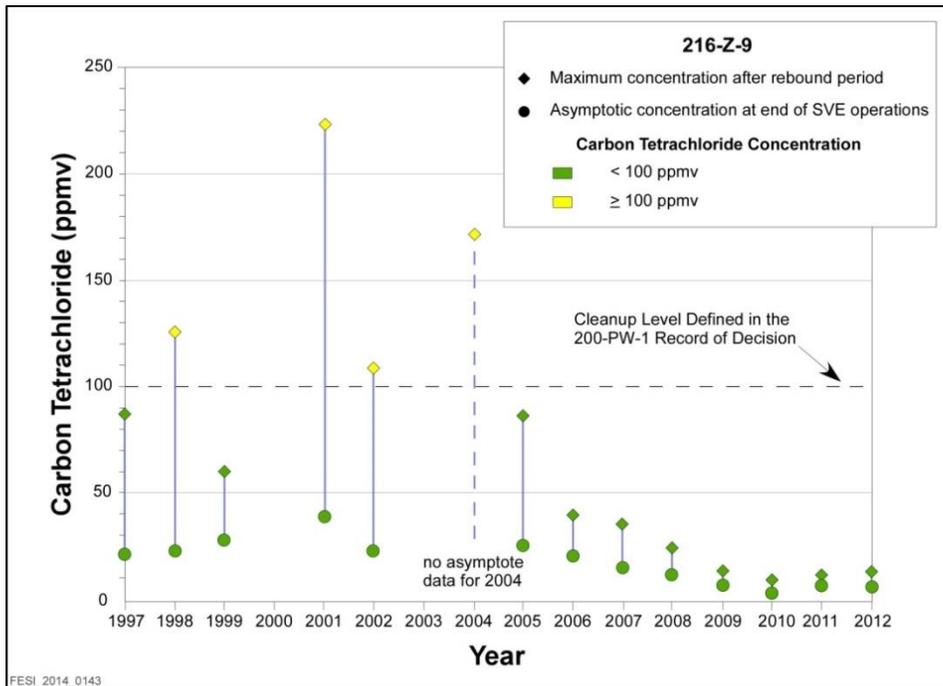
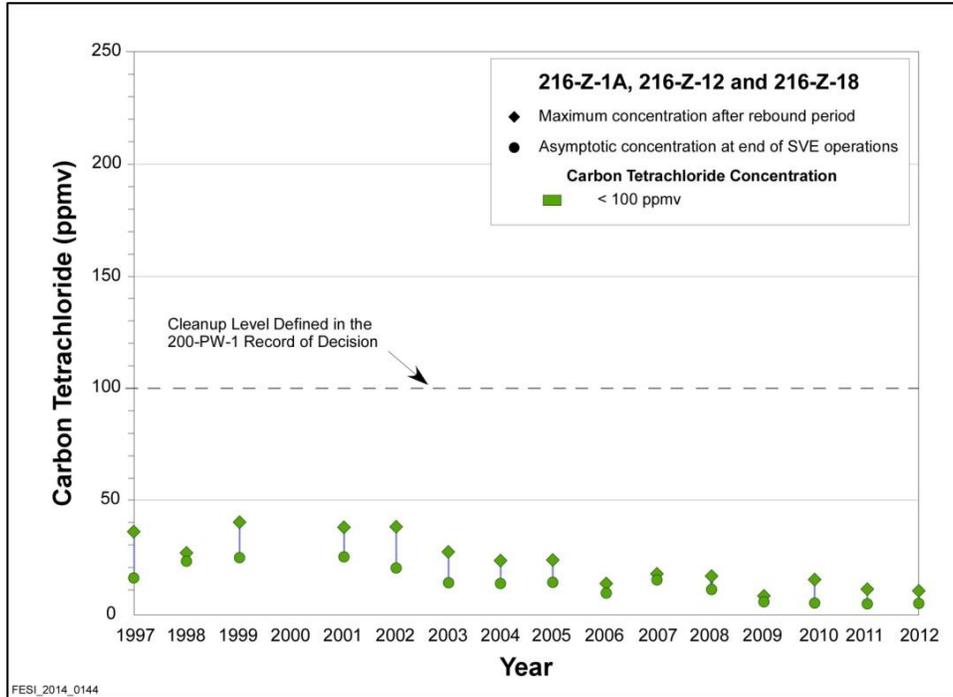


Figure 3-10. Cumulative Carbon Tetrachloride Mass Removed from the 216-Z-9 and 216-Z-1A/216-Z-18 Sites



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

Figure 3-11. 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 3-12. Rebound and Final Concentrations for Operational Cycles of the 216-Z-1A/216-Z-18/216-Z-12 SVE System from 1997 to 2012

1
2
3
4
5

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

17 Given the source location in the CCU and diffusion of carbon tetrachloride into the more permeable
18 sediments below the CCU, there is potential for an impact to the 200-ZP-1 OU groundwater, which is
19 the receptor for the 200-PW-1 OU vadose zone contamination. Receptors are discussed in more detail
20 in Chapter 4.

21 The one complicating factor relevant to the vadose zone contamination is the fact that the groundwater
22 is already contaminated with carbon tetrachloride, and it is possible for contaminant mass transfer to be
23 out of the groundwater and into the vadose zone, depending on the relative concentrations in these
24 two zones. A separate and concurrent remedy ongoing for groundwater treatment, the 200-ZP-1 OU
25 groundwater remedy, consists of applying a P&T system for 25 years (through 2037) to extract carbon
26 tetrachloride-contaminated groundwater and reduce concentrations to approximately 100 µg/L.
27 The remedy then transitions to a 100-year period of MNA, during which time the residual carbon

tetrachloride in the groundwater is expected to decline sufficiently to meet the cleanup goal of 3.4 µg/L established in EPA et al., 2008, *Record of Decision, Hanford 200 Area, 200-ZP-1 Superfund Site, Benton County, Washington* (hereafter referred to as the 200-ZP-1 OU ROD). The groundwater contaminant concentrations are important as part of the CSM because they need to be considered in regard to carbon tetrachloride transport. 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.

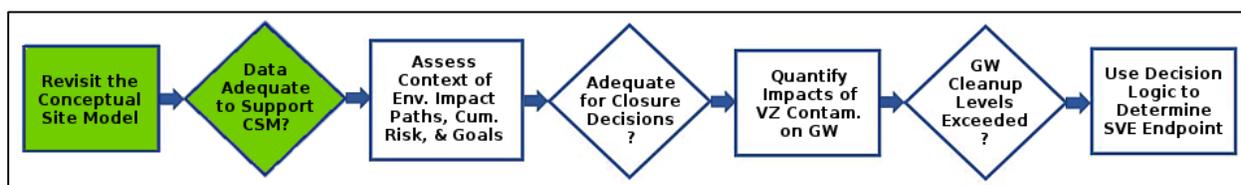
3.2 Methylene Chloride Conceptual Site Model

Methylene chloride was not a component of the disposed waste. Its presence in the subsurface would be due to anaerobic degradation of chloroform, which 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 these reactions. These conditions may have existed during (and for some time after) disposal, when the subsurface moisture content was high (due to the presence of disposed water and organics such as lard oil). Over time, the potential for generation of methylene chloride in the subsurface would decrease as the organic material was degraded, the moisture content decreased, and the subsurface transitioned to more aerobic conditions, especially with the onset of SVE. Under current conditions, the methylene chloride contamination is viewed as a dispersed remnant of these previous conditions, with no continuing source of methylene chloride in the vadose zone. In addition, methylene chloride can be biodegraded by anaerobic or aerobic direct metabolism mechanisms as attenuation processes that further reduce its concentration over time in the subsurface (WSRC-STI-2006-00096). The end product of these 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 (Appendix B). Based on these low concentrations, it is likely that the 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 concentrations are expected to stay low and diminish over time in the vadose zone.

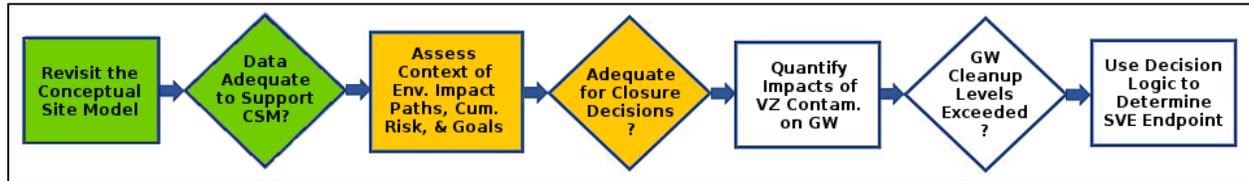
3.3 Conclusions

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



4 Environmental Pathways and Regulatory Compliance Context

Having reviewed/updated the CSM, the next step (per Chapter 2) 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 3) provides the framework to revisit these aspects and determine whether they are adequate to support SVE endpoint decisions.



4.1 Environmental Impact Pathways

The CSM describes the current extent of the 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 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 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 baseline risk assessment determined that the vapor inhalation pathway was insignificant.

The remaining potential environmental pathway is exposure via groundwater (e.g., exposure through drinking, irrigation, and discharge to surface water). Referring to the current CSM, the remaining carbon tetrachloride contamination is primarily in the CCU sediments. Currently, diffusive transport of carbon tetrachloride in the soil gas below the CCU is a potential pathway to the groundwater, where interphase mass transfer could result in an impact to the groundwater receptor. This pathway from the vadose zone source (CCU sediments) to contamination of groundwater needs to 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.

4.2 Cumulative Risk

Given the CSM framework and the existence of a single relevant environmental impact pathway (from vadose zone to groundwater), the applicable cumulative risk is simply the exposure risk due to carbon tetrachloride in the groundwater via exposure to groundwater. This risk from groundwater exposure is assessed as part of the 200-ZP-1 OU groundwater remedy and is not directly applicable to the 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

1 of risk assessment as part of the groundwater remedy and a groundwater carbon tetrachloride
2 concentration cleanup goal of 3.4 µg/L.

3 **4.3 Remediation Goals and Regulatory Setting**

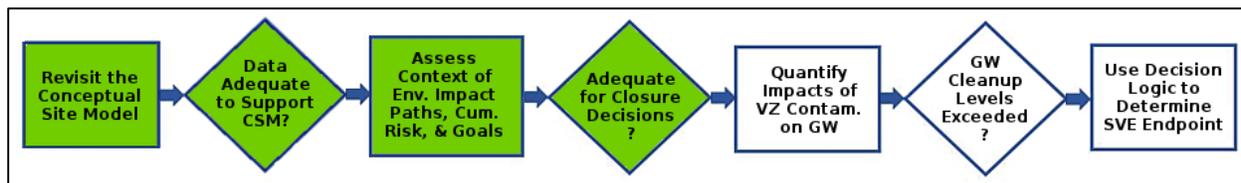
4 To support decisions regarding SVE endpoints, it is important to assess the remediation goal context to
5 ensure that the goals have been defined and are appropriate for the site based on current knowledge.

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

15 The 200-PW-1 OU ROD (EPA et al., 2011) established a final cleanup level of 100 ppmv for carbon
16 tetrachloride and 50 ppmv for methylene chloride in soil vapor to meet the intent of RAO 3 for the
17 200-PW-1 OU. Because this cleanup level was based on the objective of protecting groundwater, the
18 ROD specified that “...soil vapor concentration cleanup levels will be further refined and assessed to
19 ensure they are protective of groundwater...” and that cleanup is subject to WAC 173-340, “Model
20 Toxics Control Act—Cleanup.” The data and analyses present in the treatability test report
21 (PNNL-21326) and in Chapter 5 provide the refined consideration of vadose zone conditions that are
22 protective of groundwater. The 200-PW-1 OU ROD also noted that, “As long as residual contamination
23 remains above levels that allow for unrestricted use, institutional controls will be required.”

24 **4.4 Conclusion for Environmental Pathways and Regulatory Compliance**

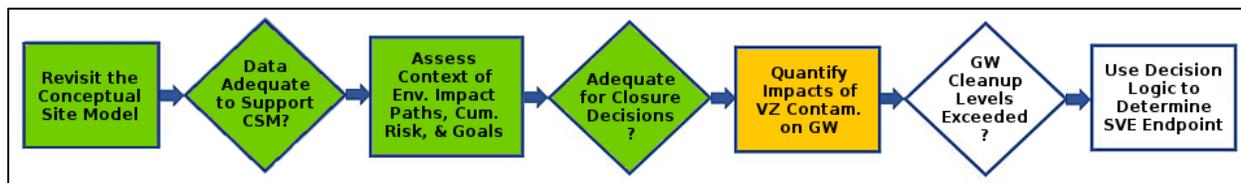
25 As previously described, the environmental impact pathway, cumulative risk, and regulatory compliance
26 context have been adequately determined and defined to support evaluation of the impact of vadose zone
27 contamination on the groundwater concentrations and subsequent decisions regarding disposition of the
28 200-PW-1 OU SVE systems.



29
30

5 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 chapter. The evaluation for carbon tetrachloride contamination is presented in Section 5.1, followed by an evaluation for methylene chloride in Section 5.2.



5.1 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 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). These 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 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.

5.1.1 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 Chapter 3. 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 waste site have removed approximately 55,000 kg of contaminant mass compared to approximately 25,000 kg removed at the combined 216-Z-1A/216-Z-18 sites. 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 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). Appendix C provides the SVEET calculation details. For the 216-Z-9 waste 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 waste 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

1 below the detection limit. As expected from the source strengths, the 216-Z-9 waste site is estimated to
 2 have the most significant impact on groundwater. The impacts to groundwater from the 216-Z-1A and
 3 216-Z-18 sites are estimated to be about 40 and 55 percent less than the estimated impact of the vadose
 4 zone contamination at the 216-Z-9 site. This indicates that the 216-Z-9 vadose zone contamination would
 5 be the limiting, worst-case scenario when considering termination of SVE operations.

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

6
 7 The SVEET results presented in Table 5-1 are conservative for two reasons:

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

15 **5.1.2 Predicted Impacts to Groundwater Using 216-Z-9 Treatability Test**
 16 **Results – Current Mass Discharges (Step 2)**

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

22 The treatability test applied the method of Brusseau et al. (2010) to estimate the vadose source discharge
 23 to be 265 L/d (70 g/d) in 2010, the last year’s data to be analyzed. The treatability test also determined
 24 that the CCU is the primary remaining source of carbon tetrachloride in the vadose zone with areal extent
 25 90 by 90 m (295 by 295 ft).

26 The modeling technique provided in Carroll et al., 2012, “Assessing Performance and Closure for Soil
 27 Vapor Extraction: Integrating Vapor Discharge and Impact to Groundwater Quality,” was used to predict
 28 the groundwater impact from a 90 by 90 m (295 by 295 ft) vadose zone source with varying mass release
 29 rates. For the 2010 measured source mass release rate of 265 L/d (70 g/d), the maximum groundwater
 30 concentration for carbon tetrachloride would be approximately 24 µg/L. As described in the treatability
 31 test report (PNNL-21326) and in Section 5.1.3, the source mass release rate and resulting groundwater
 32 carbon tetrachloride concentration will continue to decline over time and reach a condition that meets the
 33 groundwater remediation goal.

1 **5.1.3 Comparison of the Soil Vapor Extraction Endstate Tool and**
2 **the 216-Z-9 Treatability Test Report Results (Step 3)**

3 As previously discussed, both SVEET (PNNL-21843, SVE Closure Guidance) and the treatability test
4 (PNNL-21326) analyses were conducted for the 216-Z-9 site. SVEET estimates that the groundwater
5 carbon tetrachloride concentration would be approximately 27 µg/L (based on soil vapor concentration of
6 24.7 ppmv at the source). This estimate is consistent with the 24 µg/L groundwater concentration
7 calculated in the treatability test and corroborates the SVEET calculations. Thus, the relative comparisons
8 of SVEET estimates shown in Section 5.1.1 for the three waste sites are appropriate. The SVEET results
9 demonstrate that the 216-Z-9 waste site has the highest impact to groundwater. Because the treatability
10 test uses a more detailed site-specific analysis than SVEET, it provides a more accurate estimate of the
11 groundwater carbon tetrachloride concentrations resulting from the 216-Z-9 vadose zone contaminant
12 source. Therefore, it is appropriate to proceed with the evaluation of SVE impact to groundwater using
13 the 216-Z-9 treatability test analyses.

14 **5.1.4 Predicted Impacts to Groundwater Using 216-Z-9 Treatability Test**
15 **Report Results – Future Mass Discharges (Step 4)**

16 The mass discharge from the vadose zone source will continue to decrease after termination of SVE
17 operations. During cyclic SVE operations, the higher permeability materials around the source zone were
18 periodically cleaned out, allowing vapor-phase contaminants to diffuse from the source zone into the
19 clean zone. As described in the treatability test report (PNNL-21326), the source mass release rate will
20 continue to decline over time due to diffusive mass transfer. Figure 5-1 shows how the maximum
21 groundwater carbon tetrachloride concentrations decline over time based on the post-SVE decline in the
22 source mass release rate described in the treatability test and summarized as follows. With termination of
23 the SVE system, the vadose zone source at the 216-Z-9 site will be below levels of concern within
24 40 years.

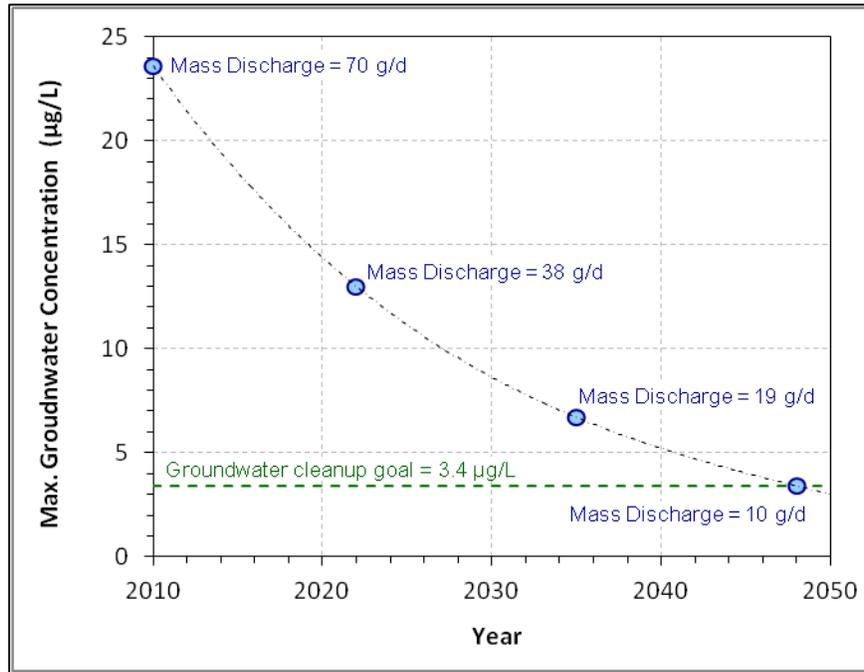
25 Carroll et al. (2012) examined the mass discharge rates for vadose sources comparable in size to the
26 216-Z-9 waste site. The study found the post-SVE diffusion rate was about five times lower than the
27 rate under cyclic SVE conditions (see Appendix E). A source mass discharge rate of 265 L/d (70 g/d)
28 (i.e., the calculated mass discharge for the 216-Z-9 site in 2010 during SVE operations) is expected to
29 decrease to 38 L/d (10 g/d) about 40 years after termination of SVE operations (i.e., about 2050).
30 The mass discharge value of 38 L/d (10 g/d) is significant because it corresponds (Figure 5-1) to
31 a predicted groundwater concentration below 3.4 µg/L, the carbon tetrachloride cleanup level specified
32 for groundwater in the 200-ZP-1 OU ROD (EPA et al., 2008).

33 The P&T system for the 200-ZP-1 OU will be operated for 25 years (through 2037) to extract carbon
34 tetrachloride-contaminated groundwater and reduce concentrations to approximately 100 µg/L. In the
35 100 years following P&T operation, the residual carbon tetrachloride in the groundwater is expected to
36 decline during the MNA phase to meet the ultimate goal of 3.4 µg/L.

37 Figure 5-2 shows the 2013 carbon tetrachloride concentrations in the groundwater below the 216-Z-9
38 waste site to be approximately 500 µg/L. These elevated groundwater concentrations preclude the
39 migration of carbon tetrachloride vapor from the vadose zone into the groundwater due to Henry's law
40 equilibrium calculations (Appendix D).

41 Thus, while groundwater concentrations remain relatively high (e.g., in the 10s to 100s of µg/L), residual
42 carbon tetrachloride concentration in the vadose zone will not migrate downward and poses no additional
43 risk to 200-ZP-1 OU groundwater. However, within about 40 years, the vadose zone contamination will

1 have dissipated to approximately 38 L/d (10 g/d) mass discharge and will pose no threat to clean
2 groundwater. This time frame is well within the groundwater remedy timespan of 125 years.



3
4 Source: Adapted from PNNL-21326, *Treatability Test Report: Characterization of*
5 *Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the*
6 *216-Z-9 Site.*

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

11 **Figure 5-1. Predicted Maximum Groundwater Carbon Tetrachloride**
12 **Concentrations over Time for the 216-Z-9 Trench**

13 5.2 Methylene Chloride Impact on Groundwater

14 Methylene chloride concentrations in the vadose zone are below the 50 ppmv cleanup level in the
15 200-PW-1 OU ROD (EPA et al., 2011) (Section A5 in Appendix A; Appendix B). To further investigate
16 the potential impact of residual methylene chloride contamination in the vadose zone beneath the
17 216-Z-9 waste site, the Hanford Environmental Information System database was queried for
18 groundwater sampling results in the underlying 200-ZP-1 OU aquifer. The wells that were queried are
19 shown in Figure 5-3, and the results from the query are summarized as follows:

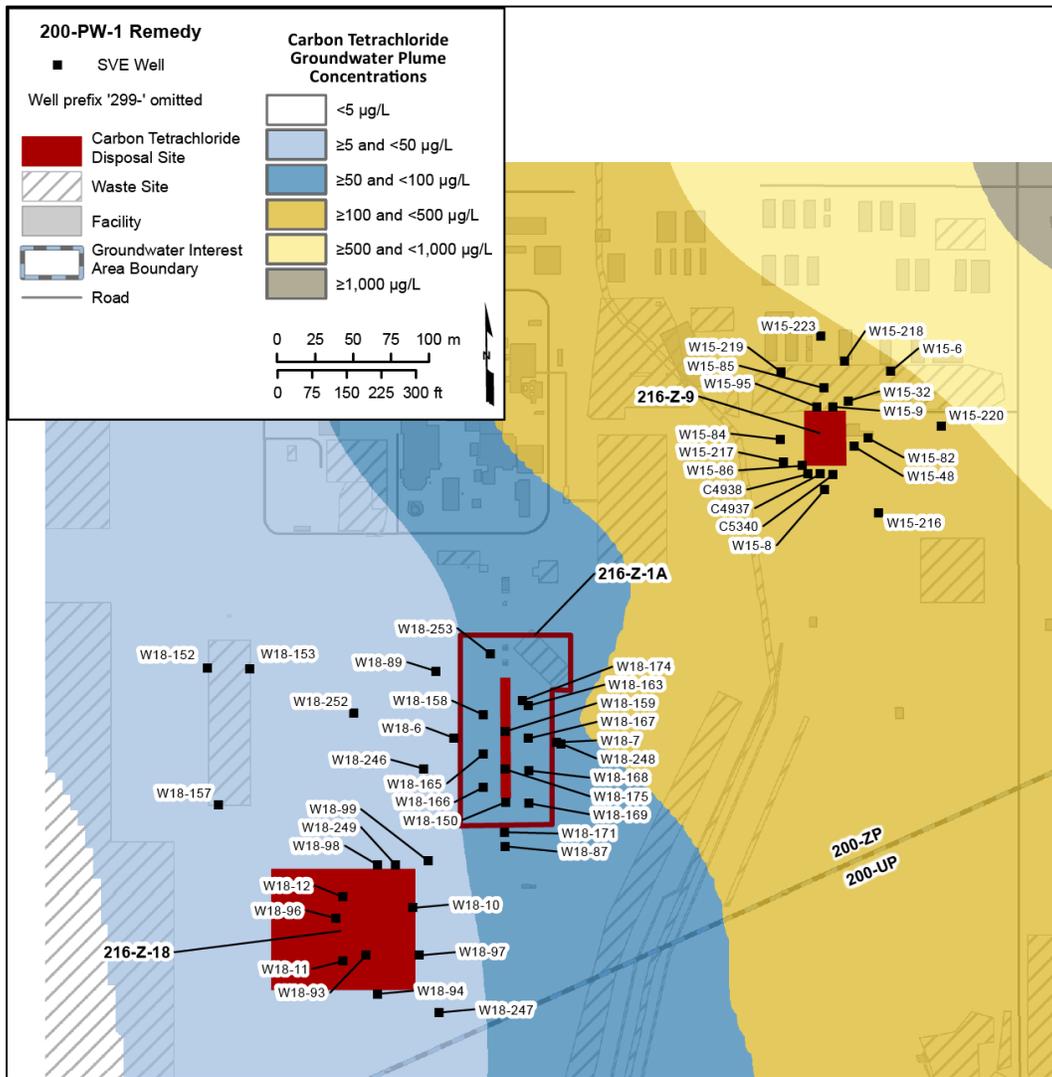
- 20 • Well 299-W15-46 has been continuously monitored since 2004 (including in 2014), with methylene
21 chloride measurements below the detection limit (1 µg/L) since 2006.
- 22 • Well 299-W15-47 has been continuously monitored since 2004, with methylene chloride
23 measurements below the detection limit (1 µg/L) since 2008. Sampling was discontinued after 2010
24 because the measurements did not exceed the maximum contaminant level (MCL) of 5 µg/L.
- 25 • Well 299-W15-6 has been continuously monitored since 1990, with methylene chloride
26 measurements below the MCL (5 µg/L) since 2008. Only three measurements exceeded the detection

1 limit (1 µg/L) since 2008 with measurements at or below 3 µg/L. Sampling was discontinued after
2 2011 because the measurements did not exceed the MCL.

3 • Wells 216-W15-32, 216-W15-38, and 216-W15-39 were continuously monitored since 1997, with
4 methylene chloride measurements below the MCL since 2004. Sampling was discontinued after
5 2008 because the measurements did not exceed the MCL.

6 Thus, there appears to be no significant methylene chloride contamination beneath the 216-Z-9 waste site
7 in the 200-ZP-1 OU aquifer.

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



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

Figure 5-2. 2013 Carbon Tetrachloride Groundwater Concentrations Underlying the Carbon Tetrachloride Waste Sites

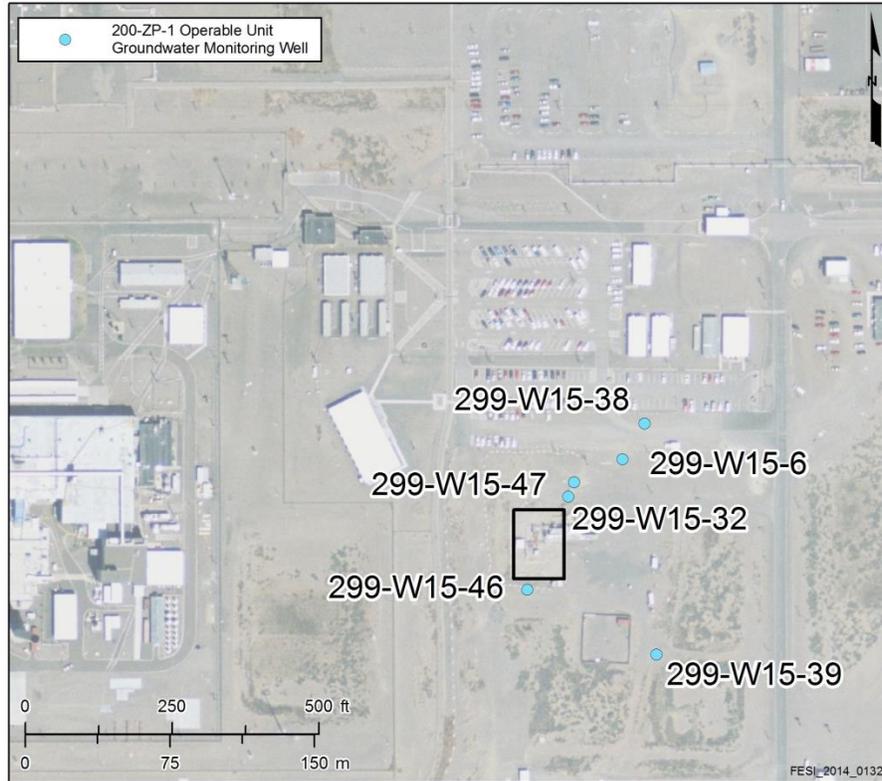
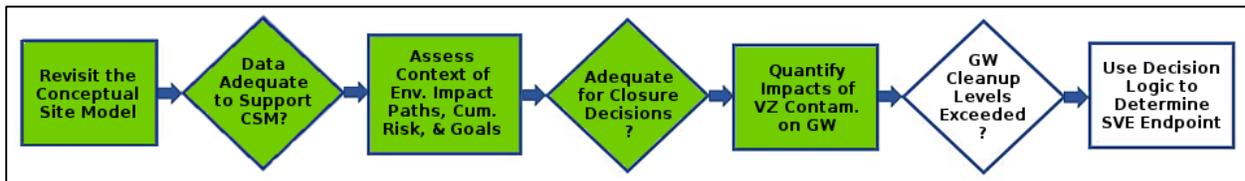


Figure 5-3. Groundwater Monitoring Wells for the 216-Z-9 Waste Site

5.3 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 $\mu\text{g/L}$ (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.

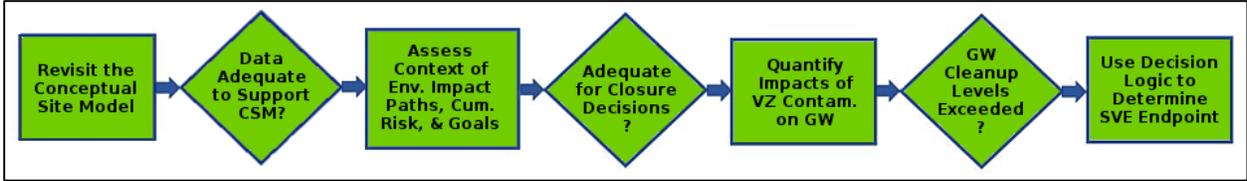


6 Decision Logic Assessment and Recommendations

The final step of the site-specific assessment approach is to combine the outcomes from the prior elements (discussed in Chapters 3, 4, and 5) and apply the decision logic shown in Figure 2-2 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 the time this goal is required for the groundwater. This information, as presented in this document, meets the steps outlined in SVE Closure Guidance (PNNL-21843) (Chapter 2) and demonstrates that groundwater cleanup levels will not be exceeded. Thus, closure of the SVE remedy (i.e., permanently discontinuing operation of the SVE systems) within the 200-PW-1 OU is recommended. EPA concurrence with this report will initiate activities to terminate SVE operations and define any necessary continued monitoring.



1

2

This page intentionally left blank

3

7 References

- 1
2 BHI-01105, 1997, *Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site,*
3 *Fiscal Year 1997*, Rev. 0, Bechtel Hanford, Inc., Richland, Washington. Available at:
4 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D198067101>.
- 5 Brusseau, M.L., V. Rohay, and M.J. Truex, 2010, "Analysis of Soil Vapor Extraction Data to Evaluate
6 Mass-Transfer Constraints and Estimate Source-Zone Mass Flux," *Ground Water Monit.*
7 *Remediat.* 30(3):57-64. Available at:
8 <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3600985/pdf/nihms437408.pdf>.
- 9 Carroll, K.C., M. Oostrom, M.J. Truex, V.J. Rohay, and M.L. Brusseau, 2012, "Assessing Performance
10 and Closure for Soil Vapor Extraction: Integrating Vapor Discharge and Impact to Groundwater
11 Quality," *J. Contam. Hydrol.* 128(1-4):71-82.
- 12 *Comprehensive Environmental Response, Compensation, and Liability Act of 1980*, 42 USC 9601, et seq.,
13 Pub. L. 107-377, December 31, 2002. Available at: <http://epw.senate.gov/cercla.pdf>.
- 14 DOE/RL-2006-51, 2007, *Remedial Investigation Report for the Plutonium/Organic-Rich Process*
15 *Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and*
16 *200-PW-6 Operable Units*, Rev. 0, U.S. Department of Energy, Richland Operations Office,
17 Richland, Washington. Available at:
18 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA05807591>.
19 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA05807868>.
20 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0805130070>.
21 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0805130071>.
- 22 DOE/RL-2007-27, 2011, *Feasibility Study for the Plutonium/Organic-Rich Process Condensate/Process*
23 *Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6 Operable Units,*
24 Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
25 Available at:
26 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093807>.
27 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093806>.
28 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093805>.
29 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093804>.
30 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093803>.
31 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093802>.
32 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093801>.
33 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093800>.
34 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093799>.
35 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093798>.
36 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093797>.
- 37 DOE/RL-2014-18, 2014, *Path Forward For Future 200-PW-1 Operable Unit Soil Vapor Extraction*
38 *Operations*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland,
39 Washington. Available at:
40 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0082285H>.
- 41 DOE/RL-2014-32, 2014, *Hanford Site Groundwater Monitoring Report for 2013*, Rev. 0,
42 U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at:
43 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0084842>.

- 1 EPA and Ecology, 1992, *Action Memorandum: Expedited Response Action Proposal for 200 West Area*
2 *Carbon Tetrachloride Plume*, U.S. Environmental Protection Agency and Washington State
3 Department of Ecology, Olympia, Washington. Available at:
4 <http://pdw.hanford.gov/arpir/pdf.cfm?accession=D196088487>.
- 5 EPA, Ecology, and DOE, 2008, *Record of Decision, Hanford 200 Area, 200-ZP-1 Superfund Site, Benton*
6 *County, Washington*, U.S. Environmental Protection Agency, U.S. Department of Energy, and
7 Washington State Department of Ecology, Olympia, Washington. Available at:
8 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=00098825>.
- 9 EPA, Ecology, and DOE, 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and*
10 *200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*, U.S. Environmental Protection Agency,
11 U.S. Department of Energy, and Washington State Department of Ecology, Olympia,
12 Washington. Available at: <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093644>.
- 13 PNNL-21326, 2012, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride*
14 *Source Strength Using Tomographic Methods at the 216-Z-9 Site*, Pacific Northwest National
15 Laboratory, Richland, Washington. Available at:
16 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1210310436>.
- 17 PNNL-21843, 2013, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance*,
18 Pacific Northwest National Laboratory, Richland, Washington. Available at:
19 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0088374>.
- 20 RCW 49.17, “Washington Industrial Safety and Health Act,” *Revised Code of Washington*, Olympia,
21 Washington. Available at: <http://apps.leg.wa.gov/rcW/default.aspx?cite=49.17>.
- 22 WAC 173-340, “Model Toxics Control Act—Cleanup,” *Washington Administrative Code*, Olympia,
23 Washington. Available at: <http://apps.leg.wa.gov/wac/default.aspx?cite=173-340>.
- 24 WSRC-STI-2006-00096, 2007, *Scenarios Evaluation Tool for Chlorinated Solvent MNA*, Rev. 2,
25 Washington Savannah River Company, Aiken, South Carolina. Available at:
26 <http://www.osti.gov/scitech/biblio/899964>.

1

Appendix A

2

Summary of Investigations and Remedial Activities

3

1

2

This page intentionally left blank.

1 **Contents**

2 **A1 Introduction..... A-1**

3 **A2 Chronology A-1**

4 **A3 Investigation of Carbon Tetrachloride Sources at 200-PW-1 Operable Unit**

5 **Waste Disposal Sites A-1**

6 A3.1 Remediation and Characterization of Carbon Tetrachloride at 200-PW-1

7 Operable Unit Carbon Tetrachloride Waste Sites..... A-8

8 A3.2 Soil Vapor Extraction Performance A-10

9 **A4 Investigation of Carbon Tetrachloride Sources beyond the 200-PW-1**

10 **Operable Unit Waste Disposal Sites A-24**

11 A4.1 Characterization Beyond the 200-PW-1 Operable Unit Carbon

12 Tetrachloride Waste Sites A-24

13 A4.2 Key Findings and Results of the Remedial Investigation A-27

14 **A5 Methylene Chloride at 200-PW-1 Operable Unit Waste Disposal Sites..... A-34**

15 **A6 Feasibility Study..... A-39**

16 **A7 Proposed Plan and Record of Decision A-39**

17 **A8 Path Forward A-39**

18 **A9 References..... A-40**

19

20 **Figures**

21 Figure A-1. Timeline for Investigations and Remedial Activities for Carbon Tetrachloride at

22 the 200-PW-1 OU A-1

23 Figure A-2. Carbon Tetrachloride Waste Sites and SVE Systems for the 200-PW-1 OU A-9

24 Figure A-3. Cumulative Carbon Tetrachloride Mass Removed from the 216-Z-9 and

25 216-Z-1A/216-Z-18 Waste Sites..... A-10

26 Figure A-4. Carbon Tetrachloride Mass Removal Using Active SVE, Depicting a

27 Two-Order-of-Magnitude Decrease between the Early 1990s and Recent Times..... A-11

28 Figure A-5. Carbon Tetrachloride Mass Removal Using Passive SVE, Depicting an Order-of-

29 Magnitude Less than the Active SVE Systems..... A-12

30 Figure A-6. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at

31 Online Active SVE Wells with Screened Intervals above the CCU (1992 to 2012) A-13

32 Figure A-7. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at

33 Online Active SVE Wells with Screened Intervals below the CCU (1992 to 2012) A-14

34 Figure A-8. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most

35 Recent Carbon Tetrachloride Concentrations (1993 to 2012) for 216-Z-9 Online

36 Active SVE Wells A-15

1 Figure A-9. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most
2 Recent Carbon Tetrachloride Concentrations (1993 to 2012) for
3 216-Z-1A/216-Z-12 Online Active SVE Wells A-16
4 Figure A-10. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most
5 Recent Carbon Tetrachloride Concentrations (1993 to 2012) for 216-Z-18 Online
6 Active SVE Wells A-17
7 Figure A-11. Rebound and Final Concentrations for Operational Cycles of the 216-Z-9 SVE
8 System, 1997 to 2012..... A-18
9 Figure A-12. Rebound and Final Concentrations for Operational Cycles of the
10 216-Z-1A/216-Z-18/216-Z-12 SVE System, 1997 to 2012 A-19
11 Figure A-13. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at
12 Offline Monitoring Wells and Soil Vapor Probes at 216-Z-9 (1996 to 2014) A-20
13 Figure A-14. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at
14 Offline Monitoring Wells and Soil Vapor Probes at
15 216-Z-1A/216-Z-12/216-Z-18 (1996 to 2014)..... A-21
16 Figure A-15. 2014 Carbon Tetrachloride Concentrations (ppmv) for Samples Collected from
17 Soil Vapor Probes and Offline Monitoring Wells Screened above and within
18 the CCU..... A-22
19 Figure A-16. 2014 Carbon Tetrachloride Concentrations (ppmv) for Samples Collected from
20 Offline Monitoring Wells Screened below the CCU A-23
21 Figure A-17. Carbon Tetrachloride Sampling Locations during the Remedial Investigation,
22 Overlaid on the 2005 Groundwater Carbon Tetrachloride Plume Contours A-25
23 Figure A-18. Passive Soil Gas Vapor Sampling Results from the Remedial Investigation A-26
24 Figure A-19. Remedial Investigation Active Soil Vapor Sampling Results for Locations above
25 the CCU..... A-28
26 Figure A-20. Remedial Investigation Active Soil Vapor Sampling Results for Locations within
27 the CCU..... A-29
28 Figure A-21. Remedial Investigation Active Soil Vapor Sampling Results for Locations below
29 the CCU..... A-30
30 Figure A-22. Remedial Investigation Soil Sampling Results for Locations above the CCU A-31
31 Figure A-23. Remedial Investigation Soil Sampling Results for Locations within the CCU A-32
32 Figure A-24. Remedial Investigation Soil Sampling Results for Locations below the CCU..... A-33
33 Figure A-25. Historical Maximum and Most Recent Methylene Chloride Concentrations at
34 Online SVE Wells with Screened Intervals above the CCU (1993 to 2012) A-35
35 Figure A-26. Historical Maximum and Most Recent Methylene Chloride Concentrations at
36 Online SVE Wells with Screened Intervals below the CCU (1993 to 2012)..... A-36
37 Figure A-27. Maximum Methylene Chloride Concentrations at Offline Monitoring Wells and
38 Soil Vapor Probes at 216-Z-9 (1997 to 2013)..... A-37
39 Figure A-28. Maximum Methylene Chloride Concentrations at Offline Monitoring Wells and
40 Soil Vapor Probes at 216-Z-1A/216-Z-18/216-Z-12 (1997 to 2013)..... A-38
41

42 **Table**

43 Table A-1. Summary of Investigation and Remediation Activities at the 200-PW-1 OU A-2
44

Terms

| | | |
|----|---------|--|
| 1 | | |
| 2 | B&K | Brüel & Kjær |
| 3 | CCU | Cold Creek unit |
| 4 | CPT | cone penetrometer |
| 5 | CSM | conceptual site model |
| 6 | CY | calendar year |
| 7 | DNAPL | dense nonaqueous-phase liquid |
| 8 | DOE | U.S. Department of Energy |
| 9 | Ecology | Washington State Department of Ecology |
| 10 | EPA | U.S. Environmental Protection Agency |
| 11 | OU | operable unit |
| 12 | ppmv | parts per million by volume |
| 13 | ROD | Record of Decision |
| 14 | SVE | soil vapor extraction |
| 15 | | |

1

2

This page intentionally left blank.

1

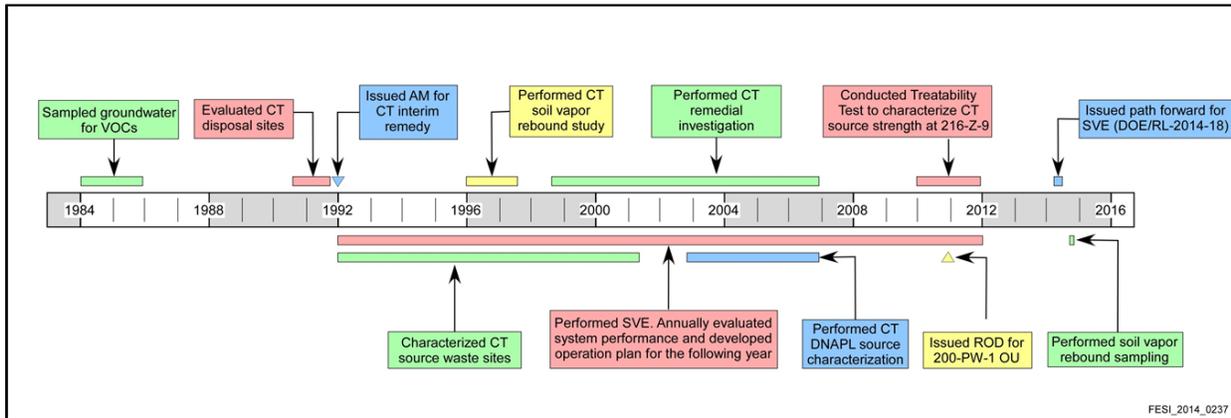
A1 Introduction

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

5

A2 Chronology

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



9

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

12

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

13

14 Carbon tetrachloride was disposed to the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib in
15 the 200-PW-1 OU from 1955 to 1973. SVE was implemented in 1992 to remove carbon tetrachloride
16 from the vadose zone in the vicinities of the three waste sites. Characterization of the carbon tetrachloride
17 distribution in the vadose zone was conducted in the vicinities of the three waste sites to support
18 implementation of SVE. At that time, carbon tetrachloride was present throughout the vadose zone.

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

27

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, <i>Hanford Site Ground-Water Surveillance for 1989</i> |
| 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 systems. | Proposed the use of SVE in the engineering evaluation/cost analysis as the preferred alternative. | DOE/RL-91-32, 1991, <i>Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon Tetrachloride Plume</i> |
| 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 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. | <i>Action Memorandum: Expedited Response Action Proposal for 200 West Area Carbon Tetrachloride Plume</i> (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, <i>FY92 Site Characterization Status Report and Data Package for the Carbon Tetrachloride Site</i> WHC-SD-EN-TI-202, 1993, <i>FY93 Site Characterization Status Report and Data Package for the Carbon Tetrachloride Site</i> WHC-SD-EN-TI-248, 1994, <i>1994 Conceptual Model of the Carbon Tetrachloride Contamination in the 200 West Area at the Hanford Site</i> BHI-00105, 1995, <i>FY 1993 Wellfield Enhancement Status Report and Data Package for the 200 West Area Carbon Tetrachloride Expedited Response Action</i> |

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 2014. | SGW-54566, 2013, <i>Performance Evaluation Report for Soil Vapor Extraction Operations at the 200-PW-1 Operable Unit Carbon Tetrachloride Site, Calendar Year 2012</i> (Note that 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, <i>Carbon Tetrachloride Soil Vapor Extraction System Operating and Monitoring Plan for CY 2015</i> (Note that 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: <ul style="list-style-type: none"> • Readily accessible mass has been removed. • The availability of additional carbon tetrachloride is limited due to the lower permeability zone. • 8-month suspended operation caused no additional degradation of groundwater quality. Recommendations included the following: <ul style="list-style-type: none"> • 4 to 8 weeks of operations 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, <i>Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site, Fiscal Year 1997</i> BHI-01105-00-CN-01, 1997, <i>Change Notice: Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site</i> |

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 | <p>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:</p> <ul style="list-style-type: none"> • 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: <ul style="list-style-type: none"> – 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 <p>Conducted numerical simulations of carbon tetrachloride disposal and migration at the 216-Z-9, 216-Z-1A, and 216-Z-18 sites.</p> | <p>Updated the conceptual models of carbon tetrachloride for 216-Z-9, 216-Z-1A, and the dispersed plume.</p> <p>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.</p> <p>Highest carbon tetrachloride concentrations beneath the waste sites are located in fine-grained layers.</p> <p>Found carbon tetrachloride DNAPL in soil sample within a silt layer above the CCU at 216-Z-9.</p> <p>No evidence of significant lateral migration of carbon tetrachloride along the top of the CCU. No evidence of downward migration from an undocumented source.</p> <p>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.</p> <p>Sampling result 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.</p> | <p>DOE/RL-2001-01, 2004, <i>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</i></p> <p>DOE/RL-2006-51, 2007, <i>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</i></p> |

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, <i>Carbon Tetrachloride Dense Non-Aqueous Phase Liquid (DNAPL) Source Term Interim Characterization Report</i> DOE/RL-2007-22, 2007, <i>Carbon Tetrachloride Dense Non-Aqueous Phase Liquid (DNAPL) Source Term Interim Characterization Report Addendum</i> |
| 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, <i>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</i> |
| 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: <ul style="list-style-type: none"> • 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, <i>Treatability Test Plan for Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site</i> PNNL-21326, 2012, <i>Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site</i> |

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 continued 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, <i>Proposed Plan for the Remediation of the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units</i> |
| 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, <i>Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units</i> |
| 2012 | SVE system operational strategy | Provided the strategy to sample, modify, and operate the SVE systems. | Recommended the following: <ul style="list-style-type: none"> • 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, <i>200-PW-1 Operable Unit Soil Vapor Extraction System Operational Strategy</i> |

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 | <p>This document provided the following:</p> <ul style="list-style-type: none"> • 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, <i>Path Forward for Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations</i> |
| 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, <i>Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2014 Rebound Sampling</i> |

Note: The references cited in this table are included in the “References” section of this appendix.

CCU = Cold Creek unit

EPA = U.S. Environmental Protection Agency

CSM = conceptual site model

OU = operable unit

CY = calendar year

ppmv = parts per million by volume

DNAPL = dense nonaqueous-phase liquid

SVE = soil vapor extraction

DOE = U.S. Department of Energy

Ecology = Washington State Department of Ecology

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

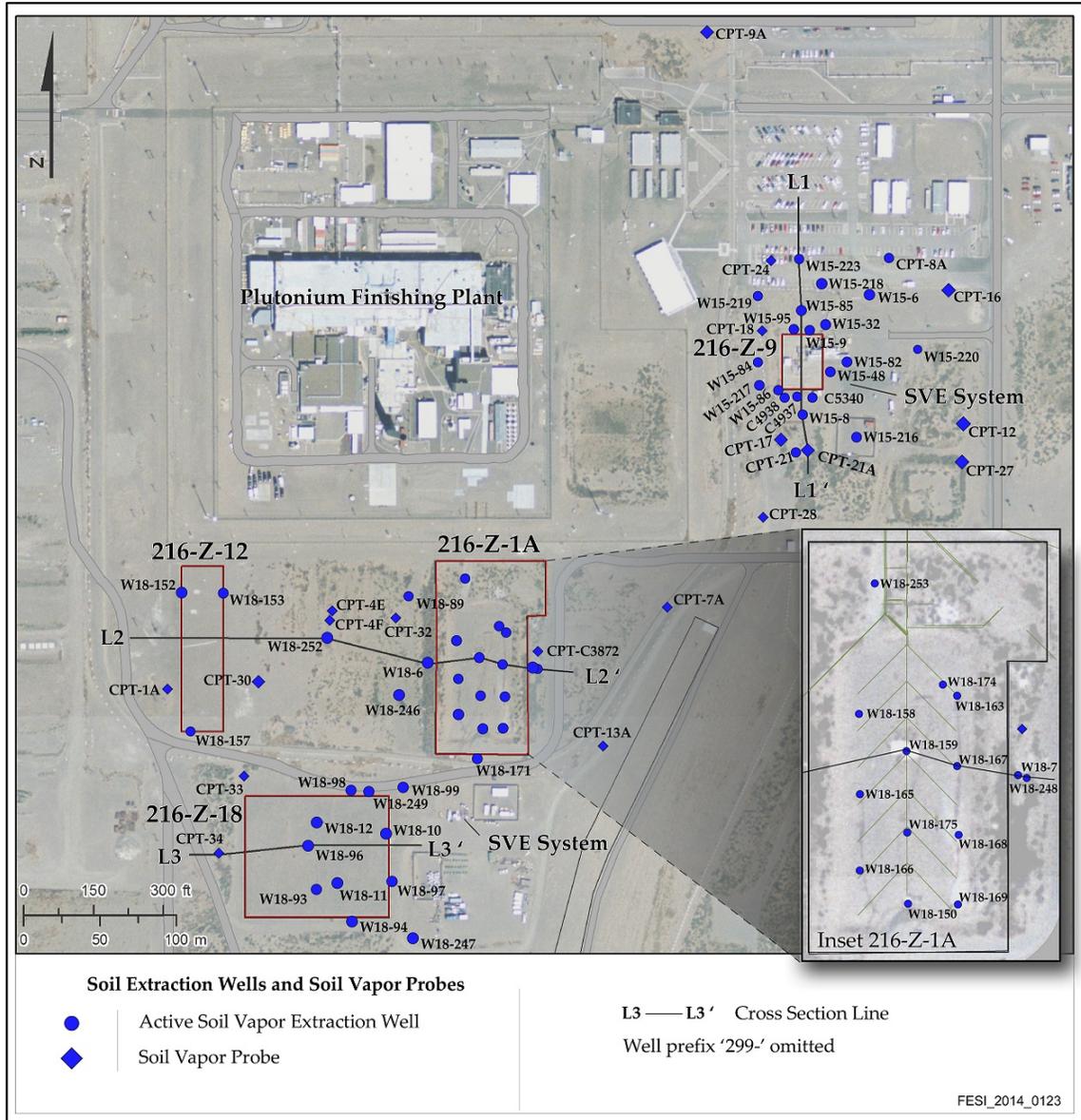
7 **A3.1 Remediation and Characterization of Carbon Tetrachloride** 8 **at 200-PW-1 Operable Unit Carbon Tetrachloride Waste Sites**

9 At the Hanford Site, carbon tetrachloride was used in mixtures with other organics to recover plutonium
10 in aqueous waste streams at the Plutonium Finishing Plant in the 200 West Area. From 1955 to 1973,
11 carbon tetrachloride contained in aqueous and organic liquid wastes was discharged primarily to three
12 subsurface infiltration sites: 216-Z-9 Trench (1955 to 1962), 216-Z-1A Tile Field (1964 to 1969), and
13 216-Z-18 Crib (1969 to 1973). Additionally, a small volume of carbon tetrachloride was discharged to the
14 216-Z-12 Crib. Figure A-2 provides a map of carbon tetrachloride waste sites within the 200-PW-1 OU.
15 The subsurface below the waste sites is comprised of higher-permeability Hanford formation materials
16 (about 34 m [112 ft] thick) and Ringold Formation material (about 25 m [82 ft] thick above the water
17 table), which are separated by the low-permeability CCU sediments (about 6 m [20 ft] thick). Thus, as the
18 liquid waste containing carbon tetrachloride infiltrated into the ground, these soils under the disposal sites
19 became contaminated. In the mid-1980s, a widespread carbon tetrachloride plume was discovered in the
20 underlying groundwater.

21 In 1992, the U.S. Environmental Protection Agency (EPA) and the Washington State Department of
22 Ecology (Ecology) issued the *Action Memorandum: Expedited Response Action Proposal for 200 West*
23 *Area Carbon Tetrachloride Plume* (EPA and Ecology, 1992) to authorize an interim remedy for the
24 removal of carbon tetrachloride from the 200-PW-1 OU vadose zone using SVE systems. Between
25 February 1992 and October 2011, the SVE systems were operated as an interim remedial action in
26 accordance with the action memorandum. In October 2011, EPA, Ecology, and the U.S. Department of
27 Energy (DOE) issued the *Record of Decision for the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6*
28 *Operable Units* (hereafter referred to as 200-PW-1 OU Record of Decision [ROD]) (EPA et al., 2011).
29 Between October 2011 and October 2014, the SVE systems were operated as a final remedial action in
30 accordance with the 200-PW-1 OU ROD.

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

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



1

2

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

3

During the remedial investigation for the 200-PW-1 OU 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.

10

The remedial investigation 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.

11

12

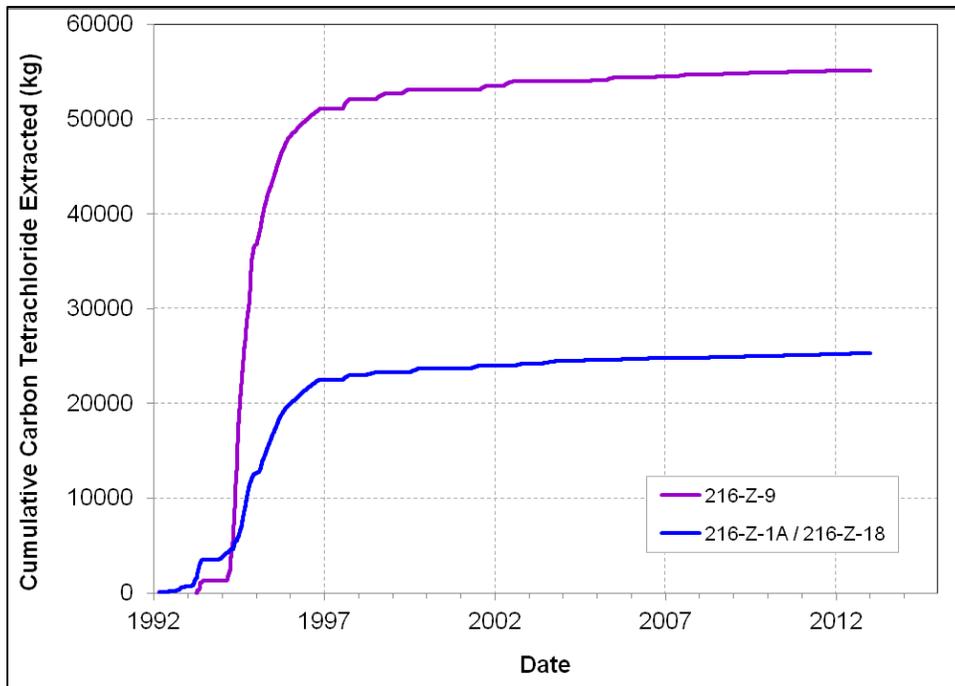
13

14

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

6 A3.2 Soil Vapor Extraction Performance

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



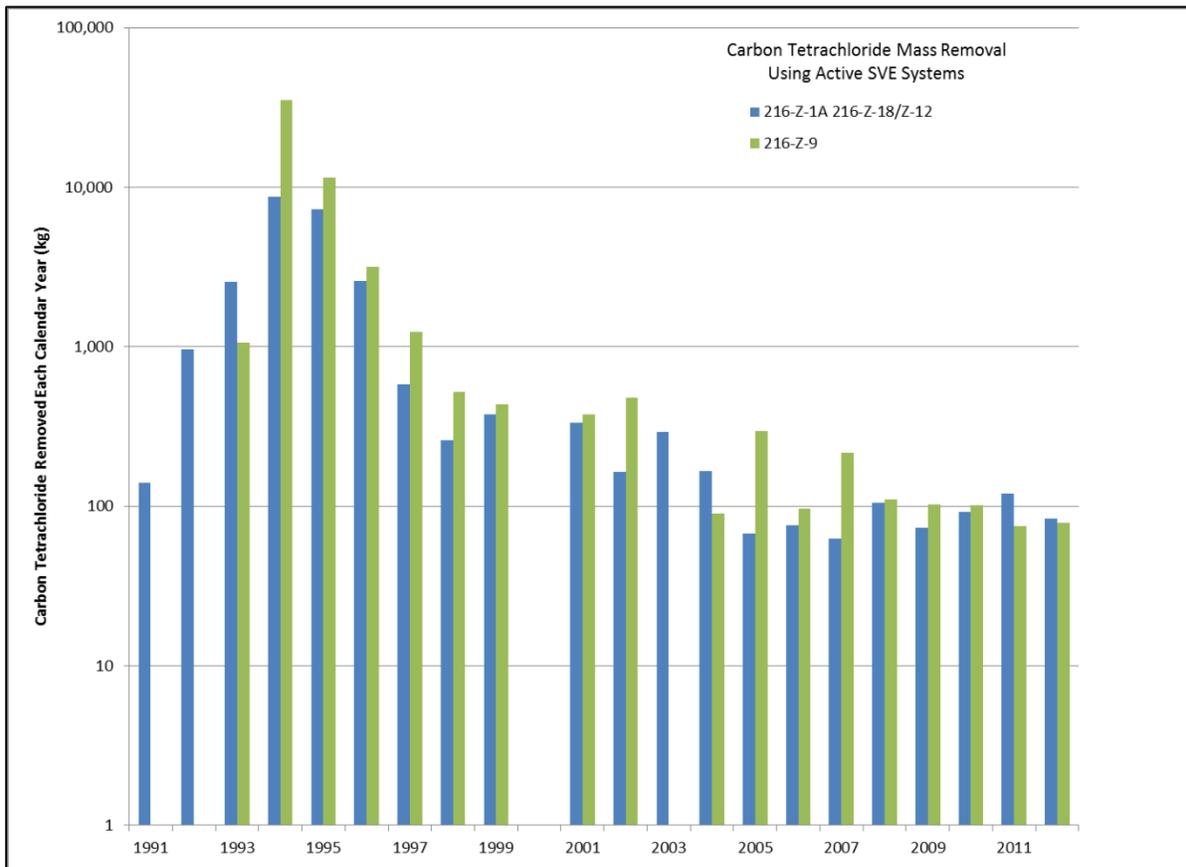
14
15 **Figure A-3. Cumulative Carbon Tetrachloride Mass**
16 **Removed from the 216-Z-9 and 216-Z-1A/216-Z-18 Waste Sites**

17 Between 1992 and 1997, the strategy for SVE operations was to run throughout the year using up to three
18 SVE systems with design capacities of 14.2, 28.3, and 42.5 m³/min (500, 1,000, and 1,500 ft³/min).
19 The SVE systems were shut down from November 1996 through July 1997 for a rebound study to
20 determine the increase in carbon tetrachloride vapor concentrations resulting from the temporary system
21 shutdown (BHI-01105, *Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site,*
22 *Fiscal Year 1997*). The study concluded that (1) in many areas, the readily accessible mass had been
23 removed from the high-permeability zones; (2) the availability of additional carbon tetrachloride for
24 capture is limited by diffusion from the lower permeability zones; and (3) the 8 months of suspended
25 operation caused no additional degradation of groundwater quality. The study recommended that the SVE
26 systems be operated in a cyclic mode (e.g., 4 to 8 weeks of active operation, followed by 8 to 16 weeks

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

3 The operating strategy was modified based on the results of the rebound study and the declining rate of
4 carbon tetrachloride removal during continuous extraction operations. Rather than operating all three
5 SVE systems, only the 14.2 m³/min (500 ft³/min) system was used for carbon tetrachloride removal from
6 1998 through 2008. The system typically operated from April through September each year, alternating
7 between the 216-Z-9 site and the 216-Z-1A/216-Z-18/216-Z-12 site (for approximately 3 months at each
8 site). The system was maintained in standby mode from October through March each year to allow time
9 for carbon tetrachloride vapor concentrations to rebound.

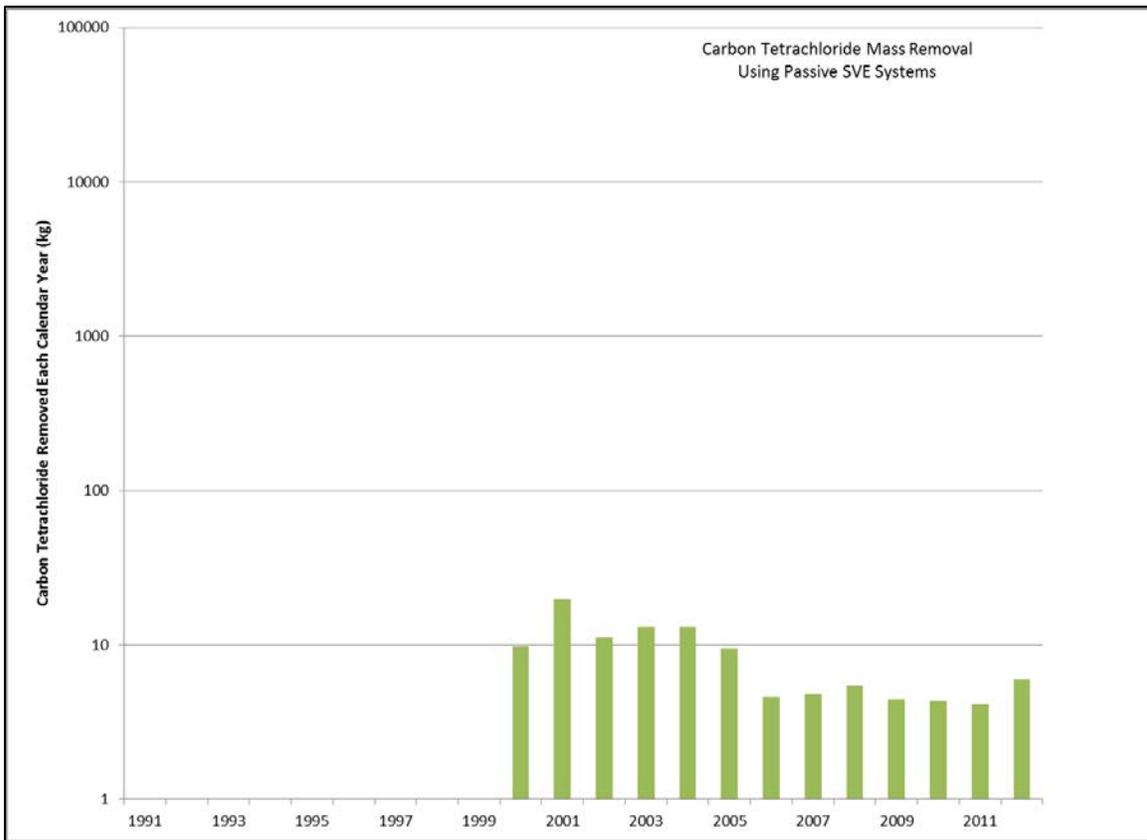
10 Two new SVE systems, each with a design capacity of 14.2 m³/min (500 ft³/min), were operated from
11 2009 through 2012. One system was operated at the 216-Z-1A/216-Z-18/216-Z-12 site, and one system at
12 the 216-Z-9 site. Each system operated for 6 months in 2009, for 8 months in 2010, for 8 months in 2011,
13 and for 6 months in 2012. The systems were not operated in 2013 or 2014 to allow carbon tetrachloride
14 concentrations to rebound. Figure A-4 summarizes the mass removal history for the 216-Z-9 and
15 216-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

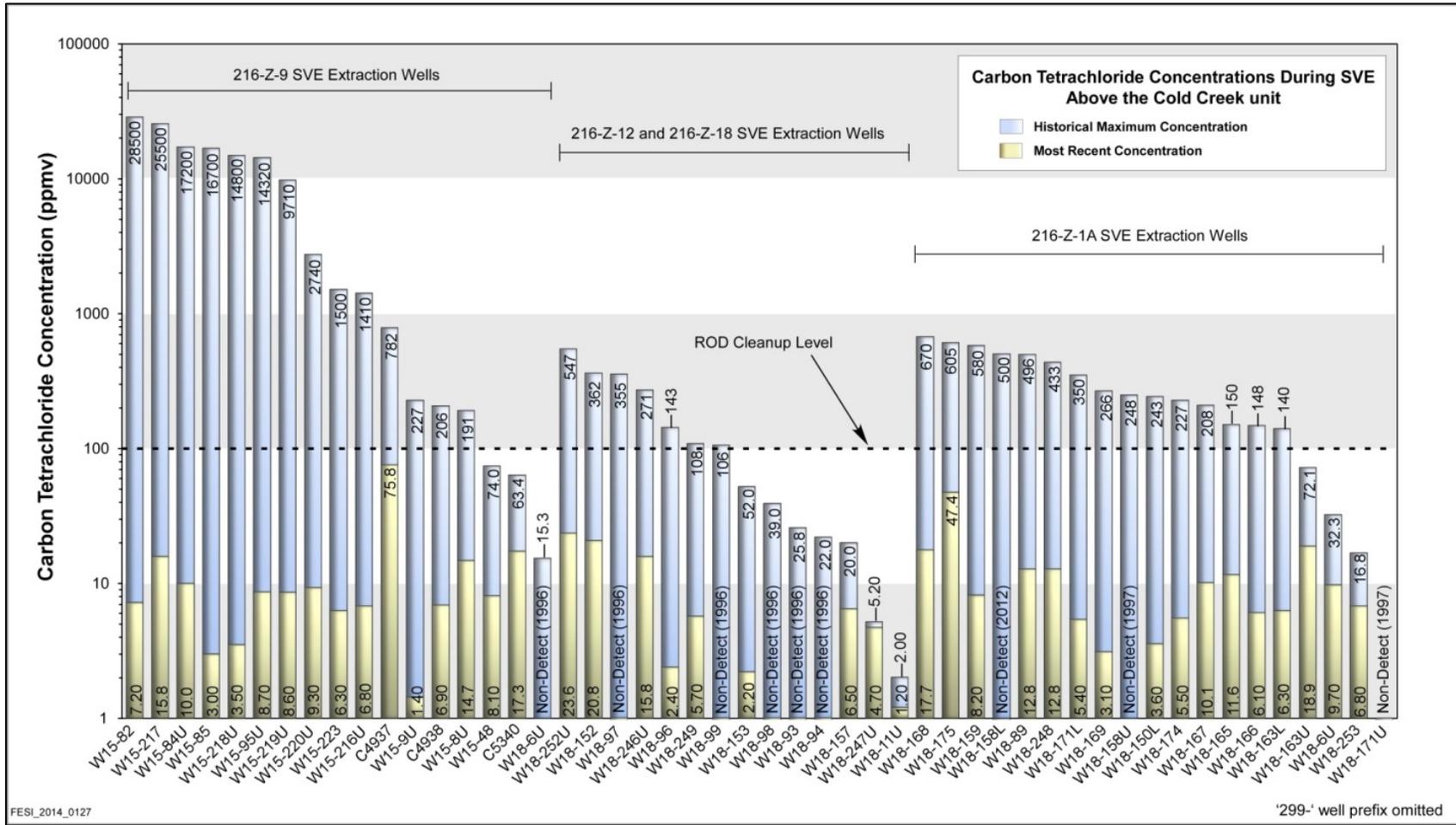
1 Eight wells were installed as passive SVE systems during 1999 at the 216-Z-1A and 216-Z-18 waste sites.
2 The passive SVE systems use naturally occurring changes in barometric pressure to extract carbon
3 tetrachloride vapor, a process also referred to as “barometric pumping.” In general, falling atmospheric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



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

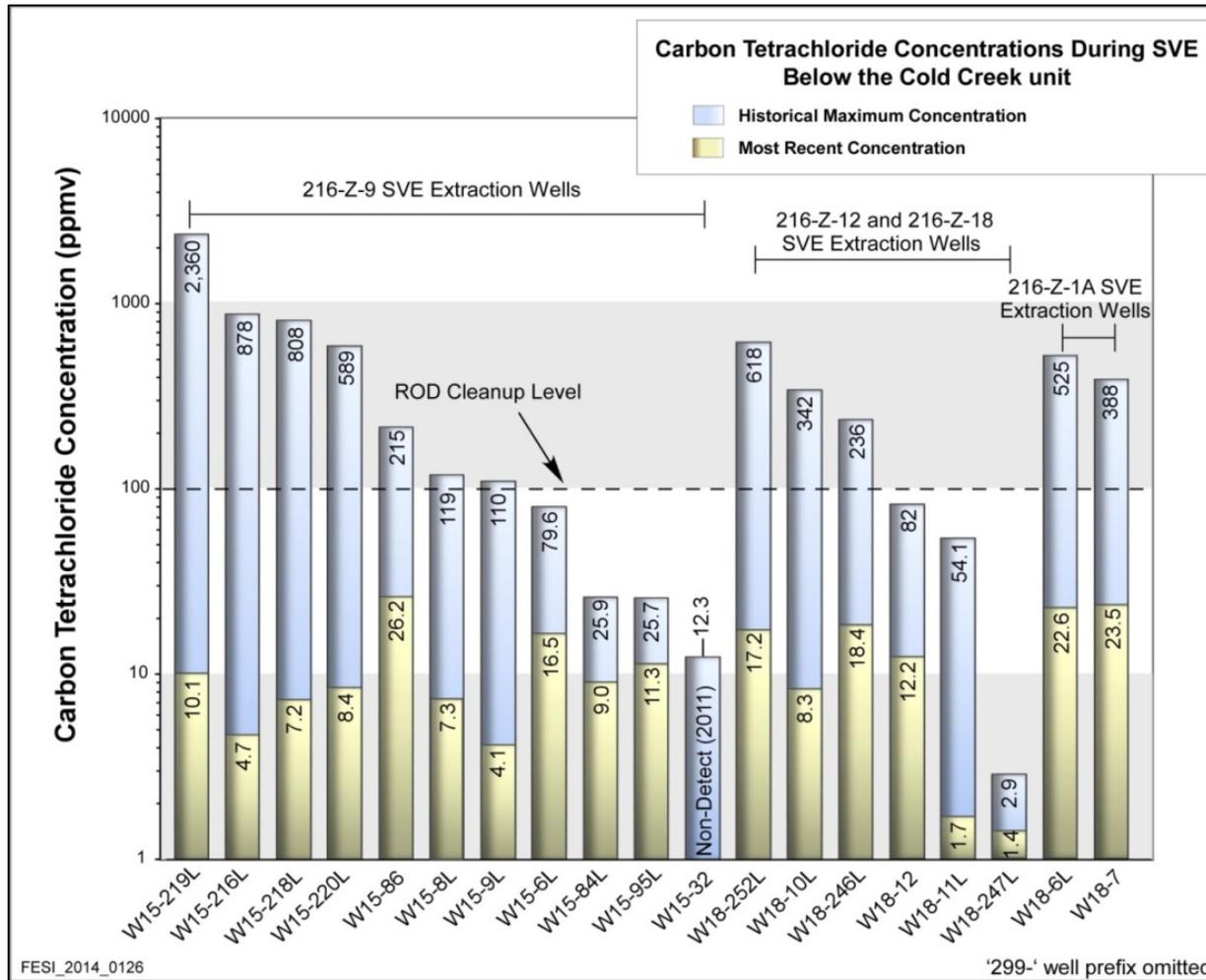
Figure A-5. Carbon Tetrachloride Mass Removal Using Passive SVE,
Depicting an Order-of-Magnitude Less than the Active SVE Systems

16 Contaminant concentrations were measured at each online active extraction well during SVE operations.
17 Figure A-6 depicts (on a logarithmic scale) the historical maximum and most recent carbon tetrachloride
18 concentrations measured in online SVE wells with open (screened or perforated) intervals above the CCU
19 from 1992 to 2012 (the most recent year of SVE operations). Figure A-7 depicts (on a logarithmic scale)
20 the historical maximum and most recent carbon tetrachloride concentrations measured in online active
21 SVE wells with open intervals below the CCU from 1992 through 2012. Concentrations have decreased
22 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)

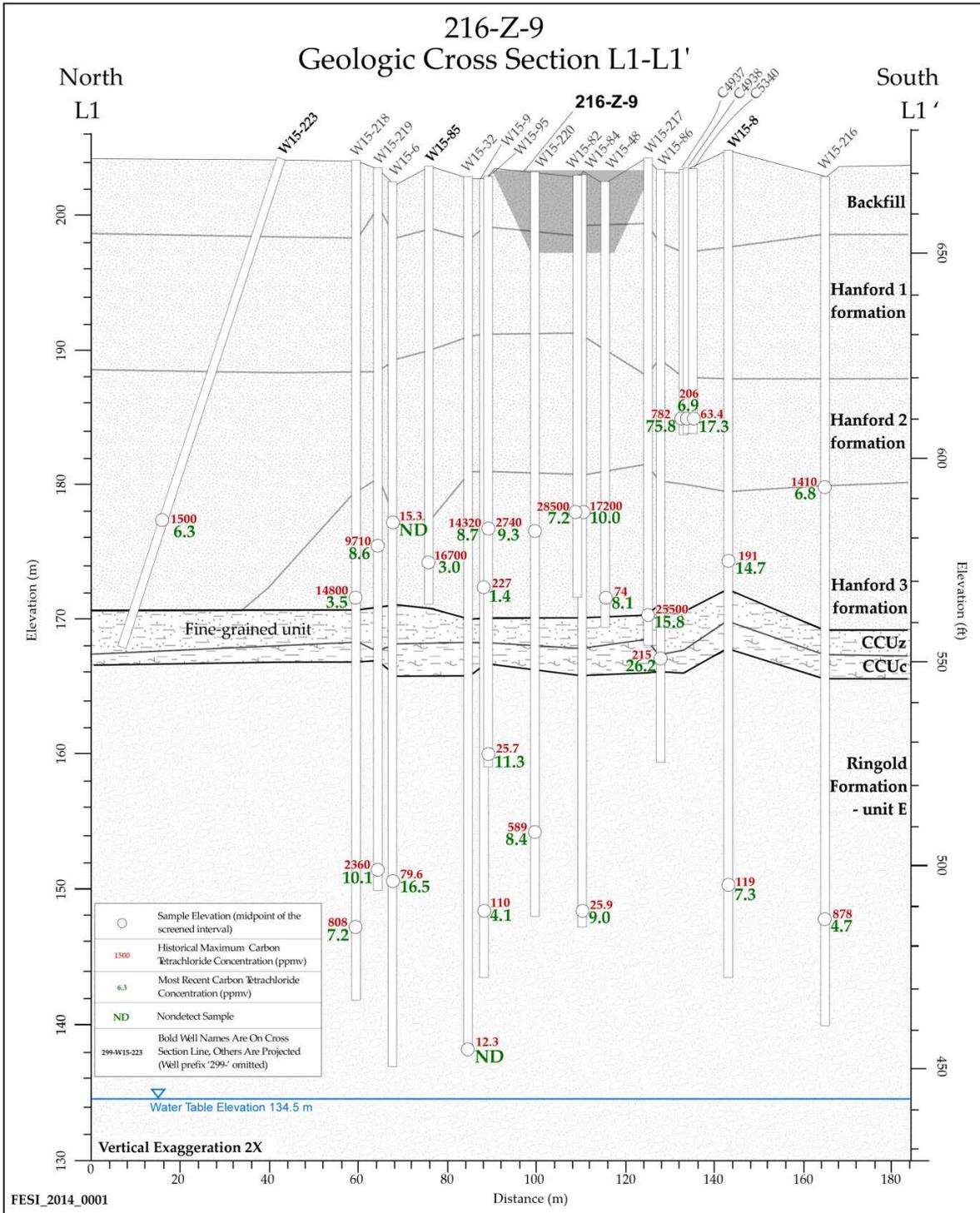


Note: The logarithmic scale is provided on the Y-axis.

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)

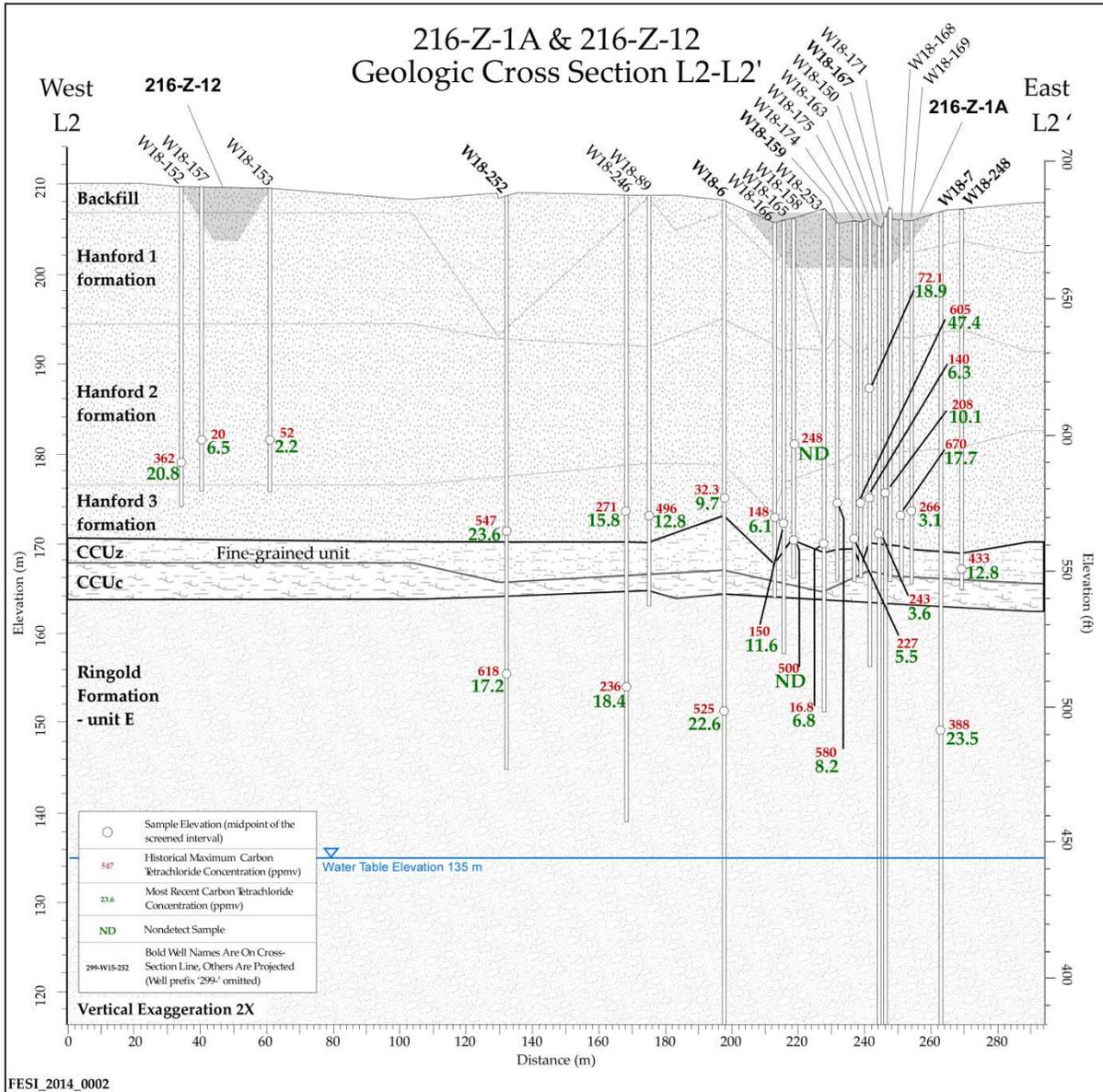
1
2
3
4

1 Figures A-8, A-9, and A-10 show cross-sectional representations of carbon tetrachloride at the 216-Z-9,
 2 216-Z-1A/216-Z-12, and 216-Z-18 waste sites, respectively. The locations of the cross sections are shown
 3 in Figure A-2. The carbon tetrachloride values shown on these cross sections are the historical maximum
 4 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.

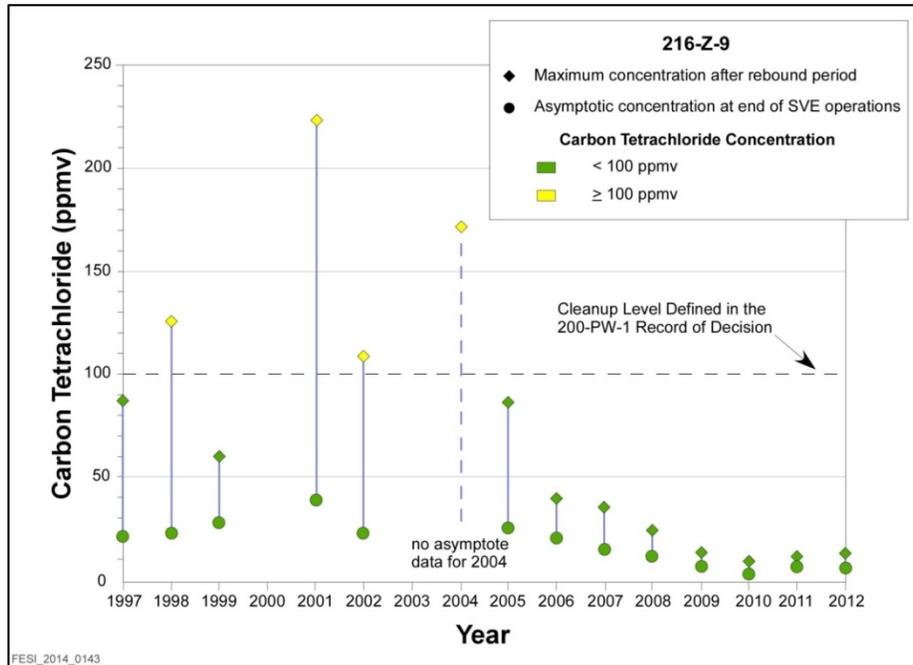
Figure A-8. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent Carbon Tetrachloride Concentrations (1993 to 2012) for 216-Z-9 Online Active SVE Wells



1
2 Note: The cross section location is shown in Figure A-2.

3 **Figure A-9. Cross-Sectional View of Site Stratigraphy with Historical Maximum and Most Recent**
4 **Carbon Tetrachloride Concentrations (1993 to 2012) for 216-Z-1A/216-Z-12 Online Active SVE Wells**

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



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

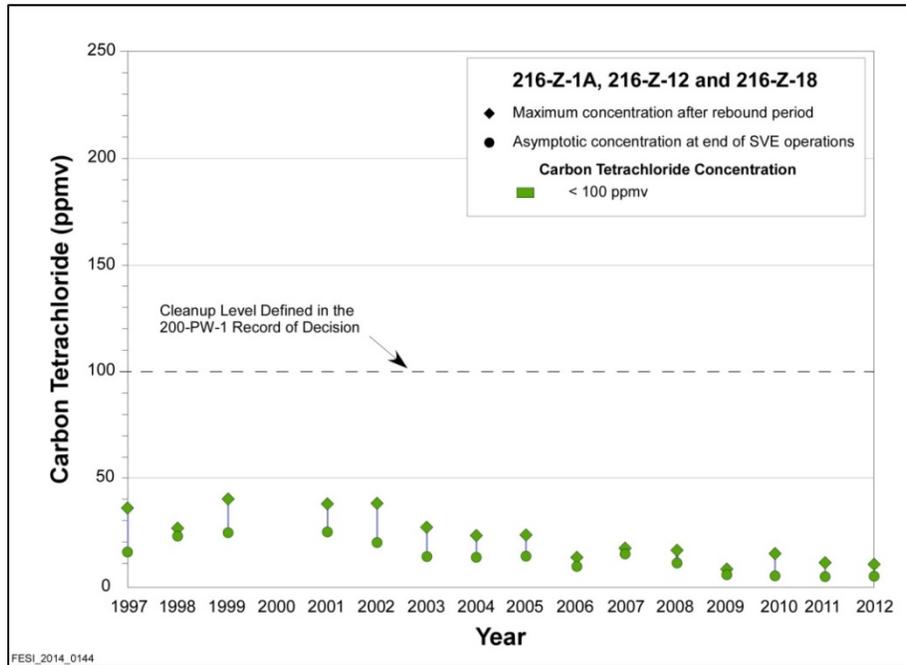
Figure A-11. Rebound and Final Concentrations for Operational Cycles of the 216-Z-9 SVE System, 1997 to 2012

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27

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 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 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).

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 the *Treatability Test Plan for Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site* (DOE/RL-2010-79). Test results were provided in the *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site* (PNNL-21326). 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.

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

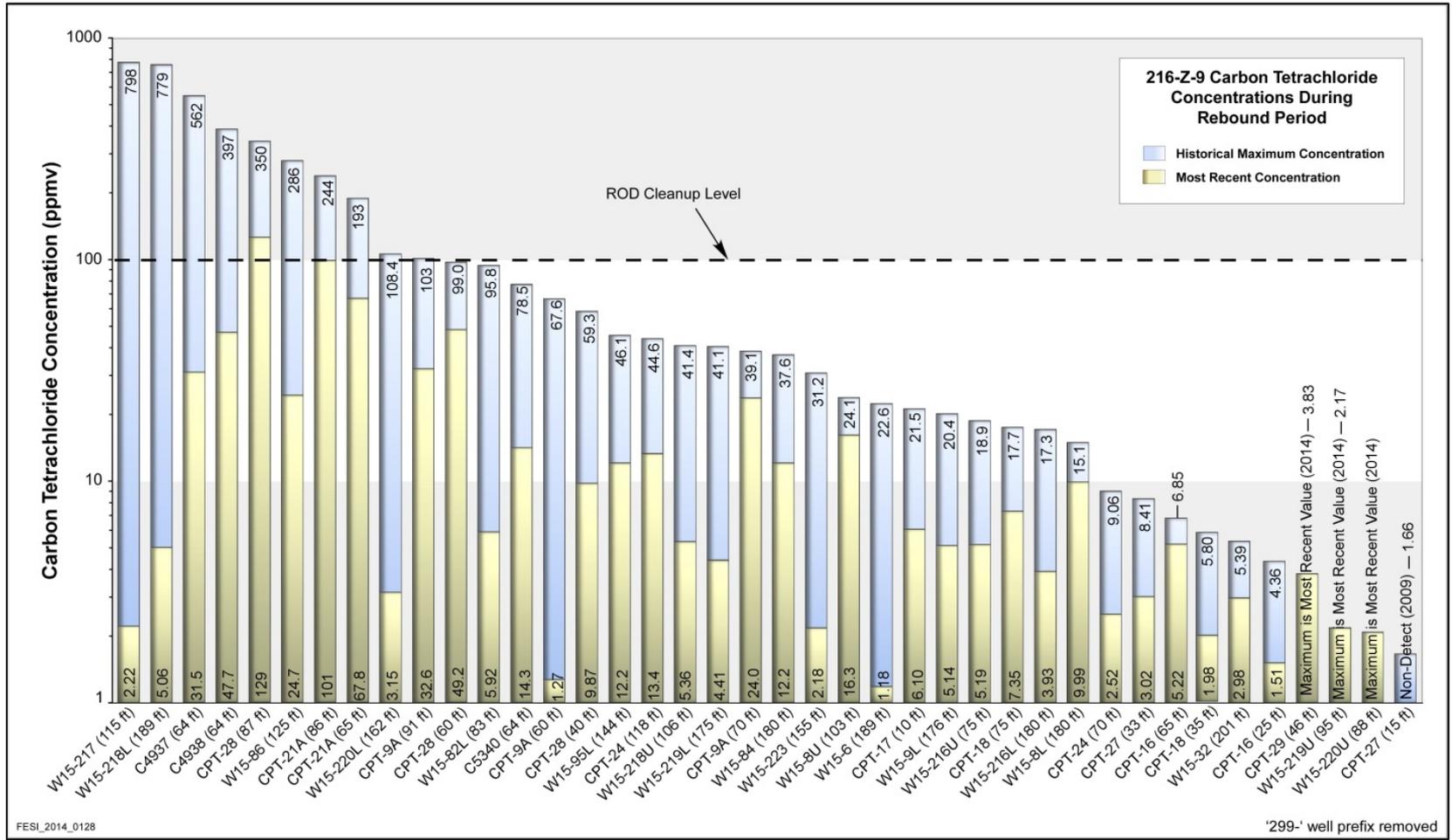


Figure A-13. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at Offline Monitoring Wells and Soil Vapor Probes at 216-Z-9 (1996 to 2014)

1
2
3

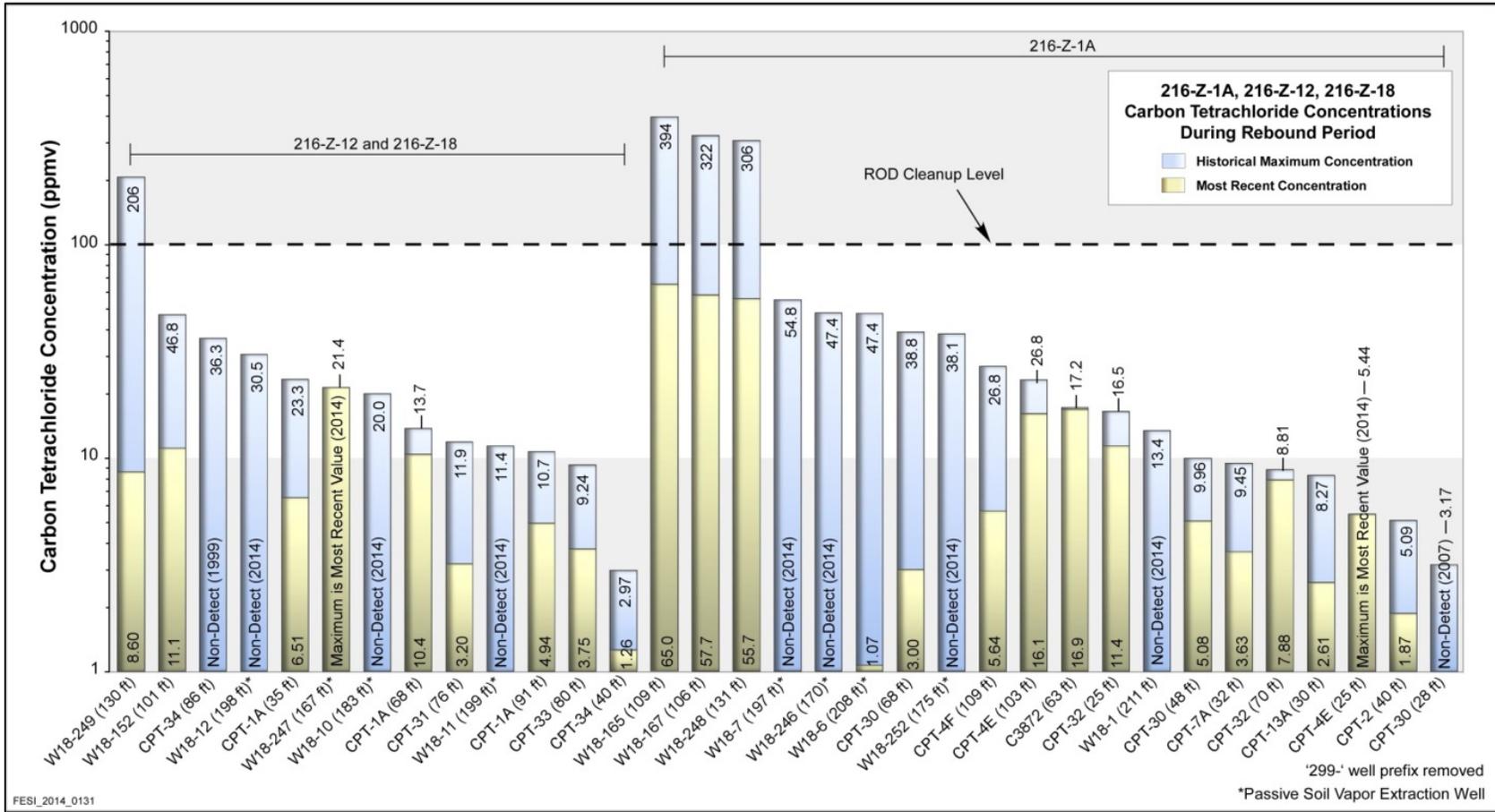
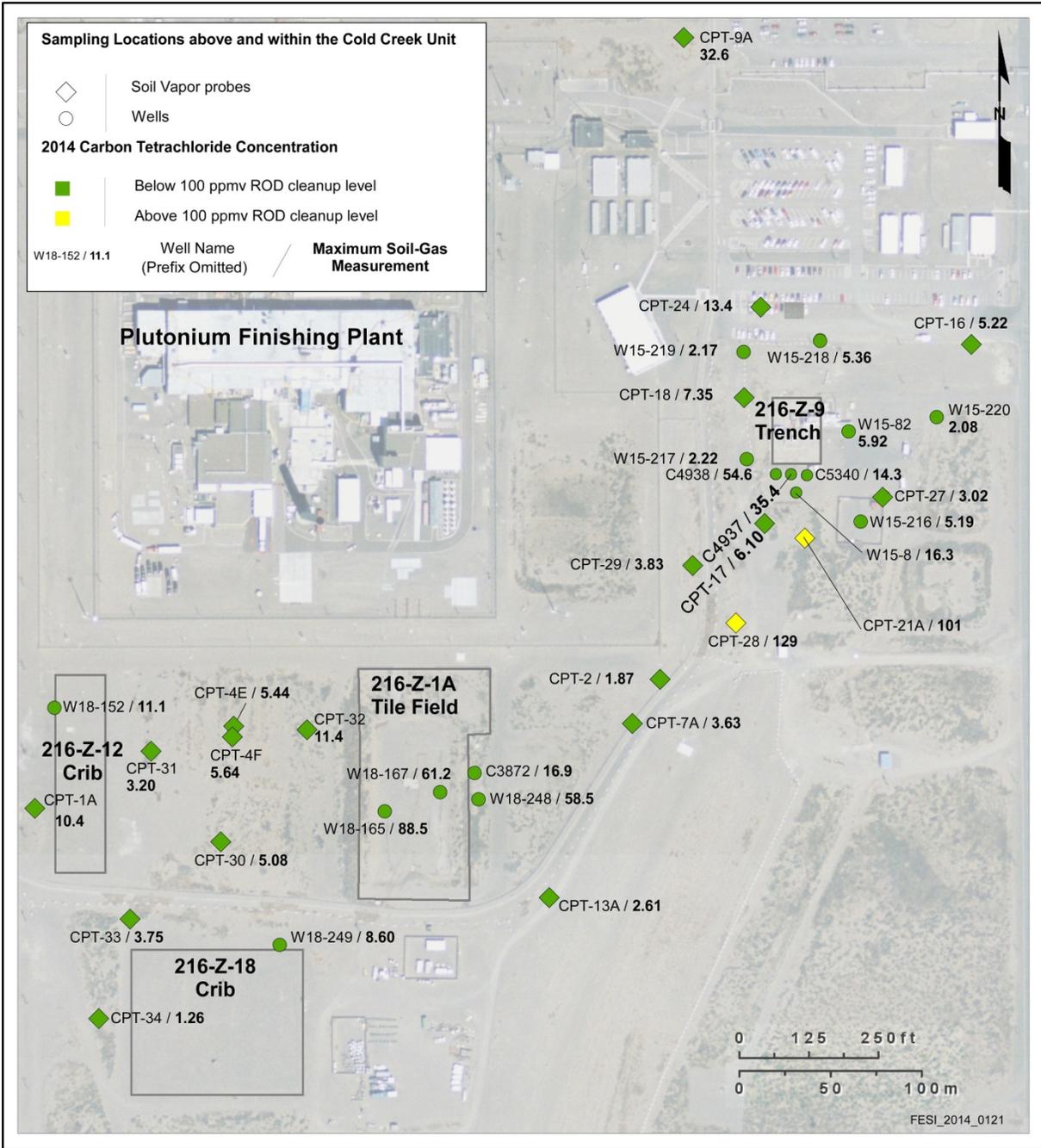


Figure A-14. Historical Maximum and Most Recent Carbon Tetrachloride Concentrations at Offline Monitoring Wells and Soil Vapor Probes at 216-Z-1A/216-Z-12/216-Z-18 (1996 to 2014)

1
2
3

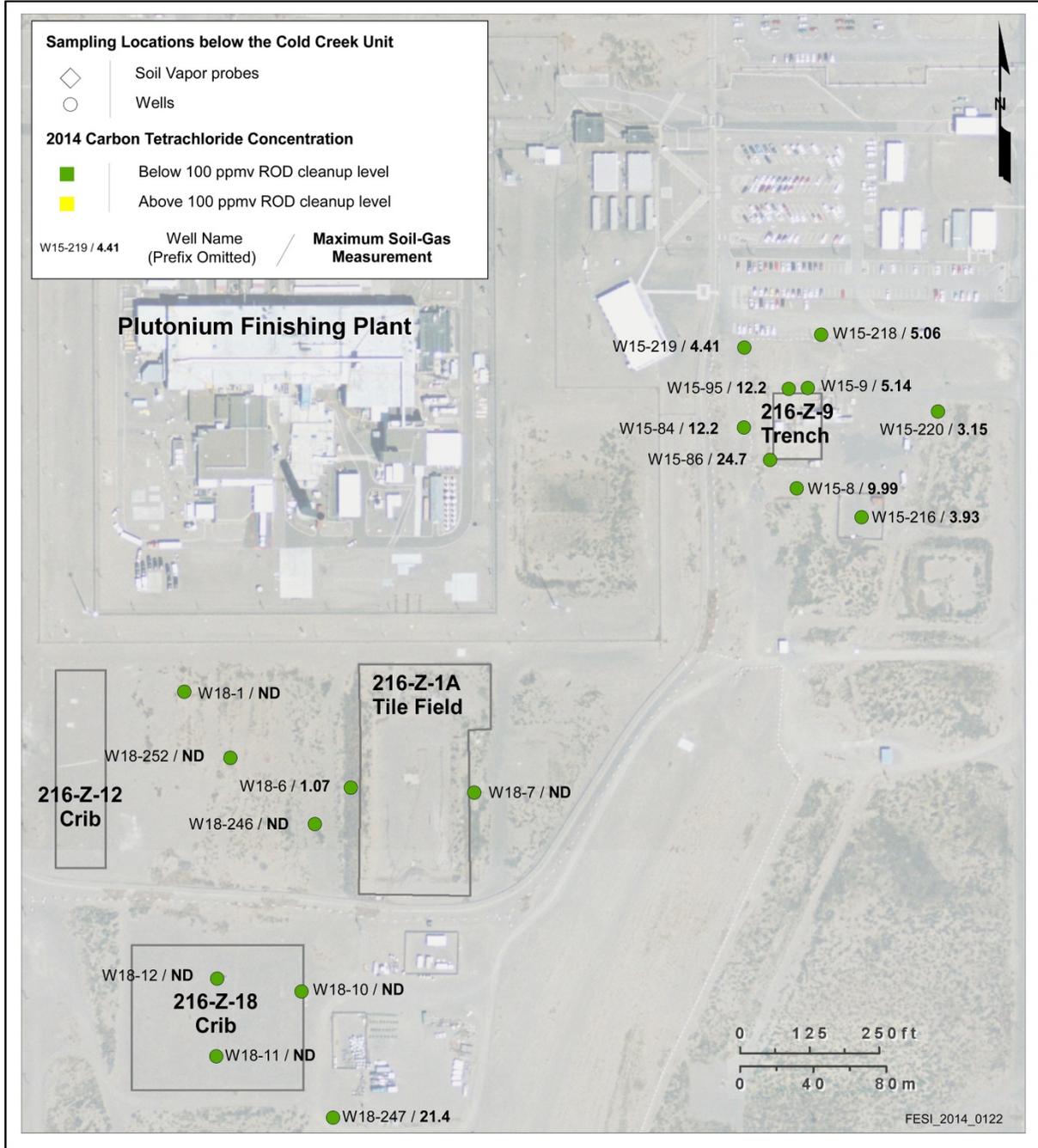


1
2 Note: Carbon tetrachloride concentrations were measured in the field using a B&K (a trade name of Brüel & Kjær [Sound and
3 Vibration Measurement A/S], Nærum, Denmark) multi-gas analyzer.

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

6 Based on the recommendations provided in the treatability test report (PNNL-21326), DOE and EPA
7 determined that the active SVE systems would not be operated or monitored during calendar year
8 (CY) 2013 to allow for a longer rebound period (DOE/RL-2014-39, *Carbon Tetrachloride Soil Vapor*
9 *Extraction System Operating and Monitoring Plan for CY 2015*). DOE and EPA agreed that the option of
10 resuming active SVE operations in CY 2014 would be considered following an evaluation of the carbon

1 tetrachloride rebound monitoring data collected during the spring of CY 2014. Rebound monitoring data
2 were collected in May and June 2014 in accordance with the *Sampling and Analysis Plan for the*
3 *200-PW-1 Operable Unit CY2014 Rebound Sampling* (DOE/RL-2014-20). Based on the 2014 results
4 (Figures A-15 and A-16), DOE and EPA agreed to extend the rebound period through CY 2014 with no
5 SVE operations or monitoring.



6 Note: Carbon tetrachloride concentrations were measured in the field using a B&K (a trade name of Brüel & Kjær [Sound and
7 Vibration Measurement A/S], Nærum, Denmark) multi-gas analyzer.
8 There are no soil vapor probes below the CCU.
9

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

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

The remedial investigation of the 200-PW-1 OU (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 remedial investigation 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 remedial investigation 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.

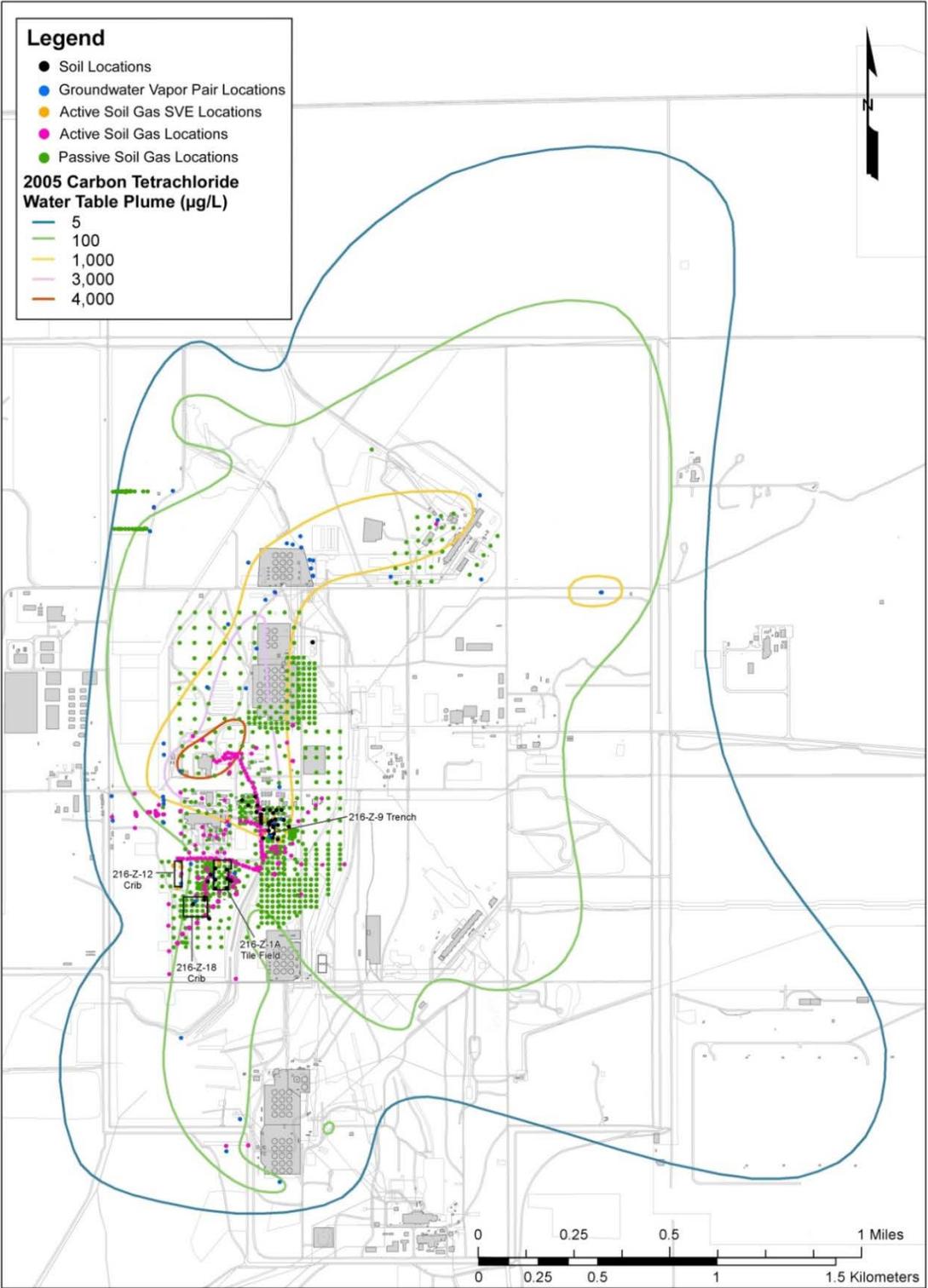
A4.1 Characterization Beyond the 200-PW-1 Operable Unit Carbon Tetrachloride Waste Sites

All of the sampling locations to characterize the carbon tetrachloride lateral and vertical extent during the remedial investigation (DOE/RL-2006-51) are shown in Figure A-17. The remedial investigation 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.

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.

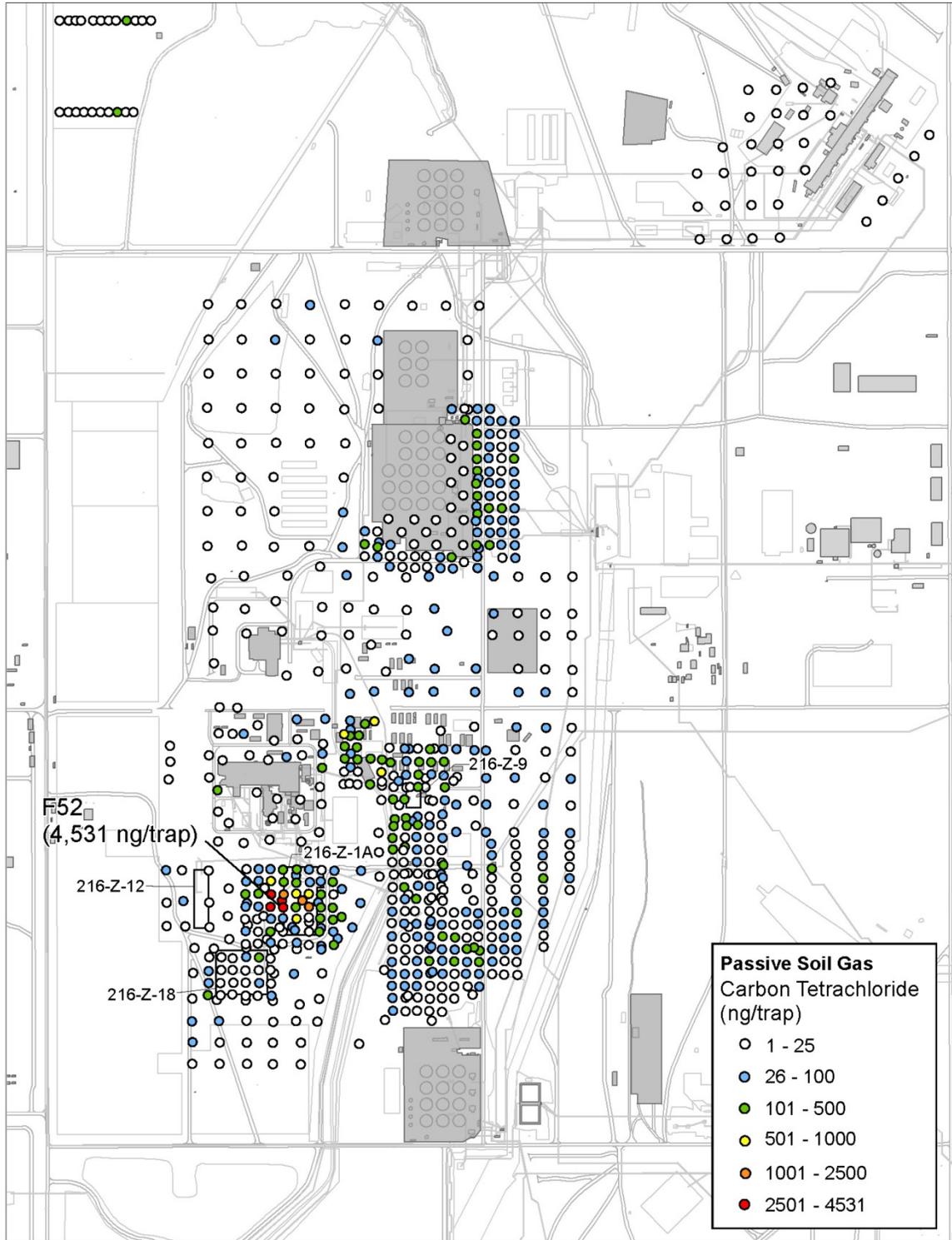
All of the passive soil gas sampling locations are shown on Figure A-17 in green. These same sampling locations are shown in Figure A-18. In Figure A-18, the sampling location “dots” are color-coded based on sample concentration results. The density of sampling locations is higher in areas where passive 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.



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

5 **Figure A-17. Carbon Tetrachloride Sampling Locations during the Remedial Investigation,**
6 **Overlaid on the 2005 Groundwater Carbon Tetrachloride Plume Contours**



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

4 **Figure A-18. Passive Soil Gas Vapor Sampling Results from the Remedial Investigation**

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

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

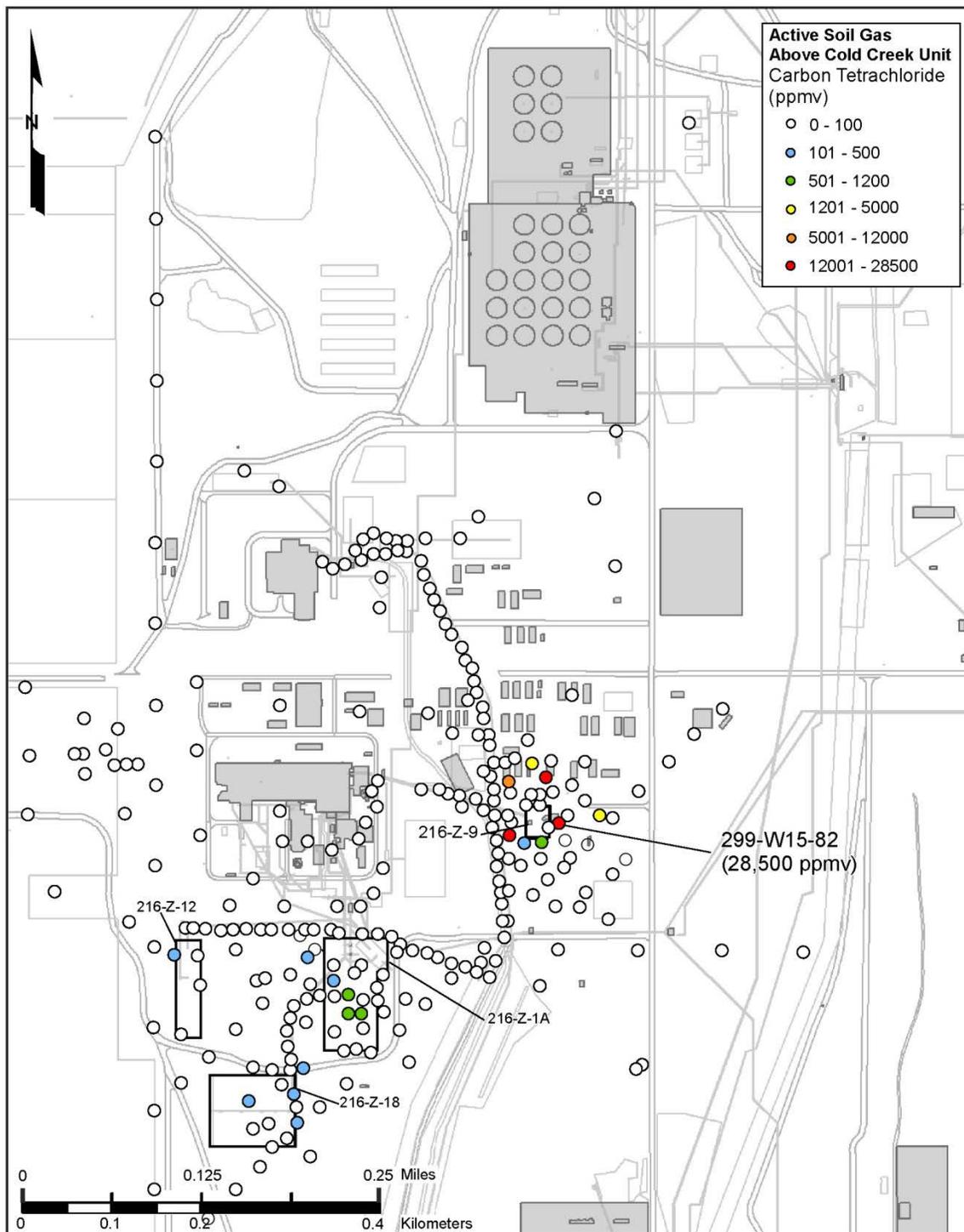
14 Elevated hot spots of carbon tetrachloride concentrations in the groundwater were also used to focus the
15 vadose zone investigation. At these locations, soil vapor samples were collected just above the water
16 table in wells, and groundwater samples were collected at the water table in the same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

21 **A4.2 Key Findings and Results of the Remedial Investigation**

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

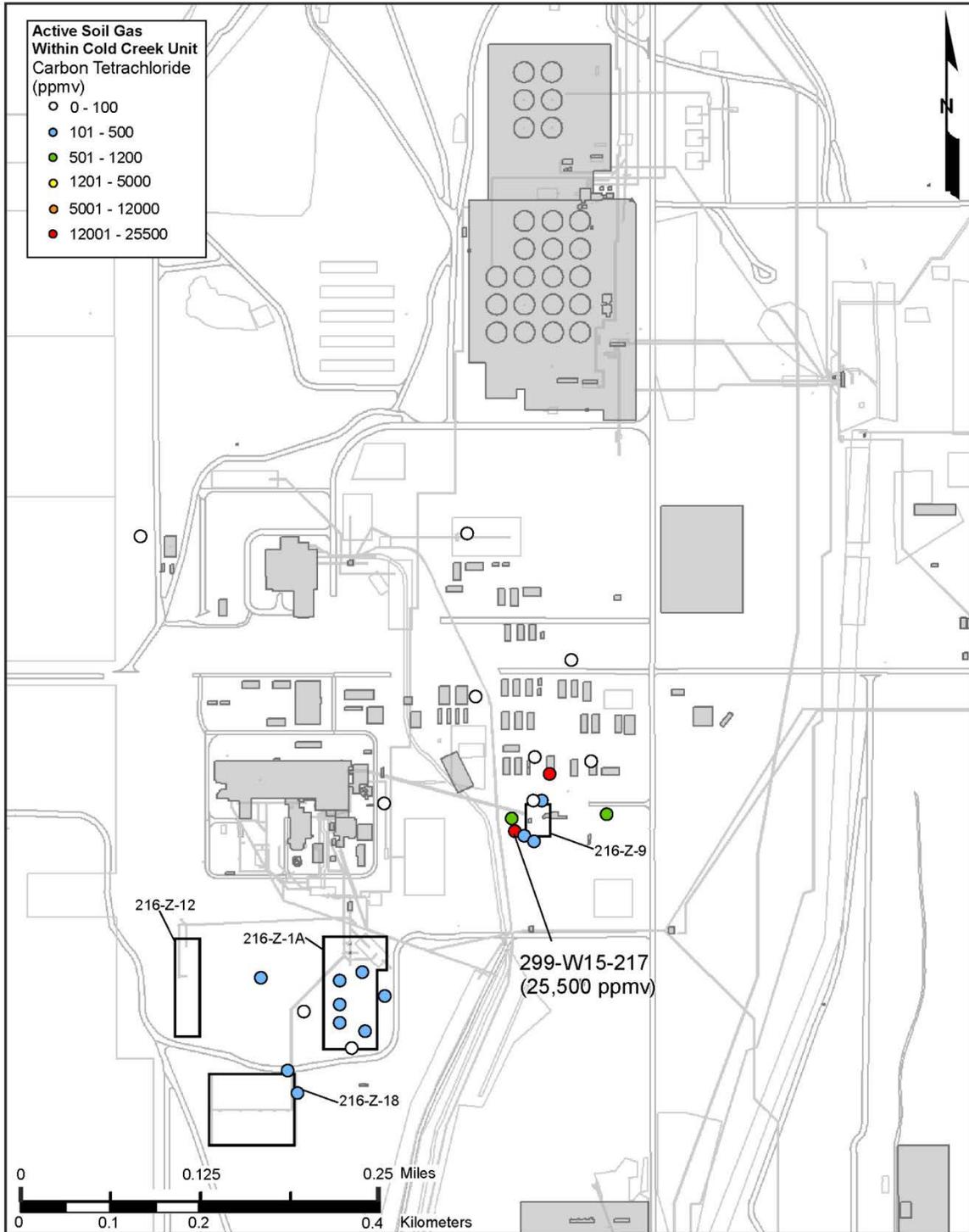
26 Key findings and results in the remedial investigation report included the following:

- 27 • The highest carbon tetrachloride concentrations in the vadose zone generally are located within about
28 75 to 150 m (246 to 492 ft) laterally from the source sites.
- 29 • The highest carbon tetrachloride concentrations are located in fine-grained layers, particularly within
30 the CCU.
- 31 • No evidence was found to indicate significant lateral migration of carbon tetrachloride along the top
32 of the CCU.
- 33 • There was no evidence of downward migration of carbon tetrachloride from an undocumented source.
- 34 • In areas away from the carbon tetrachloride waste sites, carbon tetrachloride soil vapor concentrations
35 were less than 10 to 12 ppmv. These concentrations were not considered to have significant impact on
36 groundwater quality. In particular, areas located south of the 216-Z-9 Trench (near the present
37 location of CPT-28) and south of the 216-Z-9 Trench east of the 216-Z-20 Ditch showed no evidence
38 of elevated carbon tetrachloride concentrations. Based on these investigations, it can be concluded
39 that the area south of the 216-Z-9 Trench does not contain any undocumented contamination sources.



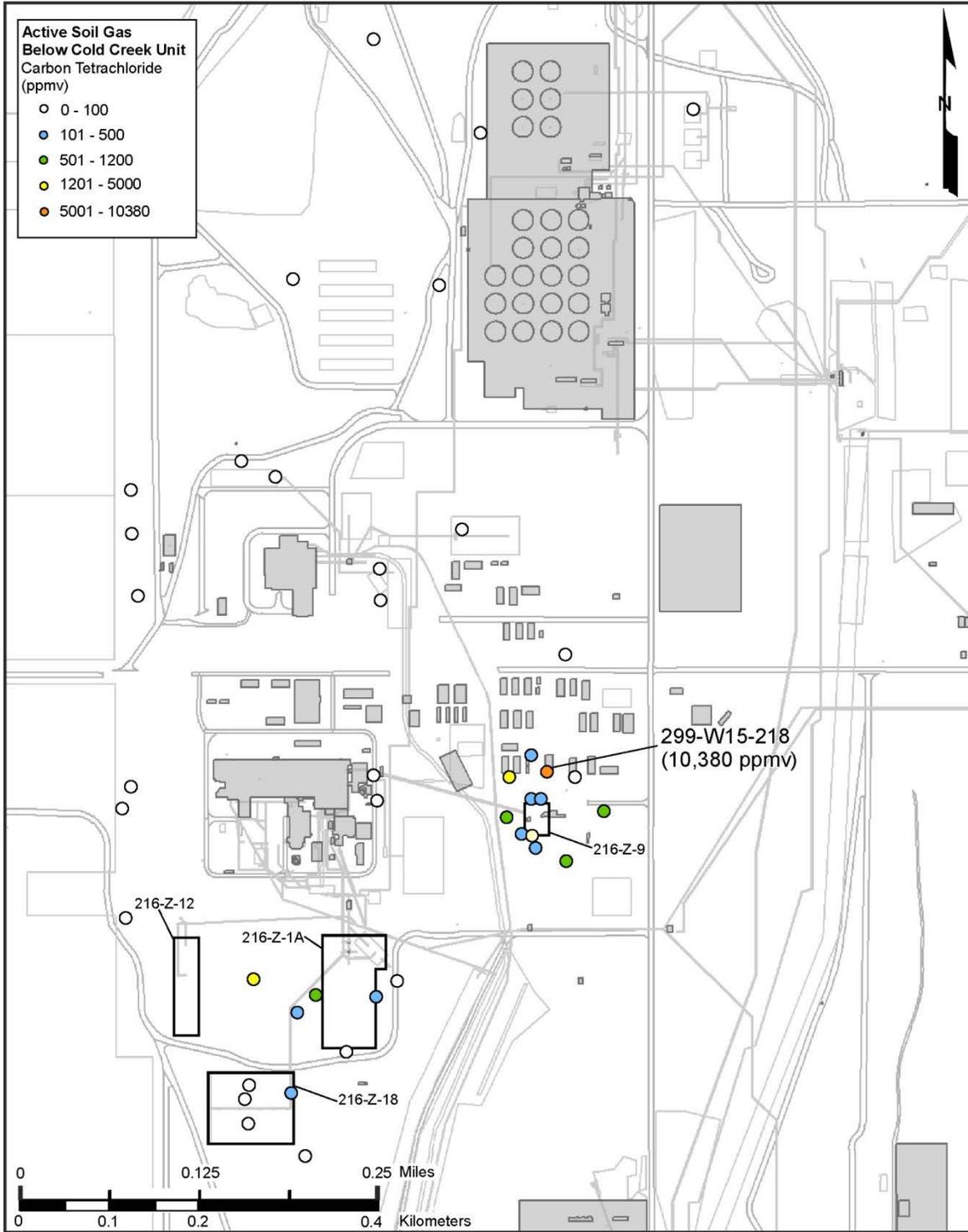
1
2 Source: Derived from Figure 3-23 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich*
3 *Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6*
4 *Operable Units.*

5 **Figure A-19. Remedial Investigation Active Soil Vapor Sampling Results for Locations above the CCU**



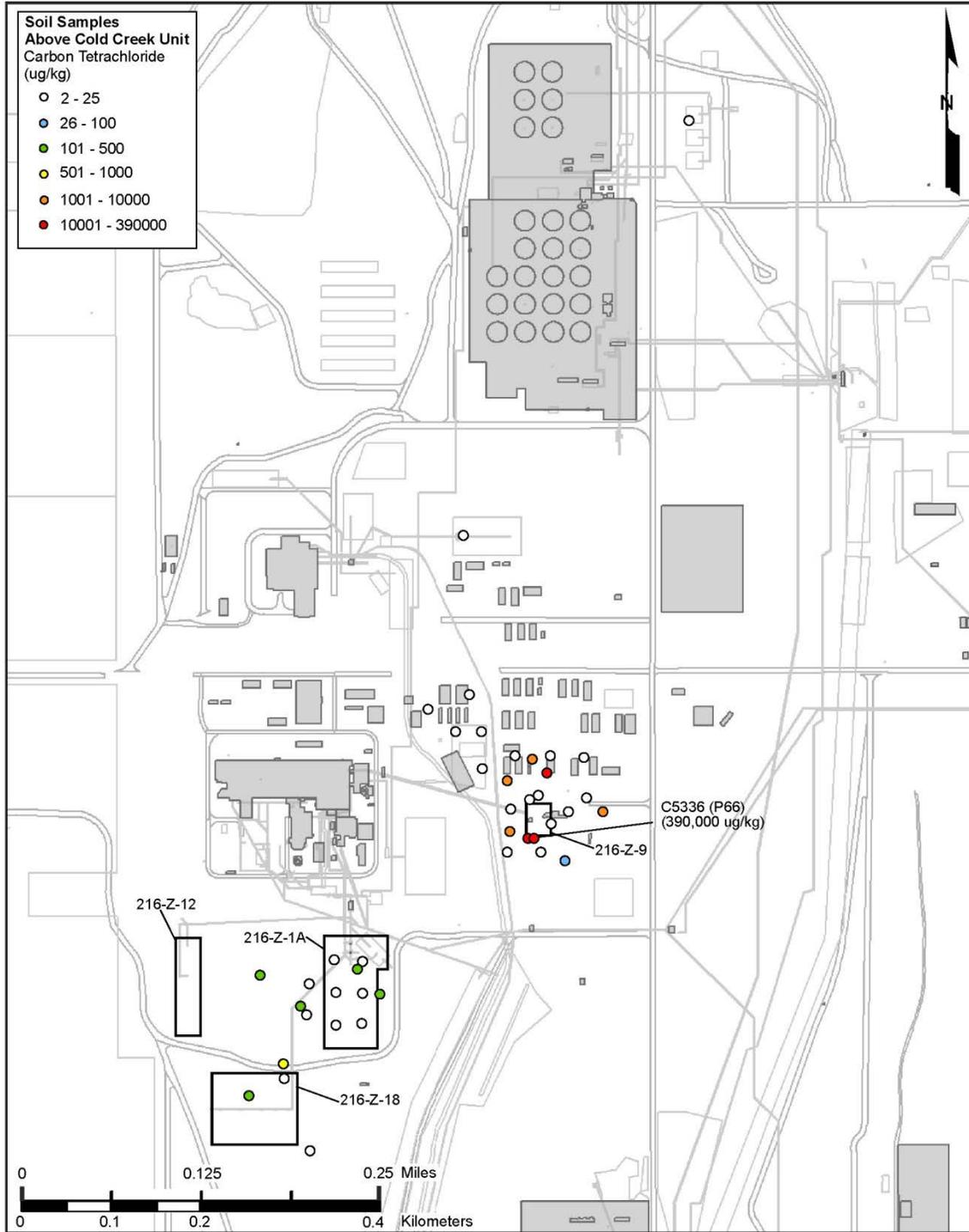
1
2 Source: Derived from Figure 3-25 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich*
3 *Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6*
4 *Operable Units.*

5 **Figure A-20. Remedial Investigation Active Soil Vapor Sampling Results for Locations within the CCU**



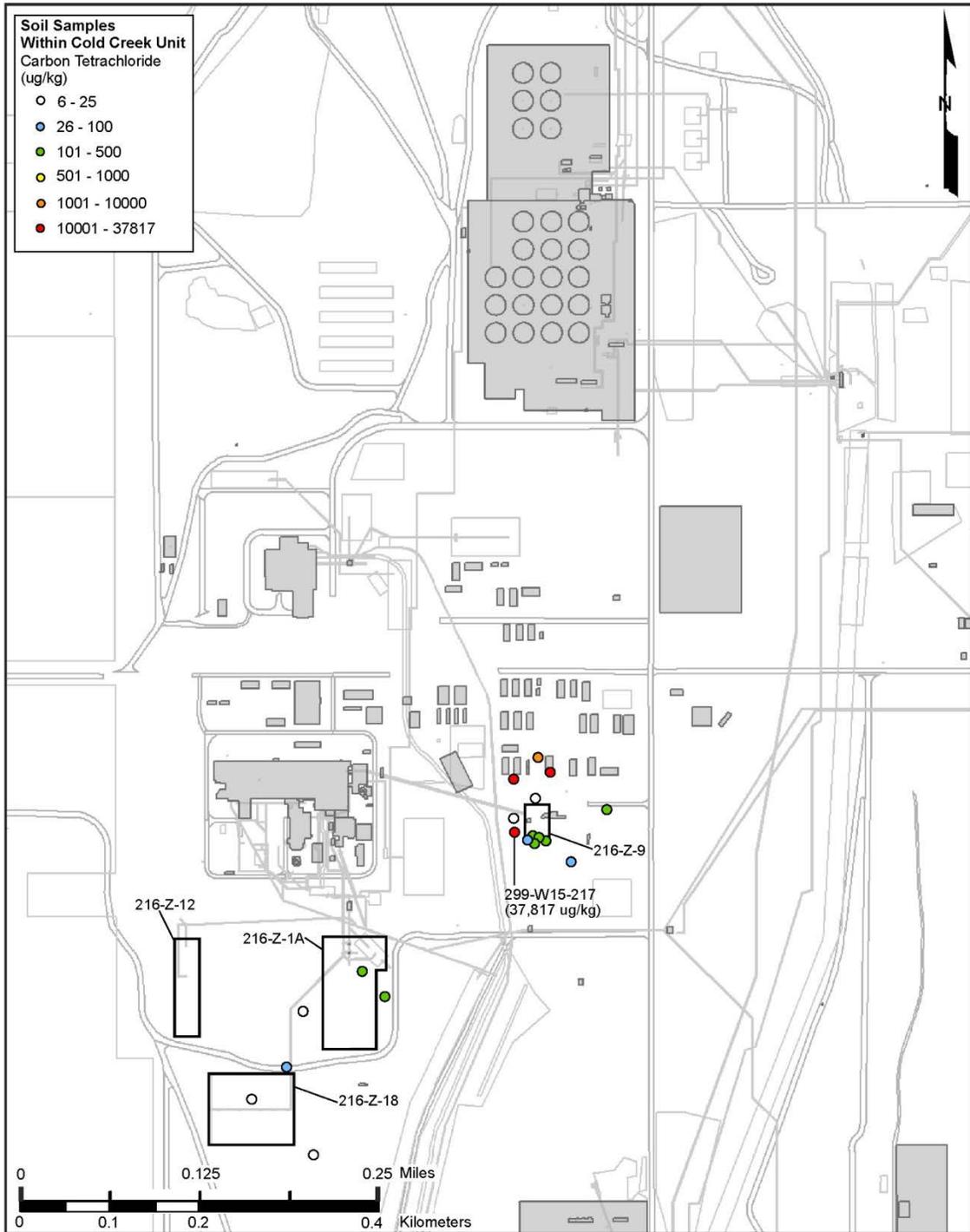
1
2 Source: Derived from Figure 3-27 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich*
3 *Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6*
4 *Operable Units.*

5 **Figure A-21. Remedial Investigation Active Soil Vapor Sampling Results for Locations below the CCU**



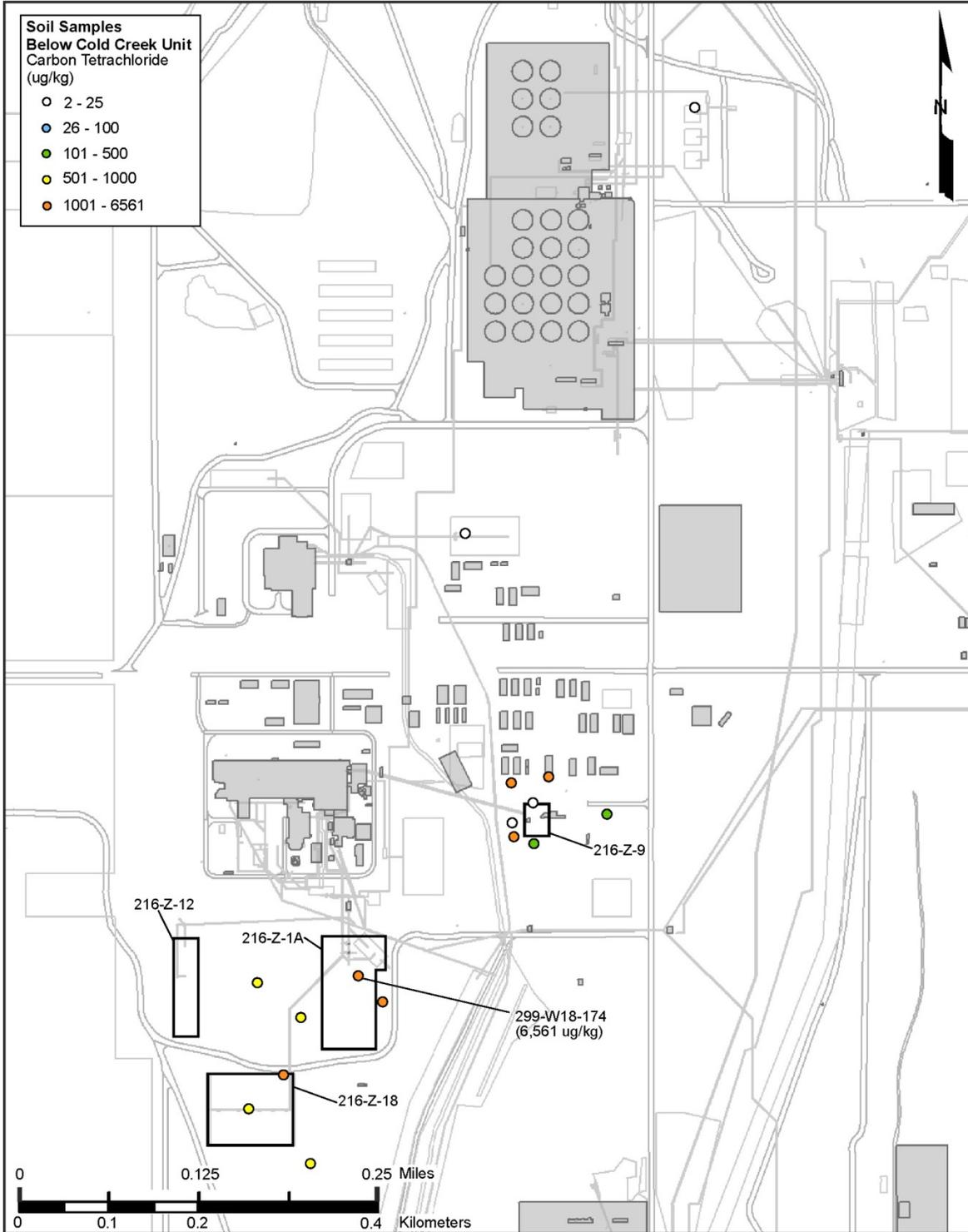
1
2 Source: Derived from Figure 3-29 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/Organic-Rich*
3 *Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6*
4 *Operable Units.*

5 **Figure A-22. Remedial Investigation Soil Sampling Results for Locations above the CCU**



1
2 Source: Derived from Figure 3-30 in DOE/RL-2006-51, *Remedial Investigation Report for the Plutonium/
3 Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and
4 200-PW-6 Operable Units.*

5 **Figure A-23. Remedial Investigation Soil Sampling Results for Locations within the CCU**



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

5 **Figure A-24. Remedial Investigation Soil Sampling Results for Locations below the CCU**

- 1 • Groundwater sampling at wells beneath hot spot areas (e.g., near waste sites) indicated that migration
2 of carbon tetrachloride in the soil vapor phase beneath the CCU is not a significant source of
3 groundwater contamination.
- 4 • An area of higher passive soil vapor detections was found northwest of the 216-Z-9 Trench near the
5 entrance to the Plutonium Finishing Plant. Active soil vapor investigation of pipelines near the area
6 did not identify any new sources in the shallow vadose zone. Active soil vapor sampling using a CPT
7 detected the highest active soil vapor measurement (119 ppmv) at a depth of 33.5 m (101 ft), just
8 above the CCU (CPT push P10A).
- 9 • Carbon tetrachloride DNAPL was found in one sample from Borehole C5335 and one sample from
10 Well 299-W15-46. Both samples were obtained from a silt lens in the shallow vadose zone (19.8 m
11 [65 ft] bgs) adjacent to the 216-Z-9 Trench.

12 Thus, extensive investigations conducted for the remedial investigation did not identify any carbon
13 tetrachloride waste sites or sources other than the 216-Z-9 Trench, 216-Z-1A Tile Field, and
14 216-Z-18 Crib. In Figures A-19 through A-24, elevated carbon tetrachloride concentrations in active
15 soil gas and soil samples were only seen in the vicinity of the 216-Z-9 Crib and the 216-Z-1A Tile Field.
16 Furthermore, continuous soil vapor monitoring of the vadose zone during the years of SVE operation has
17 not revealed any other undocumented sources. On this basis, no other carbon tetrachloride sources exist
18 within the area overlying the carbon tetrachloride groundwater plume.

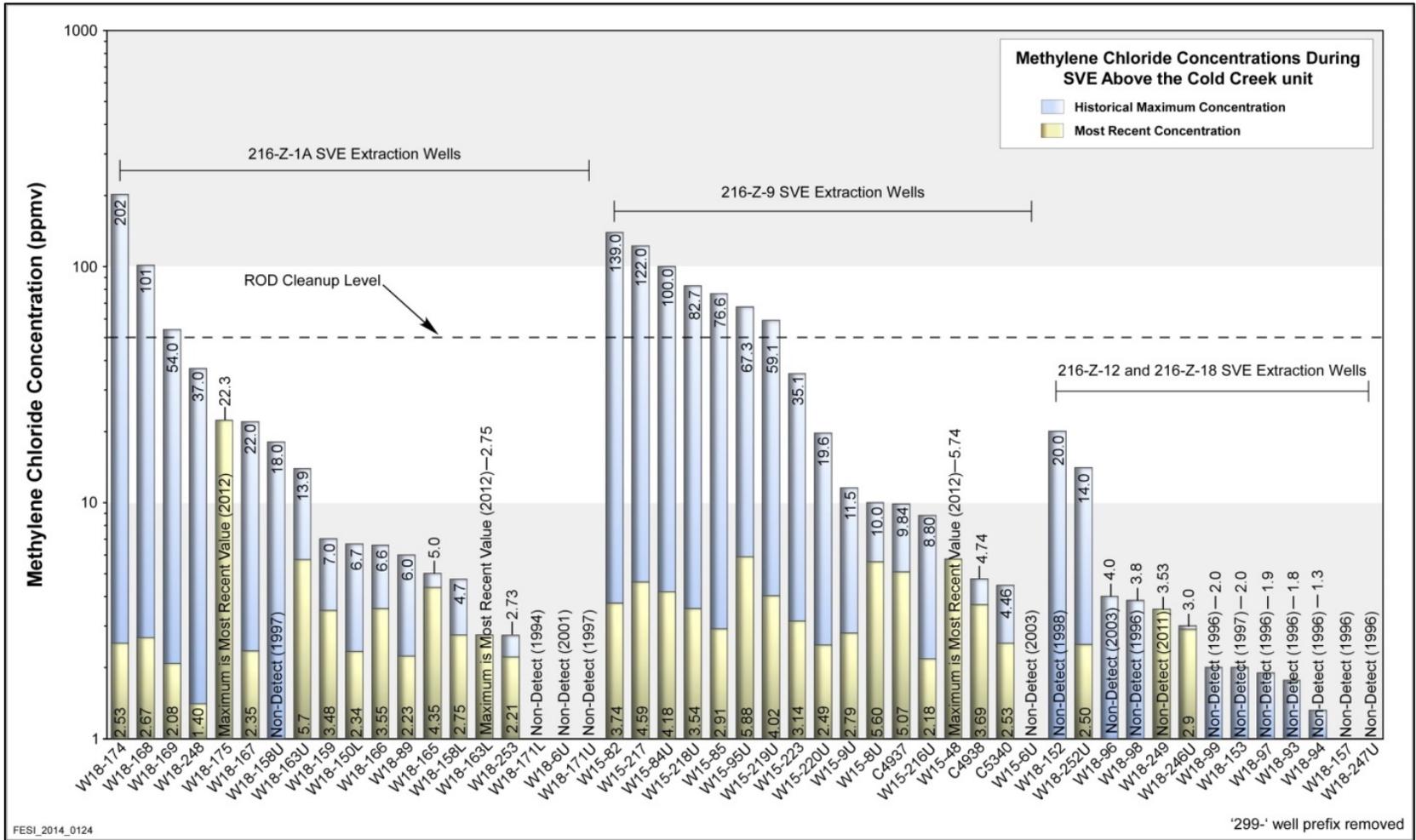
19 **A5 Methylene Chloride at 200-PW-1 Operable Unit Waste Disposal Sites**

20 Figure A-25 depicts (on a logarithmic scale) the historical maximum and most recent concentrations of
21 methylene chloride measured in online active SVE extraction wells from 1992 to 2012 for open intervals
22 above the CCU. Figure A-26 depicts (on a logarithmic scale) the historical maximum and most recent
23 concentrations of methylene chloride measured in online SVE extraction wells from 1993 to 2012 for
24 open intervals below the CCU. All methylene chloride concentrations in the online active extraction wells
25 are below the 50 ppmv cleanup level specified in the 200-PW-1 OU ROD (EPA et al., 2011).

26 Figures A-27 and A-28 show the historical maximum and most recent methylene chloride concentrations
27 measured at offline monitoring wells and soil vapor probes from 1996 (the first year of monitoring)
28 and 2013 for the 216-Z-9 well field and the combined 216-Z-1A/ 216-Z-18/216-Z-12 well field,
29 respectively. The most recent samples were collected in May and June 2014 (Appendix B). Samples were
30 collected in Tedlar² bags for analysis using the B&K analyzer in the field. Samples were also collected
31 at some locations in SUMMA³ canisters for laboratory analysis. The methylene chloride results for
32 samples collected in Tedlar bags and analyzed using the B&K analyzer were determined to be not
33 usable (Appendix B). Therefore, these results were not used in Figures A-27 and A-28. The methylene
34 chloride results for 2014 samples collected in SUMMA canisters and analyzed in the laboratory were
35 all nondetect.

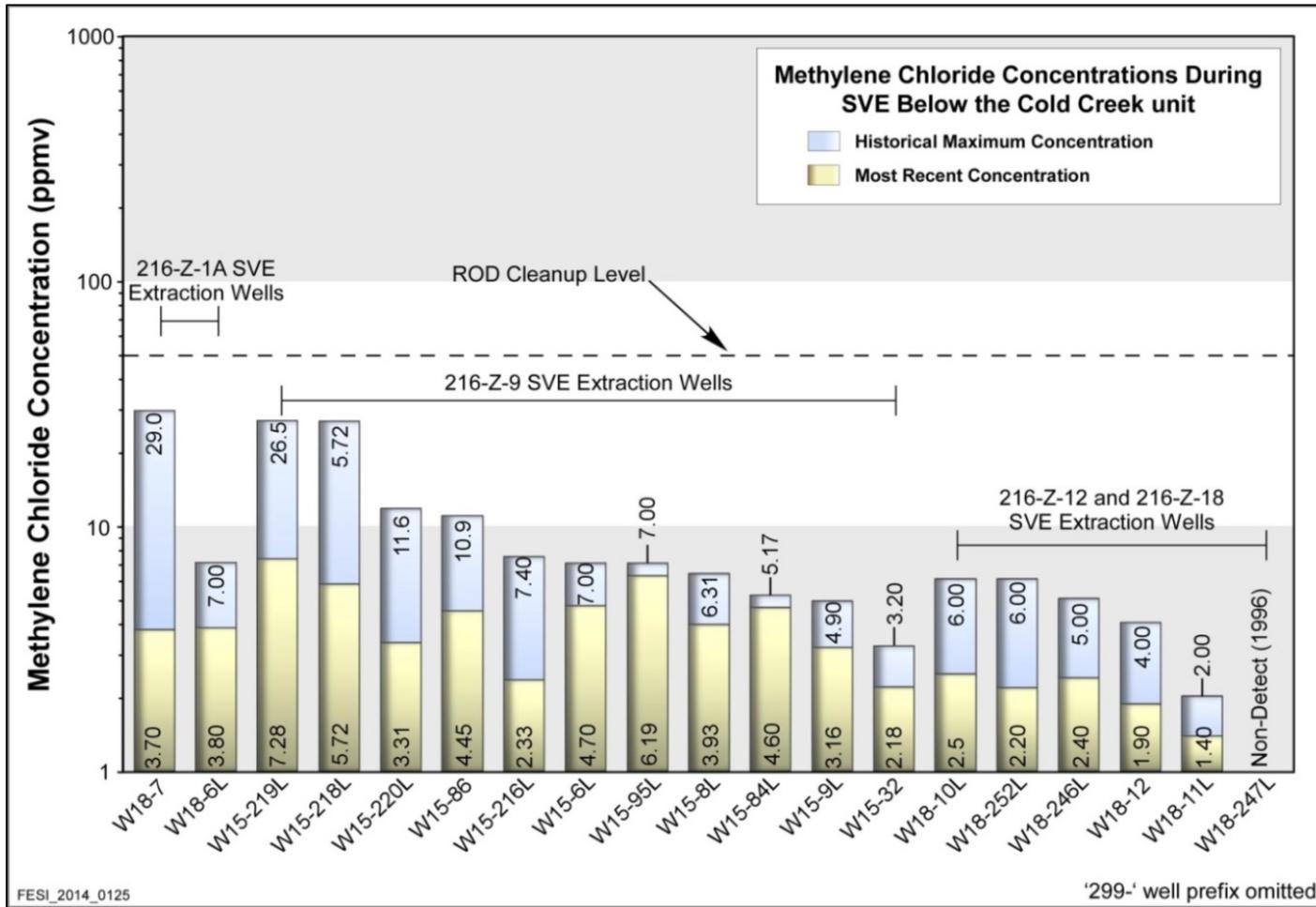
² Tedlar® is a registered trademark of E.I. du Pont de Nemours and Company, Wilmington, Delaware.

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



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

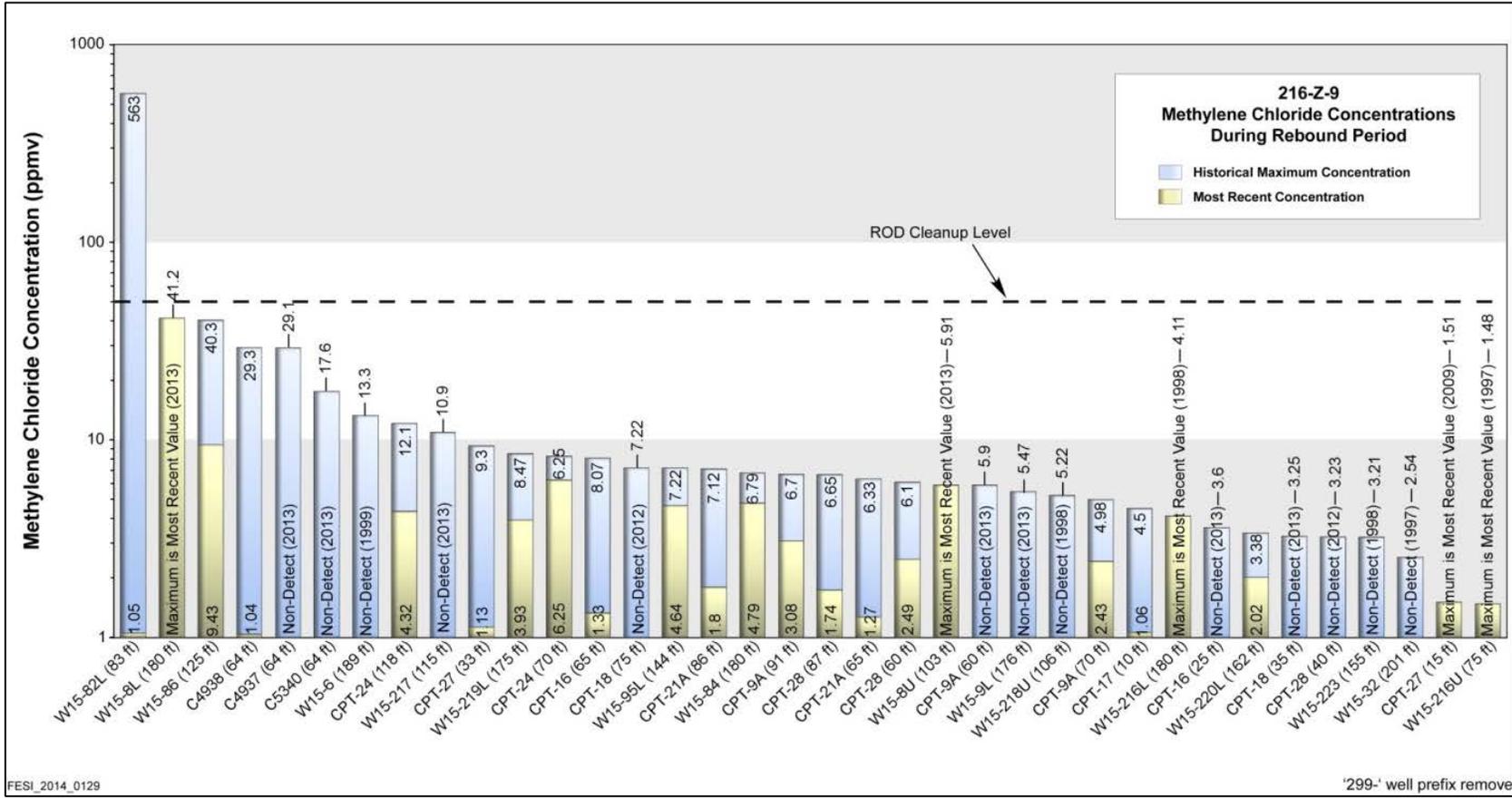
Figure A-25. Historical Maximum and Most Recent Methylene Chloride Concentrations at Online SVE Wells with Screened Intervals above the CCU (1993 to 2012)



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)

1
2
3
4



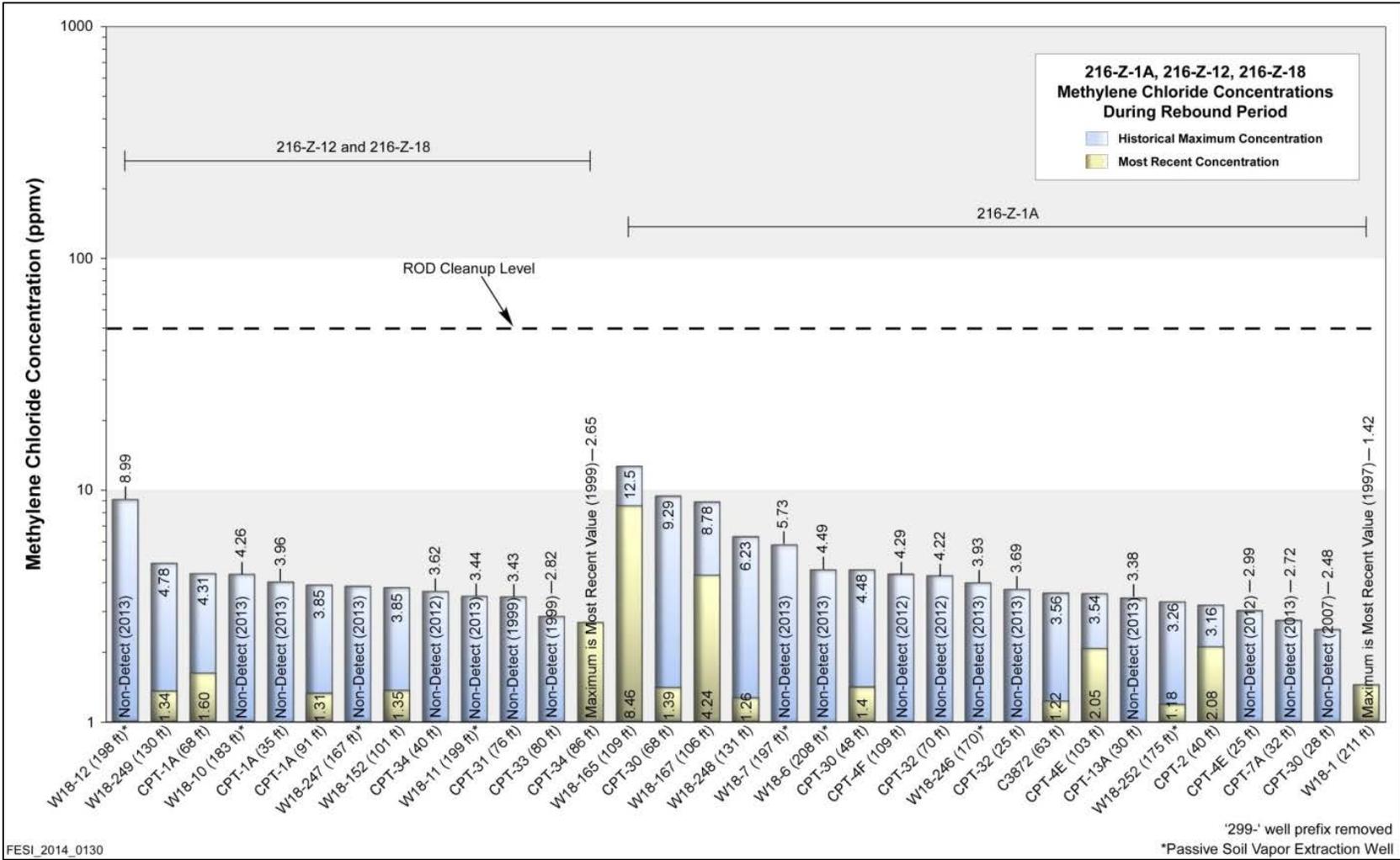
FESI_2014_0129

'299-' well prefix remove

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)

1
2
3
4



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)

1

A6 Feasibility Study

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

8

A7 Proposed Plan and Record of Decision

9 *The Proposed Plan for the Remediation of the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6*
10 *Operable Units* (DOE/RL-2009-117) was issued 2011. The Proposed Plan recommended SVE as the
11 remedial alternative for carbon tetrachloride at the three primary carbon tetrachloride waste sites:
12 216-Z-9, 216-Z-1A, and 216-Z-18. The Proposed Plan recommended that remediation using SVE
13 continue under the expedited response action until it is no longer necessary or is replaced by a component
14 of a final action remedy.

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

21 The 200-PW-1 OU ROD established cleanup levels as soil vapor concentrations for carbon tetrachloride
22 (100 ppmv) and methylene chloride (50 ppmv) and indicated that the cleanup levels will be refined and
23 assessed using the results of the treatability test to ensure protection of the groundwater.

24

A8 Path Forward

25 In May 2014, the *Path Forward for Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*
26 was issued (DOE/RL-2014-18). The path forward document provided (1) an overview of the
27 200-PW-1 OU regulatory status; (2) a summary of the history of waste disposal, investigation activities,
28 and remediation activities for the 200-PW-1 OU; and (3) an overview of SVE operations and
29 performance over the past two decades. Recent guidance on evaluating the endpoint for SVE systems
30 (PNNL-21843, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance*) was used
31 as the basis for the 200-PW-1 OU path forward to determine when SVE operations for the 200-PW-1 OU
32 can be terminated. The path forward uses site-specific evaluation and decision logic steps. EPA and DOE
33 concurred with the path forward for evaluating transition of the 200-PW-1 OU SVE systems from the
34 current cycle of active operations and monitoring to closure.

A9 References

- 1
- 2 BHI-00105, 1995, *FY 1993 Wellfield Enhancement Status Report and Data Package for the 200 West*
3 *Area Carbon Tetrachloride Expedited Response Action*, Rev. 00, Bechtel Hanford, Inc.,
4 Richland, Washington.
- 5 BHI-01105, 1997, *Rebound Study Report for the Carbon Tetrachloride Soil Vapor Extraction Site,*
6 *Fiscal Year 1997*, Rev. 0, Bechtel Hanford, Inc., Richland, Washington. Available at:
7 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D198067101>.
- 8 BHI-01105-00-CN-01, 1997, *ERC Change Notice: BHI-01105, Rev. 0, Rebound Study Report for the*
9 *Carbon Tetrachloride Soil Vapor Extraction Site*, dated December 22, Bechtel Hanford, Inc.,
10 Richland, Washington. Available at:
11 <http://pdw.hanford.gov/arpir/pdf.cfm?accession=D198066724>.
- 12 DOE/RL-91-32, 1991, *Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon*
13 *Tetrachloride Plume*, Draft B, U.S. Department of Energy, Richland Operations Office, Richland,
14 Washington. Available at:
15 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196078303>.
- 16 DOE/RL-2001-01, 2004, *Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable*
17 *Unit RI/FS Work Plan: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*, Rev. 0
18 Reissue, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
19 Available at:
20 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D4573392>.
21 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D4361348>.
22 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D4361603>.
- 23 DOE/RL-2006-51, 2007, *Remedial Investigation Report for the Plutonium/Organic-Rich Process*
24 *Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and*
25 *200-PW-6 Operable Units*, Rev. 0, U.S. Department of Energy, Richland Operations Office,
26 Richland, Washington. Available at:
27 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA05807591>.
28 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA05807868>.
29 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0805130070>.
30 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0805130071>.
- 31 DOE/RL-2006-58, 2006, *Carbon Tetrachloride Dense Non-Aqueous Phase Liquid (DNAPL) Source*
32 *Term Interim Characterization Report*, Rev. 0, U.S. Department of Energy, Richland Operations
33 Office, Richland, Washington. Available at:
34 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA04193109>.
- 35 DOE/RL-2007-22, 2007, *Carbon Tetrachloride Dense Non-Aqueous Phase Liquid (DNAPL) Source*
36 *Term Interim Characterization Report Addendum*, Rev. 0, U.S. Department of Energy, Richland
37 Operations Office, Richland, Washington. Available at:
38 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA04992076>.

- 1 DOE/RL-2007-27, 2011, *Feasibility Study for the Plutonium/Organic-Rich Process Condensate/Process*
2 *Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3 and 200-PW-6 Operable Units*,
3 Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
4 Available at:
5 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093807>.
6 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093806>.
7 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093805>.
8 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093804>.
9 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093803>.
10 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093802>.
11 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093801>.
12 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093800>.
13 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093799>.
14 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093798>.
15 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093797>.
- 16 DOE/RL-2009-117, 2011, *Proposed Plan for the Remediation of the 200-CW-5, 200-PW-1, 200-PW-3,*
17 *and 200-PW-6 Operable Units*, Rev. 0, U.S. Department of Energy, Richland Operations Office,
18 Richland, Washington. Available at:
19 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093832>.
- 20 DOE/RL-2010-79, 2010, *Treatability Test Plan for Characterization of Vadose Zone Carbon*
21 *Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*, Rev. 0,
22 U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at:
23 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1010270169>.
- 24 DOE/RL-2014-18, 2014, *Path Forward for Future 200-PW-1 Operable Unit Soil Vapor Extraction*
25 *Operations*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland,
26 Washington.
- 27 DOE/RL-2014-20, 2014, *Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2014*
28 *Rebound Sampling*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland,
29 Washington. Available at:
30 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1404210408>.
- 31 DOE/RL-2014-39, 2014, *Carbon Tetrachloride Soil Vapor Extraction System Operating and Monitoring*
32 *Plan for CY 2015*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland,
33 Washington.
- 34 EPA and Ecology, 1992, *Action Memorandum: Expedited Response Action Proposal for 200 West Area*
35 *Carbon Tetrachloride Plume*, U.S. Environmental Protection Agency and Washington State
36 Department of Ecology, Olympia, Washington.
- 37 EPA, Ecology, and DOE, 2011, *Record of Decision, Hanford 200 Area Superfund Site: 200-CW-5 and*
38 *200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*, U.S. Environmental Protection Agency,
39 U.S. Department of Energy, and Washington State Department of Ecology, Olympia, Washington
40 Available at: <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0093644>.
- 41 PNL-7396, 1990, *Hanford Site Ground-Water Surveillance for 1989*, Pacific National Laboratory,
42 Richland, Washington. Available at:
43 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196055127>.

- 1 PNNL-21326, 2012, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride*
2 *Source Strength Using Tomographic Methods at the 216-Z-9 Site*, Pacific Northwest National
3 Laboratory, Richland, Washington. Available at:
4 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1210310436>.
- 5 PNNL-21843, 2013, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance*,
6 Pacific Northwest National Laboratory, Richland, Washington. Available at:
7 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0088374>.
- 8 SGW-53024, 2012, *200-PW-1 Operable Unit Soil Vapor Extraction System Operational Strategy*,
9 Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.
- 10 SGW-54566, 2013, *Performance Evaluation Report for Soil Vapor Extraction Operations at the*
11 *200-PW-1 Operable Unit Carbon Tetrachloride Site, Calendar Year 2012*, Rev. 0, CH2M HILL
12 Plateau Remediation Company, Richland, Washington. Available at:
13 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0086023>.
- 14 WHC-SD-EN-TI-063, 1992, *FY92 Site Characterization Status Report and Data Package for the*
15 *Carbon Tetrachloride Site*, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
16 Available at: <http://pdw.hanford.gov/arpir/pdf.cfm?accession=D196113606>.
- 17 WHC-SD-EN-TI-202, 1993, *FY93 Site Characterization Status Report and Data Package for the Carbon*
18 *Tetrachloride Site*, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
19 Available at: <http://pdw.hanford.gov/arpir/pdf.cfm?accession=D196108184>.
- 20 WHC-SD-EN-TI-248, 1994, *1994 Conceptual Model of the Carbon Tetrachloride Contamination in the*
21 *200 West Area at the Hanford Site*, Rev. 0, Westinghouse Hanford Company, Richland,
22 Washington.

1
2
3
4

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

1

2

This page intentionally left blank.

1

2 Contents

3 **B1 Introduction..... B-1**

4 **B2 Summary..... B-1**

5 **B3 References B-2**

6

7 Figures

8 Figure B-1. Carbon Tetrachloride Concentrations Measured during 2014 Rebound
9 Sampling for the 200-PW-1 OU B-7

10 Figure B-2. Methylene Chloride Concentrations Measured during 2014 Rebound
11 Sampling for the 200-PW-1 OU B-8

12

13 Table

14 Table B-1. Analytical Results for CY 2014 Soil Vapor Rebound Samples..... B-3

Terms

| | | |
|----|-------|--|
| 1 | | |
| 2 | B&K | Brüel & Kjær |
| 3 | CCU | Cold Creek unit |
| 4 | CPT | cone penetrometer |
| 5 | CY | calendar year |
| 6 | GC/MS | gas chromatography/mass spectrometry |
| 7 | HEIS | Hanford Environmental Information System |
| 8 | ND | not detected |
| 9 | OU | operable unit |
| 10 | ppmv | parts per million by volume |
| 11 | ROD | Record of Decision |
| 12 | SAP | sampling and analysis plan |
| 13 | SVE | soil vapor extraction |
| 14 | | |

B1 Introduction

Initial 2014 rebound sampling was conducted on May 14 and 15, 2014, in accordance with the *Sampling and Analysis Plan for the 200-PW-1 Operable Unit CY2014 Rebound Sampling* (DOE/RL-2014-20). 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 brand new Tedlar¹ bags and were analyzed using a Brüel & Kjær (B&K)² analyzer in the field (Table B-1). Four split samples were collected in SUMMA³ 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 sampling 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.

The B&K and laboratory analyses for carbon tetrachloride in samples collected during both sampling events showed good agreement (Figure B-1). The cleanup level for carbon tetrachloride (100 parts per million by volume [ppmv]) in the *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 Operable Unit [OU] Record of Decision [ROD]) (EPA et al., 2011) 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.

The 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, the 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, and it appears to be interfering with the B&K analysis of methylene chloride; the source of this compound is probably the new Tedlar bags. The cleanup level for methylene chloride (50 parts per million by volume [ppmv]) in the 200-PW-1 OU ROD 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 Tedlar bag.

B2 Summary

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

¹ Tedlar® is a registered trademark of E.I. du Pont 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.

B3 References

1
2
3
4
5
6
7
8
9
10

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>.

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>.

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

| Well/Probe and Depth | Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer) | | | | SUMMA Canister Samples (Analyzed in Laboratory Using GC/MS) | | | | | 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/60 ft | 1.27 | 5.38 | — | — | — | — | — | — | — | — |
| CPT-9A/50 ft | 32.6 | 8.28 | — | — | — | — | — | — | — | — |
| CPT-9A/64 ft | 24.0 | 8.25 | — | — | — | — | — | — | — | — |
| CPT-29/46 ft | 3.83 | 5.29 | — | — | — | — | — | — | — | — |
| CPT-2/40 ft | 1.9 | 6.68 | — | — | — | — | — | — | — | — |
| CPT-7A/32 ft | 3.63 | 5.45 | — | — | 5.1 | ND | — | — | B2WJB2 | — |
| CPT-C3872/63 ft | 16.9 | 9.22 | — | — | — | — | — | — | — | — |
| 299-W18-7/197 ft | ND | 6.44 | — | — | — | — | — | — | — | — |
| 299-W18-248/131 ft | 58.5 | 8.12 | 55.7 | 3.63 | — | — | 71 | ND | B2WWH9 | — |
| 299-W18-165/109 ft | 88.5 | 16.1 | 65.0 | 13.6 | — | — | 68 | ND | B2WWJ0 | — |
| 299-W18-167/106 ft | 61.2 | 11.6 | 57.7 | 8.00 | — | — | 65 | ND | B2WWJ1 | — |
| CPT-32/25 ft | 11.4 | 7.22 | — | — | — | — | — | — | — | — |
| CPT-32/70 ft | 7.88 | 8.67 | — | — | — | — | — | — | — | — |
| 299-W18-6L/208 ft | 1.07 | 6.90 | — | — | — | — | — | — | — | — |
| 299-W18-246L/170 ft | ND | 6.39 | — | — | — | — | — | — | — | — |
| CPT-30/48 ft | 5.08 | 8.70 | — | — | — | — | — | — | — | — |
| CPT-30/68 ft | 3.00 | 8.06 | — | — | — | — | — | — | — | — |
| CPT-30/68 ft | 2.93 | 8.67 | — | — | — | — | — | — | — | Duplicate |
| CPT-31/76 ft | 3.20 | 6.85 | — | — | — | — | — | — | — | — |
| 299-W18-252L/175 ft | ND | 6.10 | — | — | — | — | — | — | — | — |

B-3

DOE/RL-2014-48, DRAFT A
MARCH 2015

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

| Well/Probe and Depth | Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer) | | | | SUMMA Canister Samples (Analyzed in Laboratory Using GC/MS) | | | | | 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) | | | |
| CPT-4F/109 ft | 5.64 | 7.36 | — | — | — | — | — | — | — | — | |
| CPT-4E/25 ft | 5.44 | 7.12 | — | — | — | — | — | — | — | — | |
| 299-W18-1/211 ft | ND | 6.14 | — | — | — | — | — | — | — | — | |
| 299-W18-152/101 ft | 11.1 | 7.50 | — | — | — | — | — | — | — | — | |
| CPT-1A/35 ft | 6.51 | 7.14 | — | — | — | — | — | — | — | — | |
| CPT-1A/68 ft | 10.4 | 7.77 | — | — | — | — | — | — | — | — | |
| CPT-1A/91 ft | 4.94 | 6.62 | — | — | 1.7 | ND | — | — | B2WJB3 | — | |
| CPT-33/80 ft | 3.75 | 7.79 | — | — | — | — | — | — | — | — | |
| CPT-34/40 ft | 1.26 | 8.85 | — | — | — | — | — | — | — | — | |
| 299-W18-12/198 ft | ND | 4.41 | — | — | — | — | — | — | — | — | |
| 299-W18-11L/199 ft | ND | 4.54 | — | — | — | — | — | — | — | — | |
| 299-W18-10L/183 ft | ND | 5.02 | — | — | — | — | — | — | — | — | |
| 299-W18-249/130 ft | 8.60 | 6.70 | — | — | — | — | — | — | — | — | |
| 299-W18-247L/167 ft | 21.4 | 5.96 | — | — | — | — | — | — | — | — | |
| 299-W18-247L/167 ft | 20.1 | 6.54 | — | — | — | — | — | — | — | Duplicate | |
| CPT-13A/30 ft | 2.61 | 5.16 | — | — | — | — | — | — | — | — | |
| CPT-28/60 ft | 48.6 | 4.71 | 49.2 | 3.89 | — | — | 51 | ND | B2WWJ2 | — | |
| CPT-28/87 ft | 128 | 6.55 | 129.0 | 5.52 | — | — | 120 | ND | B2WWJ3 | — | |
| CPT-17 /10 ft | 6.10 | 5.47 | — | — | — | — | — | — | — | — | |
| 299-W15-217/114 ft | 2.22 | 4.95 | — | — | — | — | — | — | — | — | |

B-4

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

| Well/Probe and Depth | Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer) | | | | SUMMA Canister Samples (Analyzed in Laboratory Using GC/MS) | | | | | 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) | | |
| 299-W15-84/181 ft | 12.2 | 7.98 | — | — | — | — | — | — | — | — |
| CPT-18/35 ft | 1.98 | 5.60 | — | — | — | — | — | — | — | — |
| CPT-18/75 ft | 7.35 | 8.06 | — | — | — | — | — | — | — | — |
| 299-W15-219U/95 ft | 2.17 | 5.76 | — | — | 3.1 | ND | — | — | B2WJB4 | — |
| 299-W15-219L/175 ft | 4.41 | 7.70 | — | — | — | — | — | — | — | — |
| CPT-24/118 ft | 13.4 | 8.39 | — | — | — | — | — | — | — | — |
| 299-W15-218U/106 ft | 5.36 | 4.43 | — | — | — | — | — | — | — | — |
| 299-W15-218L/188 ft | 5.06 | 5.33 | — | — | — | — | — | — | — | — |
| 299-W15-86/125 ft | 24.7 | 8.74 | — | — | — | — | — | — | — | — |
| 299-W15-8U/103 ft | 16.3 | 16.4 | — | — | — | — | — | — | — | — |
| 299-W15-8U/103 ft | 16.2 | 16.2 | — | — | — | — | — | — | — | Duplicate |
| 299-W15-8L/180 ft | 7.00 | 38.5 | 10.0 | 78.0 | — | — | 7.6 | ND | B2WWJ4 | — |
| C4938 (P69C) 64 ft | 54.6 | 31.0 | 47.7 | 27.7 | — | — | 48 | ND | B2WWJ5 | — |
| C4937 (P66D) 64 ft | 35.4 | 36.2 | 31.5 | 28.9 | — | — | 30 | ND | B2WWJ6 | — |
| C5340 (P68C) 64 ft | 14.3 | 23.8 | — | — | — | — | — | — | — | — |
| CPT-21A/65 ft | 66.4 | 7.56 | 67.8 | 6.13 | — | — | 69 | ND | B2WWJ7 | — |
| CPT-21A/86 ft | 98.8 | 7.06 | 101.0 | 5.72 | 140 | ND | 100 | ND | B2WJB5, B2WWJ8 | — |
| 299-W15-216U/75 ft | 5.19 | 3.42 | — | — | — | — | — | — | — | — |
| 299-W15-216L/179 ft | 3.93 | 3.61 | — | — | — | — | — | — | — | — |
| CPT-27/33 ft | 3.02 | 4.56 | — | — | — | — | — | — | — | — |

B-5

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

| Well/Probe and Depth | Tedlar Bag Samples (Analyzed in Field Using B&K Analyzer) | | | | SUMMA Canister Samples (Analyzed in Laboratory Using GC/MS) | | | | | 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) | | |
| 299-W15-82L/83 ft | 5.92 | 10.5 | — | — | — | — | — | — | — | — |
| 299-W15-9L/176 ft | 5.14 | 6.74 | — | — | — | — | — | — | — | — |
| 299-W15-95L/144 ft | 12.2 | 7.59 | — | — | — | — | — | — | — | — |
| CPT-16/25 ft | 1.51 | 5.33 | — | — | — | — | — | — | — | — |
| CPT-16/65 ft | 5.22 | 5.11 | — | — | — | — | — | — | — | — |
| 299-W15-220U/88 ft | 2.08 | 4.12 | — | — | — | — | — | — | — | — |
| 299-W15-220L/162 ft | 2.98 | 3.74 | — | — | — | — | — | — | — | — |
| 299-W15-220L/162 ft | 3.15 | 4.55 | — | — | — | — | — | — | — | Duplicate |
| Field blank | ND | 5.06 | — | — | — | — | — | — | — | — |
| Field blank | ND | 4.33 | 3.59 | 3.12 | — | — | — | — | — | — |

B&K = Brüel & Kjær

CPT = cone penetrometer

GC/MS = gas chromatography/mass spectrometry

HEIS = Hanford Environmental Information System (database)

ND = not detected

ppmv = parts per million by volume

B-6

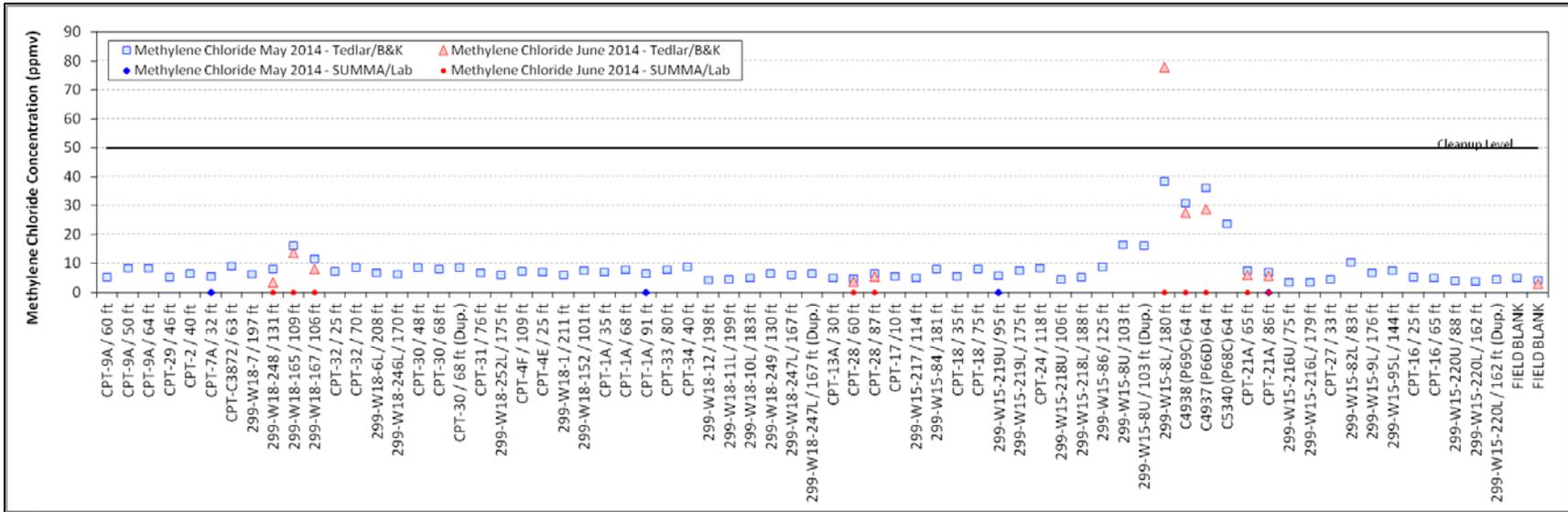


Figure B-2. Methylene Chloride Concentrations Measured during 2014 Rebound Sampling for the 200-PW-1 OU

1
2
3

Appendix C

Soil Vapor Extraction Endstate Tool (SVEET) Calculations

1

2

This page intentionally left blank.

3

1

2 Contents

3 **C1 Introduction..... C-1**

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

5 **C3 SVEET Versus Treatability Test Results..... C-7**

6 **C4 References..... C-8**

7

8 Figures

9 Figure C-1. Generalized Conceptual Model for SVEET C-2

10 Figure C-2. SVEET Results Extrapolated to a Source Width of 90 m..... C-6

11

12 Tables

13 Table C-1. Estimated Groundwater Concentrations at the
216-Z-9/216-Z-1A/216-Z-18 Waste Sites Using the SVEET Spreadsheet..... C-2

14 Table C-2. SVEET Inputs, Calculated Parameters, and Results for Source Widths of
15 10, 20, 30, and 50 m at All Three Waste Sites..... C-5

16 Table C-3. SVEET Analysis Results for All Three Waste Site (90 m Source Width,
17 25 m from Source Center)..... C-7

18

| | Terms | |
|---|-------|---|
| 1 | | |
| 2 | CCU | Cold Creek unit |
| 3 | OU | operable unit |
| 4 | ppmv | parts per million by volume |
| 5 | STOMP | Subsurface Transport Over Multiple Phases |
| 6 | SVE | soil vapor extraction |
| 7 | SVEET | Soil Vapor Extraction Endstate Tool |
| 8 | | |

C1 Introduction

1
2 The *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance* (hereafter referred to
3 as Soil Vapor Extraction [SVE] Closure Guidance) (PNNL-21843), authored by Pacific Northwest
4 National Laboratory, the U.S. Army Corps of Engineers, and the U.S. Environmental Protection Agency,
5 provides a procedure for calculating and estimating the groundwater contaminant concentration resulting
6 from a vadose zone source. The procedure is based on a generalized conceptual model defined by key
7 parameters describing the contaminant of interest, the location/extent of the vadose zone source, the
8 source strength, vadose zone porous media properties, groundwater flow characteristics, and the
9 magnitude of recharge (infiltration). For the calculation, 972 pre-modeled scenarios were simulated with
10 the Subsurface Transport Over Multiple Phases (STOMP) code (PNNL-15782, *STOMP Subsurface*
11 *Transport Over Multiple Phases, Version 4.0, User's Guide*) to obtain groundwater concentration results.
12 The pre-modeled scenarios represent combinations of parameter values for those parameters where the
13 groundwater concentration results exhibit a nonlinear relationship with the parameter value. The STOMP
14 simulation results are tabulated and the estimated impact to groundwater can be determined for
15 site-specific combinations of parameters by interpolation between the relevant pre-modeled scenario
16 results. The interpolated site-specific result is further scaled to account for parameters having a linear
17 relationship with groundwater concentration (e.g., recharge or Henry's law constant).

18 The calculation procedure from the SVE Closure Guidance has been implemented in the Soil
19 Vapor Extraction Endstate Tool (SVEET) software.¹ SVEET is a spreadsheet tool that allows the user to
20 easily enter data and calculate the estimated groundwater concentration for one or more scenarios
21 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

22
23 SVEET was used to estimate the groundwater concentrations resulting from vadose zone sources at the
24 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib. Prior studies (e.g., PNNL-21326, *Treatability*
25 *Test Report: Characterization of Vadose Zone Carbon Tetrachloride Source Strength Using Tomographic*
26 *Methods at the 216-Z-9 Site*) have determined that remaining vadose zone contamination is primarily
27 located within the fine-grained Cold Creek unit (CCU), which is taken to be the source zone for the
28 purposes of SVEET. Parameters for the generalized conceptual model, upon which SVEET is based
29 (Figure C-1), were generally taken from the treatability test, although three aspects required additional
30 consideration: definition of the source strength, location/thickness of the source, and the lateral extent of
31 the source area. These three aspects are discussed below. The full set of SVEET inputs are listed in
32 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.

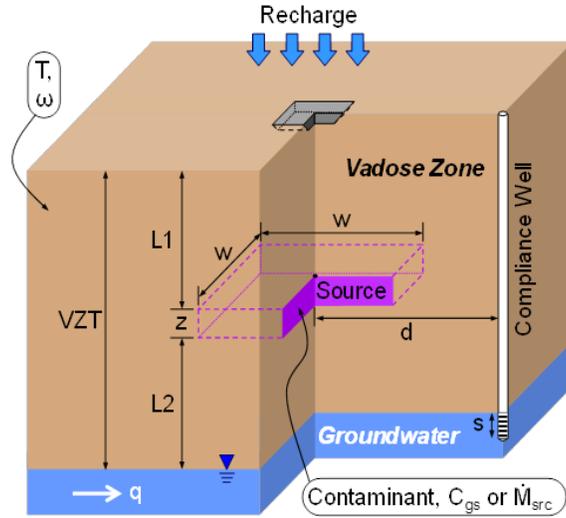


Figure C-1. Generalized Conceptual Model for SVEET

1
2
3

Table C-1. Estimated Groundwater Concentrations at the 216-Z-9/216-Z-1A/216-Z-18 Waste Sites Using the SVEET Spreadsheet

| 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 |

Table C-1. Estimated Groundwater Concentrations at the 216-Z-9/216-Z-1A/216-Z-18 Waste Sites Using the SVEET Spreadsheet

| User Input Source/Transport Parameters | 216-Z-9 | 216-Z-1A | 216-Z-18 | Data Source |
|---|---------|----------|----------|-------------|
|---|---------|----------|----------|-------------|

Note: 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

1 One aspect required for SVEET is a definition of the vadose zone source strength. Examination of soil
2 vapor monitoring data demonstrated that the level of contamination above the CCU was greater than the
3 contamination below the CCU at all sites, and that the contamination below the CCU at the 216-Z-1A and
4 216-Z-18 sites is lower than the contamination below the CCU at the 216-Z-9 site. Because the key factor
5 for impact on groundwater concentrations is the contamination emanating from the CCU into the zone
6 below the CCU, the determination of source strength focused on data from below the CCU. Of the
7 samples collected at the 216-Z-9 site in 2014 (Appendix B), the highest concentration detected was
8 24.7 parts per million by volume (ppmv) at Well 299-W15-86 on May 15, 2014. The 2014 measurements
9 beneath the 216-Z-1A and 216-Z-18 sites were all below detection limits, except for an atypical result of
10 21.4 ppmv at Well 299-W18-247L. Thus, the maximum result from the 2012–2013 time period was
11 selected as a conservative soil gas concentration below the CCU at 216-Z-1A and 216-Z-18 for SVEET
12 calculations. At the 216-Z-1A site, Well 299-W18-246L had an average result of 13.9 ppmv on
13 July 15, 2012. At the 216-Z-18 site, Well 299-W18-247L had a result of 9.65 ppmv on May 20, 2012
14 (SGW-54566, *Performance Evaluation Report for Soil Vapor Extraction Operations at the 200-PW-1*
15 *Operable Unit Carbon Tetrachloride Site, Calendar Year 2012*).

16 A second aspect is the vertical position and thickness of the source zone. The vadose zone thickness of
17 nominally 60 m (197 ft) can be represented in SVEET. However, SVEET constrains the source zone
18 thickness to be between 10 and 50 percent of the vadose zone thickness, so the nominal 4 m (13 ft)
19 thickness of the CCU source zone must be represented as 6 m (20 ft) thick. Because the thickness of
20 the CCU source zone was adjusted, the distance between ground surface and the top of the source zone
21 was also adjusted so the distance between the bottom of the CCU source and the groundwater was
22 accurate. The distance between the source and the groundwater is a key aspect with respect to the
23 influence of vadose contamination on concentrations in the groundwater. The distance from the bottom
24 of the CCU to groundwater is nominally 30 m (98 ft) at the 216-Z-9 site and 25 m (82 ft) at the
25 216-Z-1A/216-Z-18 sites.

26 The final aspect to consider was the size of the source area (i.e., lateral footprint). The size of the source
27 area at the 216-Z-9 site was determined in the treatability test report (PNNL-21326) to be nominally
28 90 m by 90 m (295 ft by 295 ft). However, data are not available to calculate the source size in the same
29 manner for the 216-Z-1A and 216-Z-18 sites; thus, the conservative approach was to use the same source
30 dimensions for all three sites. This selection of the same source size for 216-Z-1A and 216-Z-18 as used
31 for 216-Z-9 is conservative because when the source strength is defined by a given soil gas concentration,

1 the impact to groundwater increases linearly as the size increases (i.e., there is more mass impacting the
2 groundwater as the source size increases). Although the SVEET software tool does not allow for entry of
3 a source size greater than a 50 m by 50 m (164 ft by 164 ft) area, it is straightforward to linearly
4 extrapolate from key sizes (10, 20, 30, and 50 m [33, 66, 98, and 164 ft]) to the 90 m (295 ft) side length,
5 as discussed below.

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

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

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

29 The SVEET results are conservative for two reasons:

- 30 • SVEET estimates the impact of vadose zone contamination on clean groundwater. Appendix D
31 discusses the conditions for which mass transfer (e.g., via vapor diffusion) will be going either into
32 the groundwater from the vadose zone or out of the groundwater into the vadose zone. Under the
33 current contaminated conditions in the underlying 200-ZP-1 Operable Unit (OU) aquifer, mass
34 transfer from the vadose zone into the groundwater would be inhibited.
- 35 • The SVEET calculations assume that the vadose zone contaminant source remains constant over time.
36 In reality, the source becomes depleted by diffusive mass transfer. The constant source strength is
37 conservative because it computes the maximum contribution of the vadose zone source to
38 a groundwater contaminant plume.

39

1
2

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 |
| 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 |
| 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 |
| 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 |

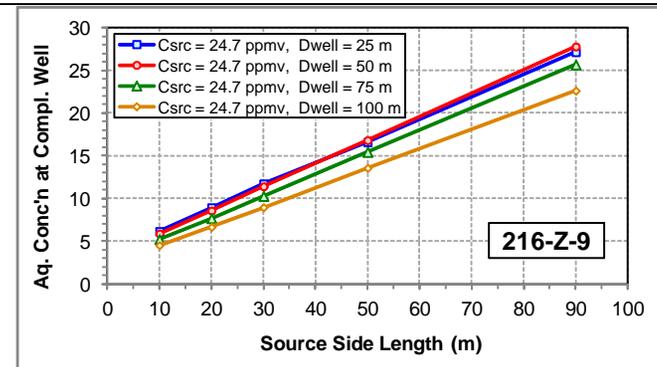
C-5

3

4

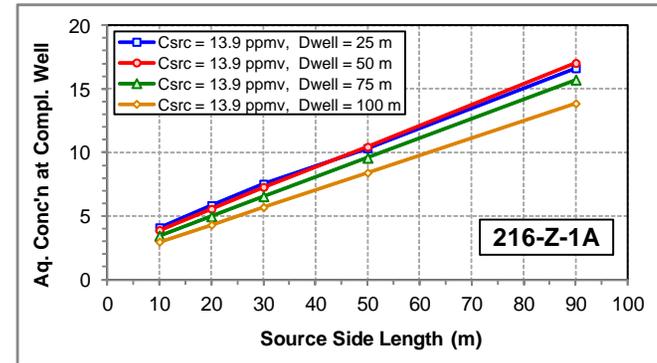
Area = **216-Z-9**
 Csrc = 24.7 (well 299-W15-86 on 5/15/2014)

| w (m): D _{well} (m) | SVEET Output (µg/L) | | | | Values Calculated Outside of SVEET | | | |
|---------------------------------|---------------------|-----|------|------|------------------------------------|-------|-----------|----------------|
| | 10 | 20 | 30 | 50 | 90 | slope | intercept | r ² |
| 25 | 6.2 | 8.9 | 11.7 | 16.6 | 27 | 0.260 | 3.696 | 0.9985 |
| 50 | 5.9 | 8.6 | 11.4 | 16.8 | 28 | 0.274 | 3.151 | 0.9999 |
| 75 | 5.2 | 7.7 | 10.3 | 15.4 | 26 | 0.256 | 2.612 | 0.9999 |
| 100 | 4.5 | 6.7 | 9.0 | 13.6 | 23 | 0.227 | 2.183 | 0.9997 |



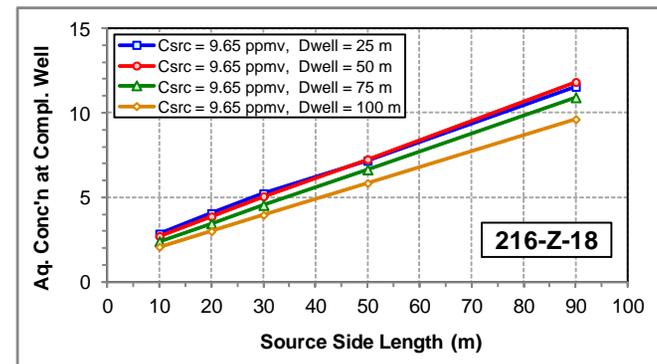
Area = **216-Z-1A**
 Csrc = 13.9 (well 299-W18-246L on 7/15/2012)

| w (m): D _{well} (m) | SVEET Output (µg/L) | | | | Values Calculated Outside of SVEET | | | |
|---------------------------------|---------------------|-----|-----|------|------------------------------------|-------|-----------|----------------|
| | 10 | 20 | 30 | 50 | 90 | slope | intercept | r ² |
| 25 | 4.1 | 5.8 | 7.5 | 10.3 | 17 | 0.155 | 2.691 | 0.9964 |
| 50 | 3.9 | 5.6 | 7.3 | 10.4 | 17 | 0.164 | 2.297 | 0.9996 |
| 75 | 3.4 | 5.0 | 6.5 | 9.6 | 16 | 0.153 | 1.915 | 0.9999 |
| 100 | 3.0 | 4.3 | 5.7 | 8.4 | 14 | 0.136 | 1.606 | 1.0000 |



Area = **216-Z-18**
 Csrc = 9.65 (well 299-W18-247L on 5/20/2012)

| w (m): D _{well} (m) | SVEET Output (µg/L) | | | | Values Calculated Outside of SVEET | | | |
|---------------------------------|---------------------|-----|-----|-----|------------------------------------|-------|-----------|----------------|
| | 10 | 20 | 30 | 50 | 90 | slope | intercept | r ² |
| 25 | 2.8 | 4.1 | 5.2 | 7.2 | 12 | 0.107 | 1.868 | 0.9964 |
| 50 | 2.7 | 3.9 | 5.1 | 7.3 | 12 | 0.114 | 1.595 | 0.9996 |
| 75 | 2.4 | 3.4 | 4.5 | 6.6 | 11 | 0.107 | 1.330 | 0.9999 |
| 100 | 2.1 | 3.0 | 4.0 | 5.8 | 10 | 0.095 | 1.115 | 1.0000 |



D_{well} (m) = the distance to the "compliance well" from the center of the source
 w (m) = the side length of the source area (square this number to get the areal footprint of the source)

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

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

| Waste Site | 216-Z-9 | 216-Z-1A | 216-Z-18 |
|---|---------|----------|----------|
| Estimated groundwater concentration ($\mu\text{g/L}$) | 27 | 17 | 12 |

C3 SVEET versus Treatability Test Results

1

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

12 As previously discussed, both SVEET and the treatability test analyses were conducted for the 216-Z-9
13 site. The SVEET estimated that the groundwater carbon tetrachloride concentration would be
14 approximately 27 $\mu\text{g/L}$ (based on soil vapor concentration of 24.7 ppmv at the source). This estimate is
15 consistent with the 24 $\mu\text{g/L}$ groundwater concentration calculated in the treatability test and corroborates
16 the SVEET calculations. Thus, the relative comparisons between the SVEET estimates for the three waste
17 sites (discussed in Sections 5.1.1 in the main text and in Section C2 of this appendix) are appropriate.

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

- 21 • The treatability test analysis used the actual CCU thickness in the analysis (about 4 m [13 ft]),
22 whereas the SVEET analysis was constrained to apply a CCU thickness of 6 m (19.7 ft) (10 percent
23 of the total vadose zone thickness). Thus, the surface area of the source is larger in SVEET and
24 results in a somewhat higher, more conservative estimate for the groundwater concentration.
- 25 • The treatability test analysis used a dimensionless Henry's law coefficient value of 0.813 (based on
26 available literature). The SVEET tool incorporates a calculation method for the Henry's law
27 coefficient as a function of temperature based on published vapor pressure and solubility data as
28 functions of temperature (see Appendix D, Section D2). SVEET calculated the value of the
29 dimensionless Henry's law coefficient to be 0.761, which is lower than the value used in the
30 treatability test. A lower, dimensionless Henry's law coefficient will result in a higher and more
31 conservative estimate for the groundwater concentration.
- 32 • The treatability test analysis incorporated a vadose zone moisture content distribution based on the
33 variation in sediment properties at the site through multiple geological layers. In contrast, the SVEET
34 analysis was constrained to use a single moisture content to represent the entire vadose zone.
35 The moisture content impacts the vapor diffusion coefficients. Differences in magnitude and

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

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

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

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

21 C4 References

- 22 PNNL-15782, 2006, *STOMP Subsurface Transport Over Multiple Phases, Version 4.0, User's Guide*,
23 Pacific Northwest National Laboratory, Richland, Washington. Available at:
24 <http://www.osti.gov/scitech/servlets/purl/1012530>.
- 25 PNNL-21326, 2012, *Treatability Test Report: Characterization of Vadose Zone Carbon Tetrachloride*
26 *Source Strength Using Tomographic Methods at the 216-Z-9 Site*, Pacific Northwest National
27 Laboratory, Richland, Washington. Available at:
28 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1210310436>.
- 29 PNNL-21843, 2013, *Soil Vapor Extraction System Optimization, Transition, and Closure Guidance*,
30 Pacific Northwest National Laboratory, Richland, Washington. Available at:
31 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0088374>.
- 32 PNNL-22062, 2012, *Abiotic Degradation Rates for Carbon Tetrachloride and Chloroform: Final Report*,
33 Pacific Northwest National Laboratory, Richland, Washington. Available at:
34 http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22062.pdf.
- 35 SGW-54566, 2013, *Performance Evaluation Report for Soil Vapor Extraction Operations at the*
36 *200-PW-1 Operable Unit Carbon Tetrachloride Site, Calendar Year 2012*, Rev. 0, CH2M HILL
37 Plateau Remediation Company, Richland, Washington. Available at:
38 <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0086023>.

1

Appendix D

2

Carbon Tetrachloride Mass Transfer from Vadose Zone to Groundwater

3

1

2

This page intentionally left blank.

3

1 **Contents**

2 **D1 Introduction..... D-1**

3 **D2 Henry’s Law and Temperature Relationship..... D-1**

4 **D3 References D-4**

5

6 **Figure**

7 Figure D-1. Gas and Aqueous Phase Equilibrium Concentrations for Carbon Tetrachloride..... D-2

8

9 **Table**

10 Table D-1. Correlation Coefficients for Vapor Pressure and Solubility for Carbon Tetrachloride D-2

11

12

1

2

3

This page intentionally left blank.

4

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:

$$C_g = H \cdot C_w \quad \text{(Equation D-1)}$$

where:

C_g = concentration in the gas phase ($\mu\text{g/L}$)

H = Henry's law constant (dimensionless)

C_w = concentration in the aqueous phase ($\mu\text{g/L}$)

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)/ $\mu\text{g/L}$. When the groundwater concentration at the water table is $1,000 \mu\text{g/L}$, 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., "A Critical Compilation of Henry's Law Constant Temperature Dependence Relations for Organic Compounds in Dilute Aqueous Solutions" [Staudinger and Roberts, 2001]; "A Review of Henry's Law Coefficients for Chlorine-Containing C_1 and C_2 Hydrocarbons" [Warneck, 2007]; "Henry's Law Constants of Chlorinated Solvents at Elevated Temperatures" [Chen et al., 2012]). "Comparison of Predictive Methods for Henry's Law Coefficients of Organic Chemicals" (Brennan et al., 1998) 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.

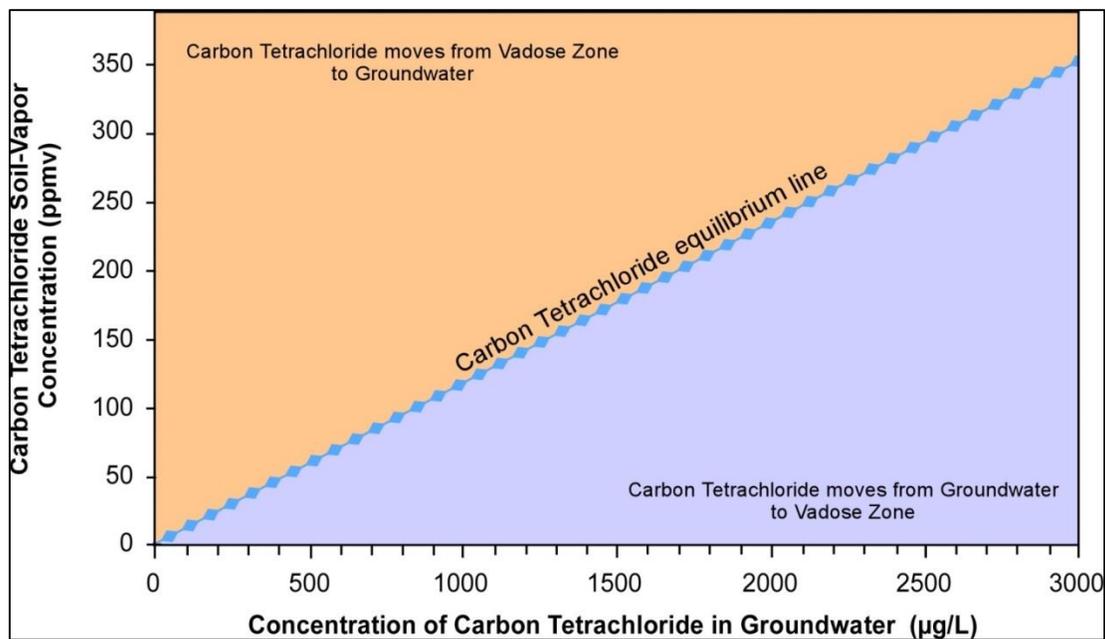


Figure D-1. Gas and Aqueous Phase Equilibrium Concentrations for Carbon Tetrachloride

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

$$\text{Log}_{10}(P_{vap}) = A - \frac{B}{T + C} \quad \text{(Equation D-2)}$$

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) | Vapor Pressure (mm/Hg) | | | Solubility (Mass Fraction) | | | |
|--------------------------|----------------------|--------------------------|------------------------|----------|---------|----------------------------|-------------|------------|------------|
| | | | 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 |

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

$$5 \quad x_p = A + B \cdot T + C \cdot T^2 + D \cdot T^3 \quad \text{(Equation D-3)}$$

6 where:

7 x_p = mass fraction (wt %)

8 T = temperature (°C)

9 $A, B, C,$ and D = tabulated contaminant-specific correlation coefficients

10 The mass fraction is converted to a mole fraction, x , in Equation D-4 by multiplying by the ratio of the
11 molecular weight of water to the molecular weight of carbon tetrachloride. Molecular weights are
12 calculated from the molecular formula and the atomic weights in the “IUPAC Periodic Table of the
13 Elements” (IUPAC, 2011).

$$14 \quad x = \frac{x_p}{100} \cdot \frac{MW_w}{MW_{CT}} \quad \text{(Equation D-4)}$$

15 where:

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

17 MW_w = molecular weight of water (18.01528 g/mol)

18 x = mole fraction

19 x_p = mass fraction (wt %)

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

$$30 \quad H = \frac{P_{vap}}{x} \cdot \frac{MW_w}{\rho_w \cdot R_{gas} \cdot T} \cdot \frac{1 L}{1000 mL} \cdot \frac{1 atm}{760 mmHg} \quad \text{(Equation D-5)}$$

31 where:

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

33 MW_w = molecular weight of water (18.01528 g/mol)

34 P_{vap} = vapor pressure

35 ρ_w = temperature-dependent density of water (g/mL)

36 R_{gas} = gas constant (0.08206 L·atm·K⁻¹·mol⁻¹)

1 T = average subsurface temperature (K)

2 x = mole fraction

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

$$\hat{C}_g = C_g \cdot \frac{R_{gas} \cdot T}{MW_{CT}} \quad \text{(Equation D-6)}$$

5
6 where:

7 C_g = concentration in the gas phase ($\mu\text{g/L}$)

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

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

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

11 T = average subsurface temperature (K)

12 Using a Hanford-specific subsurface temperature of 16°C (PNNL-22062, *Abiotic Degradation Rates for*
13 *Carbon Tetrachloride and Chloroform: Final Report*) and an aqueous carbon tetrachloride concentration
14 (C_w) of $100 \mu\text{g/L}$, the following values are calculated:

15 $P_{vap} = 74.89 \text{ mmHg}$ (from Equation D-2)

16 $x_p = 0.0840 \text{ wt \%} \rightarrow x = 9.84\text{E-}05$ (from Equations D-3 and D-4)

17 $H = 0.7609$ (from Equation D-5)

18 $C_g = H \cdot C_w = (0.7609)(100 \mu\text{g/L}) = 76.09 \mu\text{g/L}$ (from Equation D-1)

19 $\hat{C}_g = 11.7 \text{ ppmv at the water table}$ (from Equation D-6)

20

21 D3 References

22 Brennan, R.A., N. Nirmalakhandan, and R.E. Speece, 1998, "Comparison of Predictive Methods for
23 Henrys Law Coefficients of Organic Chemicals," *Water Res.* 32(6):1901-1911.

24 Chen, F., D.L. Freedman, R.W. Falta, and L.C. Murdoch, 2012, "Henry's Law Constants of Chlorinated
25 Solvents at Elevated Temperatures," *Chemosphere* 86(2):156-165.

26 CRC, 2011, "Standard Density of Water," *CRC Handbook of Chemistry and Physics*, 91st Edition
27 (Internet Edition 2011), W.M. Haynes (ed.), CRC Press/Taylor and Francis, Boca Raton, Florida.

28 IUPAC, 2011, "IUPAC Periodic Table of the Elements," International Union of Pure and Applied
29 Chemistry, Research Triangle Park, North Carolina.

30 Mackay, D, W.Y. Shiu, K. Ma, and S.C. Lee, 2006, *Handbook of Physical-Chemical Properties and*
31 *Environmental Fate for Organic Chemicals*, Second Edition, Volume II, Halogenated
32 Hydrocarbons. CRC Press, Boca Raton, Florida.

- 1 Mohr, P.J., B.N. Taylor, and D.B. Newell, 2011, “The 2010 CODATA Recommended Values of the
2 Fundamental Physical Constants” (Web Version 6.0), database developed by J. Baker,
3 M. Douma, and S. Kotochigova, National Institute of Standards and Technology, Gaithersburg,
4 Maryland. Available at: <http://physics.nist.gov/constants> (accessed April 26, 2013).
- 5 PNNL-22062, 2012, *Abiotic Degradation Rates for Carbon Tetrachloride and Chloroform: Final Report*,
6 Pacific Northwest National Laboratory, Richland, Washington. Available at:
7 http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22062.pdf.
- 8 Sander, R., 1999, “Modeling Atmospheric Chemistry: Interactions Between Gas-Phase Species and
9 Liquid Cloud/Aerosol Particles,” *Surv. Geophys.* 20(1):1-31.
- 10 Staudinger, J. and P.V. Roberts, 2001, “A Critical Compilation of Henry’s Law Constant Temperature
11 Dependence Relations for Organic Compounds in Dilute Aqueous Solutions,” *Chemosphere*
12 44(4):561-576.
- 13 Warneck, P., 2007, “A Review of Henry’s Law Coefficients for Chlorine-Containing C₁ and C₂
14 Hydrocarbons,” *Chemosphere* 69(3):347-361.
- 15 Yaws, C.L., P.K. Narasimhan, and C. Gabbula, 2009, *Yaws’ Handbook of Antoine Coefficients for Vapor
16 Pressure* (2nd Electronic Edition), Knovel, New York.
- 17

1

2

This page intentionally left blank.

1

Appendix E

2

Degradation and Future Impacts of Vadose Zone Sources

3

1

2

This page intentionally left blank.

3

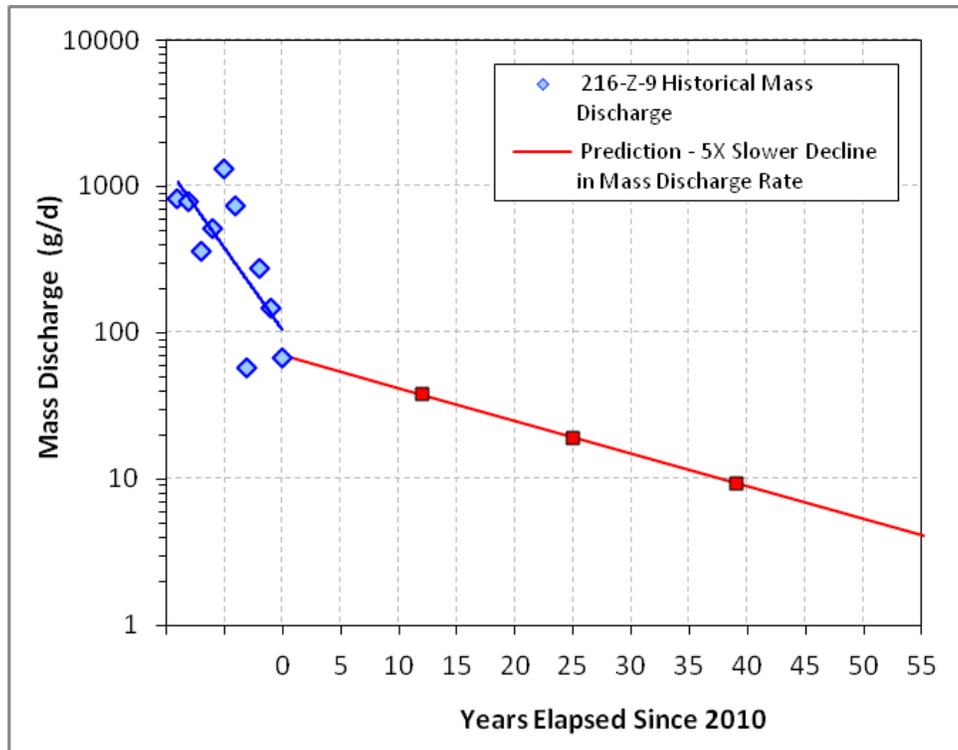
| 1 | | Terms |
|---|-------|-------------------------------------|
| 2 | MNA | monitored natural attenuation |
| 3 | OU | operable unit |
| 4 | SVE | soil vapor extraction |
| 5 | SVEET | Soil Vapor Extraction Endstate Tool |
| 6 | | |

E1 Discussion

1
2 As noted in Appendix C, the Soil Vapor Extraction Endstate Tool (SVEET) and treatability test
3 calculations (PNNL-21326, *Treatability Test Report: Characterization of Vadose Zone Carbon*
4 *Tetrachloride Source Strength Using Tomographic Methods at the 216-Z-9 Site*) assume that (1) the
5 vadose zone source maintains a constant mass discharge over time, and (2) there is not a contaminant
6 source in the groundwater. These are conservative assumptions with regard to estimating the impact of the
7 vadose zone source on groundwater contaminant concentrations. However, the mass discharge from the
8 vadose zone source is expected to continue decreasing after the termination of soil vapor extraction (SVE)
9 operations, as shown in “Assessing Performance and Closure for Soil Vapor Extraction: Integrating
10 Vapor Discharge and Impact to Groundwater Quality” (Carroll et al., 2012). In addition, the underlying
11 groundwater in the 200-ZP-1 Operable Unit (OU) already contains carbon tetrachloride contamination,
12 which affects the impact of vadose zone contamination on the groundwater. Therefore, the analyses based
13 on the current mass discharge are overly conservative. This appendix discusses the effects of a reduced
14 mass discharge from the vadose zone source at the 216-Z-9 site and the existing carbon tetrachloride
15 groundwater contamination with respect to the impact on future groundwater concentrations. Future
16 impacts are evaluated in the context of the defined remedy (25 years of pump-and-treat, followed by
17 100 years of monitored natural attenuation [MNA]) for the underlying aquifer of the 200-ZP-1 OU.

18 The magnitude of mass discharge from the vadose zone source will continue to decrease after termination
19 of SVE operations. During cyclic SVE operations, the higher permeability materials around the source
20 zone were periodically “cleaned out” and vapor-phase contaminants diffused out of the source zone into
21 this clean area. As demonstrated in the treatability test (PNNL-21326) by the series of measurements over
22 time, the source mass discharge declined over time (i.e., the source strength was diminished over time).
23 Once SVE is terminated, contaminants will still emanate from the source zone over time and will
24 continue to diminish the source strength. However, the rate of this process will be slower because the
25 SVE systems will not be periodically cleaning out the higher permeability zones. The decline in source
26 strength is controlled by diffusion of contaminants out of the source zone. The diffusion rate is governed
27 by a constant related to the contaminant properties, subsurface conditions, and the concentration gradient
28 (i.e., change in concentration over change in distance). When SVE is applied, the concentration gradient
29 remains high between the source and the surrounding subsurface. Without SVE, the concentration
30 gradient will be lower and over time become controlled by the gradient between the source zone and the
31 ground surface (upper portion of the vadose zone) and between the source zone and the groundwater
32 (lower portion of the vadose zone).

33 Carroll et al. (2012) examined the diffusion rate and associated source mass discharge under these two
34 conditions and found that, for sources of the size found at the 216-Z-9 site, the post-SVE diffusion rate
35 was about five times lower than the rate under cyclic SVE conditions. Thus, the source strength will
36 continue to diminish at a rate about five times slower than the observed rate of diminishing source
37 strength during SVE operations. Figure E-1 shows the data during SVE operations and the associated
38 rate of source strength reduction. This figure also shows the projected change after SVE is terminated.
39 In the treatability test, this type of evaluation was conducted and indicated that (as shown in Figure E-1)
40 a source mass discharge starting at a value of 70 g/d (i.e., the calculated mass discharge for the 216-Z-9
41 site in 2010 during SVE operations) is expected to drop below 10 g/d in about 40 years after termination
42 of SVE operations (i.e., in about 2050). The decrease in source mass discharge to about 10 g/d is
43 significant because that level of mass discharge is predicted to result in groundwater concentrations at or
44 below 3.4 µg/L (see Figure 5-1 in the main text), which is the carbon tetrachloride cleanup level specified
45 for the groundwater (post-MNA) in the *Record of Decision, Hanford 200 Area, 200-ZP-1 Superfund Site,*
46 *Benton County, Washington* (EPA et al., 2008).



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

4 E2 References

5 Carroll, K.C., M. Oostrom, M.J. Truex, V.J. Rohay, and M.L. Brusseau, 2012, "Assessing Performance
6 and Closure for Soil Vapor Extraction: Integrating Vapor Discharge and Impact to Groundwater
7 Quality," *J. Contam. Hydrol.* 128:71-82.

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

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