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ARID SITE CHARACTERIZATION AND TECHNOLOGY ASSESSMENT: VOLATILE ORGANIC COMPOUNDS - ARID INTEGRATED DEMONSTRATION

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Summary

Areas of common technology interests between the Volatile Organic Compounds-Arid Integrated Demonstration (VOC-Arid ID) and selected U.S. Department of Energy (DOE) arid and semiarid sites were identified based on identification, evaluation, and integration of the following information: 1) technologies currently being assessed in the VOC-Arid ID program, 2) data on subsurface contamination at DOE arid and semiarid sites, and 3) assessments of perceived technology needs to support waste site remediation activities at other DOE arid/semiarid sites.

Technologies under evaluation as part of DOE's VOC-Arid ID program fall into seven technical categories: 1) drilling and access technologies; 2) monitoring VOCs in situ and ex situ; 3) characterization (i.e., sampling and analysis) of chemical, geologic, and hydrologic properties; 4) enhanced extraction or containment of VOCs; 5) ex situ treatment of VOCs and co-contaminants; 6) in situ treatment (i.e., destruction) of VOCs and co-contaminants; and 7) data interpretation and design and evaluation of remediation systems. Specific technologies are identified in each category and the rationale for their need are described.

Subsurface contamination is described for 12 sites that were selected from a screening of 8 DOE arid/semiarid sites, using the chemistry of the subsurface of the Hanford Site's 200 West Area as a guideline. Sites selected contained known VOC contamination in the vadose zone and/or groundwater and, in many cases, also contained co-contaminants. The general nature of subsurface contamination ranged from complex mixtures in the vadose zone and/or groundwater to contamination confined to a limited area of the vadose zone and separated by hundreds of meters (hundreds to thousands of feet) from the underlying uncontaminated aquifer.

Technology needs for the 12 selected sites were assessed based on information gathered through discussions with technical professionals familiar with environmental restoration activities at their sites and documents that address characterization and environmental restoration activities. This information was used in combination with VOC-Arid ID program technologies to identify areas of common interest between Hanford's VOC-Arid ID and other DOE arid/semiarid sites. Ex situ treatment and monitoring technologies appeared to be areas of greatest common interest; however, it is anticipated that interest in the broader spectrum of VOC-Arid ID technologies will increase as characterization data become more available and remediation strategies are identified and implemented at DOE sites.

Technology development, evaluation, and deployment at DOE sites is a dynamic process. Readers of this report, therefore, are encouraged to provide constructive

comments on improving the accuracy and completeness of site characterization information and technology activities and how they were depicted in relation to VOC-Arid ID for sites described herein. All feedback will be given serious consideration for inclusion in future updates of this report. All comments should be addressed to VOC-Arid ID Coordinator, Steve Stein, at Pacific Northwest Laboratory, Seattle Research Center, 4000 N.E. 41st Street, Seattle, WA 98105 or the VOC-Arid ID Pacific Northwest Laboratory Program Manager, Tom Brouns, at Pacific Northwest Laboratory, P.O. Box 999, MS K6-80, Richland, WA 99352.

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1.0 Introduction

The U.S. Department of Energy's (DOE's) Volatile Organic Compounds-Arid Integrated Demonstration (VOC-Arid ID) program was initiated in March 1991 to evaluate technologies for all phases of remediation of VOCs in soils and groundwater at DOE arid/semiarid sites. The primary site for field demonstrations under the VOC-Arid ID program is the Hanford Site.

The purpose of this report is to describe 1) the bases for technologies currently under evaluation in the VOC-Arid ID program; 2) the types of subsurface contamination at DOE arid/semiarid sites; and 3) the areas of potential common technology interests based on perceived technology needs at other DOE sites.

This report was compiled by Pacific Northwest Laboratory[a] in response to DOE's Office of Technology Development's mission to carry out an aggressive program to accelerate the development and implementation of new and existing technologies to meet a 30-year goal set by DOE in June 1989 to clean up all of its sites and to bring all sites into compliance with current and future environmental regulations. A key component of this program is the development of technologies that are better, faster, safer, and cheaper than those technologies currently available.

Included in this report are an evaluation of technologies currently (fiscal year 1993) being pursued at the Hanford Site under the auspices of the VOC-Arid ID program (Section 2.0), an assessment of subsurface contaminants at arid/semiarid sites (Section 3.0), a summarization of technologies under consideration at other DOE sites (Section 4.0), a discussion of areas of potential common technology interests (Section 5.0), and the conclusions (Section 6.0). Also included are Section 7.0 (references cited in the text of the report); Appendix A, a summary of the extent of contamination at the DOE arid/semiarid sites under consideration; and Appendix B, a bibliography of source documents from which this report was prepared.

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2.0 Arid Technology Evaluation

The bases for the technologies currently being evaluated in the VOC-Arid ID program are summarized in Table 1. The technical areas, needs, and proposed technology solutions described are dynamic and subject to modification. The modifications would be based on the relative success of technology development and demonstration at the Hanford Site and augmented with the guidance/support that the program can obtain from other technical assessments (e.g., Chem-Nuclear Geotech, Inc. 1991; Junk 1992), experiences, needs, capabilities, information exchange, and collaboration with other DOE sites, universities, and the private sector. University participation is promoted through the subcontract process, and capabilities in the commercial sector are solicited through procurements or establishment of Cooperative Research and Development Agreements.

Technology development and demonstration by the VOC-Arid ID program are currently being driven by two factors:

- the need to provide the next generation of technology supporting the DOE's ongoing Environmental Restoration Program, such as the Expedited Response Action in the Hanford Site's 200 West Area; there, current technology is focused on the vacuum extraction of large quantities (hundreds of metric tons) of carbon tetrachloride (CCl_4) from the vadose zone underlying three cribs

- the need to develop and demonstrate technologies that can be deployed to address subsurface VOC contamination at all DOE's arid sites (and measure remediation effectiveness) especially where remediation may be significantly impacted by the presence of co-contaminants (e.g., heavy metals, radionuclides, significant quantities of other semivolatile and nonvolatile organics).

Example near-term technology needs include 1) sensors for real-time monitoring of VOCs in vacuum-pumped gas streams, vadose zone, and groundwater and 2) cost-effective ex situ treatment of VOCs and associated co-contaminants in gas and liquid streams. In parallel, there is a need for more efficient and effective deployment and application of advanced tools for characterization of the vadose zone and groundwater underlying the site. Associated with some of these tools are devices that will allow their effective deployment in the subsurface. Information from demonstration of such tools will provide 1) insight on VOC depletion from the vadose zone; 2) data for planning the demonstration of the remediation of residual VOCs and associated co-contaminants, based on developing in situ and ex situ treatment technologies; and 3) development of complex data integration/interpretation capabilities and predictive tools to enhance statistical evaluation and assessment and to design, monitor, and control technology deployment. Applied in situ technologies emphasize biodegradation, chemical destruction, enhanced removal, or techniques to remove (bulk or residual VOCs) or contain VOCs in the ground. In the case

of in situ technologies, better access to the vadose zone and/or groundwater is needed to increase the potential for success of in situ treatment. This issue is being addressed through the testing of directional drilling and penetration techniques and use of novel multiscreened wells to enhance both physical and biological treatment.

Table 1 Technology Evaluation: Volatile Organic Compounds - Arid Integrated Demonstration

Technology Category	Technology Requirement	Selected Technology
Drilling and access technologies for subsurface characterization, monitoring, and remediation	Access to the subsurface to sample or characterize the extent of contamination, install monitoring systems for compliance or process control, or install injection or extraction wells for remediation. Techniques are needed to minimize secondary waste generation and reduce costs	1. Sonic drilling (vertical and angle) 2. Horizontal drilling with air turbine tool 3. Cone penetrometer
VOC monitoring in situ and ex situ	Real-time or near-real-time monitoring of VOCs for off-gas compliance, worker health and safety, site boundary release, or to evaluate remediation performance and/or compliance in boreholes, sediments, and groundwaters	1. HaloSnif, optical emission sensor 2. Portable acoustic wave sensor 3. Fiber-optic sensor, solvochromatic dye and reagent based 4. Odyssey chlorinated hydrocarbon sensor
Characterization (sampling and analysis) of chemical, geologic, and hydrologic properties	More representative and cost-effective methods for sampling or detecting VOCs, characterizing subsurface stratigraphy, detecting dense nonaqueous-phase liquid, or organic, metal, or radionuclide co-contaminants, and measuring contaminant flux	1. Science and Engineering Associates, Inc., Membrane, Instrumentation and Sampling Techniques (SEAMIST) 2. Borehole sampler, borehole soil-gas, and groundwater-sampling tool 3. Borehole geophysical logging 4. Supercritical fluid extraction, field screening for organic contaminants 5. Unsaturated flow apparatus for vadose zone soil properties 6. Surface and cross-borehole seismic tomography 7. Soil-gas flux-measurement systems 8. Cone penetrometer with rugged, integrated sensor systems

Table 1 (contd)

Technology Category	Technology Requirement	Selected Technology
Enhanced extraction or containment of VOCs	Methods to enhance extraction or removal of VOCs from saturated and unsaturated soils, or subsurface containment of these highly mobile contaminants	1. Six-phase ohmic heating of arid soils (VOC-Arid ID and nonarid IDs) 2. Passive VOC extraction using barometric pumping 3. In situ vapor stripping of VOCs in groundwater 4. Viscous fluid or thermal precipitation barriers (In Situ Remediation Integrated Program and VOC-Arid ID)
Ex situ treatment of VOCs and co-contaminants	Processes to reduce the cost of treatment or recovery of VOCs and co-contaminants from extracted soil gas or groundwater	1. Off-gas membrane separation 2. Steam reforming for granular-activated carbon regeneration 3. Tunable hybrid plasma for in-line destruction 4. Supported liquid membranes for co-contaminant (metals, radionuclides) removal from groundwater
In situ treatment (destruction) of VOCs and co-contaminants	Methods to destroy organic contaminants in saturated or unsaturated soils to "polish" residual contamination, or for bulk contaminant destruction to minimize the costs of extraction and treatment	1. In situ corona destruction for vadose zone soils (In Situ Remediation Integrated Program, VOC Nonarid ID, VOC-Arid ID) 2. In situ groundwater bioremediation (anaerobic, aerobic)
Data interpretation and design and evaluation of remediation systems	Methods, algorithms, and hardware to collect, interpret, integrate, and display chemical, geologic, and hydrologic site data to facilitate decision making. Tools to allow cleanup staff to design and evaluate the performance of alternative remediation systems. Methods and hardware to collect the necessary contaminant data for conceptual model development, remediation design, and evaluation	1. Data fusion for site characterization and monitoring (Characterization, Monitoring, and Sensor Technology Integrated Program and VOC-Arid ID) 2. Engineering simulator/predictive tool 3. Dual-gamma analysis of three-phase fluid properties 4. Unsaturated flow apparatus for VOC transport properties

3.0 Subsurface Contaminant Assessment

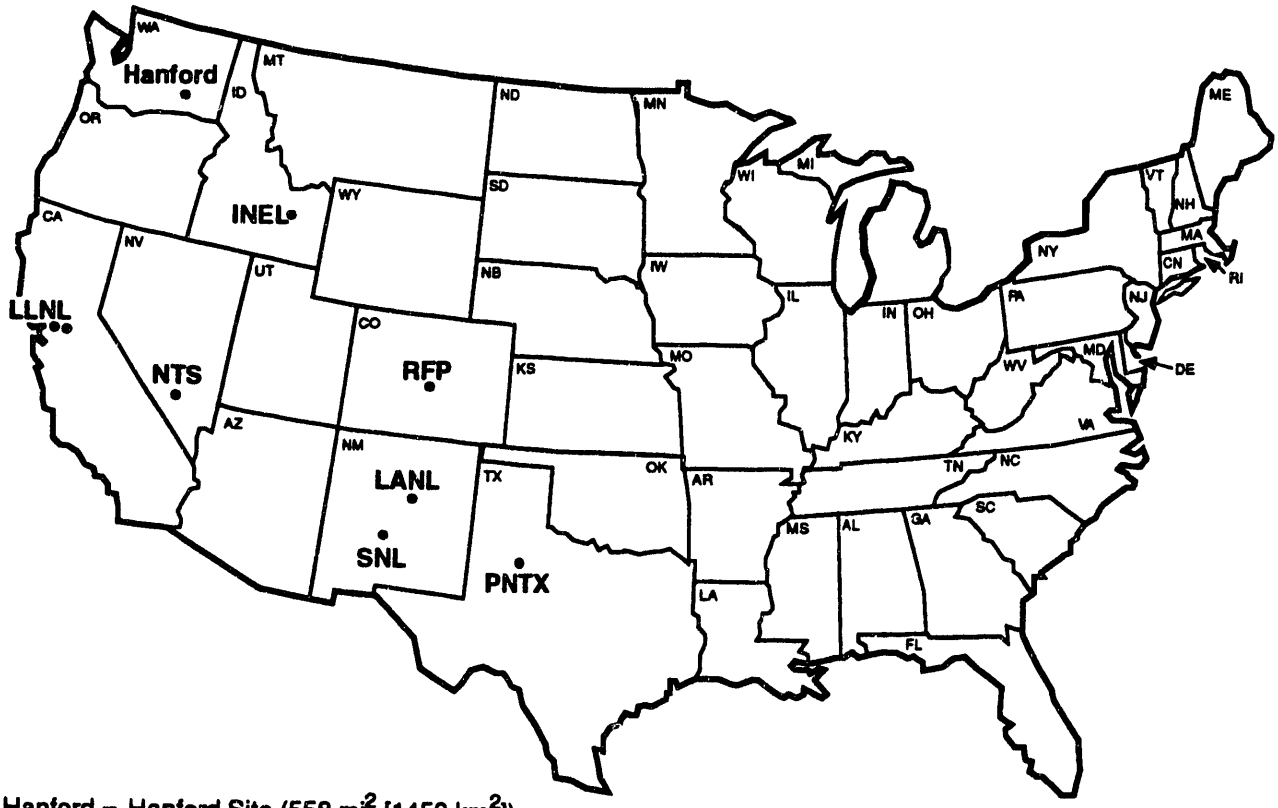
Because the primary focus of the program is the VOCs in the vadose zone and/or groundwater of arid/semiarid sites, with an emphasis on CCl_4 and associated co-contaminants (e.g., metals, anions, radionuclides, and other organics), sites at eight DOE installations with similar subsurface environments (Hanford Site, Idaho National Engineering Laboratory, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Nevada Test Site, Pantex Plant, Rocky Flats Plant, and Sandia National Laboratories; Figure 1) were selected, based on a history of subsurface VOC contamination, for assessment.

The general nature of the subsurface contamination at the selected sites is summarized in Table 2. The contamination ranges from complex mixtures in the vadose zone and/or groundwater (e.g., surface disposal of wastes or injection of wastes into deep wells) to contamination confined to a limited area of the vadose zone and separated by hundreds of meters (hundreds to thousands of feet) from the underlying uncontaminated aquifer. More specific descriptions of the nature of subsurface contamination at selected sites can be found in Appendix A. References used to obtain the information provided in Appendix A are listed in Appendix B. Some general observations follow.

Significant concentrations (100 to 10,000 μg/L) of CCl_4 have been measured in groundwater (or perched water) at three sites: Hanford's 200 West Area, Idaho's Radioactive Waste Management Complex, and Rocky Flats' East Trenches/903 Pad Operable Unit 2. Like Hanford, the Idaho and Rocky Flats sites have a history of near-surface codisposal of VOCs with significant quantities of metals, anions, radionuclides, and other organics. The injection well at Idaho's Test Area North has been used to release VOCs, metals, and radionuclides to the underlying Snake River Plain aquifer, while the surrounding vadose zone has remained virtually unimpacted.

The chemistry of contamination at Livermore's Main Site differs from the more complex sites, in that it consists mainly of VOCs, though there are isolated areas of fuel hydrocarbon, tritium, and metals contamination. Contamination exists in both the vadose zone and groundwater at the Livermore site.

The main VOC contamination at Livermore's 834 Complex is trichloroethylene (TCE), commingled with other oily organics. The organic mixture is contaminating the vadose zone and a zone of perched water but not the underlying confined aquifer. Similarly, Pantex's Zone 12 contains a highly contaminated vadose zone (solvents, metals, pesticides, polychlorinated biphenyls, fuel hydrocarbons, high explosives, uranium, etc.) and an underlying zone of perched water is contaminated with measurable quantities of chlorinated hydrocarbons, metals, and high explosives.



Hanford = Hanford Site (558 mi^2 [1450 km^2])

INEL = Idaho National Engineering Laboratory (894 mi^2 [2316 km^2])

LLNL = Lawrence Livermore National Laboratory (Main Site 1.3 mi^2 [3.4 km^2]; Site 300 10.2 mi^2 [26.4 km^2])

LANL = Los Alamos National Laboratory (43.5 mi^2 [112.7 km^2])

NTS = Nevada Test Site (965 mi^2 [2500 km^2])

PNTX = Pantex Plant (15.9 mi^2 [41.2 km^2])

RFP = Rocky Flats Plant (10.2 mi^2 [26.4 km^2])

SNL = Sandia National Laboratories (11.6 mi^2 [30.1 km^2])

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Figure 1 Location and Size of Selected Arid/Semiarid Sites

The Los Alamos and Sandia waste sites contain VOCs codisposed with other chemical contaminants. At these sites, contamination appears to be limited to the vadose zone, though trace concentrations of TCE have been detected recently in the underlying groundwater aquifer at Sandia's Chemical Waste Landfill. Areas of perched water have not been detected at these sites.

Table 2 Subsurface Contamination at Selected Arid/Semiarid Sites

Location	Volatile Organic Compounds	Metals	Anions	Radionuclides	Other Organics
Hanford Site					
200 West Area	G,S (CCl_4)	P(G,S)	P(G,S)	P(G,S)	P(S)
Idaho National Engineering Laboratory					
Radioactive Waste Management Complex	G,S (CCl_4)	P(S)	P(S)	P(S)	P (S)
Test Area North	G,S	P(G)		P(G)	
Lawrence Livermore National Laboratory					
Main Site	G,S	P(G)		P(G,S)	P(G,S)
Site 300	G,S				P(G,S)
Los Alamos National Laboratory					
Test Area 54	S	P(S)			P(S)
Nevada Test Site (no data)					
Pantex Plant					
Zone 12	G,S	P(G,S)		P(S)	P(G,S)
Rocky Flats Plant					
Operable Unit 1	G,S	P(G,S)	P(G)	P(G,S)	
Operable Unit 2	G (CCl_4), S	P(G)	P(G)	P(G)	
Operable Unit 4	G,S	P(S)	P(G,S)	P(G,S)	
Sandia National Laboratories					
Chemical Waste Landfill	G,S	P(S)	P(S)		P(S)

G = Measured in groundwater.
S = Measured in soil/sediment or soil gas.
P = Present based on historical record or measurement data.

4.0 Technology Considerations: Other DOE Sites

This section summarizes technology needs at DOE arid and semiarid sites other than Hanford. Information resources for this section included 1) discussions with technical professionals familiar with environmental restoration activities at the sites discussed in Section 3.0 and 2) review of the technical information documents referenced in Appendix B.

Idaho National Engineering Laboratory

Radioactive Waste Management Complex

Vacuum extraction of VOCs from the vadose zone is being considered as a possible option, with subsequent ex situ treatment (catalytic destruction of VOC vapors). Enhanced modeling capabilities are needed to predict vadose zone transport of VOCs in a complex subsurface environment, consisting of fractured basaltic lava flows with layers of sedimentary interbeds. From this perspective, interest has also been expressed in the capabilities of the unsaturated flow apparatus (UFA™; Beckman Instruments, Inc., Palo Alto, California). Reliable sampling and analytical tools (e.g., renewable vapor-phase sensor) are needed to measure vapor-phase VOCs and solid/liquid VOCs in fractured basalts. Along these lines, interest has been expressed in the cone penetrometer and its linkage to rugged integrated sensor systems.

As the designated site for the conduct of the Buried Waste Integrated Demonstration (BWID) program, other areas of technology needs include 1) intrusive (e.g., locating critical radiological and chemical risk assessment source terms) and nonintrusive site characterization; 2) nondestructive assay; 3) waste retrieval, followed by ex situ treatment; 4) ex situ treatment (pretreatment, primary and secondary [e.g., off-gas-treatment technology]) and in situ treatment, followed by long-term monitoring or retrieval; 5) retrieval, followed by in situ stabilization or retrieval; 6) contaminant/waste containment and stabilization; and 7) waste disposal/storage.

Test Area North

Remediation strategies for the Test Area North/Technical Support Facility injection well are currently focused on removal (bailing of sludges and solids and removing a potentially present VOC liquid layer) of contaminants and contaminated materials from source term and treatment of groundwater. There does not appear to be a need for vadose zone characterization/treatment because of the history of the nature of disposal. A Resource Conservation and Recovery Act of 1976 (RCRA)-permitted water-treatment facility is to be used at the injection well to pump and treat (carbon adsorption of VOCs, ion exchange

of metals and radionuclides) the groundwater. More cost-effective methods for ex situ treatment of contaminated groundwater are of interest. Consideration is being given to testing a German in situ air-stripping technology for removing VOCs from peripheral wells. In situ bioremediation is a possible option for consideration at this site.

Lawrence Livermore National Laboratory

Main Site

At Livermore's Main Site, a "smart" remediation strategy is being implemented that involves pumping and treatment of groundwater, subsurface characterization (lithology and contaminant distribution), and modeling. Subsurface characterization information and modeling are used to direct pump-and-treat activities (e.g., rate and duration of pumping, selection of wells to pump), including the evaluation of pump-and-treat performance and the close monitoring of VOC distribution to prevent movement into less permeable zones (making matters worse). Subsurface data (e.g., distribution coefficients, retardation factors, and lithology) and advances in model development are needed to improve 1) predictive models where data obtained from additional well placement may be limited and 2) pump-and-treat strategy design and performance.

Vacuum-induced venting is currently being evaluated for application at selected vadose zone source terms of VOC at the Main Site. Deployment of the "smart" remediation strategy currently suggests a 30-year time frame for restoration of the groundwater. Improvements in the overall strategy are anticipated to reduce restoration time.

Site 300

834 Complex

Soil-vapor extraction is currently being evaluated for the removal of VOCs (i.e., TCE) from the vadose zone in low-permeability sediments. Generation of high vacuum in the vadose zone has led to mounding of the shallow water table, resulting in the need to simultaneously remove water to the surface for treatment. The presence of oily co-contaminants in the extracted water led to emulsions that made simple aeration for the removal of TCE difficult. Manifolding to a greater number of wells, coupled with lower vacuum, has allowed for the separation of vapor extraction and liquid pumping. Future treatment of the liquid includes skimming of the oily material prior to aeration. Vapor-phase air-treatment activities include 1) in situ regeneration of adsorbant carbon by steam distillation/co-condensation of TCE and steam with TCE recovery from a phase separator, 2) pulsed high-energy ultraviolet light to photolyze the TCE in the vapor phase, and 3) pilot-scale pyrolysis. Vapor-stream monitoring will be by computer-controlled,

low-cost, dual-detector gas chromatography. In situ microbial filters in the shallow groundwater upgradient of the vacuum-induced venting system are being considered as a polishing technology.

Landfill Pit 6

Because the primary source of VOCs in groundwater is Landfill Pit 6 and because of the potential for offsite migration, remedial options under consideration include soil-vapor and groundwater extraction, with treatment of removed chemical by such approaches as volatilization to the atmosphere, thermal oxidation, ultraviolet/H_2O_2, carbon adsorption and recovery, and land farming/biodegradation.

Los Alamos National Laboratory

Technical Area 54

Los Alamos is currently taking voluntary corrective action at this site because of its desire to contain the VOC plume such that expansion of the adjacent radioactive waste site toward the chemical waste site can be done without potentially creating an area of mixed waste. Interest is focused on characterization of the surge beds. Along this line, interest has been expressed in 1) the drilling of a new borehole for testing of the SEAMIST device to obtain information on the vertical extent of VOC contamination and 2) the permanent finish of the port with the SEAMIST bed for continuous monitoring. There is also interest in some form of in situ barrier technology (e.g., active biobarrier) that could be placed at the intersection of the surge beds and boreholes to eliminate the vertical transport of VOCs via open boreholes. Technology to cost effectively determine contaminant distribution coefficients in unsaturated rock and other porous media would be valuable in understanding contaminant sorption behavior as a function of the remediation strategy applied.

Nevada Test Site

The technology needed at this site is unknown at this time.

Pantex Plant

Site characterization activities are in the early stages of development and are being carried out under a RCRA permit. These activities have consisted of soil-gas surveys and analyses of perched water and sediment samples from well-drilling activities. Evaluation of results to date indicate a subsurface that consists of tight clay and caliche layers.

Characterization work to date has not identified any significant groundwater (perched water) plumes. Because of the highly impermeable nature of the subsurface underlying Pantex, the focus is on the conduct of sufficient cost-effective subsurface characterization to identify the best remediation strategies. Interest has been expressed in field-transportable analytical technologies, including real-time measurement devices to further characterize the site and reduce characterization costs.

Rocky Flats Plant

Operable Unit 2

Vacuum extraction of VOCs in the vadose zone is being considered a possible option for treating the VOC source term. Horizontal characterization of subsurface contamination is reasonably defined; however, the vertical distribution of contamination is not well-defined. Real-time sensor capability for measuring VOCs (and other contaminants, such as uranium) in vadose zone and groundwater would be valuable. In situ bioremediation is considered a promising technology for application at this site.

Operable Unit 4

There is extreme interest in the potential application of directional drilling techniques at this site. In addition, interest has been expressed in the VOC-Arid ID engineering simulator as a technique to evaluate bioremediation of nitrates.

Sandia National Laboratories

Chemical Waste and Mixed Waste Landfills

Areas of characterization technology needs include 1) in situ sensors and sampling devices (must include radionuclides) that are deployable with directionally drilled boreholes and membrane borehole liners, 2) sampling strategy and optimization for risk estimation (with application to directionally drilled holes), 3) nonintrusive characterization methods (for delineation of pit boundaries and estimating waste type and volumes), 4) field-screening characterization technologies (for metals, VOCs, and low-level radioactivity), 5) vadose zone postclosure monitoring (for metals, VOCs, and radionuclides), and 6) subsurface access and sampling. Sandia has an interest in future development of the cone penetrometer capabilities.

Areas of remediation technology needs include 1) in situ extraction (e.g., active and passive soil ventilation, soil washing, eletrokinetics), 2) transformation (e.g., reduce toxicity and mobility of contaminants), 3) containment (aboveground and belowground), and 4) stabilization (e.g., creating in situ waste forms by binding of waste to stabilization agents).

5.0 Areas of Potential Common Technology Interests

In this section, areas of potential common technology interests between the VOC-Arid ID program and other DOE installations are briefly described. Resources used for this assessment include Sections 2.0 and 4.0 and information gained from discussions with technical professionals familiar with environmental restoration strategies under implementation or consideration at specific sites. Table 3 summarizes the areas of potential common technology interest, based on integration of the different information resources. In integrating the information, the author, in some cases, took the liberty to infer possible interest in Hanford technology at other sites. For example, Livermore indicated application of soil-vapor extraction to selected vadose source terms. In application of this technology, they might be interested in ex situ VOC-monitoring tools under evaluation at Hanford. A blank in the table for selected technologies at specific sites does not imply lack of potential applicability of the technology at a site; rather, the table reflects information available to the author at the time of its preparation.

There appears to be a significant potential common interest in the areas of ex situ VOC destruction, separation, and monitoring technology. Several of the sites (Idaho, Livermore, Rocky Flats) are using or have plans to use vacuum-extraction technology for the removal of VOCs from the vadose zone. Ex situ treatment of VOC off-gas streams is currently being done with conventional technologies (e.g., carbon adsorption, aeration), with technology development at other sites focused on systems such as membrane separation and catalytic destruction.

There is a possible opportunity for collaboration on the application of fiber-optic sensors to off-gas streams containing CCl_4 between the VOC-Arid ID and Idaho's Radioactive Waste Management Complex or Rocky Flats' Operable Unit 2.

Common interest has also been expressed in the areas of characterization and monitoring technologies. For example, a few sites have expressed interest in advanced borehole completion techniques for testing of devices (such as SEAMIST), while others have expressed specific interest in in-situ sensors for measurement of VOCs (Rocky Flats) and metals and anions (Rocky Flats and Sandia). In the latter case, technology transfer is under way through Sandia's Mixed Waste Landfill ID for onsite analysis of metals in soils/sediments. The focus of Pantex is on the conduct of sufficient cost-effective subsurface characterization to justify the best possible remediation strategies; thus, the interest is in vadose-zone- and groundwater-monitoring tools. Possible opportunities for testing field-screening technologies for the measurement of organic co-contaminants include Idaho's Radioactive Waste Management Complex, Livermore's Site 300, and Rocky Flats' Operable Units 1 and 2.

Table 3 Areas of Potential Common Technology Interest at U.S. Department of Energy Arid/Semiarid Sites

Technology Category/Technology Type	Idaho		Lawrence Livermore		Los Alamos TA-54	Pantex Zone 12	Rocky Flats Op. Unit 1, 2, or 4	Sandia CWL/MWL
	RWMC	TAN	Main Site	Site 300				
Drilling and Access Technologies								
Sonic Drilling (vertical and angle)					X		X	X
Horizontal Drilling (air turbine tool)					X			X
Cone Penetrometer	X					X	X	X
VOC Monitoring (in situ/ex situ)								
HaloSnif	X	X	X	X			X	
Portable Acoustic Wave Sensor						X		
Fiber-Optic Sensor (solvochromatic dye and reagent based)	X					X	X	X
Odyssey Chlorinated Hydrocarbon Sensor	X	X	X	X			X	
Characterization (Sampling and Analysis)								
Membrane Sampling System (SEAMIST)					X	X		X
Bore Sampler (soil gas and groundwater)								X
Borehole Geophysical Logging	X					X		X
Supercritical Fluid Extraction (field screening)	X			X		X	X	
UFA™	X		X		X			
Seismic Tomography (surface and cross-borehole)	X							X
Soil-Gas Flux-Measurement Systems								
Cone Penetrometer/Integrated Sensors	X					X		X

Table 3 (contd)

Technology Category/Technology Type	Idaho		Lawrence Livermore		Los Alamos TA-54	Pantex Zone 12	Rocky Flats Op. Unit 1, 2, or 4	Sandia CWL/MWL
	RWMC	TAN	Main Site	Site 300				
Enhanced Extraction or Containment of VOCs								
Six-Phase Ohmic Heating								X
Passive VOC Extraction Using Barometric Pumping								X
In Situ Vapor Stripping (groundwater)	X	X		X			X	
Barriers (viscous fluid or thermal precipitation)	X				X			X
Ex Situ Treatment of VOCs and Co-Contaminants								
Off-Gas Membrane Separation	X	X	X	X			X	
Steam Reforming for Granular-Activated Carbon Regeneration	X	X	X	X			X	
Tunable Hybrid Plasma	X	X	X	X			X	
Supported Liquid Membranes		X						
In Situ Treatment (Destruction) of VOCs and Co-Contaminants								
In Situ Corona Destruction	X							
In Situ Groundwater Bioremediation (anaerobic, aerobic)		X		X			X	
Data Interpretation and Design and Evaluation of Remediation Systems								
Data Fusion								
Engineering Simulator/Predictive Tool	X		X		X		X	
Dual-Gamma Analysis of Three-Phase Fluid Properties								
UFA™	X		X		X			

CWL = Chemical Waste Landfill/MWL = Mixed Waste Landfill.
Op. Unit = Operable Unit.
RWMC = Radioactive Waste Management Complex.
TA = Technical Area.
TAN = Test Area North.

Interest has been expressed in developments in drilling and access technology. Rocky Flats is very interested in potential application of directional drilling techniques to their Operable Unit 4. Sandia and Idaho have expressed interest in application of the cone penetrometer to their site problems.

Of the sites expressing interest in in-situ microbiological destruction of VOCs, Rocky Flats' Operable Unit 2 appears to have the greatest commonality (and greatest opportunity for initial collaboration) with Hanford because of the presence of significant quantities of CCl_4. Other sites focused on possible application of in situ microbiological destruction of TCE in groundwater (e.g., Idaho's Test Area North and Livermore's Site 300) may be able to take advantage of knowledge gained from ongoing studies of bioremediation of CCl_4 in Hanford groundwater and bioremediation of TCE at the VOC-Nonarid ID (Savannah River).

Three sites (Idaho's Radioactive Waste Management Complex, Livermore's Main Site, and Los Alamos' Technical Area 54) expressed strong interest in obtaining cost-effective and reliable subsurface physicochemical and hydrologic data (e.g., diffusion coefficients, hydraulic conductivity, distribution coefficients, and retardation factors). These data will support characterization of their sites and will assist development and application of predictive tools to enhance performance assessment capabilities and to design, monitor, and control remediation technology deployment. There appears to be strong opportunity for future technology transfer of VOC-Arid ID UFA™ and remediation engineering simulator technologies to other DOE arid/semiarid sites. In the case of the engineering simulator technology, Rocky Flats has expressed interest in its potential application to bioremediation of nitrates in groundwater at Operable Unit 4.

6.0 Conclusions

The VOC-Arid ID program is evaluating a number of technologies that, through technology transfer, would improve the cost effectiveness of environmental restoration activities at DOE sites. Advanced technologies under investigation involve the areas of 1) drilling to obtain subsurface access; 2) VOC monitoring (in situ and ex situ); 3) characterization for sampling and analysis of chemical, geologic, and hydrogeologic properties; 4) enhanced extraction or containment of VOCs; 5) ex situ treatment of VOCs and co-contaminants; 6) in situ treatment (destruction) of VOCs and co-containments; and 7) data interpretation and design and evaluation of remediation systems.

Subsurface chemistry at Hanford's 200 West Area was compared to other DOE arid/semiarid sites that are contaminated by VOCs. Idaho's Radioactive Waste Management Complex and Rocky Flats' Operable Unit 2 indicated a history of subsurface disposal of CCl_4 and other co-contaminants comparable in complexity to Hanford. The nature of subsurface contamination at other sites appeared less complex (e.g., Livermore's Main Site), though this perception is likely to change at some sites (e.g., Pantex) as additional characterization data become available.

Information on technology under evaluation in the VOC-Arid ID program at Hanford was compared to technology needs at the other DOE arid/semiarid sites as a basis for identifying areas of potential common technology interests. Areas of potential common interest appear to be many, with opportunities for increased interest as additional data from contaminant characterization of DOE waste sites become available and remediation strategies are identified and implemented.

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Appendix A

Site Subsurface Characterization Summaries

Appendix A

Site Subsurface Characterization Summaries

Hanford Site

Aqueous and organic wastes containing carbon tetrachloride (CCl_4) from plutonium-recovery processes at the Hanford Site's Plutonium Finishing Plant (200 West Area) were discharged primarily to three liquid waste disposal facilities: the 216-Z-1A tile field, the 216-Z-9 trench, and the 216-Z-18 crib. An estimated 363,000 to 580,000 L[a] (96,000 to 153,000 gal)[a] of CCl_4 were disposed to the subsurface in the 200 West Area. Co-contaminants and/or degradation products include chloroform; mono-, di-, and tributyl phosphates; dibutyl butyl phosphonate; lard oil (a complex mixture of triglycerides); cadmium; nitrates; hydroxides; fluorides; sulfates; and various radionuclides, primarily plutonium and americium.

The CCl_4 plume (Figure A.1) covers at least 5 km^2 (1.9 mi^2), virtually all of Hanford's 200 West Area north and east of the CCl_4 discharge area. The highest concentration measured in the upper part of the aquifer (8700 μg/L) was found approximately 450 m (1476 ft) downgradient from the liquid disposal facilities. Concentrations of CCl_4, as high as 72.7 μg/mL (soil gas), were detected in underlying soils at a depth of 1.2 m (4 ft) (Figure A.2). Chloroform, trichloroethylene (TCE), and tetrachloroethylene were also detected in the soil gas at maximum concentrations of 10 to 100 times lower than CCl_4 (e.g., see chloroform plume map in Figure A.3). Other contaminants that partially intersect the groundwater plume include cyanide, fluoride, hexavalent chromium, TCE, nitrate, tritium, ^{99}Tc, ^{129}I, and uranium.

Idaho National Engineering Laboratory

Radioactive Waste Management Complex

At Idaho's Radioactive Waste Management Complex, several volatile organic compound (VOC) plumes (Figure A.4) have been identified in the vadose zone underlying the Solid Waste Disposal Area as a result of the release, prior to 1970, of 334,620 L (88,400 gal) of organic waste. This organic waste consisted of 90,847 L (24,000 gal) of

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(a) The referenced material, from which units cited in this report were taken, often used only English or only metric; therefore, for ease of cross referencing, this report gives both units of measure.

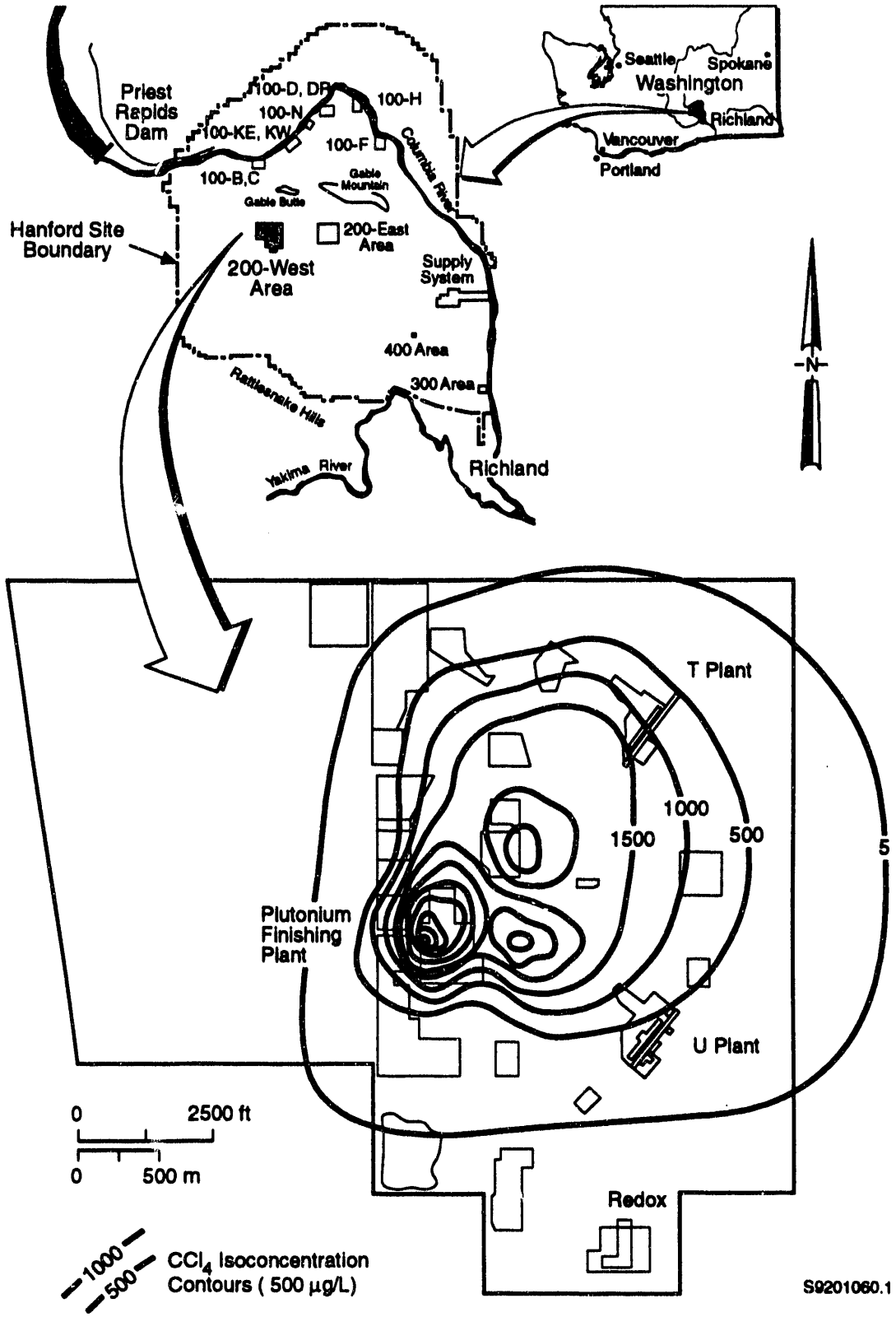

Figure A.1 Carbon Tetrachloride Groundwater Plume at Hanford's 200 West Area

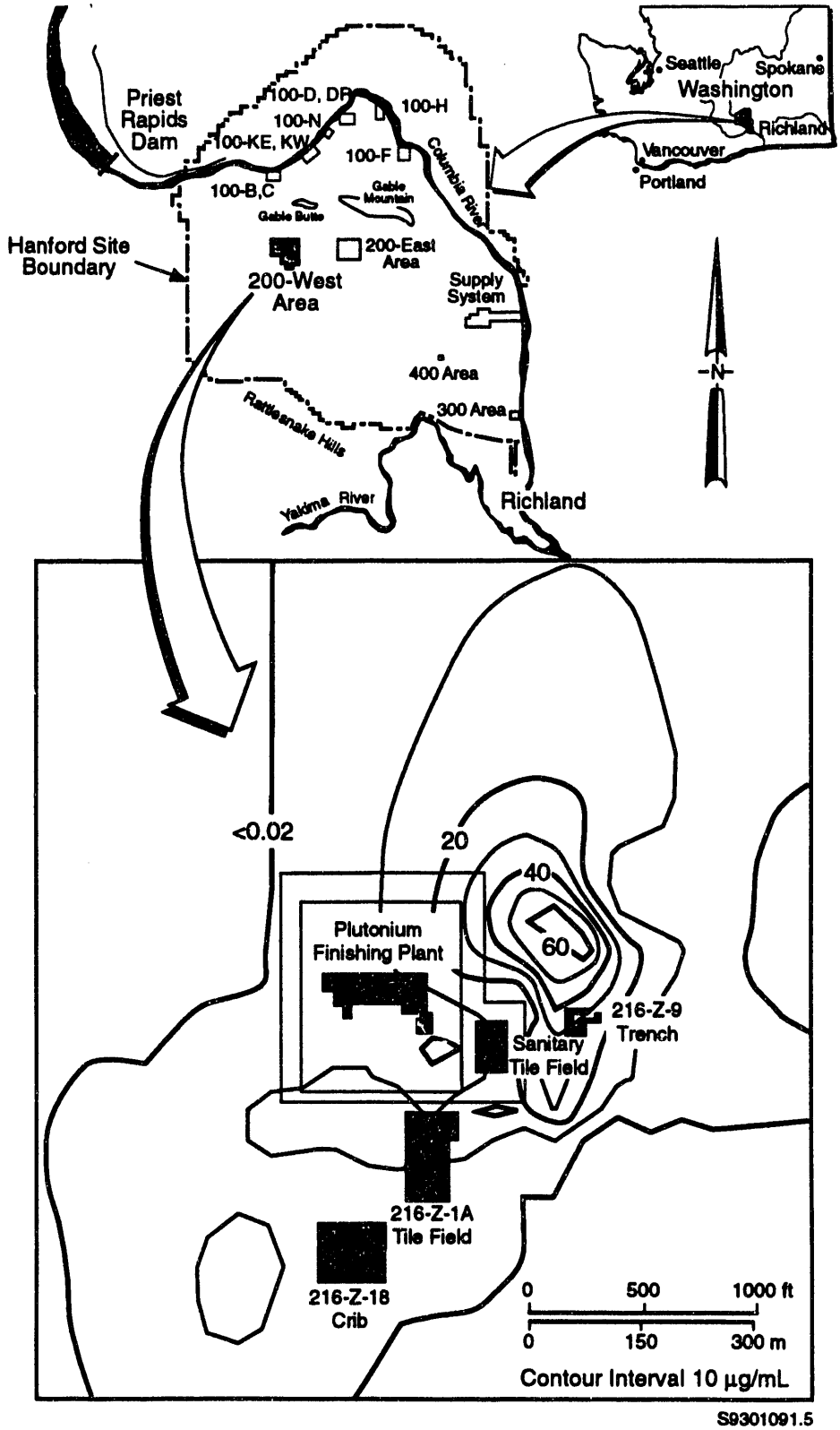

Figure A.2 Contour Map of Carbon Tetrachloride Concentrations in Soil Gas at Hanford's 200 West Area - May 1992

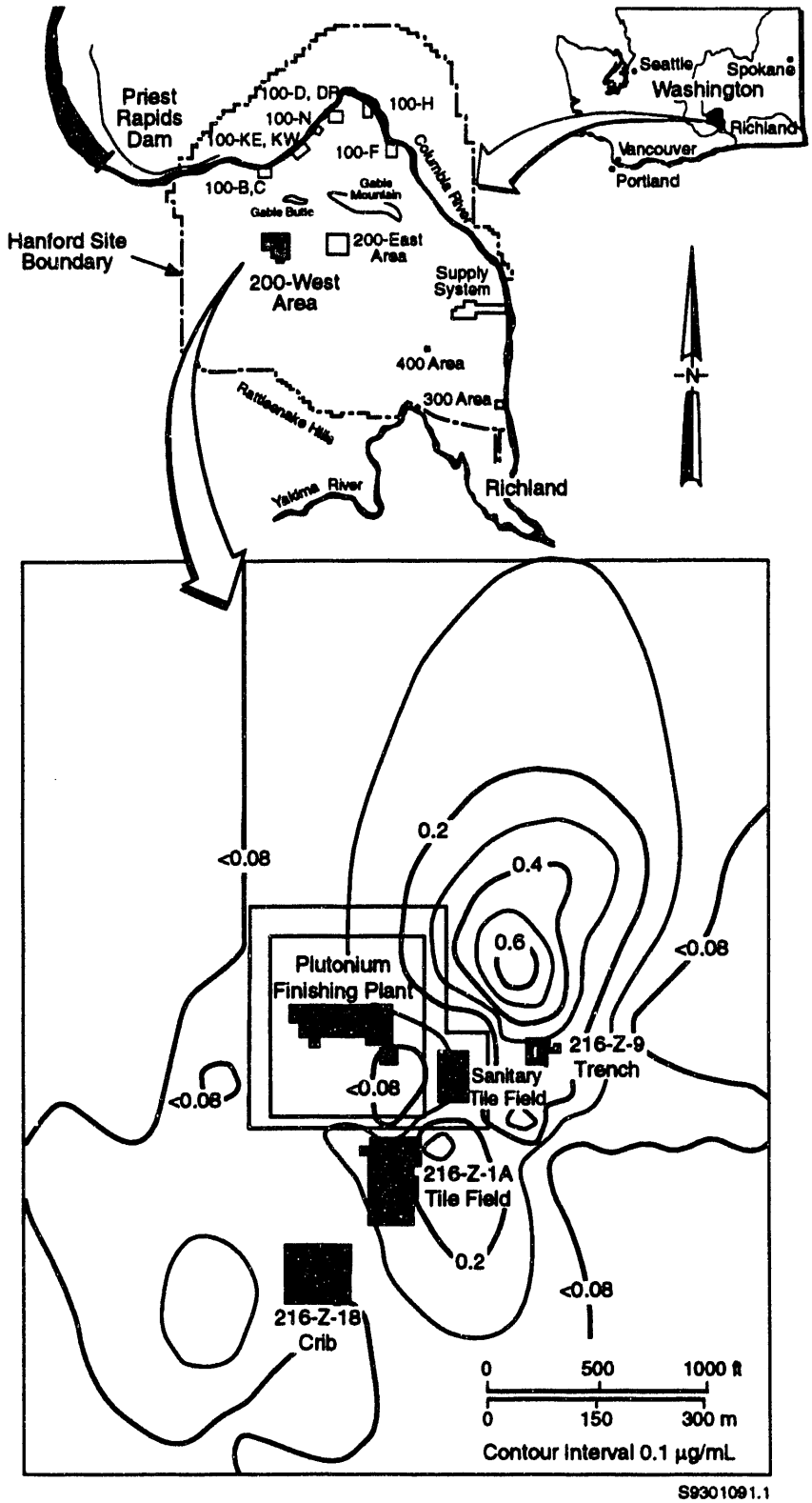

Figure A.3 Contour Map of Chloroform Concentrations in Soil Gas at Hanford's 200 West Area - May 1992

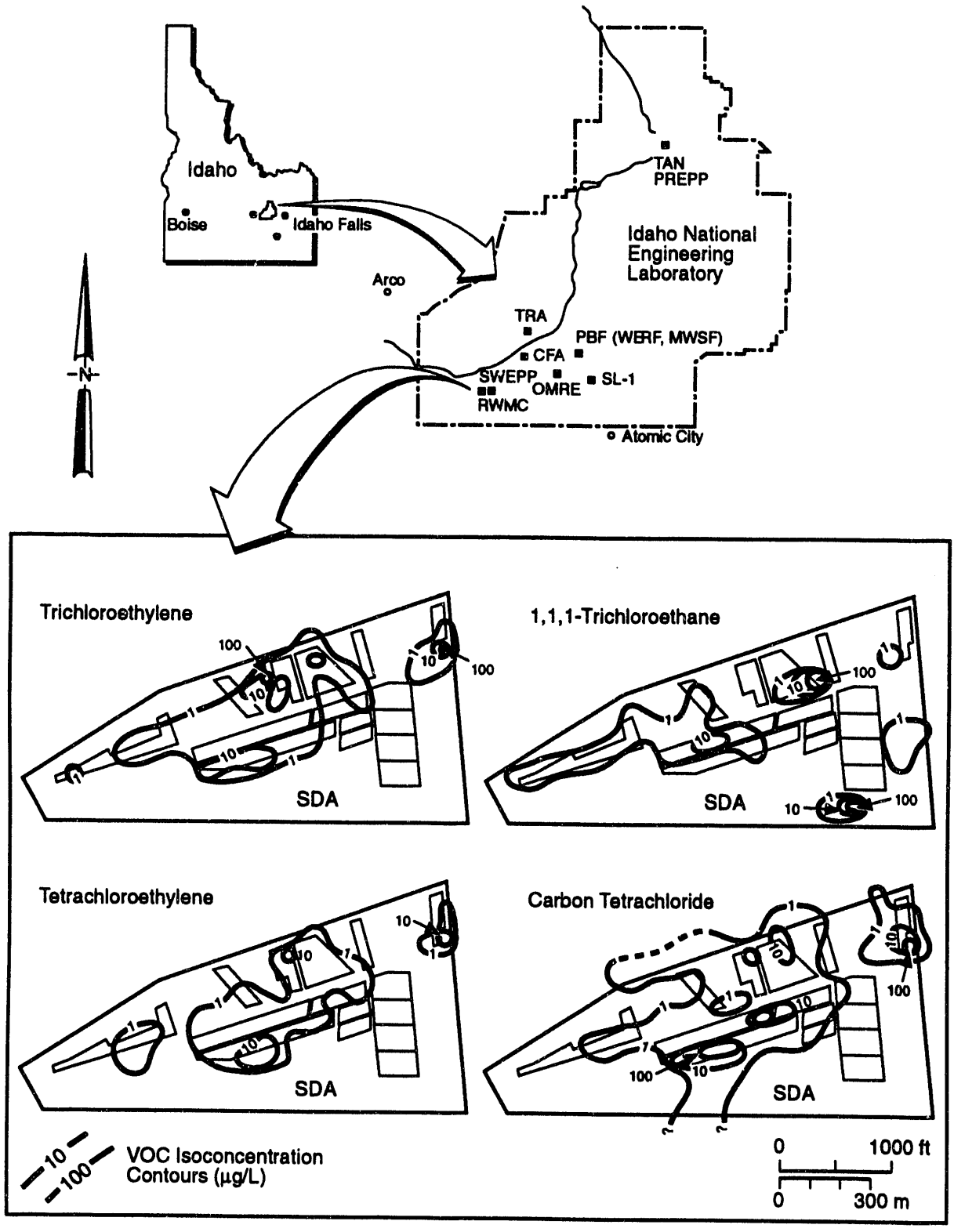

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Figure A.4 Volatile Organic Compound Vadose Zone Plumes at Idaho's Radioactive Waste Management Complex

CCl_4, 147,627 L (39,000 gal) of lubricating oil, and 94,633 L (25,000 gal) of other organic compounds (trichloroethane, TCE, tetrachloroethylene, toluene, and benzene). The VOCs in perched water at the Idaho site are shown in Figure A.5. Current data suggest that the confined aquifer has not been contaminated.

Test Area North

The Test Area North/Technical Support Facility injection well received low-level radioactive waste, process waste waters, and treated sanitary sewage. Suspected constituents disposed include mercury, lead, chromium, chlorinated solvents (e.g., TCE), and radionuclides (e.g., ^{90}Sr, ^{134}Cs, ^{137}Cs). Concentrations of VOCs at the bottom of the injection well have been measured at 35,000 μg/L. Discharge has been into the Snake River Plain aquifer, creating a TCE plume estimated to be 1.6 km (1 mile) wide and 3.2 km (2 miles) long. TCE concentration at the plume front has been measured at 7.5 μg/L (Figure A.6).

Lawrence Livermore National Laboratory

Main Site

The VOC contamination in groundwater includes approximately 85% of Livermore's Main Site and covers a total of 3.4 km^2 (1.3 mi^2) (involving areas of offsite contamination). A main source of the VOC contamination is believed to have been aircraft service operations conducted between 1942 and 1951 during Livermore Naval Air Station's and its successors' occupancy of the site. Offsite areas of contamination include a plume that extends 762 m (2500 ft) to the west onto private property and another plume 244 m (800 ft) south of the southeastern portion of the site onto U.S. Department of Energy property administered by Sandia National Laboratories (Figure A.7). The predominant VOC in the groundwater is TCE, exceeding 1,000 μg/L in the eastern site, with significant concentrations of tetrachloroethylene also present. Smaller quantities of six other chlorinated hydrocarbons (1,1-dichloroethylene, 1,2-dichloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, CCl_4, and chloroform) have been identified in the groundwater. The concentrations of VOCs in the vadose zone have been measured predominantly in the range of <5 to 500 μg/L, with levels exceeding 1000 μg/L in one area only. In some areas, VOC contamination is accompanied by fuel hydrocarbon contamination of the vadose zone (up to 11,000 μg/mL total fuel hydrocarbons) and groundwater (0.001 to 100 μg/mL total fuel hydrocarbons). Tritium (900 to 20,000 pCi/L), chromium, and lead have been identified in groundwater in isolated areas of the site.

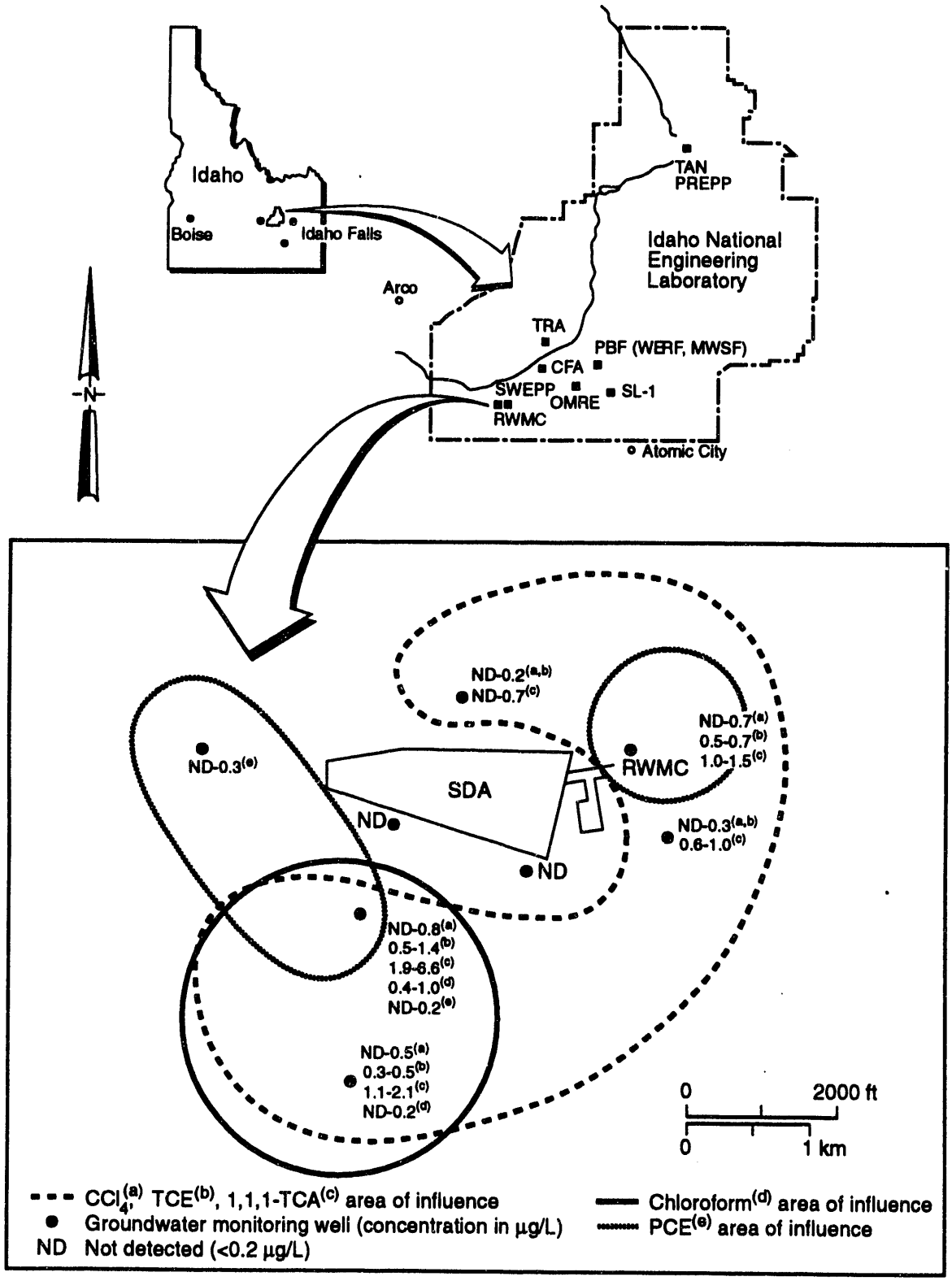

Figure A.5 Volatile Organic Compound Areas of Influence in Perched Water at Idaho's Radioactive Waste Management Complex

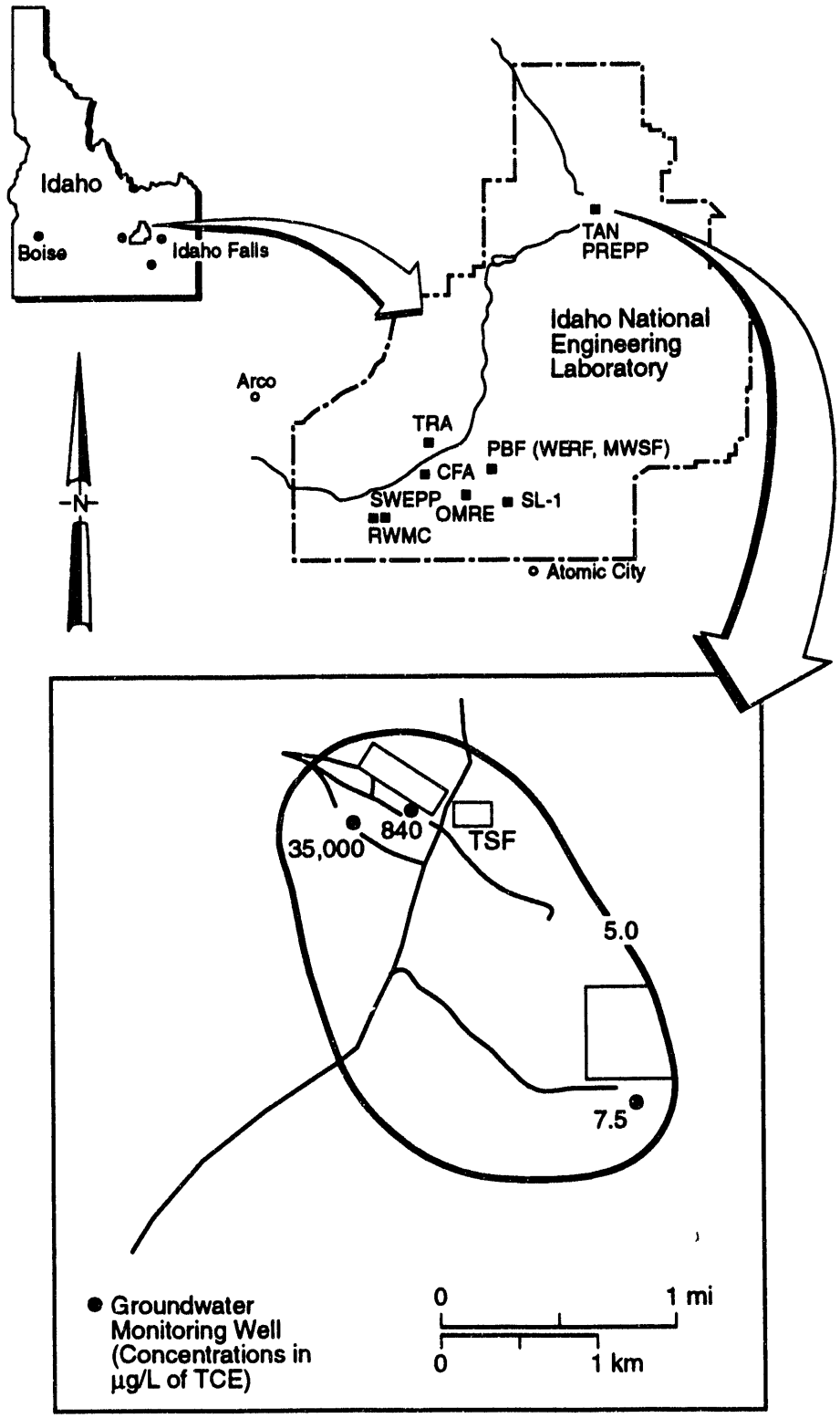

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Figure A.6 Trichloroethylene Groundwater Plume at Idaho's Test Area North

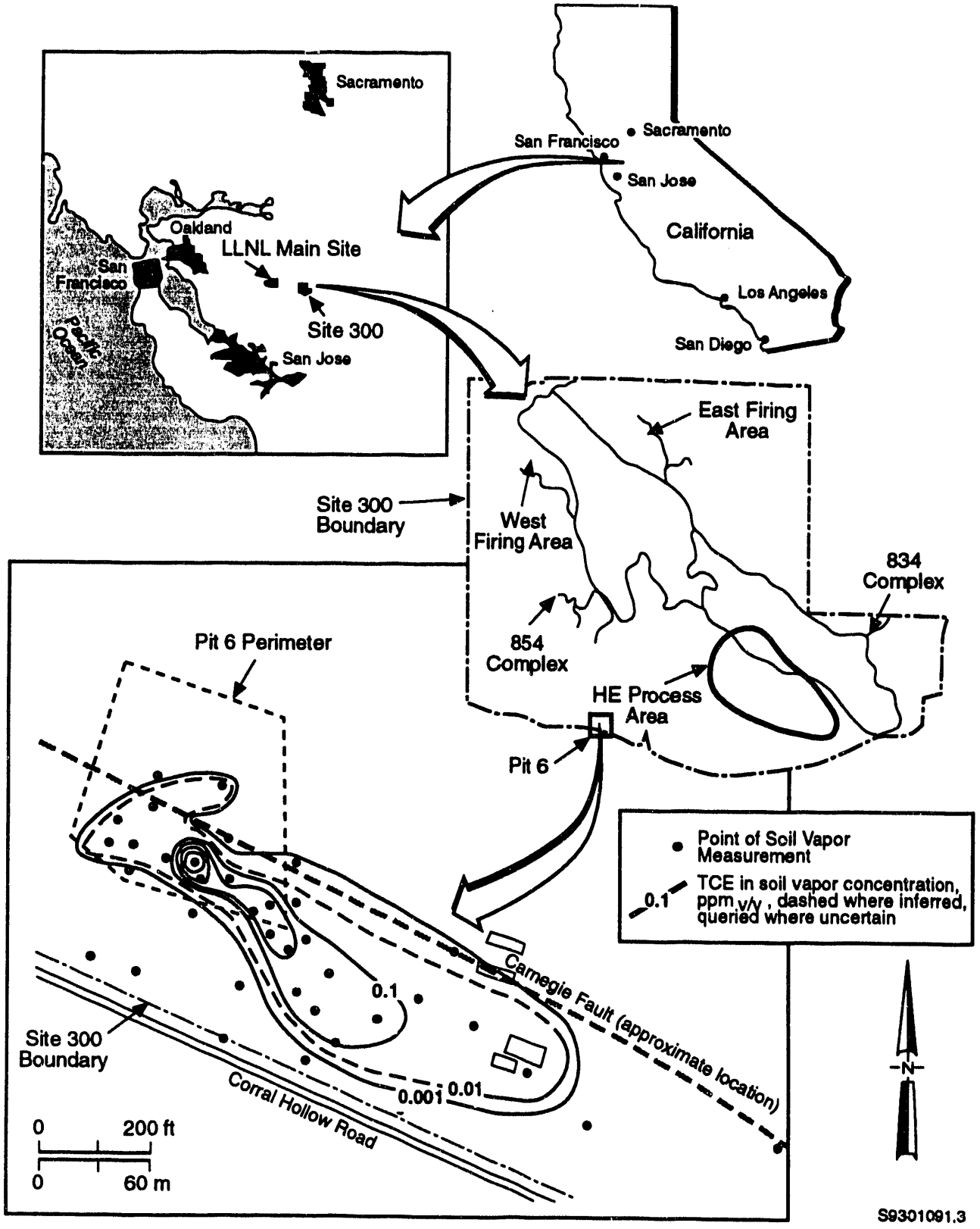

Figure A.7 Volatile Organic Compound Groundwater Plume at Livermore's Main Site

Site 300

834 Complex

The 834 Complex has been the source of leakage of TCE and other oily organic co-contaminants for a number of years into the surrounding ground. Vadose zone contamination consists of an approximate 4.3-m (14-ft) interval, 7.6 m (25 ft) below the surface, and approximately 91 m (300 ft) in diameter. The lower portion of soil contamination lies in perched water. The perched water plume extends approximately 0.4 km (0.25 mi) southwest of the 834 Complex, with VOC concentrations exceeding 100,000 μg/L at a distance of 122 m (400 ft) from the complex (Figure A.8). The perched water zone is bounded underneath by a dense clay layer, and there is no evidence of TCE migration through this clay layer to the underlying regional aquifer.

Landfill Pit 6

Landfill Pit 6 received organic, inorganic, and radioactive wastes for 9 years. Vadose zone contamination included polychlorinated biphenyls (PCBs) and other organic chemicals, beryllium, mercury, depleted uranium, and miscellaneous radioisotopes. Depth to the water-bearing zone underlying the pit averages 9.1 m (30 ft), with an average zone thickness of 6.1 m (20 ft). A TCE groundwater plume (183 m [600 ft] long by 76.2 m [250 ft] wide), moving at a rate of 45 m/yr (148 ft/yr) emanates from the southeastern corner of the pit (Figure A.9). The highest concentration of TCE measured in groundwater has been 250 μg/L. Other chlorinated hydrocarbons detected include tetrachloroethylene and 1,2-dichloroethylene. Significant concentrations of other organics (e.g., PCBs, explosives, fuel hydrocarbons), uranium, other inorganic constituents, and radioisotopes have not been detected in the groundwater. TCE has been detected in core samples as deep as 7.7 m (25.4 ft), with highest concentrations (330 and 450 μg/kg) at 1.8 and 2.7 m (6 and 9 ft), respectively. The distribution of TCE in the soil vapor (Figure A.10) closely resembles the distribution found in the groundwater. The maximum concentration of TCE detected in the soil gas was 160 μg/mL. The chlorinated hydrocarbons detected in the soil gas were tetrachloroethylene, 3.4 μg/mL; 1,1,1-trichloroethane, 0.61 μg/mL; 1,2-dichloroethane, 0.042 μg/mL; 1,1-dichloroethylene, 8.93 μg/mL; and 1,2-dichloroethylene, 0.003 μg/mL.

Los Alamos National Laboratory

Technical Area 54 served as the Los Alamos principal chemical waste disposal area from 1964 to 1985. Liquid wastes were disposed to a pit, and containerized wastes (with and without adsorbents) were disposed in 34 shafts (0.9 to 2.4 m [3 to 8 ft] dia. and 18.3 m [60 ft] deep) and spaced 4.6 m (15 ft) apart. Waste disposal logs indicate that the

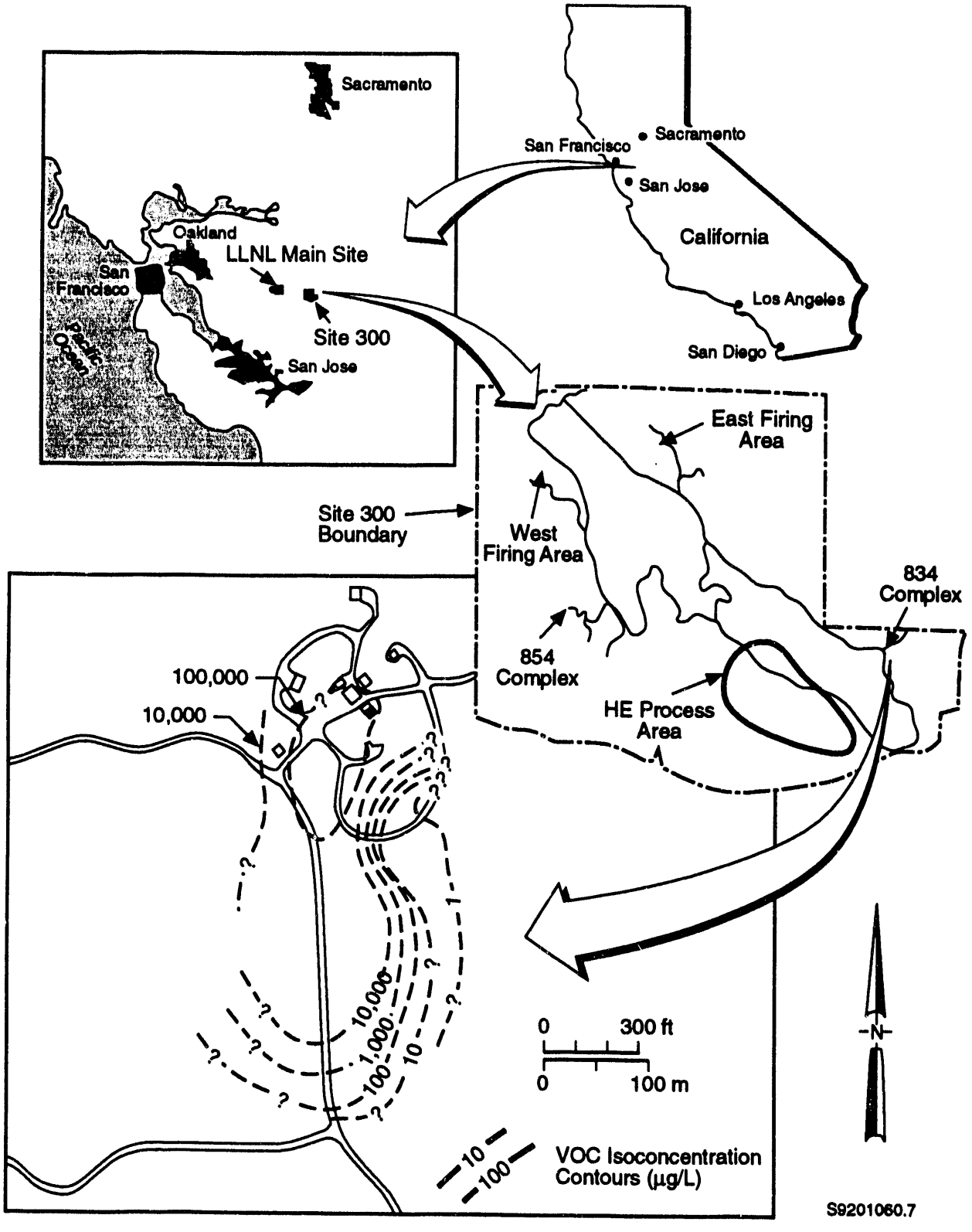

Figure A.8 Volatile Organic Compound Vadose Zone Plume at Livermore's 834 Complex

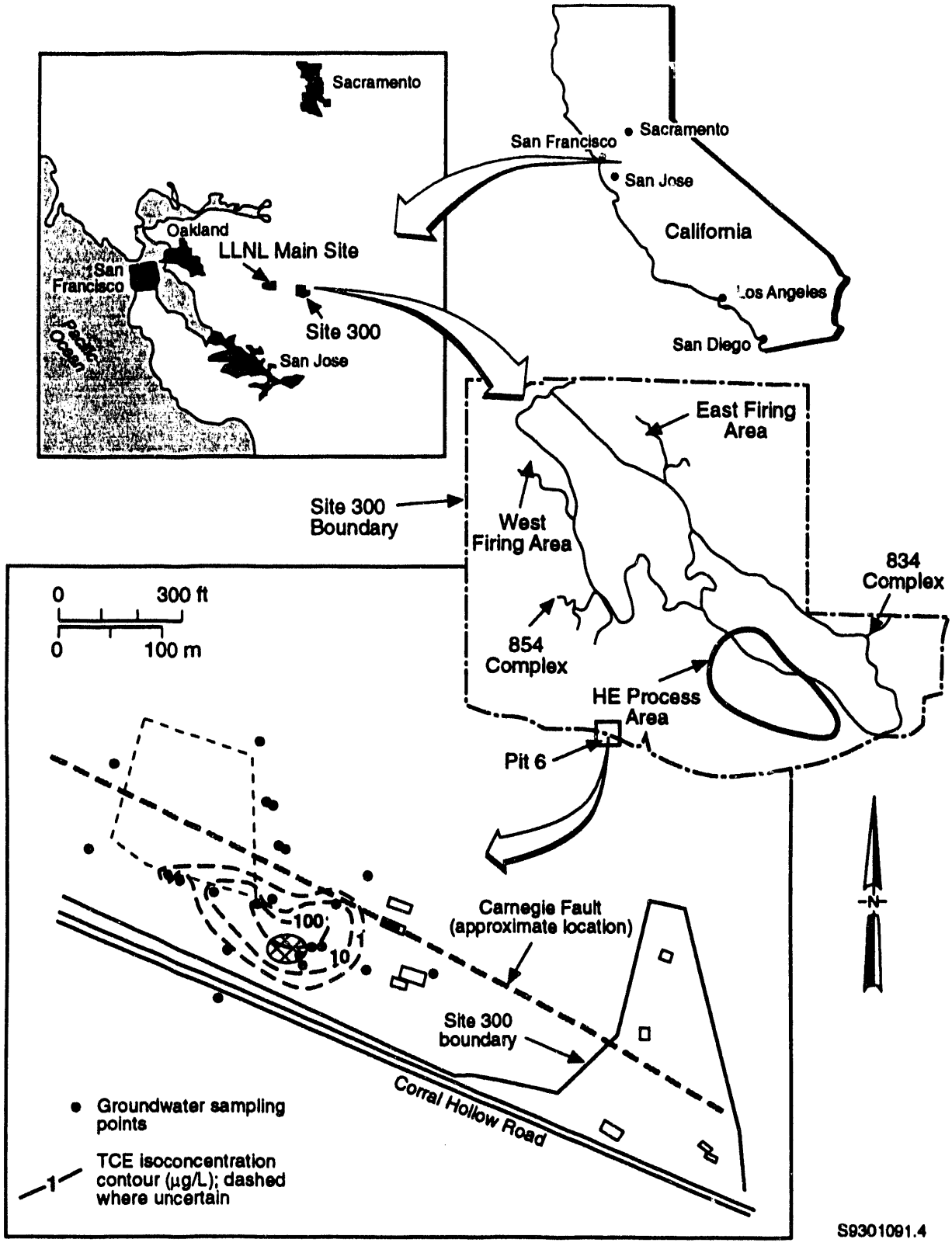

Figure A.9 Contour Map of Trichloroethylene Concentrations in Groundwater at Livermore's Landfill Pit 6

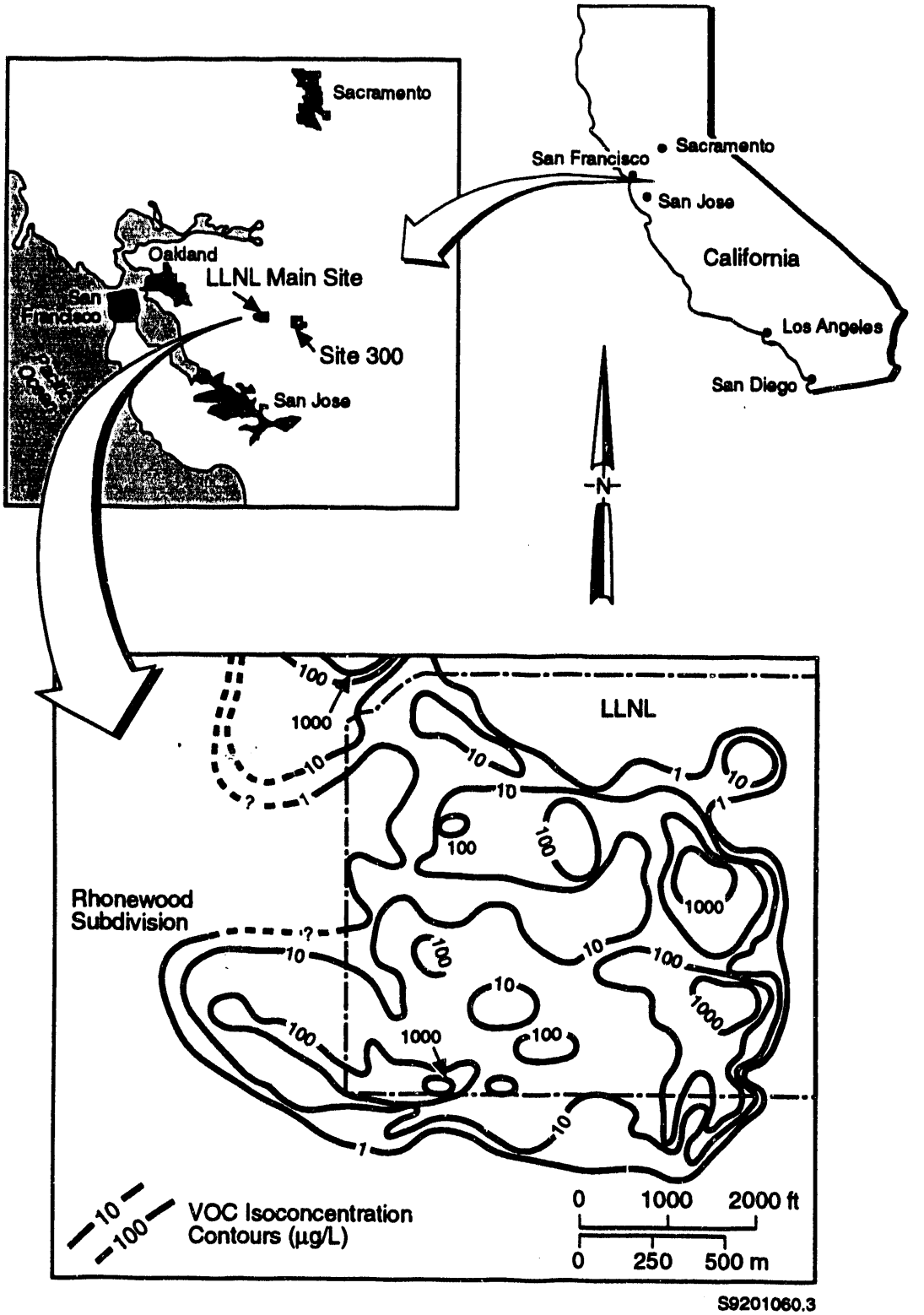

Figure A.10 Contour Map of Trichloroethylene Concentrations in Soil Vapor at Livermore's Landfill Pit 6

amounts disposed to individual shafts ranged from 798 to 15,505 kg (1762 to 34,227 lb). VOCs have been detected in rock core and pore gas samples (e.g., 171 μg/mL TCE) (Figure A.11). Aqueous transport of contaminants by unsaturated flow is not considered a viable mechanism for contaminant migration at this site. Near-vertical fractures in the tuff are often partially or completely filled with caliche, brown clay, or lemonitic material, thus reducing the potential for fractures as the major vertical pathway for contaminant transport. It is currently speculated that VOC vapor transport, from source term to intersecting shafts via laterally permeable surge beds, with subsequent movement downward through the open borehole, may be a major pathway of further movement of VOCs both horizontally and vertically at this site.

Nevada Test Site

During the course of testing operations, wastes have been disposed in 18 sumps and injection wells located in 7 areas on the Nevada Test Site and may be point sources of groundwater contamination (Area 15 EPA Farm Complex, Area 4 BJY Race Sump, Area 3 UD-6 Disposal Holes, Area 3 Core Storage Yard, Area 3 Subdock Complex, Area 9 U9Y Crater, and Area 8 U8d Crater). Contaminants disposed include tritium, plutonium, cesium, strontium, radioactive iodine; heavy metals; solvents, containing VOCs; potential PCBs; and semivolatiles. There are also eight abandoned or inactive leach fields (Area 6 CP2 and CP6; Area 23 Building 155; Area 25 R-MAD, E-MAD, Test Cells A, and C; Area 26 Building 401) that are known to have received radioactive wastes and are suspected to have received mixed wastes. Known or suspected contaminants include radionuclides, chemical solvents, and degreasing agents, including caustics and acids. Initiation of environmental restoration activities for these areas is planned for the 1992-1994 time frame.

Pantex Plant

Zone 12 of the Pantex Plant, consisting of 200 acres located in the eastern portion of the site, is the subject of a groundwater contamination assessment. Historical activities at this site have led to spills and discharges of solvents, metals, pesticides, PCBs, petroleum hydrocarbons, acids, inorganics, and high-explosive waste water. Total BTEX concentrations in the soils have been reported in the range of 25,000 to 250,000 μg/kg. Analyses of water from wells drilled into a zone of perched water underlying the area at a depth of 62.5 to 85.3 m (205 to 280 ft) indicate the presence of various metals, volatiles, and high explosives. There is at this time no evidence of contamination in the Ogallala aquifer, located at a depth of approximately 128 m (420 ft) below ground surface. TCE has been measured in a concentration range of 10 to 17 μg/L in the perched water. The possible source of this TCE contamination is a leaking underground waste oil storage tank.

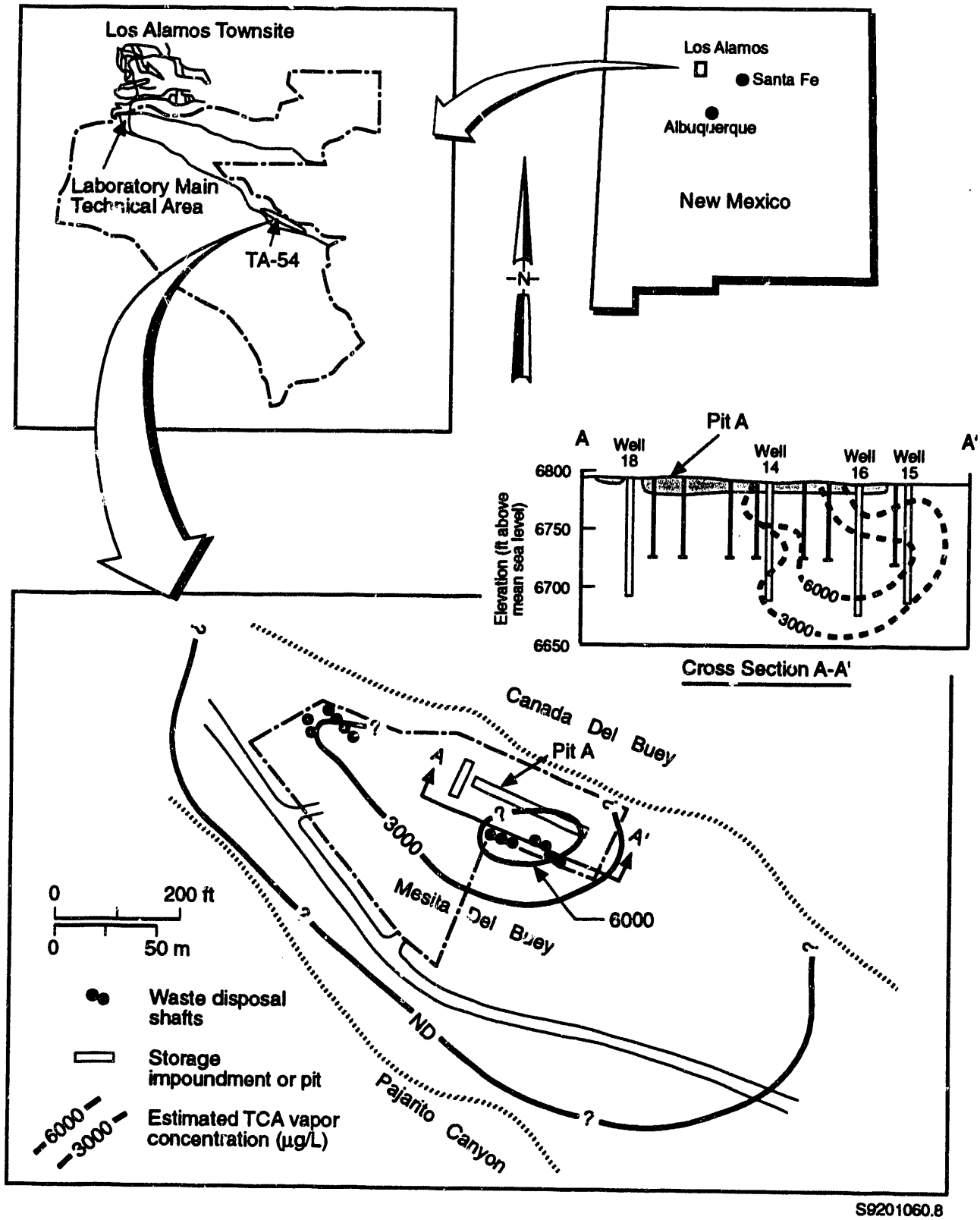

Figure A.11 Trichloroethane Plume in the Vadose Zone at Los Alamos Test Area 54

Rocky Flats Plant

Operable Unit 1

Rocky Flats' Operable Unit 1 (881 Hillside) was an area used for barrel waste storage. VOCs have contaminated the underlying shallow groundwater. TCE, tetrachloroethylene, 1,1,1-trichloroethane, and 1,1-dichloroethylene have been detected at levels up to 13,000, 5900, 19,000, and 13,000 μg/L, respectively. Concentrations of VOCs in groundwater drop significantly (<5 μg/L) within 61 m (200 ft) of the original area of storage. Above-background levels of nickel, strontium, selenium, zinc, and uranium also have been detected in the groundwater.

Operable Unit 2

Operable Unit 2, consisting of the 903 Pad, Mound Area, and East Trenches, was used as a storage and disposal area. Waste materials stored in the area (903 Pad) included radioactively and chemically contaminated (e.g., plutonium, uranium, and CCl_4) machine and cutting oils. The 903 Pad is probably one of several storage sites that has led to the contamination of the underlying groundwater. The VOC plume in this area is best described by the distribution of TCE contamination that extends approximately 183 m (600 ft) southeast and 457 m (1500 ft) northeast of the 903 Pad (Figure A.12). Concentrations of VOCs measured in the shallow bedrock groundwater include 96,000 μg/L TCE, 45,000 μg/L perchlorethylene, and 1100 μg/L CCl_4. Above-background levels of selected inorganic (e.g., strontium, barium, copper, and nickel and, to a lesser extent, chromium, manganese, selenium, lead, zinc, and molybdenum) and radioactive (predominantly ^{238}U, with lower concentrations of americium and plutonium) constituents are also present in the groundwater. Current data suggest that the confined bedrock groundwater system has not been impacted.

Operable Unit 4

Releases of contaminants to Operable Unit 4 (solar evaporation ponds) include primarily nitrate/nitrite, radionuclides, and VOCs. Nitrate concentrations as high as 12,100 mg/L have been detected in wells on the northern side of the ponds. The highest concentrations of uranium (428 pCi/L) and tritium (9000 pCi/L) have been detected on the eastern side of the ponds. The VOCs have been detected in shallow wells southeast of the ponds (e.g., vinyl chloride, 950 μg/L). Low concentrations of VOCs (i.e., acetone, 110 μg/kg; chloromethane, 52 μg/kg; dichloromethane, 29 μg/kg) have been detected in pond sediments. The ponds were historically used to store/evaporate various process aqueous wastes, including those with low-level radioactivity, high nitrates, acids, and aluminum hydroxide.

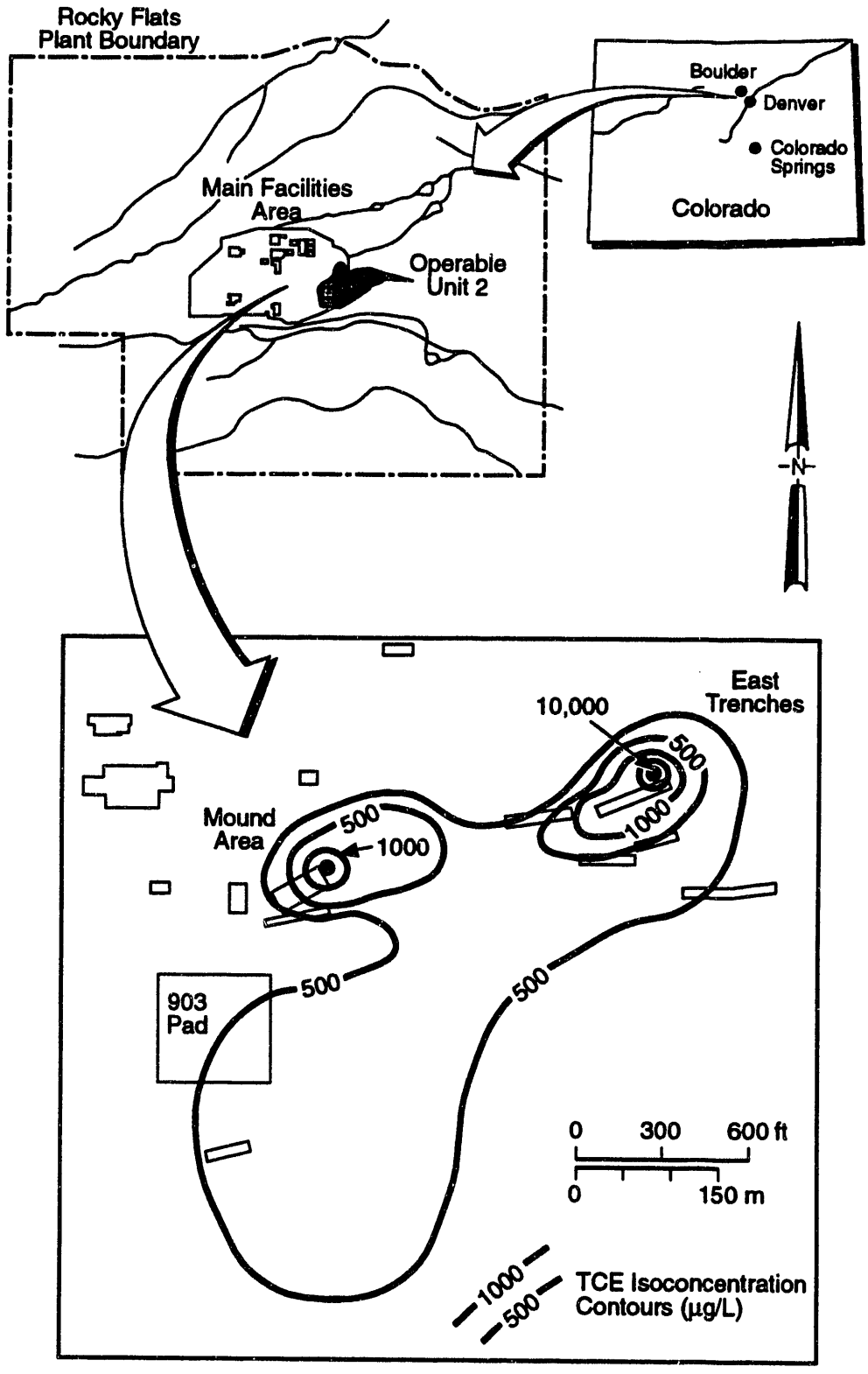

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Figure A.12 Trichloroethylene Plume in Groundwater at Rocky Flats' Operable Unit 2

Sandia National Laboratories

The Mixed Waste Landfill Integrated Demonstration at Sandia is focused on integrating new and emerging technologies and conventional methods to characterize heavy metal contaminant sources (source characterization and plume definition) and contaminant migration beneath landfills. The Sandia demonstration has targeted two sites (approximately 0.8 hectare [2 acres] each) for technology demonstration: 1) the Chemical Waste Landfill, in which the waste forms include acids, reactives, organics (e.g., TCE and TCE mixes), and metals (chromium, beryllium, mercury, arsenic, lead, cadmium, and antimony) and 2) the Mixed Waste Landfill, in which the waste forms include approximately 2832 m^3 (100,000 ft^3) of transuranic, uranium/thorium, fission products, tritium-containing and -induced activity wastes, and Resource Conservation and Recovery Act of 1976-regulated wastes (metals and acids). Previous characterization activities at the Chemical Waste Landfill have revealed chromium to a depth of 23 m (75 ft) beneath one disposal cell. TCE has been detected in groundwater underlying the site at low levels (20 μg/L). At the Mixed Waste Landfill, tritium has been detected in the underlying soil to a depth of approximately 30 m (100 ft). Currently, no contamination of the groundwater underlying the Mixed Waste Landfill has been detected.

Appendix B

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Appendix B

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