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ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN **189915**
Proj. ECN

2290-2203135
9313027-0622

2. ECN Category (mark one) Supplemental <input type="checkbox"/> Direct Revision <input checked="" type="checkbox"/> Change ECN <input type="checkbox"/> Temporary <input type="checkbox"/> Standby <input type="checkbox"/> Supersedure <input type="checkbox"/> Cancel/Void <input type="checkbox"/>	3. Originator's Name, Organization, MSIN, and Telephone No. R. R. Lehrschall, Environmental Restoration Safety Support, H4-67, 376-6788		4. Date 8/11/93
	5. Project Title/No./Work Order No. Remediation of Carbon Tetrachloride	6. Bldg./Sys./Fac. No. 200 West Area	7. Impact Level 2 ESQ
	8. Document Numbers Changed by this ECN (includes sheet no. and rev.) WHC-SD-EN-SAD-004, Rev. 1-A	9. Related ECN No(s). 169357 (0-A) 186789 (0-B) 189902 (Rev.1) 189905 (Rev.1-A)	10. Related PO No. N/A

11a. Modification Work <input type="checkbox"/> Yes (fill out Blk. 11b) <input checked="" type="checkbox"/> No (NA Blks. 11b, 11c, 11d)	11b. Work Package No. N/A	11c. Modification Work Complete N/A _____ Cog. Engineer Signature & Date	11d. Restored to Original Condition (Temp. or Standby ECN only) N/A _____ Cog. Engineer Signature & Date
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12. Description of Change

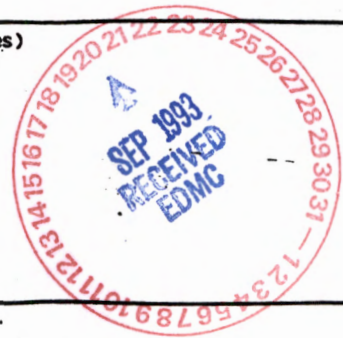
Changes have been made that address the potential consequences associated with a granular activated carbon (GAC) overheating event. This accident scenario has been incorporated into the safety assessment. Additional information is provided regarding hazardous materials that may be produced if an overheating event occurs. The controls that should be considered for preventing an overheating event are also provided.

13a. Justification (mark one)	Criteria Change <input checked="" type="checkbox"/>	Design Improvement <input type="checkbox"/>	Environmental <input type="checkbox"/>
As-Found <input type="checkbox"/>	Facilitate Const. <input type="checkbox"/>	Const. Error/Omission <input type="checkbox"/>	Design Error/Omission <input type="checkbox"/>

13b. Justification Details

The proposed changes are justified based on (1) the need to understand the potential hazards involving a GAC overheating event; (2) the discussion of potential consequences if an overheating event occurs; and (3) controls that are required to mitigate the potential consequences from overheating a GAC canister.

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18. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 12. Enter the affected document number in Block 19.

SDD/DD	<input type="checkbox"/>	Seismic/Stress Analysis	<input type="checkbox"/>	Tank Calibration Manual	<input type="checkbox"/>
Functional Design Criteria	<input type="checkbox"/>	Stress/Design Report	<input type="checkbox"/>	Health Physics Procedure	<input type="checkbox"/>
Operating Specification	<input type="checkbox"/>	Interface Control Drawing	<input type="checkbox"/>	Spares Multiple Unit Listing	<input type="checkbox"/>
Criticality Specification	<input type="checkbox"/>	Calibration Procedure	<input type="checkbox"/>	Test Procedures/Specification	<input type="checkbox"/>
Conceptual Design Report	<input type="checkbox"/>	Installation Procedure	<input type="checkbox"/>	Component Index	<input type="checkbox"/>
Equipment Spec.	<input type="checkbox"/>	Maintenance Procedure	<input type="checkbox"/>	ASME Coded Item	<input type="checkbox"/>
Const. Spec.	<input type="checkbox"/>	Engineering Procedure	<input type="checkbox"/>	Human Factor Consideration	<input type="checkbox"/>
Procurement Spec.	<input type="checkbox"/>	Operating Instruction	<input type="checkbox"/>	Computer Software	<input type="checkbox"/>
Vendor Information	<input type="checkbox"/>	Operating Procedure	<input checked="" type="checkbox"/>	Electric Circuit Schedule	<input type="checkbox"/>
OM Manual	<input type="checkbox"/>	Operational Safety Requirement	<input type="checkbox"/>	ICRS Procedure	<input type="checkbox"/>
FSAR/SAR	<input type="checkbox"/>	IEFD Drawing	<input type="checkbox"/>	Process Control Manual/Plan	<input type="checkbox"/>
Safety Equipment List	<input type="checkbox"/>	Cell Arrangement Drawing	<input type="checkbox"/>	Process Flow Chart	<input type="checkbox"/>
Radiation Work Permit	<input checked="" type="checkbox"/>	Essential Material Specification	<input type="checkbox"/>	Purchase Requisition	<input type="checkbox"/>
Environmental Impact Statement	<input type="checkbox"/>	Fac. Proc. Samp. Schedule	<input type="checkbox"/>	Hazardous Waste Operations Permit	<input checked="" type="checkbox"/>
Environmental Report	<input type="checkbox"/>	Inspection Plan	<input type="checkbox"/>		<input type="checkbox"/>
Environmental Permit	<input type="checkbox"/>	Inventory Adjustment Request	<input type="checkbox"/>		<input type="checkbox"/>

19. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

Document Number/Revision	Document Number/Revision	Document Number/Revision
N/A		

20. Approvals

Signature	Date	Signature	Date
OPERATIONS AND ENGINEERING		ARCHITECT-ENGINEER	
Cog Engineer S. A. Driggers <i>S.A. Driggers</i>	<u>8/30/93</u>	PE	_____
Cog. Mgr. M. C. Hagood <i>M.C. Hagood</i>	<u>8/30/93</u>	QA	_____
QA T. L. Bennington <i>T.L. Bennington</i>	<u>8/31/93</u>	Safety	_____
Safety M. A. Tredway <i>M.A. Tredway</i>	<u>8/30/93</u>	Design	_____
Security		Environ.	_____
Environ. K. A. Gano <i>K.A. Gano</i>	<u>8/30/93</u>	Other	_____
Projects/Programs			_____
Tank Waste Remediation System			_____
Environ. Field Services D. J. Moak <i>D.J. Moak</i>	<u>9-1-93</u>	DEPARTMENT OF ENERGY	_____
Restoration & Remediation		Signature or Letter No.	_____
Operations & Support Services			_____
IRM		ADDITIONAL	_____
ERSS W. R. Kerr <i>WRK</i>	<u>8/30/93</u>		_____
RRSA J. J. Zimmer <i>J.J. Zimmer</i>	<u>8/30/93</u>		_____

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SUPPORTING DOCUMENT

1. Total Pages **293**

2. Title

Safety Assessment for the 200 West Area Expedited Response Action for Remediation of Carbon Tetrachloride

3. Number

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1-B

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safety assessment
gas membrane separation system
low hazard

6. Author

Name: R. R. Lehrschall

Signature *R.R. Lehrschall*

Organization/Charge Code 29550/HIBBE

APPROVED FOR PUBLIC RELEASE
V. Bickley 9/2/93

7. Abstract

Revisions were made to address the potential consequences associated with a granular activated carbon (GAC) overheating event. The controls for preventing an overheating event are also provided. Calculations on HCl gas production from carbon catalyzed hydrolysis of CCl₄ have also been made to Attachment G.

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<p>Title Safety Assessment for the 200 West Area Expedited Response Action for Remediation of Carbon Tetrachloride</p>	<p>Unclassified Category</p> <p>UC-</p>	<p>Impact Level 2</p> <p>ESQ</p>
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RECORD OF REVISION

(1) Document Number

WHC-SD-EN-SAD-004

Page 5

(2) Title

Safety Assessment for the 200 West Area Expedited Response Action for Remediation of Carbon Tetrachloride

CHANGE CONTROL RECORD

(3) Revision	(4) Description of Change - Replace, Add, and Delete Pages	Authorized for Release	
		(5) Cog. Engr.	(6) Cog. Mgr. Date
1-A	Rev. 0 released per EDT 129408 Rev. 0-A released per ECN 169357 Rev. 0-B released per ECN 786789 Rev. 1 released per ECN 189902 Rev. 1-A released per ECN 189905 Rev. 1-B released per ECN 189915		
1-A	Revisions have been made to the table of contents and pages 3, 4, 5, 33, 39, 40, and 41. Revisions were made to reflect a change in operational safety limit 2 to address the operation of several vapor extraction units at two different sites. The specific changes provide the sampling frequencies required at the stack sample port based on the maximum concentrations of CCl ₄ anticipated and lower concentrations that may be encountered. Attachment G has been replaced.	J. W. Green (signature on file)	M. C. Hagood (signature on file)
1-B RS	Revisions have been made to the table of contents and pages 2, 3, 5, 23, 27, 28, 31, 33, 36, 46, 47, 48, and 50. The entire main text has been replaced to reflect new page numbers. Revisions were made to address the potential consequences associated with a granular activated carbon (GAC) overheating event. The controls for preventing an overheating event are also provided. Calculations on HCl gas production from carbon catalyzed hydrolysis of CCl ₄ have also been made to Attachment G. Attachment J has been added that explains the monitoring for ketones.	S. A. Driggers <i>Signature</i> 9/3/93	M. C. Hagood <i>R.R. Schmitt</i> for M.C. Hagood per Telco 9-3-93

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LIST OF TERMS

acfm	actual cubic feet per minute
CAM	continuous air monitor
CCl ₄	carbon tetrachloride
cfm	cubic feet per minute
cpm	counts per minute
DAC	derived air concentration
DAS	Data Acquisition System
DOE	U. S. Department of Energy
DOT	Department of Transportation
EPA	Environmental Protection Agency
ERA	expedited response action
GAC	granular activated carbon
GMSS	Gas Membrane Separation System
HEPA	high efficiency particulate air
HCl	hydrogen chloride
HMS	Hanford (Site) Meteorology Station
HWOP	Hazardous Work Operations Permit
IDLH	immediately dangerous to life or health
JSA	Job Safety Analysis
mR/h	millirem per hour
msl	mean sea level
OSHA	Occupational Safety and Health Administration
OSL	operational safety limits
PAG	protective action guidelines
pCi	pico curie
PFP	Plutonium Finishing Plant
p/M	parts per million
PRF	Plutonium Reclamation Facility
STEL	short term exposure limit
TLV	threshold limit values
TWA	time weighted average
μCi	micro curie
VES	vapor extraction system
VOC	volatile organic compound
WHC	Westinghouse Hanford Company

SAFETY ASSESSMENT FOR THE 200 WEST AREA EXPEDITED RESPONSE ACTION FOR REMEDIATION OF CARBON TETRACHLORIDE

1.0 INTRODUCTION AND SUMMARY

Westinghouse Hanford Company (WHC) is preparing to perform remediation activities to mitigate the spread of carbon tetrachloride (CCl_4) within the 200 West Area unsaturated soils located on the Hanford Site for the U.S. Department of Energy, Richland Field Office. This activity is one of three expedited response actions (ERA) that the U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (EPA), and the Washington State Department of Ecology agreed in late 1990 to undertake at the Hanford Site. This safety assessment presents the results of the remediation activities associated with the CCl_4 ERA. The purpose of this assessment is to determine the potential consequences of an inventory of material associated with a facility or activity exclusive of engineered features or administrative controls (Kerr 1990). This document complies with the criteria provided in DOE Order 5481.1B, *Safety Analysis and Review System* (DOE 1986).

1.1 WORK DESCRIPTION

The remediation activities will be conducted using a vapor extraction system (VES) for removal of CCl_4 . Granular activated carbon (GAC) contained in Department of Transportation (DOT) approved canisters are used to adsorb the CCl_4 vapors. Fully saturated canisters will be stored for an interim period and then transported offsite for regeneration. A maximum of twelve fully saturated canisters will be allowed in a storage location at the site. The VES process is used nationwide to remove a variety of volatile organic chemicals from vadose zone soils contaminated by leaks from underground storage tanks and other sources. The EPA has approved the use of vacuum extraction at more than 31 sites.

Task 7 of the Phase I site evaluation for the ERA compiled information on the volume and contaminant types found, contaminant concentration, and identification of the influence zone using the VES (Lehrschall 1990; DOE-RL 1991). Based on the test results, the VES successfully removes CCl_4 vapors from the vadose zone of the Hanford Site soils.

The scope of this assessment includes activities that will involve the use of several VES units to complete the ERA and conduct a treatability demonstration for performing a Gas Membrane Separation System (GMSS) test. The VES unit used during the Task 7 activities will be used for remediation activities until larger units are available. This assessment also addresses the hazards associated with the operation of the larger units (planned for the full scale remediation activities) based upon the current proposed design and a VES characterization unit used for sampling activities to determine the CCl_4 concentrations found at the boreholes throughout the well fields. Changes to the proposed designs will necessitate an evaluation of any new hazards and a possible addendum to this assessment. The design of the current system, larger production unit, and the characterization unit are discussed in Section 2.4.

The first phase of CCl_4 vapor removal will use existing vertical wells. The second phase will use existing vertical wells plus new vertical or horizontal wells. The installation (drilling) of any new wells is not evaluated and addressed in this safety assessment. The three major waste site locations are in close proximity to the Plutonium Finishing Plant (PFP). These sites were the major contributors of CCl_4 to the soil and groundwater and will be the focal point for the remediation activities. The extracted vapors will be treated using carbon adsorption technology.

1.2 ASSESSMENT SUMMARY

This completed assessment found the design and plans to be safe. The report summarizes the findings and conclusions of the assessment for this ERA. The potential consequences of this remediation work indicate that the toxicity of CCl_4 is the controlling hazard for an accident involving airborne releases. The calculated results are conservative.

1.3 SUMMARY OF CONTROLS AND PRUDENT ACTIONS

The recommendations and controls identified are necessary to insure the bases of the boundary inventory release. The following is the first operational safety limit (OSL) required to reduce the potential for a GAC canister fire that could be caused by an external source:

The analysis disclosed this activity would be classified as a low hazard operation provided that fuel sources (other than the fork truck or similar equipment having small quantities of fuel) are maintained a minimum of 15 m (50 ft) away from the GAC canisters. The electric generator must also be maintained a minimum of 8 m (25 ft) away from the GAC canisters. A maximum of twelve fully saturated canisters will be allowed per storage location at the work site.

The analysis indicates that the primary cause of a CCl_4 release is high temperatures intense enough to regenerate the carbon, thereby stripping the CCl_4 . Removing the fuel sources that could support a fire intense enough to strip the CCl_4 eliminates the only credible postulated mechanisms for a release that would result in consequences to the uninvolved individual and the public exceeding the threshold limit values (TLV) for a low hazard operation.

The analysis also disclosed that concentrations of CCl_4 at 100 m (330 ft) from the work site could exceed the time weighted average (TWA) limit and the concentrations of hydrogen chloride (HCl) could exceed the ceiling limit. Two OSLs have been established indicating the requirements needed to mitigate the potential consequences to the uninvolved worker. The following are the mitigating requirements based upon system design features:

- Placement of a CCl_4 detector downstream of the final GAC canister (stack monitor) that is set to alarm (production units are interlocked with the logic system to shut down the blower) if concentrations of CCl_4 exceed 25 p/M if the system is operating in automated mode.

- Flow rate meters, located upstream of the primary GAC canister and downstream of the final GAC canister, will be in place and interlocked with the logic system to shut down the blower if there is a flow rate variance greater than 10%. Reliability of the system (flow rate meters and logic system) must ensure instruments fail safely to assure shutdown of the blower.
- A minimum of two GAC canisters in place (two in series) to adsorb any CCl_4 if breakthrough of the first GAC canister occurs when operating in automated mode.

The following are the mitigating requirements based upon administrative controls:

- The sampling frequency (by operations personnel) at the 216-Z-1A and Z-1B well fields will be required once a day during the day shift to assure concentrations of CCl_4 at the point of discharge do not exceed 25 p/M. The sampling frequency is based upon a maximum concentration of 2,500 p/M CCl_4 . The sampling frequencies at the Z-9 well field will be required based on measured concentrations at the CT-1 sample port. The assumed maximum flow rate in the analysis is 480 cfm. The maximum time required for breakthrough of CCl_4 through the GAC is also considered in the analysis. There shall be a minimum of three GAC canisters in place (in the production units) at all times when operating in manual mode.
- Verification of the hose configuration for the GACs and piping is required by the responsible operating organization before startup.
- Monitoring of flow rate meters will be required by operations personnel as prescribed in the work procedures if interlocks are not operable to detect a flow rate variance of greater than 10% (exceeding 10% variance for more than one minute will require shutdown of the VES). If flow rate meters and interlocks are not operable, constant monitoring (with instruments for detection of CCl_4 vapors) is required around the portion of the VES under positive air pressure. Detection of CCl_4 vapors that achieve ≥ 2 p/M will require shutdown of the VES.
- Constant monitoring (with instruments for detection of CCl_4 vapors) is required around the portion of the characterization unit under positive air pressure during operation. Detection of CCl_4 vapors that achieve ≥ 2 p/M will require shutdown of the VES.
- Personnel training shall be verified for personnel responsible for operating, sampling, and shutting down the VES before initial startup.
- The GAC canister inlet CCl_4 concentrations will be determined based on sampling at two hour intervals. The results of a second consecutive sample shall be $\leq 1,000$ p/M. The variance between the inlet and outlet air stream temperature shall not exceed $> 11^\circ C$ ($20^\circ F$).

Three OSLs and eighteen prudent actions are provided in Section 4.0.

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The following recommended prudent actions are provided to minimize the probability of occurrence or the consequences of a release of CCl_4 to the receptor groups of concern: the occupational workers, the uninvolved personnel, the public, and the environment.

- Monitor ambient air and workers' breathing zone for detection of CCl_4 vapors in areas where workers will be required to perform their work activities. Concentrations detected that exceed the TWA limits should require personnel (1) to be removed from the work area; or (2) to wear the appropriate protective gear as required by the Job Safety Analysis (JSA) or Hazardous Work Operations Permit (HWOP).
- Although radioactive particulate is not expected to be removed during the remediation activities, in-line monitoring should be provided. In the event continuous air monitor (CAM) alarms indicate possible radioactive contamination, the process shall be shut down. Concurrence for restart will be required from the Health Physics supervisor. The characterization unit should be surveyed for any radioactive contamination before movement to another site. A record sampler should be used during operation of the characterization unit for confirmation of no airborne radioactivity.
- Radon (^{222}Rn) gas monitoring equipment should be used to indicate the total quantities of ^{222}Rn and daughters adsorbed by the GACs during the VES operation. The quantities of ^{222}Rn measured will determine if the GAC canisters can be released from radiological controls. The ^{222}Rn gas concentrations of the stack effluent should be monitored.
- A routine survey program should be implemented to monitor the GAC canisters for potential gamma exposures that may result from ^{222}Rn buildup in the canisters. If exposure rate exceeds 2mR/h outside the canisters, the area should be posted in accordance with the requirements in WHC-CM-4-10, *Radiation Protection Manual*.
- The sites identified for remediation or site characterization work should be cleared of vegetation and combustibles not necessary to the activity.
- The electric generator should be located a minimum of 8 m (25 ft) from the propane storage tank as prescribed by fire codes.
- Replacement of existing in-line heaters should be with heater units that have a maximum air stream temperature capacity that does not exceed 400° F (205° C).
- Whenever saturated GAC canisters are removed from the process, covers will be placed over the inlet and outlet ports of the canister and verified to be secure.
- The VES components required for providing confinement of CCl_4 monitoring should be identified as safety class 3 components in a safety equipment list.

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- The fire department shall be notified of the potential hazards involving CCl_4 in a fire and the potential for production of phosgene or HCl .
- Employees (drivers) responsible for handling the saturated canisters must have completed hazardous material training.
- Maintain a 15 m (50 ft) exclusion zone around the VES operations to prevent inadvertent access by uninvolved individuals at the work site.
- The site workers should not come into close proximity to the heaters during periods of operation. The maximum air stream temperatures of 400°F (205°C) is required to be maintained. The temperatures within 2.54 cm (1 in.) of the heater cal rod may exceed the 400°F (205°C) resulting in some production of phosgene. The site workers should be made aware of potential hazards associated with the operation of the heaters during VES operations. Heater will be shut down when the blower is not running or the individual hose line is not in use.
- An emergency response kit should be available at the work site for containment of any spills. Notification to the hazardous material response team at 911 (811 if using a cellular phone) should be made in the event of a spill.
- During the GMSS test no more than one drum containing up to a maximum of 115 L (30 gal) of liquid CCl_4 should be located at the work site. The loaded drum shall be removed from the work site before continuing the GMSS test.
- Emergency notification responsibilities and response actions should be addressed in the emergency plans for the work sites where CCl_4 remedial activities are planned and in the emergency plans for the adjacent affected facilities or activities.
- Characterization analysis for ketones or other easily oxidized materials should be conducted. Detection of concentrations that exceed 100 p/M should require additional characterization before use of the affected well for vapor extraction operations.

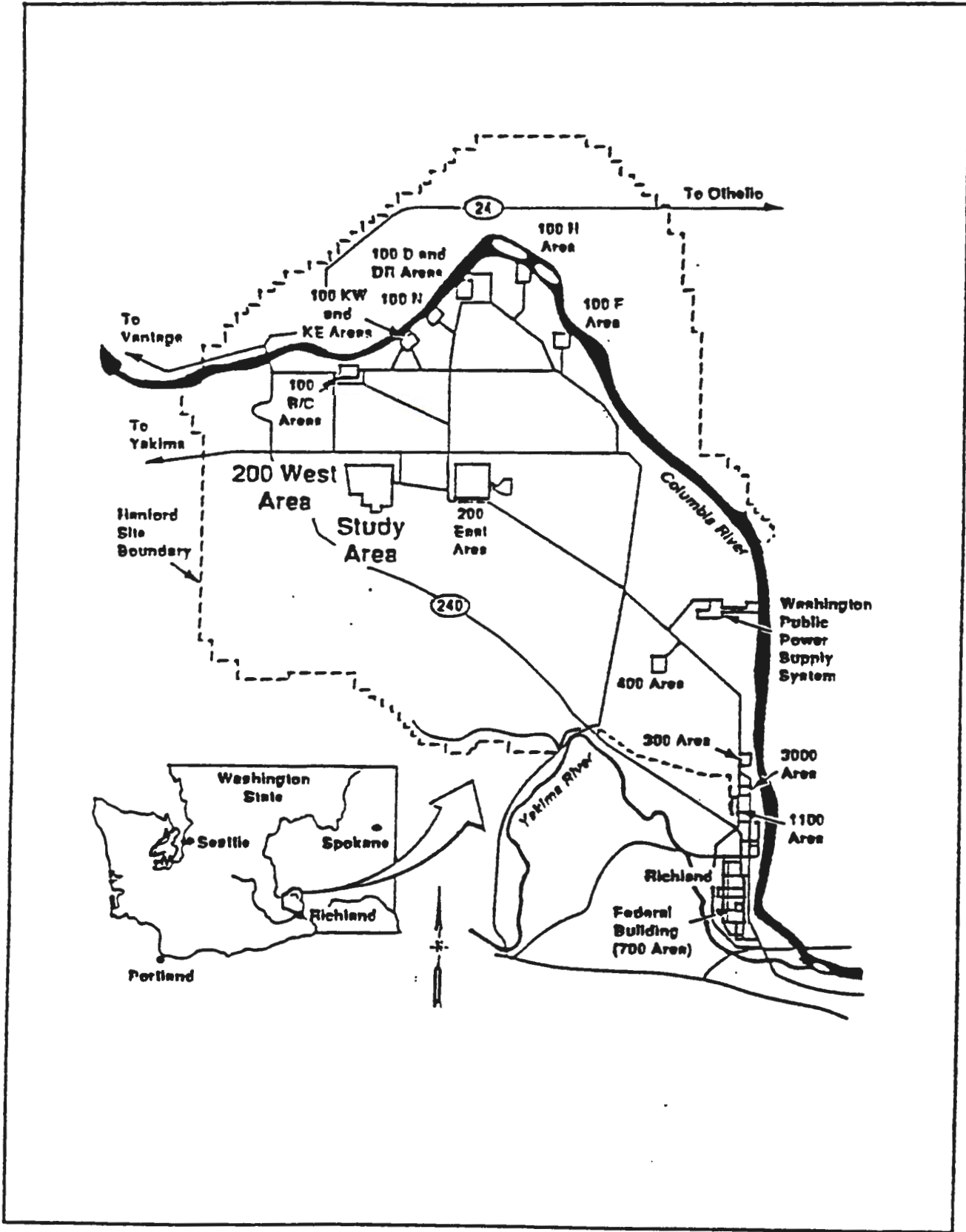
2.0 WORK DESCRIPTION

2.1 LOCATION AND DESCRIPTION OF DISPOSAL SITES

This section provides descriptions of disposal sites that were the principle contributors of the inventory of contamination to the soil and groundwater (DOE-RL 1991). Figures 1 and 2 provide a basic site orientation. Figure 3 provides the location of the three PFP waste discharge sites.

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WHC-SD-EN-SAD-004, Rev. 1-B
Figure 1. Map of the Hanford Site.



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Figure 2. Site Map of the 200 West Area.

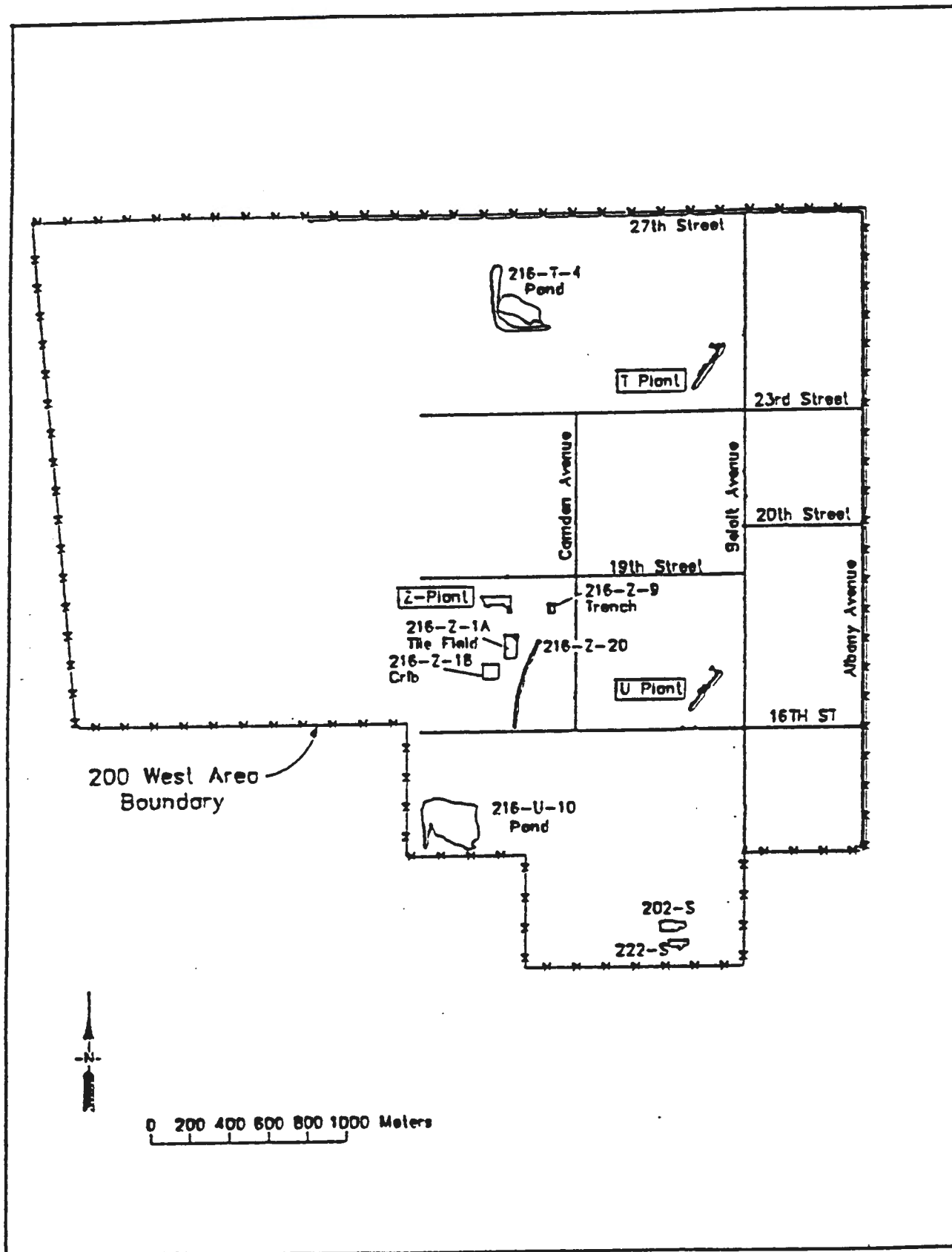
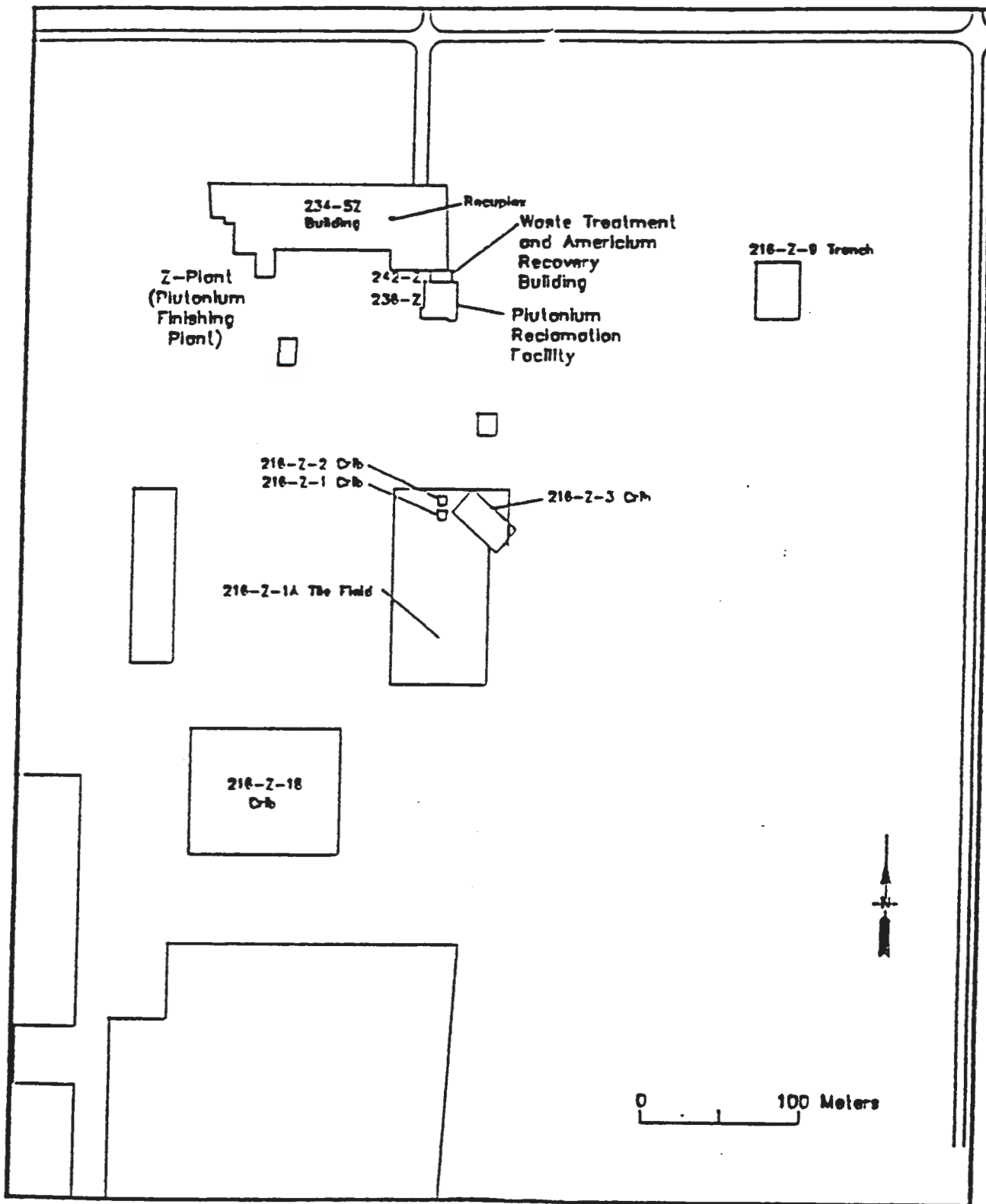


Figure 3. Site Map of Carbon Tetrachloride Disposal Sites in the Vicinity of Z Plant.



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Past waste disposal practices included the discharge of actinide-bearing liquid waste, generated from plutonium purifying processes, directly to the ground via structures called cribs. The PFP disposed of liquid CCl_4 -bearing organic solvents and associated high salt, acidic aqueous wastes primarily to three waste sites from 1955 to 1973 (when solvent discharge to soil was stopped): the 216-Z-9 Trench, the 216-Z-1A Tile Field, and the 216-Z-18 Crib.

2.1.1 216-Z-9 Trench

The 216-Z-9 Trench operated from 1955 to 1962 to receive all PFP Recuplex facility solvent and aqueous wastes discharged to the soil. The 216-Z-9 Trench is an enclosed earthen trench, located about 215 m (705 ft) east of the PFP. The trench excavation base is 18 m (60 ft) by 9 m (30 ft) and 6 m (20 ft) deep. The surface is a 36.5 m (120 ft) by 27 m (90 ft) by 0.23 m (0.75 ft) thick concrete trench cover at ground level. Six 7 m (23 ft) tall concrete columns support the cover. Waste was transferred by gravity through one of two 4-cm (1.5-in.) stainless steel pipes that entered the trench about 5 m (16 ft) above its bottom.

2.1.2 216-Z-1A Tile Field

The 216-Z-1A Tile Field operated from 1949 to 1959 to receive overflow liquid waste from three adjacent cribs. The waste stream consisted of neutral to basic (pH 7 to 10) process waste and analytical and development laboratory waste from PFP via the 241-Z-361 Settling Tank. Use of these four disposal facilities stopped in 1959. The 216-Z-1A Tile Field was reactivated in 1964 to receive aqueous and organic waste directly from the Plutonium Reclamation Facility (PRF).

Between 1964 to 1969, the tile field was divided into three working sections (Z-1AA, Z-1AB, and Z-1AC) to prevent waste buildup at the northern end of the field. No other facility received PRF wastes from 1964 to 1969 except on two brief occasions during tile field effluent piping upgrades. During this time the PRF wastes were discharged to the 216-Z-1 and 216-Z-2 cribs, located immediately north of the tile field. The 216-Z-1A Tile Field is a drain field located about 150 m (490 ft) south of the PFP and about 300 m (983 ft) west of Camden Avenue. The tile field has surface dimensions of about 60 m (195 ft) by 110 m (360 ft). The 6 m (20 ft) deep sloping sidewalls resulted in a facility floor dimension of about 35 m (115 ft) by 85 m (280 ft). The excavation floor is covered by a 1 m (3 ft) thick cobble layer with a minimum north-to-south surface slope of 1%. A 20 cm (8 in.) diameter pipe herringbone pattern, comprised of a 80 m (260 ft) long, north-south central distributor pipe and seven 20 m (65 ft) long lateral pairs are on this cobble layer. The 30 m (100 ft) by 80 m (260 ft) rectangular area covered by the piping system is overlain with 15 cm (6 in.) of cobbles and 1.5 m (5 ft) of sand and gravel. A 0.05 cm (0.02 in.) thick polyethylene sheet covered by 30 cm (12 in.) of sand and gravel was added to the facility. The 216-Z-1A Tile Field effluent piping is vitrified clay pipe. The central distributor pipe is a continuous line without perforations and with laterals divided into 0.3-m (1-ft) long segments. A 5-cm (2-in.) diameter stainless steel pipe was added inside the central distributor clay pipe when the field was modified into three operational sections. The tile field was not backfilled; the surface remains about 2.5 m (8 ft) below grade.

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2.1.3 216-Z-18 Crib

The 216-Z-18 Crib operated from 1969 to 1973 to receive PRF aqueous and organic wastes as a replacement for the 216-Z-1A Tile Field. It is a drain field type crib located southwest of 216-Z-1A and about 300 m (1,000 ft) south of the PFP. It consists of five parallel north-south oriented trench excavations. Each is 65 m (215 ft) by 3 m (10 ft) and from 4.5 m (15 ft) to 5.5 m (18 ft) deep. A 90-m (295-ft) long, 7.5-cm (3-in.) steel pipe runs east and west bisecting the length of each trench. Two 30-m (100-ft) long and perforated, fiberglass-reinforced 7.5-cm (3-in.) epoxy pipes exit each side of the steel pipe in each trench (two lines north and two lines south). These distribution lines are 0.3 m (1 ft) above the crib bottom in a 0.6 m (2 ft) thick bed of 4 cm (1.5 in.) to 7.5 cm (3 in.) gravel. The gravel cover is a membrane barrier overlain by about 15 cm (6 in.) of sand. The trenches are backfilled to grade and the western most of the five trenches were never used.

2.2 WASTE INVENTORIES

The following volumes and quantity estimates of various liquids and contaminants discharged to the three principal CCl₄ disposal facilities were derived from research provided in DOE-RL 1991. A total of 363,000 to 580,000 L of CCl₄ is estimated to have been discharged to the soil column between 1955 and 1973 as identified in Table 1.

Table 1. Contaminant Inventory in Carbon Tetrachloride Liquid Waste Disposal Sites.

Contaminant	216-Z-9	216-Z-1A ^a	216-Z-18
Carbon tetrachloride (L)	85,000 to 300,000	170,000	110,000
Plutonium (kg)	10 ^{6b}	57	23
Americium (kg)	2.5	1	0.4
Total liquid (L)	4.09 x 10 ⁶	5.2 x 10 ⁶	3.86 x 10 ⁶
Period of use	1955 to 1962	1964 to 1969	1969 to 1973

NOTES:

^aFrom 1949 to 1959, the 216-Z-1A Tile Field received about 1 x 10⁶ L of slightly basic, aqueous waste via overflow from associated 216-Z-1, 216-Z-2, and 216-Z-3 cribs. From 1964 to 1969, PRF wastes were discharged directly to 216-Z-1A.

^bA total of 58 kg were later removed.

2.3 SITE CHARACTERISTICS

This section summarizes the information about the site characteristics specific to the 200 West Area CCl₄ disposal sites, which are the major focus of this assessment (DOE-RL 1991).

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2.3.1 Topography

The topography of the Hanford Site is relatively flat although elevations range from greater than 1,000 m (3,300 ft) above mean sea level (msl) at Rattlesnake Mountain to 122 m (400 ft) above msl along the Columbia River. The 200 West Area, located on a broad, flat plateau, has elevations ranging from 200 m (665 ft) to 225 m (735 ft) above msl.

2.3.2 Meteorology

The climate of the Hanford Site is a midlatitude semiarid or midlatitude desert. The summers are warm and dry with abundant sunshine and winters are cool with occasional precipitation.

The mean surface air temperature at the Hanford Meteorology Station (HMS) [located about 0.4 km (0.3 mi) east of the 200 West Area] averages about 54° F (12° C). Temperatures average 75° F (24° C) in July and 30° F (-1° C) in January. Mean average precipitation at the HMS averages 16 cm (6 in.). The average Hanford Site atmospheric pressure is 742 mm Hg (14.4 lb). The barometric pressure is higher in the winter than in the summer, although both the highest and lowest recorded pressures occurred during winter.

Prevailing near-surface wind around the HMS is primarily from the west with an average wind speed of 4.8 km/h (3.0 mi/h). June has the highest average monthly wind speed of 3.6 mi/h (5.8 km/h), and the prevailing wind direction is from the west-northwest. In November and December, average wind speeds fall to about 3.8 km/h (2.4 mi/h) and the prevailing wind direction is from the northwest. Figure 4 shows the wind roses for the Hanford Site.

2.3.3 Surface Water Hydrology

The primary surface-water features of the Hanford Site are the Columbia and Yakima rivers. Existing surface water features within the 200 West Area are the 216-Z-21 seepage basin and the 200 West Area powerhouse ponds.

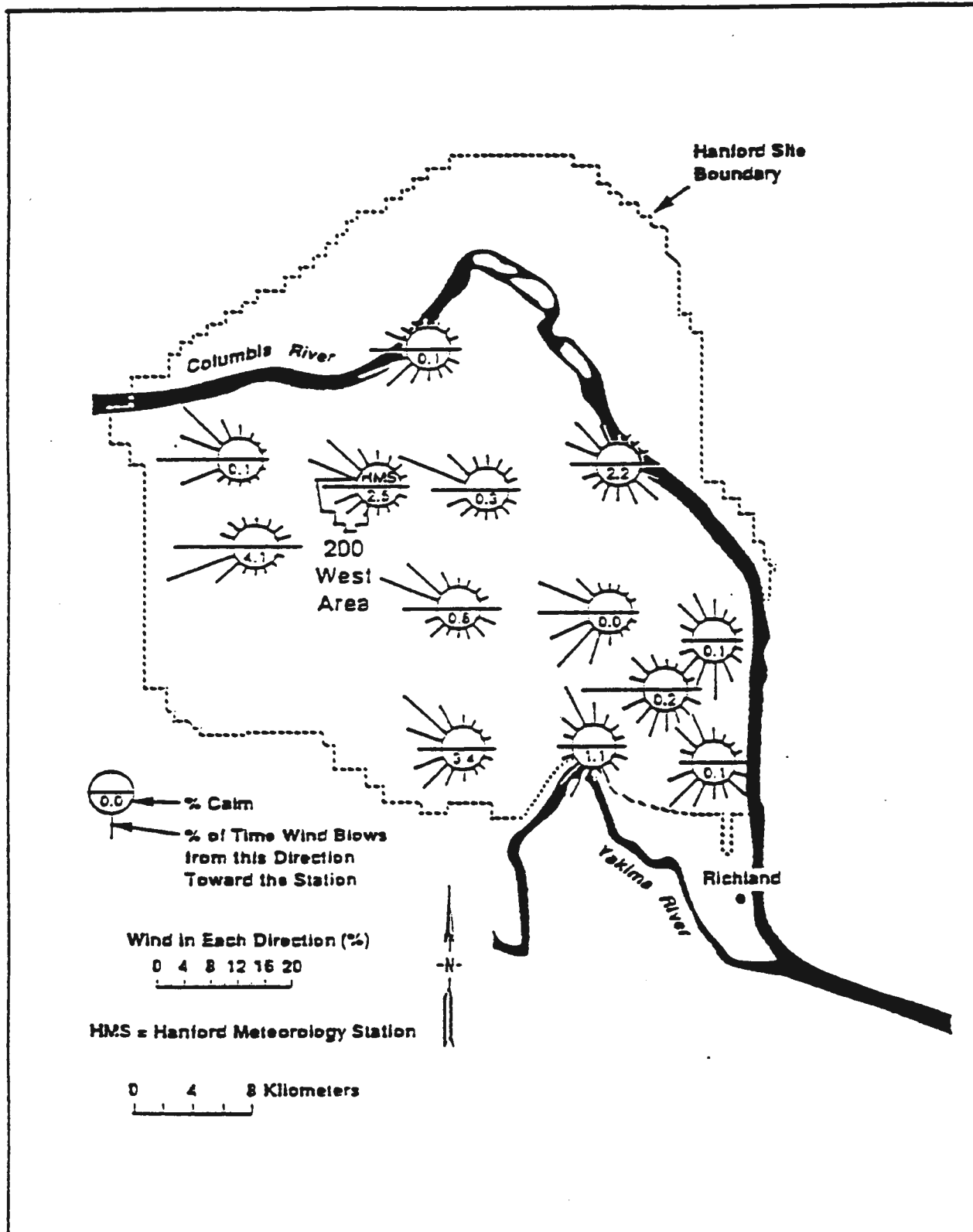
2.3.4 Geology

The geology of the 200 West Area consists primarily of basalts overlain by fluvial and glaciofluvial sediments. The following are sediments, from the oldest to the youngest:

- Ringold Formation - a series of alluvial sands and gravels, and overbank and lacustrine deposits of late Miocene to Pliocene age
- Plio-Pleistocene unit - basaltic detritus and a carbonate-rich paleosol, often referred to as the caliche layer
- Early Palouse soil - eolian silt and fine-grained sand
- Hanford Formation - glaciofluvial gravels, sands, and silts deposited by middle to late Pleistocene cataclysmic flood waters.

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Figure 4. Wind Roses for the Hanford Site.



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The hydrostratigraphic column presented in Figure 5 indicates the thickness of these units for the area underlying the CCl_4 disposal sites.

Local structural features in the vicinity of the 200 West Area include the Cold Creek syncline and the Gable Butte to Gable Mountain extension of the Umatanum Ridge anticline. The 200 West Area is located on the northern flank of the Cold Creek syncline that dips at about 5 degrees to the south. No faults have been identified beneath the 200 West Area.

The uppermost aquifer in the 200 West Area is unconfined and located within the Ringold Formation. The depth to the water table ranges from 58 m (190 ft) to 82 m (270 ft). Beneath the CCl_4 disposal sites, the depth to groundwater ranges from 60 m (197 ft) to 66 m (217 ft). The saturated thickness of the uppermost aquifer ranges from 67 m (220 ft) to 113 m (370 ft). Groundwater velocities are estimated to range from <0.1 m (<0.3 ft) to 47 m (154 ft) down. Groundwater flow directions are generally radial outward from the southwest portion of the 200 West Area primarily because of the continuing influence of the residual groundwater mound underlying the decommissioned 216-U Pond. Recharge to the aquifer is primarily artificial recharge from waste disposal activities. The groundwater in the 200 West Area is only used for monitoring. The emergency and process water come from the Columbia River.

The vadose zone consists of sediments from the Ringold Formation, Plio-Pleistocene unit, early Palouse soil, and Hanford formation. The vadose zone ranges in thickness from 58 m (190 ft) to 82 m (270 ft). Within the vadose zone, the Plio-Pleistocene unit (caliche layer) is less permeable than the other units that may result in slower travel times through this unit or perched groundwater or vapor. The vapor extraction tests indicate that the air permeability of the Hanford Site Formation is 2×10^{-8} to 5.6×10^{-8} cm^2 .

2.3.5 Demography

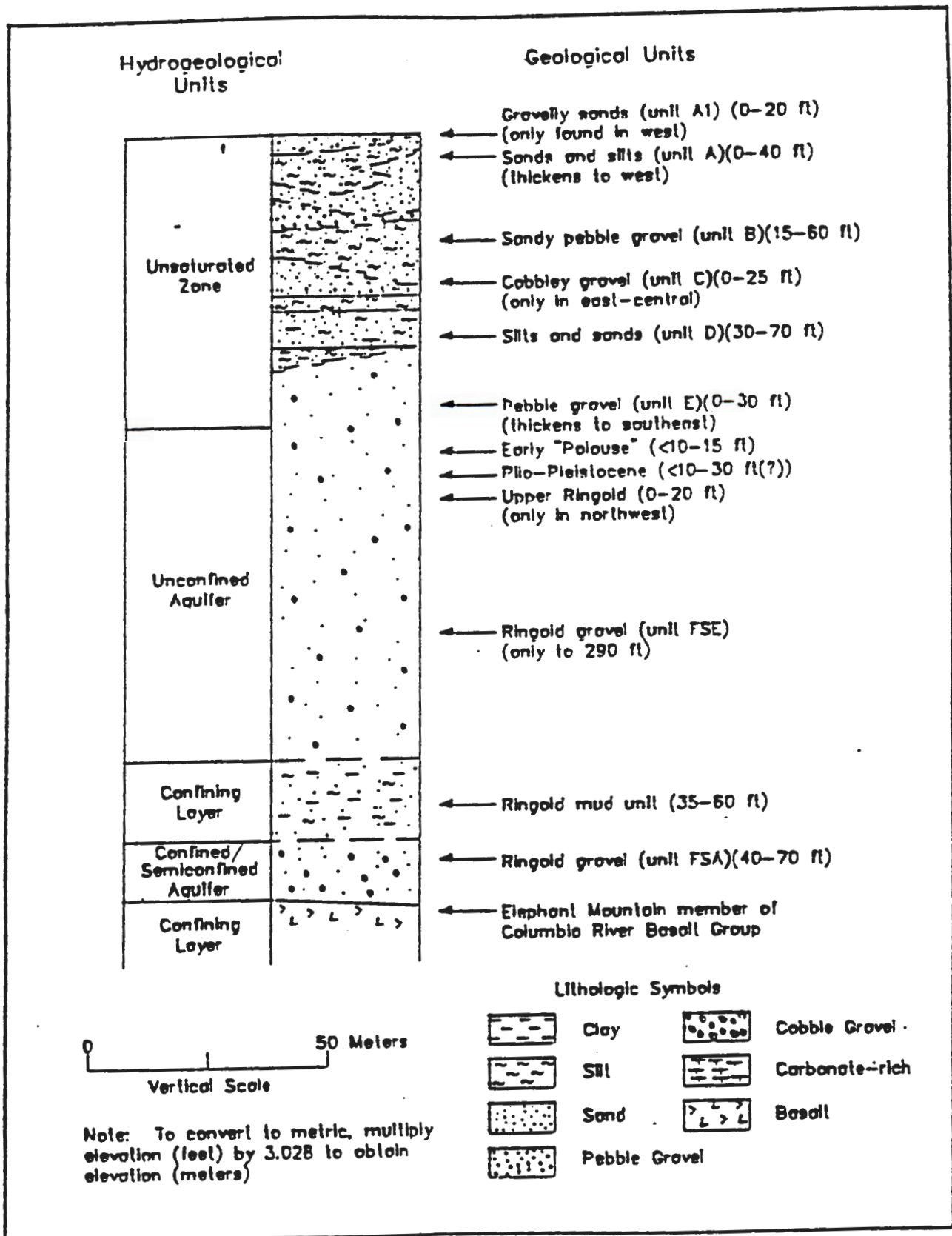
The HMS is used as the population reference point for the PFP area because of the availability of data and its proximity. About 36 people live within a 16 km (10 mi) west-southwest radius of the HMS. There are no residents within the Hanford Site boundary. Within this boundary only DOE, contractor personnel, or other authorized persons travel in areas beyond the Wye and Yakima Barricades. The closest resident to the 216-Z-9 Trench, 216-Z-1A Tile Field, and the 216-Z-18 Crib areas is 12.5 km (7.7 mi) due west at a Cold Creek ranch near State Highway 24 to Yakima. The nearest uninvolved workers are at the PFP and the patrol headquarters that are located 100 m (330 ft) from the 216-Z-9 Trench and 150 m (492 ft) from the 216-Z-18 Crib and 216-Z-1A Tile Field.

2.4 ACTIVITY DESCRIPTION AND PURPOSE

The purpose and objective of this activity is to further mitigate CCl_4 soil and groundwater contamination in the 200 West Area. The VES process will remove CCl_4 and other volatile organic soil gases from the contaminated vadose zone soil.

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Figure 5. Generalized Hydrostratigraphic Column for the 200 West Area.



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The VES process will use existing or new wells for removal of CCl_4 . The existing wells were used to collect vapor and sediment samples to define the CCl_4 plume and radionuclide configurations beneath the cribs. Some of the wells that may be used for remediation work (near the crib sites where CCl_4 vapors were detected in 1991) are shown in Figure 6. Other wells where remediation activities may occur (CCl_4 vapors detected at these sites from 1987 to 1991) in the 200 West Area are shown in Figure 7. The configuration of a typical well that will be used for extraction operations is shown in Figure 8. New wells may be drilled (as part of the remediation activities) if site characterization identifies additional CCl_4 plume areas that cannot be extracted using existing wells.

The process extracts soil gas by vacuum pumping. The processing system of the VES provides a negative pressure to the well, drawing the surrounding soil vapors out of the soil. Because CCl_4 is volatile, the negative pressure and air flow in the zone of influence of an extraction well converts any liquid CCl_4 into the vapor phase. Thus, any liquid CCl_4 mixed with artificial radioactive contaminants will separate from the artificial radioactive contaminants and release through the wells as a vapor (Attachment A).

The processing equipment of the VES is mounted on trailers to provide mobility and versatility. The trailers are connected together by electrical lines, instrumentation lines, and hoses. The VES characterization unit will be used for sampling the concentrations of CCl_4 found in the vadose zone soils.

2.4.1 Power Requirements

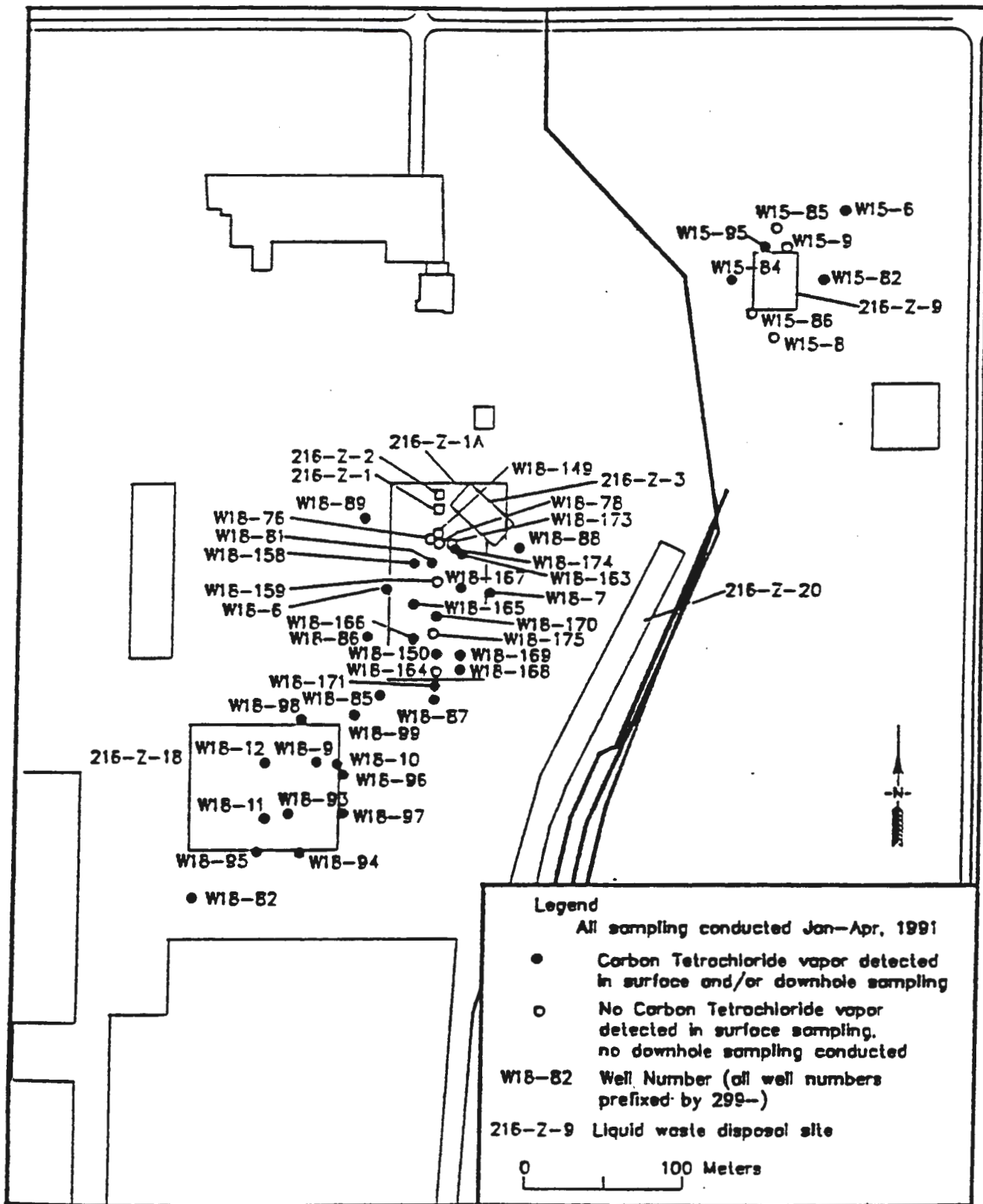
Several generators provided power for the VES during the test phase. Electrical pole power will power the VES process system. A 3,800 L (1,000 gal) propane tank will fuel a trailer mounted electric generator. The primary use of the generator will be for supplying power to the VES characterization unit (used primarily for site sampling activities) in remote locations where electrical pole power may not be available.

2.4.2 Vapor Extraction and Filter System

An overview of the VES design is discussed in this section. A more detailed description is provided in the project supporting document (Green 1991). The VES smaller production unit design will have the same form and function as the full-scale remediation unit with two major differences. The smaller production unit will have a minimum of two GAC canisters in series for removal of the CCl_4 vapors, as opposed to a minimum of six GAC canisters that will be used in the full-scale remediation unit for removal and treatment of CCl_4 vapors. The smaller production unit will operate at a maximum of 1,000 cfm while the full-scale remediation system will operate up to 1,500 cfm.

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Figure 6. Wells Located Near the Crib Sites Where Carbon Tetrachloride Vapors Have Been Found that May be Used for Remediation Work.



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Figure 8. Typical Extraction Well.

WELL CONSTRUCTION AND COMPLETION SUMMARY			
Drilling Method: <u>Cable Tool</u>	Sample Method: <u>D-Log Method</u>	WELL NUMBER: <u>200-418-17</u>	TEMPORARY WELL NO: _____
Drilling Fluid Used: <u>None</u>	Drilling Additives: <u>Not Documented</u>	Coordinates: <u>N/S 1 30 D10</u>	E/V <u>1 74 60</u>
Driller's Name: <u>Boyer</u>	MA State: _____	State: _____	Coordinates: <u>N 44 195 E 2 212.67</u>
Drilling Company: <u>Not Documented</u>	Company Location: <u>NY</u>	Start: _____	Card #: <u>Not Documented</u>
Date Started: <u>26 Jul 77</u>	Date Complete: <u>09 Aug 77</u>	Elevation Ground surface (ft): <u>675.2 ft estimator</u>	
Depth to water: <u>Not applicable</u>			
GENERALIZED Driller's STRATIGRAPHY Log			
0-25: <u>Med-very coarse SAND, PEBBLES (fill)</u> 25-27.5: <u>Med-coarse SAND</u> 27.5-37.5: <u>Med SAND</u> 37.5-43: <u>Coarse-very coarse SAND, w/PEBBLES & COBBLES</u> 43-47: <u>Fine-very coarse SAND, w/PEBBLES & COBBLES</u> 47-48: <u>Fine-very coarse SAND & GRAVEL</u> 48-49: <u>Med SAND</u> 49-51: <u>Fine-very coarse SAND & GRAVEL</u> 51-53: <u>Med SAND</u> 53-58: <u>Very fine-fine SAND</u> 58-62: <u>Fine-med-coarse SAND</u> 62-65: <u>Med SAND (Dry)</u> 65-67: <u>Very fine-fine SAND</u> 67-69: <u>Silty very fine SAND</u> 69-72.5: <u>Fine-med SAND</u> 72.5-75: <u>Fine-coarse-very coarse SAND</u> 75-87: <u>Very fine-med SAND</u> 87-88: <u>Silty-very fine-fine-med SAND</u> 88-91: <u>Med SAND</u> 91-93: <u>Med-coarse SAND</u> 93-95: <u>Fine-coarse SAND</u> 95-98: <u>Very fine-coarse SAND</u> 98-99: <u>Fine-coarse SAND w/SILT stringers, few PEBBLES, COBBLES</u> 99-102: <u>Med-very coarse SAND, w/PEBBLES, COBBLES</u> 102-103.5: <u>Fine-very coarse SAND, PEBBLES</u> 103.5-105: <u>Coarse-very coarse SAND & pea GRAVEL, few COBBLES</u> 105-107: <u>Very fine-very coarse SAND w/PEBBLES & COBBLES</u> 107-119: <u>Med-very coarse SAND, PEBBLES & COBBLES</u> 119-121: <u>Coarse-very coarse SAND, PEBBLES S/G</u> 121-125: <u>Fine-med-very coarse SAND, pea GRAVEL</u> 125-125.5: <u>Very fine-med SAND, few PEBBLES</u> 125.5-127: <u>Very fine SAND-SILT</u> 127-132: <u>SILT</u> 132-136: <u>SILT, some CaCO₃</u>	Elevation of reference point: <u>(top of casing) (577.85 ft)</u> Height of reference point above ground surface: <u>(2.5 ft)</u> Depth of surface seal: <u>(None)</u> Type of surface seal: <u>Cement grout</u> I.D. of surface casing (if present): <u>(None)</u> I.D. of riser pipe: <u>(8-in)</u> Type of riser pipe: <u>Carbon steel</u> Diameter of borehole: <u>(8-in approx)</u> Type of filler: <u>Not Documented</u> Depth to bottom, Jan 91: <u>122.2 ft (131.2 ft TOC)</u> Cement plug in bottom, not well documented Depth bottom of casing: _____ Depth bottom of borehole: <u>(136 ft)</u>		
DRILLER'S NOTES:			
Contamination encountered:			
87 ft = 20,000 cpm			
87.5 ft = 20,000 cpm			
Drawing By: <u>REL/2018-171,ASS</u> Date: <u>10 Feb 01</u>			
Reference: _____			

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The high efficiency particulate air (HEPA) trailer will filter the soil gas vapor stream before the vapor is collected in the GAC canisters (see Figure 9).

The maximum operating vacuum will not exceed 25 cm (10 in.) of mercury (254 mm Hg).

The following are system components:

- Perforated wells that may be extraction and observation intervals
- Extraction hoses heated to prevent condensate freezeup
- High efficiency particulate air trailer
 - Four inlet manifold on the test unit and seven inlet manifold on the full-scale remediation unit
 - Sample capability for soil gas upstream and downstream of the HEPA filter in a protective cabinet
 - In-line instrumentation to measure and record well head pressures, air temperatures, differential pressures, vacuum, relative humidity, and flow rate
 - High efficiency particulate air filter housing containing a prefilter and two HEPA filters in series
 - There may be a noncontact electric heater installed before the prefilter to raise the vented gas temperature and reduce its relative humidity
 - Alpha and beta process CAMs located between the HEPA filters.

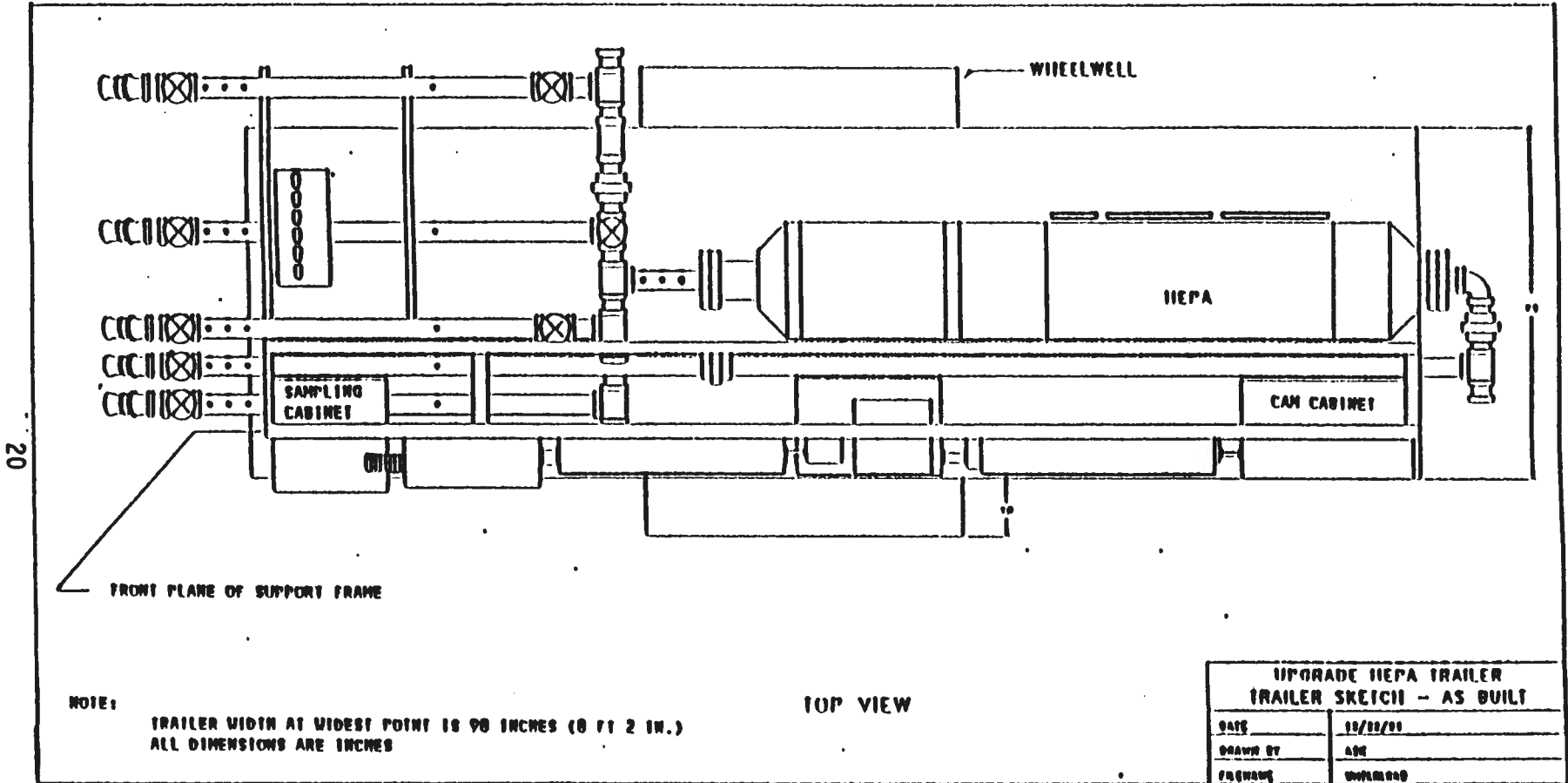
Instrumentation will connect to a Data Acquisition System (DAS). The DAS will control operations, alarms, and perform trend analysis.

2.4.3 Blower Trailer

The blower trailer shall provide the flow that extracts the soil vapor and pushes it through the GAC canisters. The purchase specifications for procurement of GAC canisters requires that these canisters are DOT approved units. A flow diagram with a description of the major parts associated with the blower trailer is identified in Figure 10.

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Figure 9. High Efficiency Particulate Air Filter Trailer.



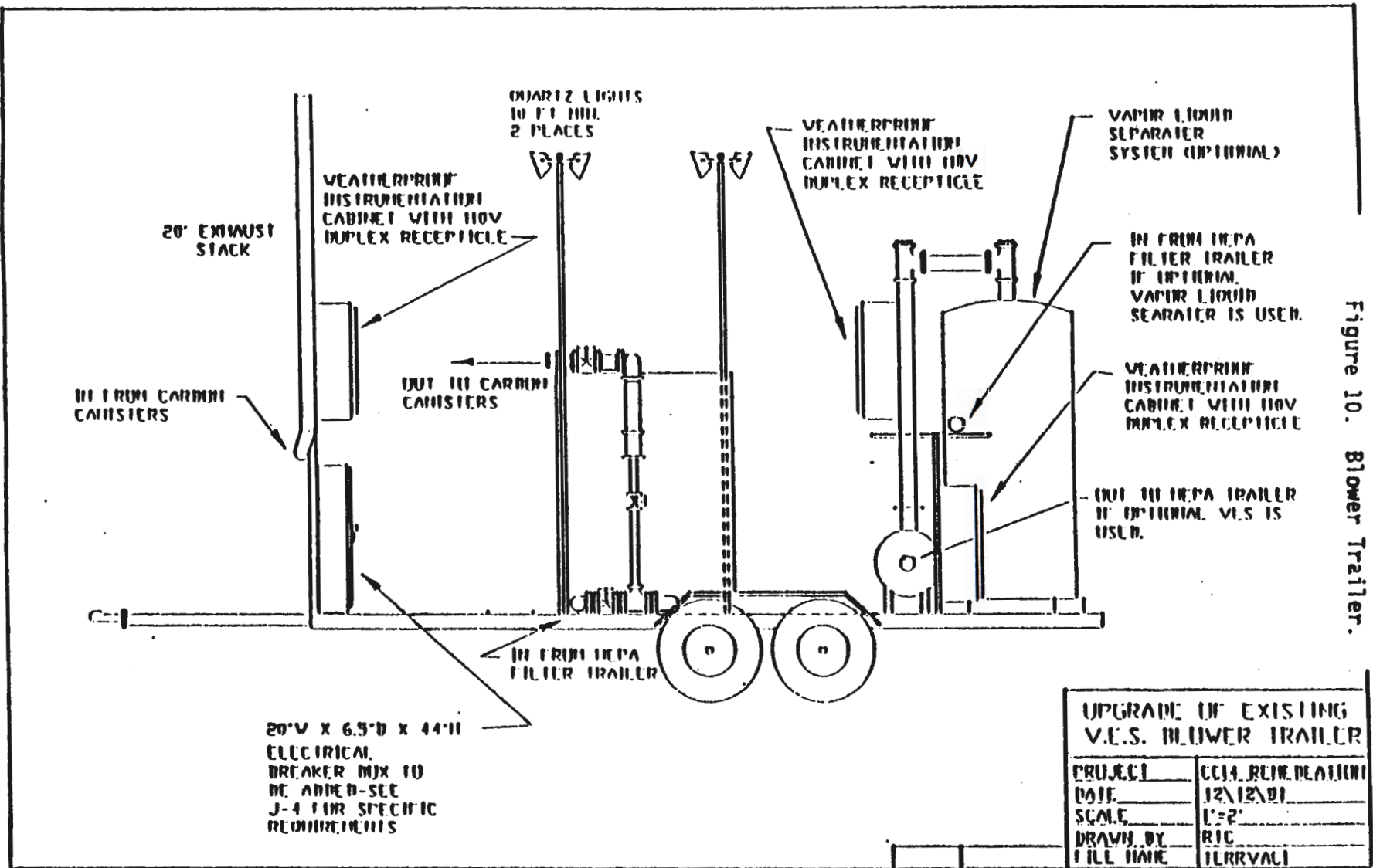


Figure 10. Blower Trailer.

The following are trailer components:

- A vacuum pump designed to produce a maximum of 750 cfm at 381 cm (150 in.) Wg. for the test unit
- Vacuum pumps designed to produce a maximum of 1,500 cfm at 381 cm (150 in.) Wg. for the full-scale remediation unit
- Outlet and return manifolds for flow to and from the GAC canisters
- One series of a minimum of two 450 kgs (1,000 lb) to a minimum of 900 kgs (2,000 lbs) GAC canisters for the test unit
- Three parallel GAC canister series with a minimum of two 900 kgs (2,000 lbs) GAC canisters in series. Specifications require DOT approved canisters
- In-line instrumentation to measure and record air temperature, pressure, vacuum, relative humidity, flow rates, ²²²Rn gas, and CCl₄ concentrations
- A sample cabinet
- A DAS that includes a computer, software for trend analysis, alarm logic, and control software
- A record sampler located at a 7 m (20 ft) tall exhaust stack.

2.4.4 Vapor Extraction System Characterization Unit

Sampling activities will be conducted using a VES characterization unit for removal of CCl₄ vapors and monitoring of the gas stream using field instruments. These field instruments will be used at the well sites identified for characterization work to establish the concentrations of CCl₄ found at each borehole. The data accumulated will assist in determining the most likely areas where full scale remediation activities for removal of CCl₄ will be required in the future.

The VES characterization unit will be operated, typically during the day shift, with a crew in attendance at all times. The duration period for sampling at each borehole will be about one hour. The portion of the VES characterization unit that is under positive pressure will be continuously monitored (using field instruments) during periods of operation.

The VES characterization unit design consists of a maximum 60 cfm system with the following components:

- Sample capability for soil gas upstream and downstream of the HEPA filter
- In-line instrumentation to measure vacuum, pressure, air, temperatures, differential pressures, relative humidity, and flow rates
- In-line HEPA filter

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- Vacuum pump designed to produce a maximum of 60 cfm at 25 cm (10 in.) Hg
- Two 900 kgs (2,000 lbs) GAC canisters for adsorbing CCl_4 vapors extracted during sampling activities.

A description of the specific components for the VES characterization unit is provided in Figure 11.

2.4.5 Gas Membrane Separation System

The GMSS test is designed to remove volatile organic compounds (VOC) from the vacuum extracted air stream and condense it to a liquid form. The air stream will be obtained by tapping into the VES. The system will require about 35 scfm. The four primary pieces of equipment for this system consist of a compressor, condenser, membrane modules, and vacuum pump. The system is a closed loop with a clean air stream being returned to the VES upstream of the GACs.

3.0 HAZARDS

3.1 BASES FOR HAZARDS CONSIDERED

An evaluation of the unmitigated intrinsic hazards associated with this project and the initiating events were assessed for their potential to create a source term release. This evaluation and inventory analysis identifies the potential accident events.

The results from the evaluations determined that process hazards involving a continuous release of CCl_4 , heated CCl_4 , GAC bed overheating, dropped canisters, vehicle accidents, and fires involving fuel sources are credible. Natural force events such as high winds/missiles, seismic events, range fires, and lightning also were considered to be credible. Process hazards involving regeneration of the carbon releasing CCl_4 were found to be incredible. Criticality was assessed and determined not to be credible as a result of the vacuum extraction operations. Natural force events involving a flood and tornado were considered to be of no significant impact or would not result in significant consequences, therefore not requiring further analyses. A basis for these conclusions is discussed in this section.

3.2 HAZARDS INVENTORY

This assessment addresses the hazards associated with removal and treatment of CCl_4 using the VES units. The dominant VES hazard inventory anticipated is CCl_4 .

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There are several other chemical contaminants found in the unsaturated zone around the three primary CCl_4 disposal sites. The contaminant distribution data comes from soil gas analysis, historical well log data, measurements of CCl_4 vapors in boreholes, soil analysis, and data collected during the VES test. The contaminant data is divided into two sections; the near field (includes the three primary CCl_4 disposal sites) and the far field (includes the 200 West Area).

The near field hazardous substances identified (before the VES test phase) were tributylphosphate, dibutyl butyl phosphorate, n-butyl alcohol [from possible hydrolysis of tributylphosphate and chloroform (a CCl_4 degradation product; DOE-RL 1991)]. The VOC substances, along with CCl_4 , will vaporize based on the vaporization pressures and temperatures.

The sample results from the test phase show that the VOC extracted were CCl_4 and 2-butanone with trace amounts of chloroform.

Far field soil samples identified other contaminants in the soils. The following are identified contaminants: acetone, benzene, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, ethyl benzene, fluoromethane, methylene chloride, methyl isobutyl ketone, tetrachloroethylene, toluene, 1,1,1-trichloroethane, trichloroethylene, p-xylene, m-xylene, and o-xylene. Samples of these contaminants from various wells indicate that the concentrations are very low. These compounds were analyzed for but not detected during the test phase.

The radionuclides discarded to the cribs are identified in Table 1. The high concentrations of radionuclides were found in sediments located immediately below the crib. The high concentration of actinides at this location is possibly due to the filtering and ion exchange by sediments of plutonium oxide particles that were originally present in the waste stream (Attachment A). The concentration of plutonium and americium in sediments generally decreases with depth beneath the bottom of the crib. An increase in plutonium and americium concentration at depth is generally associated with an increase in the silt content of sediments or with boundaries between sedimentary units. The bulk of the actinide contamination appears to be contained within the first 15 m (50 ft) of sediments beneath the bottom of a disposal site. The maximum vertical penetration of plutonium and americium contamination (defined by the 10^{-2} nCi/g isopleth that is approximately 30 m (100 ft) below the bottom of the 216-Z-1A crib [Price 1979]).

During the test phase ^{222}Rn gas was detected using spectral gamma energy logging. Readings at the outside walls of the GAC canisters showed that the GAC had collected ^{222}Rn and that the ^{222}Rn was decaying to form decay products bismuth-214 (^{214}Bi) and lead-214 (^{214}Pb), both of which have short half-lives. The test could not determine if the ^{222}Rn was from naturally occurring uranium or from uranium waste.

The test phase also indicated that the downstream GAC canister was found to emit higher gamma counts than the upstream canister [2,500 counts per minute (cpm) vs 3,800 cpm using a thin window pancake geiger monitor probe on contact with the canister], which implied that the downstream canister contained more ^{222}Rn . The ^{222}Rn that was initially captured by the first GAC column would have been gradually displaced by the CCl_4 vapors, which have a

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greater affinity for carbon adsorption than ²²²Rn. The displaced ²²²Rn would migrate from the upstream canister and be captured by the downstream canister.

Atmospheric dispersion for ²²²Rn emissions were calculated to determine if the ²²²Rn concentration in the effluent can reach or exceed the derived air concentration (DAC) guide limit (3.E-08 mCi/ml or 30 pCi/L) for controlling occupational intake through inhalation (DOE 1988a). The derived concentration guide dose limit for ²²²Rn emissions (3.E-9 mCi/ml) for members of the public was also considered for controlling intake through inhalation resulting from the VES operations (WHC-CM-7-5, *Environmental Compliance Manual*; DOE 1990). The calculations indicate it is unlikely that the emissions could be maintained at concentrations of 1 μCi/s without exceeding the DAC limit for the area surrounding the VES operations. Using the maximum operating flow rate of 1,500 cfm, the ²²²Rn concentration in the effluent can reach 1.4E-06 μCi/mL (1412 pCi/L) before exceeding 10% of the DAC limit. It is unlikely that soil gas ²²²Rn concentrations could reach the level necessary to maintain an emission rate of 1 μCi/s and would not exceed the threshold limits identified for low hazard category (Attachment B). An instantaneous release was also evaluated (Attachment B).

There could be gamma exposure problems if the ²²²Rn buildup in the GAC canisters were to reach an exposure of 2 mR/h on the outside of the GAC canisters. During the test phase, the maximum gamma exposure readings identified were < 2 mR/h. Prudent actions are discussed in Section 4.3, addressing an exposure survey program and controls required in the event the contact exposure rate exceeds 2 mR/h and if any contamination is found to have been caused by any ²²²Rn progeny contamination.

3.3 VAPORIZATION OF CONTAMINANTS

During the test phase, sample results indicated that there were only three chemical contaminants detected. The vapors extracted during testing consisted principally of CCl₄ and 2-butanone; however, 2-butanone may have resulted from laboratory contamination. Trace amounts of chloroform were also detected; the test assessment identified these contaminants as chemicals that were expected to be vaporized. Table 2 identifies the chemical contaminants expected to be vaporized and removed during the overall remediation phase.

Table 2. Chemical Contaminants Expected to be Vaporized During Remediation.

Chemical	Boiling Point	Vapor pressures at 68° (20° C)
Carbon tetrachloride	170°F (76.7°C)	1.7 lbs/in ² (90 mm Hg)
Chloroform	140°F (61°C)	3.0 lbs/in ² (160 mm Hg)
2-Butanone	175°F (79°C)	1.4 lbs/in ² (71 mm Hg)

During the test phase, no radionuclides (other than ²²²Rn) were detected during sampling of the GAC canisters, filters, or other portions of the system as expected (Attachments A and C).

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3.4 CREDIBLE SCENARIOS ANALYZED

The predominant events are those associated with activities that would cause the contaminants to become airborne. There were several scenarios postulated that could cause a release of contaminants to the environment during normal operations or as a result of an accident. The analysis of the hazard inventories and the potential release mechanisms indicated that a continuous release of CCl_4 caused by a system control or component failure would produce the maximum source term. All of the scenarios involve inventories of CCl_4 or HCl that could be released to the environment.

3.4.1 Process Hazards

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3.4.1.1 Continuous Release. This scenario illustrates the consequences associated with the recovery and release to the environment of CCl_4 (e.g., positive pressures blowing out CCl_4 around fittings, hole in a flex hose, saturation of carbon beds) during operations. This scenario encompasses any event that results in a continual release of CCl_4 as it is recovered (e.g., a control system or component failure) resulting in a source term to the receptor groups of concern. The source term identified for this scenario is 1.6 lb/min being released over a 24 hour period. This is the bounding accident condition for this assessment.

3.4.1.2 Heated Carbon Tetrachloride. In-line noncontact electric heaters will be used to reduce the humidity (condensation) in both the vacuum hoses and before entry into the HEPA filters. The noncontact electric heaters were evaluated for their potential to heat the CCl_4 , producing phosgene or regenerating the carbon releasing CCl_4 .

The heater design indicates that 275° F (135° C) is the maximum air stream temperature capacity of the heater units at 50 acfm. Hydrolysis (production of phosgene) of CCl_4 could begin to occur if temperatures exceed 400° F (205° C) in the air stream. The maximum temperature capacity of the heating units are not sufficient to produce phosgene. Additional discussion is provided in Section 3.7.

The maximum temperature capacity of the heaters may support some regeneration of the carbon (located downstream in canisters) resulting in some CCl_4 desorption. An event involving desorption of the CCl_4 resulting in unacceptable consequences was found to be incredible based on the analysis (Attachment D).

3.4.1.3 Granular Activated Carbon Bed Overheating. The GAC is used to adsorb CCl_4 as it is removed from the vadose zone soils. As a part of this process, heat from adsorption can buildup inside the GAC bed as a result of stripping the CCl_4 from the soil gas without sufficient air flow to remove the heat. Overheating the GAC bed may occur when more heat is produced than is being removed. Sufficient buildup of heat in the GAC bed can result in autoignition of the coconut-based GAC at 300°C (572°F). The CCl_4 hydrolyzes between 250°C (480°F) and 700°C (1292°F) resulting in production of phosgene or HCl . Another complicating factor would be process flow streams containing ketones or other organics. These constituents oxidize at relatively low temperatures and therefore can ignite the GAC. A scenario assuming autoignition of the GAC

and the potential consequences as a result of this type of an event is provided in Section 3.7.

3.4.1.4 Dropping Saturated Canisters During Changeout. There is a possibility for a spill of CCl_4 caused by dropping a fully loaded GAC canister during the process of changing out the canister. The CCl_4 inventory of 1,200 lbs (545 kgs) adsorbed on a 2,000 lb GAC unit is the maximum inventory; this is the highest possible saturation efficiency of the carbon. The carbon canister would be saturated with 1,200 lbs (545 kgs) of CCl_4 . The source term would be 660 lbs (300 kgs), which is the quantity that would be desorbed when exposing the contents to an unimpeded air flow of 70° F (22° C) at 1 atm. If this event were to occur, the consequences could result in concentrations of CCl_4 above the TWA limit but would still be far less than the immediately dangerous to life and health limit. The consequences of this scenario would be bounded by the scenario associated with a system control or component failure.

3.4.1.5 Vehicle Accident. An accident involving a vehicle fire (fork truck used to change out canisters) in the extraction area near the GAC canisters was evaluated to determine the probability of occurrence. The analysis determined that a vehicle fire is credible but that the sequence probability of involving the GAC canisters in the fire providing sufficient heat to support regeneration of the carbon was not credible (Attachment E).

3.4.1.6 Fire Involving Propane Fuel Source. A 3,785 L (1,000 gal) propane fuel tank will be located a minimum of 15 m (50 ft) from the GAC canisters to provide fuel to an electrical generator that will be used primarily for powering the VES test unit. The generator will be located a minimum of 8 m (25 ft) from the GAC canisters.

An analysis was developed based on the following scenarios: a fire caused by refueling the propane tank; a fire resulting from equipment damage to the propane tank; a fire involving a vehicle accident in close proximity to the propane tank; and a fire involving the generator.

Even though the analysis indicates that these initiating events are credible, the sources of fire in relationship to the generator and fuel storage area to the configuration of the canisters (accumulation in storage or location in the VES process) indicate that a significant release of CCl_4 because of a fire (heating up and regenerating the carbon releasing CCl_4) is considered to be incredible (Attachment E).

3.4.2 Natural Force Events

3.4.2.1 High Winds/Missiles. There is a remote possibility that high winds may cause airborne missiles (e.g., scrap wood, miscellaneous items around the sites) to be carried through the air, striking and penetrating a section of flex hose or a canister. The resulting release caused by a ruptured air hose would be bounded by the analysis addressing a continuous release. The release of any carbon particles are not likely to cause unacceptable consequences to the receptor groups of concern because 95% of these particles are not considered to be respirable.

3.4.2.2 Seismic Event. If a seismic event occurs, the worst case consequences would most likely result from a continuous release of CCl_4 if the system continued to operate. The analysis for a continuous release (Table 5) would bound the scenario (damage to the VES caused by a seismic event), releasing CCl_4 continuously. The VES is designed to extract CCl_4 vapors from soils (vadose zone) and is not required to operate to provide confinement. If the system is damaged and inoperable, the extraction of CCl_4 would not be possible. Any damage to the canisters may result in some desorption of CCl_4 if the contents are exposed to an unimpeded air flow. The consequences resulting from desorption of the CCl_4 would be bounded by the scenario addressing a system control or component failure.

3.4.2.3 Range Fires. Range fires were evaluated and determined to be credible. The probability associated with the fire affecting the canisters (duration of fire and sufficient heat to support regeneration of CCl_4) was found to be incredible (Attachment E).

3.4.2.4 Lightning. Thunderstorms have been observed at the HMS nearly every month of the year but are very rare during the winter months. Although severe thunderstorms are rare, the site is vulnerable to lightning strikes that occur typically in the months of July or August. If a lightning strike occurs at the work site and damages piping or a GAC canister, the worst case consequences would be bounded by the analysis addressing a continuous release.

3.5 EVENTS CONSIDERED INCREDIBLE

3.5.1 Process Systems or Materials

3.5.1.1 Regeneration of Carbon. The potential consequences of an accident involving regeneration of the carbon resulting in CCl_4 desorption was evaluated and found to be incredible. Accidental regeneration was based upon fresh air desorption (based upon experimental data and data from the carbon supplier) of the CCl_4 contained on the carbon. Desorption of CCl_4 resulting in consequences to the receptor groups of concern or the environment was found not to be credible (Attachment D).

3.5.1.2 Criticality. The criticality safety issues involving the VES process were evaluated before the VES test to ascertain whether some of the plutonium bearing waste solutions (discarded in the past to the three crib disposal sites) could possibly be vaporized and draw off plutonium with the gases.

The VES technique for extracting CCl_4 from the soil below the crib did not draw off any plutonium with the gases as expected during the test phase. The discussion provided in Attachments A and C indicate that removal of plutonium in the gases or redistribution of the material trapped in the soil would not occur. The criticality prevention specification was revised and approved by criticality engineering for allowing vapor vacuum extraction operations at the crib sites for the overall remediation activities (Attachment F).

3.5.2 Natural Forces Events

3.5.2.1 Flood. The Columbia River probable maximum flood elevations (the flood discharge that may be expected from the most severe combination of meteorologic and hydrologic conditions reasonably possible in the region) would be about 130 m (425 ft) at the 100-N Area (with respect to msl). This flood would not affect the central part of the site (the 200 East and West Areas plateau), where the cribs are located because this area has an elevation greater than 150 m (495 ft). Similarly, waters from the 100-year flood would have no effect on this area. A flood affecting this site having significant adverse effects is therefore considered incredible.

3.5.2.2 Tornado. A severe tornado of the Midwest type is highly unlikely under the Pacific Northwest climatologic and orographic conditions. There have been only two tornado funnel clouds and one small tornado (June 16, 1948) observed at the Hanford Site in the 34-year period between 1945 and 1978. Although one of these touched ground, it caused no damage. The nearest reported tornado damage was in Yakima (April 30, 1957), about 28 km (45 mi) to the west, and at Wallula Junction (June 26, 1958), about 31 km (50 mi) to the southwest; only minor damage was noted. The potential consequences in terms of airborne concentrations have been found below risk acceptance consequences (WHC-CM-4-46, *Nonreactor Facility Safety Analysis Manual*).

3.6 THRESHOLD VALUES

The inventory and resulting source terms were analyzed for CCl₄. The other VOCs that were extracted during the test phase (based upon the temperatures required to vaporize these contaminants) were 2-butanone and trace amounts of chloroform. Because these other contaminants are present in much lower quantities than of CCl₄ and the toxicity of both chloroform and 2-butanone are less than CCl₄, these contaminants are bounded by the CCl₄ analysis.

The toxicity limit values for the chemical contaminants identified in this section are provided in Table 3. These limits were derived from the guidelines using the concentration values reported in the *1990-1991 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices* (ACGIH 1990) and 29 CFR 1910.

Table 3. Toxicity Limit Values.

Inventory of contaminants	IDLH ^b		TWA ^b		STEL ^c	
	p/M	mg/m ³	p/M	mg/m ³	p/M	mg/m ³
2-Butanone	3,000	8,847	200	590	300	885
Carbon tetrachloride ^d	300	1,887	2	13	--	--
Chloroform	1,000	4,883	2	10	--	--

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NOTES:

^aThe Immediately Dangerous to Life or Health (IDLH) level represents a maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects.

^bThe Time-Weighted Average (TWA) concentration limit for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (the term "TWA" may be expressed in either p/M or mg/m³).

^cThe Short-Term Exposure Limit (STEL) is a 15-minute TWA exposure that should not be exceeded at any time during a workday.

^dAny chemical designated as "Ca" is considered to be a chemical that should be treated as an occupational carcinogen.

3.7 ASSESSMENT SUMMARY

This assessment analyzed CCl₄ as the hazardous inventory of concern because CCl₄ is the predominant contaminant found during the test phase as discussed in the ERA proposal (DOE-RL 1991). This assessment also analyzed HCl from the potential hydrolysis of CCl₄, which would result in generation of HCl if a GAC bed overheating event occurred. Scenarios were analyzed and the results have been provided in order to determine the potential consequences associated with these events. The worst case consequences have been identified and are addressed in this section.

The requirements for determination of hazard classification indicate this activity will require review and approval for that of a low hazard operation. This safety assessment satisfies the requirements of WHC-CM-4-46, Kerr 1990, and DOE 1986. The requirements considered also included the protective action guidelines (PAG) that were developed to limit inhalation exposures to the public to levels below which they would not be expected to experience or develop irreversible or other serious health effects or symptoms that could impair their ability to take appropriate protective action (WHC-CM-4-1, *Emergency Plan*).

The hazard classification criteria for this activity complies with the procedural criteria of WHC-CM-4-46 and is consistent with the guidance in Kerr 1990. Because CCl₄ is not defined in PAG concentrations (WHC-CM-4-1) or in the emergency response action guidelines provided in Kerr 1990, concentrations with conservative fractions of IDLH are used as the criteria. Onsite criteria and offsite criteria for low hazard is <0.1 of the IDLH [30 p/M CCl₄ (Kerr 1990)] and < TLV-TWA [2 p/M CCl₄ (WHC-CM-4-46)], respectively.

The assessed consequences have been evaluated against the toxicological risk acceptance curve. The potential concentrations of CCl₄ are within the acceptance guidance (WHC-CM-4-46).

The receptors of concern are the nearest onsite and offsite individuals. The closest onsite facility to the remediation sites is the PFP. The nearest offsite location is Highway 240, 4.5 km (2.8 mi) southwest of the

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216-Z-18 crib. The site boundary (nearest resident) is 7.7 mi (12.5 km) southwest of the crib sites.

The bounding postulated scenario involves the rupturing of three fully saturated canisters releasing CCl_4 , resulting in consequences to the receptors of concern. This scenario involves a vaporization rate of 2.0 lb/min of CCl_4 , with the CCl_4 vapors being released over a period of 16 hours. A summary of the receptor exposures for this scenario is provided in Table 4.

Table 4. Receptor Exposures Caused by Release of 2.0 lbs/min of Carbon Tetrachloride Over 16 hours.

Release of CCl_4 per minute over a 16-hour period (lbs)	Resultant exposures			Limits	
	Onsite 100 m (330 ft)	Nearest public access 4.5 km (2.7 mi)	Offsite	IDLH	TWA
2.0	28 p/M ³ 176 mg/m ³	0.14 p/M ³ 0.88 mg/m ³	0.05 p/M ³ 0.32 mg/m ³	300 p/M ³ 1,882 mg/m ³	2 p/M ³ 13 mg/m ³

Attachment G provides the data that includes the analysis for the receptor exposures identified in Table 4.

One postulated scenario identified the worst-case production of phosgene gas near heating units in the GAC system. There will be heaters located in the hoses that connect the well head to the GAC system (usually one heater per well), before the prefilter, and located upstream of the HEPA filtration system. The heaters should not provide sufficient temperatures to heat the GAC units that result in the production of phosgene [hydrolysis could begin to occur if temperatures exceed 400° F (205° C) in the air stream] as indicated in Attachment H because the in-line heater design will have a maximum air stream temperature capacity of 275° F (135° C) at 50 acfm.

Table 5 provides the consequences if sufficient temperatures could be achieved for phosgene production. The conversion rate of CCl_4 to phosgene assumes temperatures of 1,100° to 1,400° F (600° to 760° C) that are required for a much larger conversion (CCl_4 hydrolysis reaction goes to completion or near completion) of CCl_4 to phosgene. The conversion rate is 2.7E-4 lbs phosgene produced per pound of CCl_4 exposed to the stated temperatures in the presence of oxygen. Other assumptions show that phosgene produced is also vented to the environment without being adsorbed in the GAC unit, and does not undergo hydrolysis as the temperature decreases.

Even if sufficient temperatures are achieved, the consequences would not exceed the limits for a low hazard activity (Table 5), but the TWA limit for exposure to phosgene could be exceeded for the site worker. Prudent actions are recommended in Section 4.3, addressing the maximum air stream temperature capacity for the heaters.

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Table 5. Phosgene Production Near Upstream and Prefilter Heaters.

Flow of carbon tetrachloride per minute (lbs)	Resultant exposures			Limits		
	Onsite 100 m (330 ft)	Nearest public access 4.5 km (2.7 mi)	Offsite 12.5 km (7.7 mi)	IDLH	TWA	Ceiling* limit
1.6	.007	1.2E-5	4E-6	2 p/M 8.22 mg/m ³	0.01 p/M ³ 0.04 mg/m ³	0.02 p/M ³ 0.8 mg/m ³

NOTE:

*Ceiling limit - A permissible 15-minute TWA excursion limit above the 8-hour TWA limit that should not be exceeded during any part of the workshift.

Attachment G provides the data that includes the analysis for the receptor exposures identified in the above table.

Another scenario involves a GAC bed overheating event; an occurrence of this type would produce phosgene or HCl. A postulated scenario was developed involving hydrolysis of the CCl₄, resulting in the production and release of HCl from the GAC bed. The release of the HCl was a result of an exhaust hose failure from the heat generated.

This event would involve the primary GAC canister being heated up to sufficient temperatures to decompose the CCl₄. The production of HCl may occur in the GAC bed from two possible mechanisms: from hydrolysis of CCl₄, or by hydrolysis of phosgene that may act as an intermediate product in the conversion of CCl₄ to HCl. When sufficient water is present (> 7% relative humidity at the inlet to the GAC at CCl₄ concentrations of 1,000 p/M), the CCl₄ should be hydrolyzed to HCl at about 250°C (480°F) to 700°C (1292°F). The relative humidity during operations is typically > 50% and has never been < 20%. Assuming these factors, it is unlikely that any phosgene produced would be released--however, substantial quantities of HCl would be produced assuming sufficient CCl₄ was retained on the GAC bed and not desorbed. A maximum estimated mass flow rate (5.08 g/s of HCl) for a GAC temperature excursion taking place is addressed in Attachment G. Table 6 provides the worst case consequences associated with a release of HCl from an event involving internal overheating of a GAC canister.

Table 6. Receptor Exposures Caused by a Release of 5.08 g/s of Hydrogen Chloride .

Release of HCl (g/s)	Resultant exposures			Limits	
	Onsite 100 m (330 ft)	Nearest public access 4.5 km (2.7 mi)	Offsite	IDLH	Ceiling
5.08	5.4 p/M 8 mg/m ³	0.01 p/M 0.014 mg/m ³	0.003 p/M 0.004 mg/m ³	100 p/M 152 mg/m ³	5 p/M 8 mg/m ³

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The consequence analysis also indicated that several postulated scenarios could result in consequences to the site worker and nearest uninvolved individual that exceeds the Occupational Safety and Health Administration (OSHA) limits for exposure to CCl_4 . Table 7 identifies the system or component failures, consequences as a result of those failures and mitigative features available to reduce or eliminate the potential consequences to the site worker and nearest uninvolved worker.

Those components designed for providing or maintaining confinement of the VES are defined as safety class 3 components (WHC-CM-1-3, *Management Requirements and Procedures*). The consequences of this operation could affect the health and safety of the site workers caused by accidental releases of chemicals.

The VES production and characterization units are located in closer proximity to the PFP than has been analyzed in the PFP accident analysis. The CCl_4 workers located within the PFP safety envelope are required to be trained for emergency response actions to those accidents at the PFP that may result in any potential consequences to the VES work sites. The PFP Final Safety Analysis Report discusses the accidents and potential consequences to the site worker, onsite worker, and the public (Carlson 1990).

The mitigation features and controls required to assure concentrations to the site and nearest uninvolved worker are controlled below the OSHA limit for CCl_4 (identified in Table 7) and are discussed in Section 4.0.

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Table 7. Assessment of Hazards and Controls. (sheet 1 of 2)

Component Failure and Consequences	Mitigation Features
<p>Failure of piping (hole in a flex hose), fittings, saturation of both the GAC canisters causing CCl₄ to breakthrough, or failure of a control system could cause a continuous release resulting in consequences to the uninvolved individual. Concentrations of CCl₄ at 100 m (330 ft) would be a maximum of 17 p/M.</p>	<p>Install a calibrated VOC detector downstream of the final GAC canister for detection of CCl₄ if the VES is operating in automated mode. The alarm set point of the detector shall be set for concentrations of 25 p/M_V of CCl₄ and shall also be interlocked to shut down the blower if the 25 p/M_V concentrations are exceeded.</p> <p>A minimum of two GAC canisters shall be in place (two in series with the second canister having > adsorptive capacity than the first unit) to adsorb any CCl₄ if breakthrough of the first GAC canister occurs when operating the VES in automated mode.</p> <p>A sampling frequency (for detection of concentrations of CCl₄) is required once a day during the day shift at the 216-2-1A and 2-18 well fields and at the frequencies determined for the 2-9 well field (based upon concentrations of CCl₄) with three GAC canisters in place when operating the VES in manual mode.</p> <p>Train personnel who operate the VES production or characterization unit to monitor and shut down the blower in the event the 25 p/M_V is exceeded.</p> <p>Calibrate flow rate meters, located upstream of the blower and downstream of the final GAC, to indicate a flow rate variance of not more than 10% above the combined accuracy between the meters. Interlock flow rate meters to shut down the blower if a greater than 10% variance above the combined accuracy of the two flow rate meters is detected. Reliability of system must ensure instruments fail safely to assure shutdown of the blower.</p> <p>Monitoring of flow rate meters will be required by operations personnel as prescribed in the work procedures if interlocks are not operable to detect a flow rate variance of greater than 10% (exceeding 10% variance for more than one minute will require shutdown of the VES). If flow rate meters and interlocks are not operable, constant monitoring (with instruments for detection of CCl₄ vapors) is required around the portion of the VES under positive air pressure. Detection of CCl₄ vapors that achieve ≥ 2 p/M will require shutdown of the VES.</p>

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Table 7. Assessment of Hazards and Controls. (sheet 2 of 2)

Component Failures and Consequences.	Mitigation Features
<p>Spill of carbon involving three GAC canisters (as a result of a rupture caused by dropping a canister) that results in consequences to the uninvolved individual. Maximum concentrations of CCl_4 at 100 m (330 ft) would be 28 p/M. An emergency response kit should be available for containment of a spill. Immediate notification to hazardous material response team using the 811 emergency notification system should be made in the event of a spill.</p>	<p>An emergency response kit should be available for containment of a spill. Immediate notification to the hazardous material response team using the 811 emergency notification system should be made in the event of a spill.</p>
<p>In-line heaters that have a maximum air stream temperature capacity of 275° F (135° C) at 50 acfm. The heaters will be used to remove moisture in the process flow stream. Hydrolysis of CCl_4 can occur (resulting in the production of some phosgene gas) caused by heating the process flow stream to temperatures that exceed 400° F (205° C).</p>	<p>Replacement of failed heater units should be with units that do not exceed a maximum air stream temperature capacity of 400° F (205° C).</p>
<p>A fuel fire that occurs in close proximity to the saturated GAC canisters providing sufficient temperatures to cause regeneration of the carbon. The heat from the fuel fire would strip and release the toxic pollutants in the smoke plume within a 30-minute period.</p>	<p>Locate the fuel sources a minimum of 15 m (50 ft) away from the GAC canisters whether the canisters are in storage or are being used in the process. Locate the generator a minimum of 8 m (25 ft) away from the GAC canisters. Maintain the fuel sources and generators at the specified distances to allow adequate clearance for flames that could result from a failure of the propane tank or fuel hose to the generator. This would provide a conservative distance at which flames could affect the CCl_4 canisters.</p>

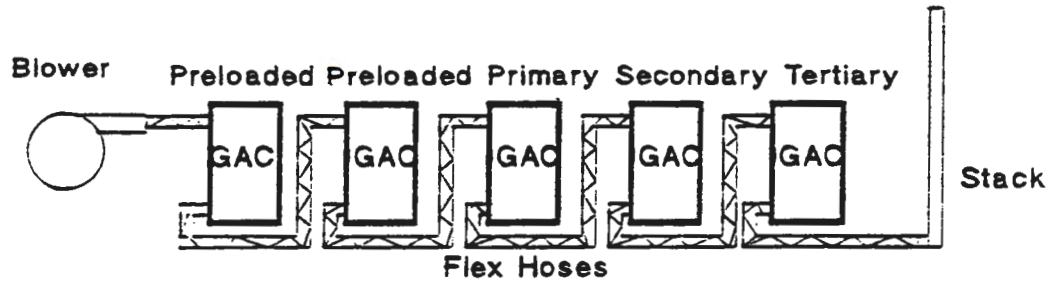
4.0 OPERATIONAL SAFETY LIMITS AND PRUDENT ACTIONS

The analysis disclosed that the VES remediation operations would be classified as a low hazard operation. The safety functions that will be provided for the remediation activities of the CCl_4 VES process are identified in OSLs. The following are the OSLs for the 200 West Area CCl_4 ERA.

The OSLs specify the requirements for the number of GAC canisters that are required to be in place based upon automated or manual modes of operation. Figure 12 provides information regarding how the configuration of the GAC canisters should be situated based on their intended function (i.e., the preloaded GAC canisters may be located upstream of the primary unit for using additional adsorptive capacity if available).

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Figure 12. Configuration and Definitions of the Granular Activated Carbon Canisters.



Preloaded: These are GAC canisters that have reached saturation during previous loading and are placed back on line to maximize the adsorptive capacity of the unit. Previous loading may have only used 20% capacity. Maximum loading capacity could be up to 60%.

Primary: This GAC canister is the first unit in series where no breakthrough of CCl₄ to the next GAC canister has occurred.

Secondary: This GAC canister would be the next unit after the primary unit and should have greater adsorptive capacity than the primary unit.

Tertiary: This GAC canister would be the next unit located after the secondary unit and would be required to have full adsorptive capacity. If no tertiary unit is used (i.e., automated mode of operation), then the secondary unit would be required to have full adsorptive capacity.

Breakthrough: The definition of breakthrough is defined as a rapid rise or increase in CCl₄ concentration at the outlet of the GAC canister.

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4.1 OPERATIONAL SAFETY LIMITS

OPERATIONAL SAFETY LIMIT 1 - FUEL SOURCES

- 1.1 TITLE: Inventory Control of Fuel Sources
- 1.2 APPLICABILITY: This OSL applies to the location of the 3,785 L (1,000 gal) propane storage tank, fuel trucks that may be used for refueling the fuel tank, and the electric generator at the site. (This limit does not apply to the fork truck or similar equipment having small quantities of fuel).
- 1.3 OBJECTIVE: The objective of this OSL is to assure that a common mode fire affecting the propane tank, fuel truck, or generator would not provide sufficient temperatures that could affect the GAC canisters resulting in regeneration of CCl_4 causing unacceptable consequences to individuals.
- 1.4 REQUIREMENTS:
 - a. The propane fuel tank or a fuel truck for refueling the propane tank shall be located a minimum of 15 m (50 ft) from the GAC canisters whether the canisters are in storage or are being used in the process.
 - b. The generator shall be located a minimum of 8 m (25 ft) from the GAC canisters.
 - c. A maximum of not more than twelve fully saturated canisters will be allowed per storage location at the work site.
- 1.5 SURVEILLANCE: The responsible operating organization shall verify daily (before startup and during periods of operation) that the work site is in compliance with the requirements of this OSL. Compliance with the stated requirements shall be documented in an auditable record.
- 1.6 RECOVERY: Noncompliance with the requirements of the OSL
 - a. Vapor extraction system operations shall cease until Health and Safety Assurance approves restart of the operation.
 - b. The fire department shall be notified requesting standby at the work site until full recovery actions are completed.
 - c. The location of the fuel source shall be reestablished at a minimum of 15 m (50 ft) as soon as reasonably possible.

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- d. The location of the electric generator shall be reestablished at a minimum of 8 m (25 ft) as soon as reasonably possible.
- e. The number of saturated canisters in storage shall be reduced to twelve as soon as reasonably possible.

The OSL violation shall be documented as an unusual occurrence report.

Noncompliance with the surveillance requirement

- a. The surveillance shall be performed immediately.
- b. If surveillance determines noncompliance with the requirement, the recovery actions identified in Section 1.6, "Noncompliance with the requirements of the OSL" shall be initiated.
- c. Failure to implement a surveillance requirement shall be documented as an off-normal occurrence.

1.7 AUDIT POINT:

An auditable log shall be maintained at the site documenting the results of the surveillance. This log shall be reviewed weekly by the operating organization assuring compliance with the requirements and surveillance. The audit and surveillance frequencies shall be determined by the Quality Assurance and Environmental Assurance organizations respectively.

1.8 BASIS:

A minimum 15 m (50 ft) separation between the propane tank and the CCl_4 canisters, whether in storage or being used at the VES production and characterization units, and a minimum 8 m (25 ft) separation between the generator and the canisters allows adequate clearance for flames that could result from a failure of the propane tank or the fuel hose to the generator. This would provide a conservative distance at which a flame could affect the CCl_4 canisters. The primary cause of a release of CCl_4 is high temperature. Removing the only potential fuel sources [3,785 L (1,000 gal) propane tank, fuel carried by a fuel truck] for a fire intense enough to strip the CCl_4 eliminates the credible postulated mechanisms for releasing the CCl_4 , causing consequences to the receptors of concern or the environment exceeding the TLV for a low hazard operation. The analysis involving other accidents in this assessment were based upon six saturated canisters that are part of the VES and twelve saturated canisters in a storage area. An accident involving not more than twelve saturated canisters in storage would ensure the integrity of this assessment.

OPERATIONAL SAFETY LIMIT 2 - LIMITING CARBON TETRACHLORIDE EXPOSURES TO THE NEAREST UNINVOLVED INDIVIDUAL

- 2.1 TITLE: Controlling the Concentrations of Carbon Tetrachloride to the Nearest Uninvolved Individual to Below the Permissible Exposure Limit.
- 2.2 APPLICABILITY: This limit applies to mitigating the consequences of a release of CCl_4 below the OSHA 8-hour TWA limit of 2 p/M to the nearest uninvolved individual during VES operation.
- 2.3 OBJECTIVE: The objective of this limit is to assure that the concentrations of CCl_4 from the VES operation do not exceed the OSHA limit causing unacceptable consequences to individuals.

2.4 REQUIREMENTS:

2.4.1 AUTOMATED MODE OF OPERATION

2.4.1.1 Monitoring for Granular Activated Carbon Breakthrough

Requirements: a. A CCl_4 detector shall be located downstream of the final GAC (stack monitor) and interlocked to shut down the blower (on the production units) if the 25 p/M CCl_4 concentrations are exceeded.

b. A minimum of two GAC canisters in place (two in series) to adsorb any CCl_4 if breakthrough of the first GAC canister occurs. The secondary GAC canister shall have full adsorptive capacity whenever installed in the system.

Surveillance: a. A weekly operability check and monthly system functional check of the CCl_4 detector located downstream of the final GAC (stack monitor) shall be required. Test data shall be recorded and documented in an auditable record.

b. The responsible operating organization shall verify before startup that two GAC canisters are in place with the secondary unit having full adsorptive capacity when installed in the system.

Recovery: **Noncompliance with the requirements**

a. Once a determination is made that the operating organization is not in compliance with the requirements of this OSL, operations shall immediately cease. The approval of Health and Safety Assurance will be required for restart of the operations in automated mode.

b. Failure of the CCl_4 detector (stack monitor located downstream of the final GAC) to initiate shutdown (if

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concentrations of CCl_4 exceed 25 p/M shall require maintenance troubleshooting and repair before restart of operations in automated mode.

- c. Failure to have two GAC canisters in place (secondary unit having full adsorptive capacity when installed) will require shutdown of the system. Restart of the VES will require verification that two GAC canisters are in place before resumption of operations.
- d. The OSL violation shall be documented as an unusual occurrence report.

Noncompliance with the surveillance

- a. The surveillance shall be performed immediately.
- b. If the surveillance determines noncompliance with the requirement, then initiate recovery actions as identified in Section 2.4.1.1.(c), "Noncompliance with the requirements."
- c. Failure to implement a surveillance requirement shall be documented as an off-normal occurrence.

2.4.1.2 Monitoring for Ambient Air Leakage of System Under Positive Air Pressure

Requirement: The flow rate meters, located upstream of the primary GAC and downstream of the final GAC, shall be calibrated. A logic system shall be in place to initiate a system shutdown (system shutdown within one minute) when flow rate variance is greater than 10% above the combined accuracy of the flow rate meters. Reliability of system (flow rate meters and logic system) must ensure instruments fail safely to assure shutdown of the blower.

Surveillance: A weekly operability check and monthly system functional check of the flow rate meters, located upstream of the primary GAC canister and downstream of the final GAC canister, shall be conducted by the responsible operating organization. Test data shall be recorded and documented in an auditable record.

Recovery: **Noncompliance with the requirements**

- a. Once a determination is made that the operating organization is not in compliance with the requirements of this OSL, operations shall immediately cease. The approval of Health and Safety Assurance will be required for restart of the operations in automated mode.

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- b. Failure to calibrate flow rate meters shall require shutdown of the VES until calibrated flow rate meters are in place. Failure of the logic system to initiate shutdown (if flow rate variance is greater than 10% and does not shut down the system within one minute) shall require maintenance troubleshooting and repair before restart of automated operations.
- c. The OSL violation shall be documented as an unusual occurrence report.

Noncompliance with the surveillance

- a. The surveillance shall be performed immediately.
- b. If the surveillance determines noncompliance with the requirement, then initiate recovery actions as identified in Section 2.4.1.2., "Noncompliance with the requirements."
- c. Failure to implement a surveillance requirement shall be documented as an off-normal occurrence.

2.4.2 MANUAL MODE OF OPERATION

2.4.2.1 Monitoring for Granular Activated Carbon Breakthrough

- Requirements:
- a. The required sampling frequencies for assuring the concentrations of CCl_4 do not exceed 25 p/M at the point of discharge (stack sample port downstream of the final GAC canister) from the VES is as follows:
 - b. The sampling frequency by operations personnel for the production units at the 216-Z-1A and Z-18 well fields will be required once a day during the day shift at the sample port between the primary and secondary GAC canister. The interval between samples shall not exceed 32 hours.
 - c. The minimum sampling frequencies for the production units at the Z-9 well field required (at the stack sample port) are based on the concentrations of CCl_4 as measured at the CT-1 sample port as identified below. The sampling frequency at the CT-1 sample port is required once every 1.5 hours (for at least the first six hours) until the concentrations of CCl_4 from each Z-9 well has been established.

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Concentrations of carbon tetrachloride at CT-1 sample port (p/M)	Sample frequencies at stack sample port (hours)
≤ 25,000	1.5
≤ 20,000	2.0
≤ 15,000	2.5
≤ 10,000	4.0
≤ 5,000	8.0

- d. The responsible operating organization shall provide a second individual to verify (at the work site) the samples are taken at the frequency required.
- e. There shall be three 2,000 lb GAC canisters in place (production units) at all times during operations with the secondary GAC canister having greater adsorptive capacity than the primary unit, and the tertiary unit having full adsorptive capacity whenever installed in the system.
- f. Personnel who operate the VES production and characterization units shall be trained to monitor, sample and shut down the blower in the event the concentrations of CCl_4 detected at the stack sample port exceed 25 p/M.
- g. Verification of the hose installation to the GACs and piping on the 1500 cfm unit is required by the responsible operating organization before startup.

- Surveillance:
- a. The sampling data shall be reviewed weekly to verify sampling frequency requirements are complied with and verification of sampling is conducted. Results of the weekly surveillance shall be documented in the field log.
 - b. The responsible operating organization shall verify the system configuration [three 2,000 lb GAC canisters in place (production units) with the secondary unit having greater adsorptive capacity than the primary unit, and the tertiary unit having full adsorptive capacity when installed in the system] before startup of the VES.
 - c. Personnel training shall be verified for those individuals responsible for operating, sampling, and shutting down the VES production and characterization units before initial startup.
 - d. Verification of the hose installation to the GACs and piping on the 1500 cfm unit is required before startup.

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Recovery:

Noncompliance with the requirements

- a. Once a determination is made that the operating organization is not in compliance with the requirements of this OSL, operations shall immediately cease. The approval of Health and Safety Assurance will be required for restart of the operation in manual mode.
- b. Failure to conduct sampling operations at the frequency identified and verification of sampling will necessitate immediate shutdown of the VES.
- c. Failure to have three 2,000 lb GAC canisters in place (production units) with the secondary unit having greater adsorptive capacity than the primary unit, and the tertiary unit having full adsorptive capacity when installed in the system will necessitate immediate shutdown of the VES. Restart will not be allowed until three canisters are verified to be in place.
- d. Failure to operate the VES production and characterization units with trained personnel shall require shutdown of sampling operations until trained personnel are provided.
- e. Failure to verify the configuration of the hoses for the GACs and piping system will require verification that the configuration is correct prior to restart of operations.
- f. The OSL violation shall be documented as an unusual occurrence report.

Noncompliance with the surveillance

- a. The surveillance shall be performed immediately.
- b. If the surveillance determines noncompliance with the requirement, then initiate recovery actions as identified in Section 2.4.2.1., "Noncompliance with the requirements."
- c. Failure to implement a surveillance requirement shall be documented as an off-normal occurrence.

2.4.2.2 Monitoring for Ambient Air Leakage of System Under Positive Air Pressure

- Requirements: a. Monitoring of flow rate meters will be required by operations personnel as prescribed in the work procedures if interlocks are not operable to detect a flow rate variance of greater than 10% (exceeding 10% variance for more than one minute will require shutdown of the VES). If flow rate meters and

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interlocks are not operable, constant monitoring (with instruments for detection of CCl_4 vapors) is required around the portion of the VES under positive air pressure. Detection of CCl_4 vapors that achieve ≥ 2 p/M will require shutdown of the VES.

- b. Personnel who operate the VES production and characterization unit shall be trained to monitor, sample, and shut down the blower in the event that CCl_4 vapors are detected around the portion of the VES under positive air pressure that achieve ≥ 2 p/M.

Surveillance: a. The data, documenting any flow variances, shall be reviewed weekly to verify compliance with these requirements. Results of the weekly surveillance shall be documented in the field log.

- b. Personnel training shall be verified for those individuals responsible for operating, sampling, and shutting down the VES production and characterization units before initial startup.

Recovery: Noncompliance with the requirements

- a. Once a determination is made that the operating organization is not in compliance with the requirements of this OSL, operations shall immediately cease. The approval of Health and Safety Assurance will be required for restart of the operation.
- b. Failure of operations personnel to monitor the readout for detecting variances in the flow rate meters (if interlocks are not functioning) or not monitoring the portion of the VES under positive air pressure (if flow rate meters and interlocks are not operable) for detection of CCl_4 vapors that achieve ≥ 2 p/M will require shutdown of the VES.
- c. Failure to operate the VES production and characterization units with trained personnel shall require shutdown of sampling operations until trained personnel are provided.
- d. The OSL violation shall be documented as an unusual occurrence report.

Noncompliance with the surveillance

- a. The surveillance shall be performed immediately.
- b. If the surveillance determines noncompliance with the requirement, then initiate recovery actions as identified in Section 2.4.2.2., "Noncompliance with the requirements."

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- c. Failure to implement a surveillance requirement shall be documented as an off-normal occurrence.

2.5 AUDIT POINT: An auditable log shall be maintained at the site documenting the results of the surveillances. This log shall be reviewed weekly by the operating organization.

2.6 BASIS: a. Sampling intervals and the number of GAC canisters required for manual mode operation are based on the time periods to achieve breakthrough of the primary, secondary, and tertiary GAC canisters, and a maximum system flow rate capacity of 480 cfm.

b. A maximum concentration of 2,500 p/M CCl_4 is assumed in the calculations for the 216-Z-1A and Z-18 well fields. Therefore, a minimum sampling frequency of once a day during the day shift is required (samples required a minimum of every 32 hours). A total of 34.4 hours adsorptive capacity is available for removal of CCl_4 before breakthrough at the tertiary GAC canister could occur (Attachment I).

c. The sampling frequencies for the production units at the Z-9 well fields are based on a maximum concentration of 25,000 p/M. Other sampling frequencies have been calculated based on lower concentrations. Reduced sampling frequencies are allowed after verification of the CCl_4 concentrations (at the CT-1 sample port) from the wells in the Z-9 well fields. The sampling frequencies are conservative (i.e., a minimum sampling frequency required every 1.5 hours for 25,000 p/M concentrations. A total of 3.4 hours adsorptive capacity are available for removal of CCl_4 before breakthrough at the tertiary GAC canister could occur).

d. Limiting the concentrations of CCl_4 to below the OSHA 8-hour TWA limit to the nearest uninvolved worker assures exposures to occupational carcinogens are maintained at levels that will reduce or eliminate adverse health effects to personnel.

OPERATIONAL SAFETY LIMIT 3 - REDUCING THE POTENTIAL FOR A GRANULAR ACTIVATED CARBON BED OVERHEATING EVENT RESULTING IN A POTENTIAL RELEASE OF HYDROGEN CHLORIDE AT THE 216-Z-1A AND 216-Z-18 CRIB SITES

3.1 TITLE: Controlling the Inlet Air Stream CCl_4 Concentrations to the GAC Bed and the Variance Between Inlet and Outlet Air Stream Temperatures for the Vacuum Extraction Unit at the 216-Z-1A and 216-Z-18 Crib Sites.

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- 3.2 APPLICABILITY: This OSL applies to the GAC inlet CCl_4 concentrations and the variance between inlet and outlet air stream temperatures.
- 3.3 OBJECTIVE: The objective of this OSL is to prevent an overheating event from occurring that could possibly result in the production and release of HCl , causing unacceptable consequences to the receptors of concern.
- 3.4 REQUIREMENTS: a. The air stream concentration of CCl_4 at the primary GAC inlet shall be determined by sampling at startup of operations and at two hour scheduled intervals. If the results of two consecutive samples $> 1,000$ p/M, then shutdown of operations shall be required.
- b. If the outlet air stream temperature exceeds the inlet air stream temperature by $> 11^\circ\text{C}$ (20°F) then bleed in ambient air, close well field lines, and run system for 30 minutes. If temperatures are still $> 11^\circ\text{C}$ (20°F) then quench the GAC bed with water or inert gas. If temperatures return to $\leq 11^\circ\text{C}$ (20°F) continue to bleed in ambient air until inlet temperature is achieved.
- 3.5 SURVEILLANCE: The responsible operating organization shall verify daily (during periods of operation) that the work site is in compliance with the requirements of this OSL. This daily surveillance shall be documented in an auditable record.
- 3.6 RECOVERY: Noncompliance with the requirements of the OSL
- a. If air stream concentrations of CCl_4 at the primary GAC inlet are $> 1,000$ p/M during operation, ambient air shall be introduced to dilute the air stream and reduce the concentration of CCl_4 to $\leq 1,000$ p/M. If the results of the second consecutive scheduled sample indicates concentration of CCl_4 is $> 1,000$ p/M, then shut down operations. The responsible operating organization shall formulate a plan to assure compliance with the requirements. The plan shall require the approval of Health and Safety Assurance before restart of operations.
- b. Failure to bleed in ambient air and close well field lines [if temperatures exceed the inlet air stream temperatures by $> 11^\circ\text{C}$ (20°F)] or remove the GAC canister and quench the GAC bed [if temperatures have not been reduced to $< 11^\circ\text{C}$ (20°F)] will require shutdown of operations. The responsible operating organization shall be required to formulate a recovery plan with concurrence from Health and Safety Assurance before restart of operations.

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- c. Violation of the OSL shall be documented as an unusual occurrence report.

Noncompliance with the surveillance

- a. The surveillance shall be performed immediately.
- b. If the surveillance determines noncompliance with the requirement, then initiate recovery actions as identified in Section 3.6 of this OSL, "Noncompliance with the requirements of this OSL."
- c. Failure to implement a surveillance requirement shall be documented as an off-normal occurrence.

3.7 **AUDIT POINT:** An auditable log shall be maintained at the work site documenting the results of the surveillances. This log shall be reviewed weekly by the operating organization.

3.8 **BASIS:** The basis of the requirements is to preclude overheating of a GAC bed. Limiting the concentration of CCl_4 , based upon a two hour sampling interval, provides sufficient controls to minimize the heat generation from a GAC bed overheating event. Controlling the outlet temperature to within $11^{\circ}C$ ($20^{\circ}F$) of the inlet temperature should help in determining if there is autoignition GAC bed occurring. These requirements are based upon data obtained from the carbon industry for preventing possible overheating events in GAC beds that are used for adsorption of hydrocarbons.

4.2 PRUDENT ACTIONS

Function 1 - Minimize occupational workers' exposures of VOCs to as low as reasonably achievable.

Prudent Action 1 - Monitor ambient air and workers' breathing zone for CCl_4 vapors in areas where workers will be required to perform their work activities. Concentrations detected that exceed the TWA limits should require personnel (1) to be removed from the work area; or (2) to wear the appropriate protective gear as required by the JSA or HWOP.

Function 2 - Monitor VES for potential radionuclide particulate contamination.

Prudent Action 2 - Monitor for radioactive contamination even though radioactive particulates are not expected to be removed during remediation activities. In the event CAM alarms indicate possible radioactive contamination, shut down the process. Concurrence for restart will be required from the Health Physics supervisor. The characterization unit should be surveyed for any radioactive contamination before movement to another site.

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A record sampler should be used during operation of the characterization unit for confirmation of no airborne radioactivity.

Function 3 - Monitor for ^{222}Rn .

Prudent Action 3 - Use ^{222}Rn monitoring equipment to indicate the total quantities of ^{222}Rn and daughters adsorbed by the GACs during the VES operation. The quantities of ^{222}Rn measured will determine if the GAC canisters can be released from radiological controls. The ^{222}Rn concentrations of the stack effluent should be monitored.

Function 4 - Survey program.

Prudent Action 4 - Implement a routine survey program to monitor the GAC canisters for potential gamma exposures that may result from ^{222}Rn buildup in the canisters. If the exposure rate exceeds 2mR/h on contact with the outside of the canisters, the area will be posted per the requirements identified in WHC-CM-4-10.

Function 5 - Assure remediation and characterization sites are free of vegetation and combustibles.

Prudent Action 5 - Clear the sites identified for remediation or site characterization of vegetation and combustibles not necessary to the project.

Function 6 - Location of generator.

Prudent Action 6 - Locate the electric generator a minimum of 8 m (25 ft) from the propane storage tank as prescribed by the fire code.

Function 7 - Control the size (temperature capacity) of the in-line heaters used in the VES design.

Prudent Action 7 - Replace failed in-line heaters with heater units that have a maximum air stream temperature capacity that does not exceed 400° F (205° C).

Function 8 - Capping of the canister ports.

Prudent Action 8 - Whenever saturated GAC canisters are removed from the process, place covers over the inlet and outlet ports of the canister and verify to be secure.

Function 9 - Establish safety equipment list.

Prudent Action 9 - Identify the components of the VES required for providing confinement of CCl_4 and monitoring as safety class 3 components in a safety equipment list.

Function 10 - Apprise fire department of hazards.

Prudent Action 10 - Notify the fire department of the potential hazards involving CCl_4 in a fire and production of phosgene or HCl .

Function 11 - Training.

Prudent Action 11 - The employees (drivers) responsible for handling the saturated GAC canisters must have completed hazardous material training.

Function 12 - Exclusion zone.

Prudent Action 12 - Maintain a 15 m (50 ft) exclusion zone around the VES operations to prevent inadvertent access by uninvolved individuals to the work site.

Function 13 - Personnel exposure to heaters during operations.

Prudent Action 13 - The site workers should not come into close proximity to the heaters during periods of operation. The maximum air stream temperatures of 400° F (205° C) is required to be maintained. The temperatures within 2.54 cm (1 in.) of the heater cal rod may exceed the 400° F (205° C) resulting in some production of phosgene. The site workers should be made aware of potential hazards associated with the operation of the heaters during VES operations. Heater will be shut down when the blower is not running or the individual hose line is not in use.

Function 14 - Minimize consequences of spilled carbon with CCl₄.

Prudent Action 14 - Have an emergency response kit available on site for containment of spills. If a spill occurs, notify 911 (811 if using a cellular phone) requesting response by hazardous material response team.

Function 15 - Inventory control of liquid CCl₄ at the GMSS test site.

Prudent Action 15 - During the GMSS test no more than one drum containing up to a maximum of 115 L (30 g) of liquid CCl₄ should be located at the work site. Remove loaded drum from the work site before continuing GMSS test.

Function 16 - Notification and emergency response actions.

Prudent Action 16 - Address the emergency notification responsibilities and response actions in the emergency plan for the CCl₄ work site and in the emergency plans for the adjacent affected facilities.

Function 17- Monitor for ketones or other easily recognized oxidized materials.

Prudent Action 17 - Monitoring should be conducted relative to the wellhead for detection of any ketones or other easily oxidized materials that may be removed during VES operations. Concentrations detected in the air stream that exceed 100 p/M should require that the identified well not be used for remedial operations until additional characterization data is provided (Attachment J).

Function 18 - Emergency response measures from a GAC canister overheating event.

Prudent Action 18 - The appropriate procedures should provide the actions required to respond to an GAC bed overheating event. The following actions should be considered:

- Personnel should evacuate the immediate work area in the event a hose failure occurs or appropriate respiratory and dermal

protection (as specified in the HWOP or emergency response procedures) should be available for personnel who are required to respond to emergency situations.

- Monitoring should be available at the site for determining when concentrations of HCl are above 5 p/M.
- Respiratory protection should be used whenever introducing any water or inert gas into a canister. Protective clothing should be worn for protection from thermally hot canister surfaces and steam that could be generated whenever adding water to a hot GAC bed.

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WHC-CM-4-46, *Nonreactor Facility Safety Analysis Manual*, Westinghouse Hanford Company, Richland, Washington.

WHC-CM-7-5, *Environmental Compliance Manual*, Appendix A, "Derived Concentration Guides for Controlling Exposure to Members of the Public," Westinghouse Hanford Company, Richland, Washington.

9313027-0682

**HYDROGEN CHLORIDE GAS PRODUCTION FROM CARBON CATALYZED
HYDROLYSIS OF CARBON TETRACHLORIDE**

An earlier report on phosgene production from carbon tetrachloride combustion concluded that in the presence of carbon and excess moisture, the hydrolysis reaction would dominate and that any phosgene generated would be quickly hydrolyzed to hydrogen chloride (HCl) gas. Thus, if any phosgene is generated by a carbon bed temperature excursion, it will be very short lived in the presence of 60% relative humidity. Note that at 60% relative humidity, the mass flow rate of water to the granular activated carbon (GAC) unit is 1.25 g/second. The earlier report was based on information taken from *Military Problems with Aerosols and Nonpersistent Gases* (NDRC 1946). The report (NDRC 1946) indicated that under normal conditions of high moisture content, it is unlikely that appreciable amounts of phosgene can be desorbed from carbon. Continued passage of air would probably remove only the hydrolysis products HCl and CO₂.

The paper discussed above (NDRC 1946) is directed at describing carbon used in military gas masks to protect soldiers from phosgene used as a military weapon. This paper does not address the situation in which carbon is being used to adsorb CCl₄, and phosgene is produced in the carbon bed as a result of a temperature excursion.

Hydrogen chloride gas may be produced in the carbon bed via two possible mechanisms: from the hydrolysis of carbon tetrachloride, or by hydrolysis of phosgene, which is produced in the bed by partial hydrolysis of the CCl₄ at elevated temperatures. An explanation was provided in NDRC 1946 that if any phosgene were adsorbed on carbon, in the presence of excess water in the gas stream, the phosgene would be hydrolyzed to HCl before it is desorbed. It should also be noted that other possible degradation products from CCl₄ include chlorine dioxide and chlorine, but these compounds would also react with water vapor to yield HCl.

The question of what concentration of HCl to expect in the offgas stream from an overheated GAC canister is complicated by the possible chemical reactions discussed in the previous paragraph. It is not reasonable to attempt to relate HCl mass flow to CCl₄ mass flow to the GAC unit. After a few hours use of a GAC unit, the inventory of carbon tetrachloride already adsorbed on the bed is very large compared to the instantaneous mass flow of the CCl₄ coming in. The rate at which the material on the bed can be hydrolyzed is a function of bed temperature and the mass flow rate of water to the bed. However, the rate at which the CCl₄ sorbed on the bed can be thermally stripped is also a function of heatup rate. The boiling point of CCl₄ is 170° F (77° C)--this is well below the temperatures reached in the temperature excursion that took place at the Z-9 crib. The loss of CCl₄ from the bed during a temperature excursion is a horse race between thermal stripping and hydrolysis.

In view of the above considerations, it is impossible to theoretically predict what the mass flow rate of hydrogen chloride gas would be from a GAC unit during a temperature excursion. The most reasonable analytical approach is to bound the HCl source term by assuming that it is the mass flow rate of water that limits the mass flow rate of HCl from the GAC canister, assuming that temperature is sufficiently high and not limiting.

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The maximum mass flow rate for HCl was estimated for a GAC unit temperature excursion taking place at Z1A Crib assuming a total GAC unit inlet flow rate of 240 SCFM, and a gas stream temperature of 70° F. This flow rate translates to a molar flowrate of 4.70 moles/second. The 60% relative humidity in the inlet gas stream is equivalent to a water vapor partial pressure of 11.3 Torr.

The mass flowrate of water is

$$(11.3/760)(4.70)(18) = 1.25 \text{ g/second}$$

The theoretical maximum flow rate for HCl production can only be twice the molar flow rate for water; therefore the HCl mass flowrate is

$$(2)(11.26/760)(4.70)(36.5) = 5.08 \text{ g/second}$$

If this mass flowrate is used as a source term in the Emergency Prediction Information¹ dispersion model, using Class D stability and a wind speed of 4.5 m/second, the maximum concentration 100 m downwind is only 5.4 ppm (Hanson 1993)². This concentration is far below the Emergency Response Prediction Guideline-3 value of 100 ppm.

If total air flowrate = 240 scfm, then

$$\text{@ } 70^{\circ}\text{F, } P_{\text{H}_2\text{O}} = 0.363 \text{ psi}$$

$$= 18.77 \text{ Torr}$$

$$\text{@ } 60\% \text{ relative humidity } (0.60) (18.77) = 11.26 \text{ mm Hg}$$

4.70 moles/s = molar flowrate air.

$$\frac{11.26}{760} (\text{molar flowrate}) (18) = \text{mass flowrate air}$$

$$= \frac{11.26}{760} (4.70) (18) = 1.25 \text{ g/s } \text{H}_2\text{O flowrate}$$

or 0.0696 moles/s = molar flowrate

Theoretical maximum HCl production rate can only be twice the molar flowrate of water; therefore, the HCl mass is

$$(2) (0.0696) (36.5) = 5.08 \text{ g/second.}$$

¹Emergency Prediction Information is a registered trademark of Homann Associates, Inc., Fremont, California.

²Recommended nonradiological hazard classification guidelines for use with DOE Order 5481.1B.

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REFERENCES

Hanson, J. L., L. H. Frauenholtz, and N. R. Kerr, 1993, *Environmental Restoration and Decontamination and Decommissioning Safety Documentation Guidance - Draft*, SRT-EG-93-0044, Westinghouse Savannah River Company, Aiken, South Carolina.

NDRC 1946, *Military Problems with Aerosols and Nonpersistent Gases*, GEH-13, 162, National Defense Research Committee, Washington D. C.



D. K. Oestreich, Engineer, Environmental
Restoration Safety Support

9313027.0685

EPICode 4.1 S/N 12149 BATTELLE
 SUBSTANCE I.D. : HYDROGEN CHLORIDE Library-91
 Molecular Weight : 36.5 gram/mole
 CAS Number: [7647-01-0]
 TWA : 5.0 ppm TWA : 7.5 mg/m³
 IDLH : 100 ppm
 ERPG-1 : 3 ppm ERPG-2 : 20 ppm ERPG-3 : 100 ppm

CONTINUOUS : 5.1E+00 gram/sec

HEIGHT-EFFECTIVE: 0 Meters
 SURFACE WIND SPEED : 4.5 Meters/second
 DEPOSITION VELOCITY: 0.100 cm/second
 STABILITY CLASS : D
 TERRAIN : STANDARD
 RECEPTOR HEIGHT (z) : 0 Meters
 LOCATION OF MAXIMUM CONCENTRATION LEVEL
 Distance : < 0.10km
 Level : > 8.0E+00 mg/m³ 5.4E+00 PPM

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DOWNWIND Distance-km áááááááááááááá	CONCENTRATION		ARRIVAL TIME hours:minutes áááááááááááááá
	mg/m ³ áááááááá	ppm áááááááá	
0.10	8.0	5.4	0: 0
0.20	2.1	1.4	0: 1
0.30	1.0	0.68	0: 1
0.40	0.60	0.40	0: 1
0.50	0.40	0.27	0: 2
0.60	0.29	0.20	0: 2
0.70	0.22	0.15	0: 3
0.80	0.18	0.12	0: 3
0.90	0.15	0.10	0: 3
1.00	0.12	0.082	0: 4
2.00	0.040	0.027	0: 7
3.00	0.022	0.015	0:11
4.00	0.014	0.010	0:15
5.00	0.010	0.0070	0:19
6.00	0.0081	0.0054	0:22
7.00	0.0066	0.0044	0:26
8.00	0.0055	0.0037	0:30
9.00	0.0047	0.0032	0:33
10.0	0.0041	0.0028	0:37
20.0	0.0017	0.0012	1:14
40.0	7.8E-04	5.2E-04	2:28
60.0	4.9E-04	3.3E-04	3:42
80.0	3.6E-04	2.4E-04	4:56
100	2.8E-04	1.9E-04	6:10

ATTACHMENT J

PROPOSED LIMIT OF KETONES IN VAPOR EXTRACTION SYSTEM SOIL GAS

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EBASCO

August 24, 1993
ERL-WHC/93-10-1-93-219

Ms. Virginia Rohay
Westinghouse Hanford Company
P.O. Box 1970 MSIN H6-06
Richland, WA 99352

SUBJECT: WHC ORDER NO. MLW-SVY-037106
TASK ORDER NO. E-93-10
PROPOSED LIMIT OF 1 ppm, KETONES IN VES SOIL GAS (CCl₄, ERA)

Dear Ms. Rohay:

The subject limit may be unnecessarily conservative in light of recent pilot-scale testing of the GAC canister as used in the VES at 216-Z-1A tile field and 216-Z-9 trench.

Pilot-scale testing, which simulated the conditions of the GAC canisters as used in the ERA, was recently performed at Washington State University. The pilot-scale tests will be fully documented and analyzed in a report to be released September 10, 1993 by Ebasco Services Incorporated.

The pilot-scale testing, which simulated 1000 ppm, carbon tetrachloride (CCl₄) and no methyl ethyl ketone (MEK), indicated an internal temperature rise of approximately 3 °C relative to inlet air temperature. The pilot-scale testing which simulated 1000 ppm, CCl₄ and 200 ppm, MEK indicated similar temperature rises. In addition, the temperature rise profiles were not distinguishable from the test without 200 ppm, MEK. It may be concluded that, under the conditions of these two tests, MEK at 200 ppm, is not contributing to any additional temperature rise in the GAC column.

Additionally, expert opinions have placed the MEK levels of concern at 100 or 200 ppm, based on experience. These levels were discussed in the Draft Summary Background Report, Rev. 1. One expert, Richard Lynch (Calgon Carbon Corp.), indicated that the level of concern for MEK was 100 to 200 ppm. Another expert, David Ainsworth (Cameron Carbon), indicated that the level of concern for MEK was 100 ppm, or above. Another expert, Mukund Ramaratnam (Westates Carbon), indicated that the level of concern for MEK was 100 to 500 ppm.

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Based on the results of the pilot-scale tests and upon expert opinions, a reasonable limit for ketone concentrations in the soil gas stream would be 100 ppm. Since MEK has been identified as the most insidious of ketones in the initiation of GAC column combustion initiation, these limits should be conservative.

Sincerely,

Marc Dippre

Marc Dippre
Ebasco Environmental, A Division of
Ebasco Services Incorporated

MD/jrl

cc: R. Cameron
J. Grover
File 2.2/3.6

9313027.0690

DISTRIBUTION SHEET

To:
DistributionFrom:
R. R. LehrschallDate:
August 13, 1993

Project Title/Work Order:

SAFETY ASSESSMENT FOR THE 200 WEST AREA EXPEDITED RESPONSE ACTION FOR REMEDIATION OF
CARBON TETRACHLORIDE, REV. 1-B

EDT No.:

ECN No.: 189915

Name	MSIN	With Attachment	EDT/ECN & Comment	EDT/ECN Only
M. R. Adams	H6-01	1		
T. L. Bennington	H4-16	1		
R. T. Coffman	N3-05	1		
S. O. Deleon	H4-16	1		
S. A. Driggers (2)	H6-04	2		
S. J. Gale	N3-05	1		
K. A. Gano	X0-21	1		
K. D. Gibson	H4-61	1		
M. C. Hagood	H6-04	1		
D. O. Hess	L4-74	1		
B. J. Hobbs	N3-06	1		
W. L. Johnson	H6-04	1		
N. R. Kerr	H4-67	1		
R. R. Lehrschall (2)	H4-67	2		
D. J. Moak	N3-05	1		
T. B. Powers	H4-65	1		
V. J. Rohay	H6-06	1		
M. A. Tredway	R3-54	1		
D. B. Tullis	L6-57	1		
B. G. Tuttle	N3-06	1		
T. M. Wintczak	H6-27	1		
J. J. Zimmer	H4-67	1		
Central Files (original + 3)	H4-22	3 2		
EDMC (2)	H6-08	2		
ERSS Files (3)	H4-67	3		
Docket Files	H5-36	2		

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