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Investigation Work Plan for Material Disposal Area L, Solid Waste Management Unit 54-006 at Technical Area 54

Los Alamos NM 87545

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Prepared by Risk Reduction and Environmental Stewardship– Remediation Services

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Investigation Work Plan for Material Disposal Area L at Technical Area 50 (SWMU 54-006)

August 2003

EXECUTIVE SUMMARY

This investigation work plan (IWP) presents recommendations for investigation activities required to complete the Resource Conservation and Recovery Act facility investigation (RFI) of material disposal area (MDA) L, solid waste management unit (SWMU) 54-006, at Technical Area (TA)-54 at Los Alamos National Laboratory (the Laboratory). The IWP also includes a description of sampling activities and analytical results for historical investigations at MDA L. The investigation activities described in this IWP are designed to address data gaps remaining after past investigations, including the Phase I RFI fieldwork conducted at MDA L.

The objectives of the IWP are to determine the nature and extent of hazardous waste constituents and/or radionuclide releases to the environment identified during the Phase I RFI. Evaluation of environmental data generated during the Phase I RFI consisted of comparisons of site data with background values and/or fallout values in environmental media, evaluation of correlations among environmental measurements, and spatial plots of contaminant concentrations in surface and subsurface environmental media. The following contaminant releases were identified at MDA L:

- methoxychlor was detected in channel sediments;
- plutonium-238 was elevated with respect to its fallout value in one channel sediment sample;
- barium, chromium, cobalt, copper, manganese, nickel, uranium, and zinc were detected in subsurface core above background beneath the disposal units;
- volatile organic compounds (VOCs) were frequently detected in pore-gas samples collected from monitoring boreholes; and
- tritium was detected in surface flux samples and in subsurface core.

The Phase I RFI data were evaluated to determine if data gaps remain related to characterizing the nature and extent of contamination. The data gaps identified include

- 1. vertical extent of metals in tuff beneath the shafts and impoundments;
- 2. nature and extent of perchlorate, nitrate, and high-explosive (HE) contamination in core;
- 3. concentrations and spatial extent of tritium in the vapor phase in subsurface core;
- 4. presence of perched groundwater beneath MDA L;
- 5. information on hydrogeologic properties to support contaminant transport modeling of the vadose zone at MDA L;
- 6. continued monitoring of vapor-phase VOC plume to track plume stability; and
- 7. collection of one supplemental channel sediment sample.

Once the additional fieldwork has been completed and the investigation report prepared and approved by NMED, a corrective measure study will be prepared and an alternative selected for the site.

To address data gap 1, two angled boreholes will be advanced under Impoundments B, C, and D, and one angled borehole will be advanced beneath the western shaft field. The objective of these boreholes is to collect samples to evaluate the extent of metals contamination in tuff. A minimum of two tuff samples will be collected from each borehole.

To address data gap 2, all core samples associated with data gap 1 will be analyzed for nitrates and perchlorate and field-screened for HE. Twenty percent of the samples screened for HE will also be submitted to an off-site contract laboratory for analysis.

To address data gap 3, a minimum of two tritium pore-gas samples will be collected from the three new angled boreholes and from eight existing boreholes. Samples will be collected directly beneath the nearest disposal unit and at the total depth of each borehole.

To address data gap 4, a vertical borehole will be advanced east of the MDA L fence line to a depth of 700 ft to investigate whether perched groundwater is present below MDA L. Moisture levels will be recorded at 1-ft intervals to the total depth of the borehole.

To address data gap 5, data on the geophysical properties of vadose zone core will be collected from the 700-ft borehole to evaluate contaminant fate and transport mechanisms in the subsurface at MDA L for the future corrective measure study.

To address data gap 6, continued monitoring in new and existing boreholes is required to track the plume's stability, its migration pattern, or a potential release from the source areas (data gap 6). However, concentrations and spatial extent of VOC vapors in subsurface tuff have been defined.

To address data gap 7, one channel sediment sample will be collected at the interface of the alluvial sediments and bedrock in the historic drainage areas.

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1.0 INTRODUCTION

1.1 General Site Information

Los Alamos National Laboratory (LANL or the Laboratory) is a multidisciplinary research facility owned by the US Department of Energy (DOE) and managed by the University of California. The Laboratory is located in north-central New Mexico, approximately 60 mi northeast of Albuquerque and 20 mi northwest of Santa Fe. The Laboratory site covers 40 mi² of the Pajarito Plateau, which consists of a series of finger-like mesas separated by deep canyons containing perennial and intermittent streams running from west to east. Mesa tops range in elevation from approximately 6200 to 7800 ft.

The Laboratory's Risk Reduction and Environmental Stewardship–Remediation Services (RRES-RS) Project, formerly the Environmental Restoration (ER) Project, is participating in a national effort by the DOE to clean up sites and facilities formerly involved in weapons research and production. The goal of RRES-RS is to ensure that past DOE operations do not threaten human or environmental health and safety in and around Los Alamos County, New Mexico. To achieve that goal, RRES-RS is currently investigating sites potentially contaminated by past Laboratory operations. The sites under investigation are either solid waste management units (SWMUs) or areas of concern (AOCs).

The SWMU addressed in this report (SWMU 54-006) contains both hazardous and radioactive components.¹ Depending on the type of contaminant(s) and the history of a SWMU, the New Mexico Environment Department (NMED) or the DOE has administrative authority over work performed by RRES-RS at the site. NMED, under the auspices of the State of New Mexico Hazardous Waste Act (NMHWA), has authority over cleanup of sites with hazardous waste or certain hazardous constituents, including the hazardous waste portion of mixed waste (i.e., waste contaminated with both radioactive and hazardous constituents). The DOE has authority over cleanup of sites with radioactive contamination. Radionuclides are regulated under DOE Order 5400.5, "Radiation Protection of the Public and the Environment," and DOE Order 435.1, "Radioactive Waste Management."

NMED enforces the Hazardous and Solid Waste Amendments (HSWA) Module VIII of the Laboratory's Hazardous Waste Facility Permit, hereafter referred to as Module VIII. Module VIII specifies conditions and requirements for investigation and cleanup activities at the Laboratory, which are performed by RRES-RS. The US Environmental Protection Agency (EPA) issued Module VIII on May 23, 1990, and revised it on May 19, 1994 (EPA 1990, 1585; EPA 1994, 44146). NMED is currently revising the Laboratory's Hazardous Waste Facility Permit.

In accordance with Module VIII, the nature and extent of releases of hazardous waste or hazardous constituents are determined through the Resource Conservation and Recovery Act (RCRA) facility investigation (RFI) process. Under RRES-RS, the Laboratory also implements the RFI process for those sites under the administrative authority of DOE.

Material disposal area (MDA) L is located on a mesa in the east-central portion of the Laboratory at Technical Area (TA)-54 (Figure 1). During the late 1950s, the Laboratory, with approval of the US Atomic Energy Commission and upon recommendation of the US Geological Survey, selected Mesita del Buey, within TA-54, for underground disposal of Laboratory-generated waste (Rogers 1977, 5707; Rogers 1977, 5708). Since that time, the main waste storage and disposal facilities for the Laboratory

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have been located at TA-54. MDA L is one of four disposal areas on Mesita del Buey between Pajarito Canyon (south) and Cañada del Buey (north) and within TA-54 (Figure 2).

MDA L is an 1100- by 3000-ft (2.5-ac) fenced area. MDA L consists of one inactive subsurface disposal pit (Pit A); three inactive subsurface treatment and disposal impoundments (Impoundments B, C, and D); and 34 inactive disposal shafts (Shafts 1 through 34) with depths ranging from 10 to 65 ft below the original ground surface, before an asphalt cover was placed over the site. The pit, impoundments, and shafts are constructed in the Tshirege Member of the Bandelier Tuff, a consolidated tuff unit. The regional aquifer is estimated to be at a depth of approximately 930 ft, based on data from other wells at the Laboratory and the predictions of the hydrogeologic conceptual model for the Pajarito Plateau (LANL 1998, 59599). The topography of MDA L is relatively flat. The majority of the surface of MDA L is paved with asphalt to house ongoing waste management activities; surface water runoff from this area is controlled and diverted to an outfall at the northeast corner of the site.

Historically, MDA L was used for disposing of non-radiological liquid chemical wastes. Disposal of these types of wastes no longer occurs at this site. LANL drawings AB113 (LANL 1993, 76052) and ENG-C-45259 (DOE 1987, 25606) have been used to identify the locations of the pit, impoundments, and shafts at MDA L. There are no visible surface expressions of the pit or the impoundments because asphalt covers most of the surface of MDA L. Most of the shaft locations (but not all) are marked with brass caps pressed into the asphalt indicating the approximate location of each shaft. The depth of the disposal units was described in the approved RFI work plan for Operable Unit (OU) 1148 (LANL 1992, 07669) based on historical records; however, elevation data was not documented. The subsequent cover material placed over the disposal units, including the asphalt pad, has increased the elevation across the site. The elevation of the disposal units at the time of excavation has been estimated from the tuff/soil interface identified in the Phase I RFI borehole logs. Figure 3 shows the locations of the pit, impoundments, and shafts as well as other site surface features and topographical lines. The entire fenced surface area over MDA L is an active RCRA-permitted hazardous waste management unit.

This investigation work plan (IWP) provides the results of historical investigations (including the Phase I RFI) of MDA L, SWMU 54-006, at TA-54 and presents recommendations for additional investigation activities required to complete the investigation. The IWP includes site background, site conditions, scope of activities necessary to complete the investigation, investigation methods, and the anticipated schedule for completing the field activities. Appendix A includes a list of acronyms and defines terms used in this report. Appendix B describes the historical RFI activities and analytical results for MDA L, including data interpretation to establish if releases had occurred from the disposal units and to make a preliminary determination of the nature and extent of the contamination. Appendix C describes results of the quality control (QC)/quality assurance (QA) process. Appendix D on CD attached to inside back cover of this report provides all of the Phase I RFI data. Appendix E describes statistical analyses to support data interpretation. Appendix F lists relevant documents for the regulatory history of the SWMUs associated with MDA L. Appendix G includes a history of pore-gas monitoring at MDA L. Appendix H includes borehole profiles and logs. Appendix I is a copy of the report "Subsurface Vapor-Phase Transport of TCA at MDA L: Model Predictions" (Stauffer et al. 2000, 69794). Appendix J contains a copy of the report "Summary Report: Conceptual Model Review and Remediation Options for Los Alamos National Laboratory Technical Area 54, Material Disposal Area L, Revision 1." Appendix K contains information on the stratigraphy of the MDA L area. Appendix L contains the Source Term and Batch Waste Source Term Databases.

1.2 Investigation Objectives

The objectives of the IWP for MDA L are to

- determine the nature and extent of hazardous waste constituents and/or radionuclide releases to the environment identified during the Phase I RFI;
- establish the rationale for data collection and analysis; and
- identify appropriate methods and protocols for collecting, analyzing, and evaluating data to finalize the characterization of MDA L.

The RRES-RS Project conducted Phase I RFI fieldwork at MDA L from 1993 to 2003. The results of these investigations are described in the historical investigation report (HIR) in Appendix B of this IWP. Based on an evaluation of existing environmental data collected at MDA L, several data gaps were identified that must be addressed to define the nature and extent of contamination in the environment and to evaluate potential risks to human and ecological receptors. These data gaps are described in the HIR and in Section 4.1 of this IWP.

2.0 BACKGROUND

2.1 Operational History

MDA L is a decommissioned (i.e., removed from service) MDA established for disposing of non-radiological liquid chemical waste, including containerized and uncontainerized liquid wastes; bulk quantities of treated aqueous waste; batch-treated salt solutions; electroplating wastes, including precipitated heavy metals; and small batch quantities of treated lithium hydride. MDA L operated from the early 1960s until it was decommissioned in 1985. A chronology of the salient information pertinent to MDA L is presented in pages 5-105 through 5-108 of the approved RFI work plan for OU 1148 (LANL 1992, 07669) and in Section 1.0 of the HIR in Appendix B.

At MDA L, 1 pit, 3 impoundments, and 34 shafts were excavated into the overlying soil and unit 2 of the Tshirege Member of the Bandelier Tuff (Figure 3). The pit, impoundments and shafts were unlined. Upon decommissioning, the pit and impoundments were filled and covered with clean, crushed, consolidated tuff. When the shafts were filled to within approximately 3 ft of the surface, steel caps were placed over the opening of each shaft, and the area above the steel plate was capped with a 3-ft concrete plug (Rogers 1977, 5707; 5708).

2.2 Land Use

MDA L is located in an industrial area within TA-54, which is currently the primary site at the Laboratory for waste management activities. The Laboratory does not anticipate that land use at TA-54 will change in the foreseeable future. Public access to the site is restricted by fencing, locked gates, and restricted access to Pajarito Road and TA-54. Under present-day conditions, only Laboratory employees or contractors may enter the site for site management activities (i.e., installing best management practices), waste management operations, or collecting environmental samples.

2.3 Relationship to Other SWMUs and AOCs

To evaluate the potential impact of MDA L and to make sound decisions regarding the need for and nature of effective remedies, it is important to understand, at least qualitatively, the potential impact of nearby SWMUs and AOCs. The most significant SWMUs/AOCs near MDA L, in terms of contaminant inventory and physical size, are MDAs G and H at TA-54 (Figure 2). MDA G is located near the eastern end of Mesita del Buey approximately 1 mi east of MDA L. This 65-ac site has been the Laboratory's primary radioactive waste disposal facility since 1959 and is scheduled to operate through 2044. Investigations to date have revealed a diffuse plume of volatile organic compounds (VOCs) (probably associated with residual solvent contamination in radioactive waste) and a plume of water vapor containing tritium. As an operating nuclear facility, MDA G is subject to intensive personnel safety and environmental protection and surveillance programs, and the VOC and tritium plumes are monitored regularly. Ongoing low-level radioactive waste disposal is authorized by the DOE, and ongoing solid lowlevel mixed-waste and transuranic (TRU) mixed-waste management activities are authorized by the DOE and permitted, as necessary, by the NMED under agreement with the EPA. MDA H is located 0.6 mi west of MDA L. This 0.3-ac site functioned as the Laboratory's primary disposal area for classified, solid-form waste from 1960 through August 1986. Investigations conducted to date indicate that a vapor-phase release of tritium and VOCs occurred from the subsurface shafts. The corrective measures study (CMS) for MDA H was submitted to NMED on May 31, 2003 (LANL 2003, 76039).

2.4 Contaminant Transport and Potential Receptors

The inventory of wastes disposed of at MDA L includes inorganic and organic chemicals. The relevant release and transport processes associated with these wastes are a function of chemical-specific properties, the physical form and/or container associated with a waste, and the nature of the transport process. The transport of tritium and VOCs, for example, occurs primarily in the gas phase and by diffusion or advection in air. Relatively water-soluble contaminants, primarily certain metals, are susceptible to release and transport via infiltration of water through the interred wastes.

The primary potential release and transport mechanisms for contaminants in subsurface wastes at MDA L include the following:

- *Volatilization, diffusion, and dispersion in air.* Gas or vapor-phase contaminants diffuse from waste and mix with air in the shafts, impoundments, or pit, and then diffuse through the air-filled pores in the subsurface rock. Migration of gas or vapor-phase contaminants from the tuff into ambient air may occur by diffusion or by advection driven by barometric pressure changes.
- *Dissolution and advective transport in water.* Residual moisture under the asphalt surface moves down through the shafts, impoundments, and pit, dissolves contaminants, and slowly transports dissolved contaminants through the subsurface rock. Transport in tuff may be facilitated by the presence of fractures, particularly when fractures have coatings with low conductivity or when sufficient liquid saturates the matrix adjacent to the fracture where flow is occurring.

In addition to the processes described above, which were described in the context of buried wastes, contaminants may also have impacted environmental media at MDA L from releases that occurred during the operation of MDA L. Dissolution of contaminants in infiltrating water, for example, may have been more prevalent during site operations when the pit, impoundments and shafts were open for waste disposal. At least two release mechanisms, currently inactive at MDA L, may have contributed to existing contamination in environmental media:

• *Subsurface solute-transport.* Although limited liquid-phase contaminant transport may have occurred in the past, as indicated by the presence of metals in core samples collected beneath the subsurface pit, impoundments, and shafts, boreholes drilled beneath MDA L have not provided evidence of residual free liquid (solvent or water). These findings indicate that no liquid source is present outside the disposal trenches and shafts. Nonetheless, because liquid VOCs

may still be present in the MDA L inventory (e.g., intact drums in shafts), the possibility of future liquid-phase solute transport is retained as a potential contaminant transport mechanism.

• *Liquid-phase transport of solvents and associated metallic residue*. If intact drums of chemicals are still present, liquids from the drums would rapidly volatilize into pore space. It is possible that a drum or drums of liquid could fail completely, adding a pulse of liquid to the system. The depth of resultant contaminant transport would be a function of the saturated and unsaturated hydraulic conductivity and the volume of liquid released. To evaluate the potential for liquid VOC flux (aqueous-phase transport) and subsequent mobilization of residual metals, the rate of volatilization was compared to the rate of saturated and unsaturated flux. Based on conservative assumptions, a 55-gal. drum of 1,1,1,-trichloroethane (TCA) that fails completely would fully volatilize within one year, resulting in vertical liquid transport of approximately 100 ft (Appendix I of this IWP). Once the volume of liquid released fully volatilizes, saturated conditions would cease to exist, after which volatile chemicals would diffuse through the pore space in the tuff. Any metals mobilized during saturated conditions would sorb onto solid particles. The introduction of liquid pulses into the subsurface at MDA L would not result in long-term saturated flow conditions or deep vertical transport of contaminants.

Movement of VOC plumes can be characterized as advective (density driven) or diffusive (concentration driven [Conant et al. 1996, 64608]). Density-driven flow increases the downward migration rate of a VOC and affects the distribution of the plume in solid media with air permeabilities greater than 10^{-11} m² (10 darcies [Stauffer et al. 2002, 69794]). This is the upper limit for air permeability in the Bandelier Tuff. Based on relatively low air permeability, vapor movement beneath MDA L is expected to be dominated by diffusion, with the rate of diffusion being determined by the concentration gradient between the source and the ambient pore gas. Assuming diffusive (concentration driven) processes are dominant and using site-specific properties (e.g., geology and air-permeability), modeling results of the VOC plume evolution match the nature and extent of the plume as measured during pore-gas sampling (Appendix I). Matching the modeling to the site-specific conditions (i.e., data) would verify that the primary mechanism for VOC transport is diffusive transport in the vapor phase.

The impacts of drum failure on the VOC plume extent are evaluated in a report contained in Appendix I (Stauffer et al. 2002, 69794) to determine whether a drum failure could be detected with pore-gas monitoring. The simulation assumed that a 55-gal. drum of TCA fails, emptying its entire contents into the subsurface. The TCA was assumed to move downward, smearing homogeneously, to a depth of 100 ft below a shaft bottom or approximately 160 ft below the MDA L surface. Next, the TCA is assumed to completely volatilize, creating a TCA cloud at a concentration of 20,000 parts per million by volume (ppmv). This addition of vapor (~300 kg) is roughly 40% of the current plume inventory. After one year, the simulation predicts that 22% of the new release is lost through the surface. According to the model, after two years, 31% would be vented, and after five years, 50% would be removed by venting through the surface to the atmosphere. The concentration increase in the subsurface following drum failure would be detected by the current monitoring program. The impact on the extent of the VOC plume would be minimal. The simulation showed that the extent of the 100-ppmv-concentration contour beneath the release would expand slightly. The outer extent (10-ppmv contour) would not change measurably. The prediction calculates that after 10 yr, 70% of the release is vented, and after 20 yr, 88% has left the system. At this point, the plume would look much like its current condition, and monitoring would no longer be able to detect the release. In summary, a single drum failure does not appear to substantially change the extent of the plume, and the current monitoring system is able to detect the release (Appendix I).

Receptors potentially exposed to contamination from MDA L include workers at MDA L and TA-54 and biota at the site. Potentially, site workers may be exposed to contaminants via inadvertent soil ingestion, inhalation of suspended soil (dust), dermal absorption from soil on the skin, and external irradiation. Inhalation of gas-phase contaminants such as tritium and/or VOCs emanating from the site into the atmosphere is also a potential means of exposure. Ecological receptors may also be exposed via these pathways as well as via plant root uptake and the food web; in addition, these receptors may be exposed to higher concentrations of gas-phase contaminants in subsurface burrows.

Perched groundwater was not encountered, nor is suspected, beneath Mesita del Buey at MDA L at TA-54 (LANL 1998, 59599). No perched water was observed in 340 ft of drilling (to 6448 ft above sea level) in the deepest borehole (borehole 54-01004, Appendix H of this IWP). No perched water was observed in 883 ft of drilling (to 5767 ft above sea level [asl]) in regional well R-22 or in 800 ft of drilling (to 5680 ft above sea level) in regional well R-21 (Figure 4). Therefore, the potential for exposure of receptors through a water-mediated pathway is unlikely. Data from other wells at the Laboratory and predictions of the hydrogeologic conceptual model for the Pajarito Plateau place the regional aquifer at a depth of approximately 930 ft below MDA L (LANL 1998, 59599). Because of the depth to the regional aquifer and the low moisture content (1% to11% gravimetric moisture content within the first 300 ft below ground surface ([bgs] (LANL 1994, 76071) of the vadose zone, it is unlikely that contamination at MDA L could reach the regional aquifer in the foreseeable future. However, contaminants from MDA L could potentially reach groundwater, and this pathway will be investigated and evaluated in the MDA L investigation report and the future CMS report.

2.5 MDA L Waste Inventory

Waste disposal records for MDA L are found in un-numbered disposal logbooks (LANL 2003, 76036). These logbooks were used to record information on the type, date, location, and volume of waste placed in MDA L. Records prior to 1974 are incomplete, and many logbook entries contain only brief descriptions of wastes disposed of at MDA L (i.e., waste types, volumes, and disposal locations are not always provided). An estimate of the types and quantities of waste disposed of at MDA L was compiled in the OU 1148 data report (LANL 1992, 23247).

Two databases were developed based on the original logbook entries. Untreated waste deposited at MDA L between May 30, 1975, and May 7, 1985, is identified in the Source Term Database and summarized in Appendix B, Section B-1.1. Information about waste that underwent treatment before disposal at MDA L from December 20, 1974, to July 25, 1984, is provided in the Batch Waste Source Term Database and is summarized in Appendix B, Section B-1.1. Given the uncertainties and lack of information in the historical records, the data are sufficient only to estimate the general nature of inventoried waste buried of in the pit, shafts, and impoundments at MDA L. The Source Term and Batch Waste Source Term databases are included in Appendix L of this IWP.

2.6 Summary of Historical Investigations

2.6.1 Pre-RFI Field Investigations

On May 7, 1985, the Laboratory received a compliance order from the New Mexico Environmental Improvement Division (NMEID, now called NMED) that addressed numerous waste management issues at the Laboratory (NMEID 1985, 75885). The 1985 order specified the following six tasks that involved site investigation activities in and around MDA L:

- Task 1 required measuring the intrinsic permeability of the tuff,
- Task 2 required determining the soil-moisture characteristic curves,
- Task 3 required determining the unsaturated hydraulic conductivity of the Bandelier Tuff,
- Task 4 required analyzing the infiltration and redistribution of meteoric water into the tuff,
- Task 5 required characterizing the core and pore gas in the vadose zone, and
- Task 6 required analyzing the potential presence of perched water.

The results and outcomes of the above six tasks are described in a report entitled "Hydrogeologic Assessment of Technical Area 54, Areas G and L" (LANL 1987, 76068), which was submitted in 1987 to the NMED in response to the 1985 compliance order/schedule. These investigations and the associated findings are described in the HIR (Section B-1.2 of Appendix B) and in the approved RFI work plan for OU 1148 (LANL 1992, 07669).

2.6.2 Phase I RFI Field Investigations

Phase I RFI activities, including sampling of ambient air, channel sediments, subsurface core, and pore gas, are summarized in Table 1.

VOC surface flux was measured across MDA L in two surveys conducted in August 1993 and August 1994. Details of the investigation are reported in two Quadrel Services reports (Quadrel 1993, 63868; Quadrel 1994, 63869). Trujillo et al. (1998, 58242) issued a report summarizing the results of the surface flux VOC measurement investigations. During the summers of 1993 and 1994, tritium flux was measured at locations on and near the surface of MDA L. Tritium flux locations are shown on Figure B-4 and the results are presented in Table B-6 (Eklund 1995, 56033).

Between September 1993, and May 1995, 184 core samples were collected from seven vertical and nine angled boreholes drilled at MDA L and submitted to an off-site contract laboratory for analysis. Depth intervals for sample collection and analytical suites varied by borehole and are described in Section B-2.3.1 in Appendix B. The depths of these boreholes ranged from 50 to 607 ft bgs. Borehole locations and trajectories are shown on Figure B-6. Boreholes are described by depth, declination, and adjacent disposal unit in Table B-7. A total of 18 boreholes were drilled during the Phase I RFI; however, core samples were not collected from boreholes 54-01017 and 54-01018.

In 1994, channel sediments from tributaries of Cañada del Buey were collected from eight locations and field screened for alpha, beta, and gamma radiation to bias sample selection. The sample with the highest gross alpha and gross beta, the sample with the highest gross gamma, and two other samples selected at random (four total) were submitted to an off-site contract laboratory for target analyte list (TAL) metals, polychlorinated biphenyls (PCBs)/pesticides, herbicides, gamma spectroscopy for radionuclides, tritium, isotopic thorium, strontium-90, isotopic uranium, and isotopic plutonium analyses (LANL 1996, 54462).

Additionally, in 1994, ambient-air samples were collected for eight days at two sampling locations along the northern perimeter of MDA L. The samples were analyzed for VOCs. This sampling event is described in Section B-2.1.2 of Appendix B and reviewed in Appendix J of this IWP.

In 1997 and 1998, the Environmental Restoration Project (now called RRES-RS) evaluated the effectiveness of passive-vapor extraction of subsurface vapor-phase VOCs at MDA L. Passive-vapor extraction uses natural changes in atmospheric barometric pressure as a pump to exhaust VOCs through open boreholes. These activities are described in Section B-2.3.2 of Appendix B.

Sampling of subsurface pore gas for VOCs has been ongoing at MDA L from 1992 to the present. Currently, there are 18 boreholes at MDA L available for this sampling, including two Phase I RFI

boreholes and 16 pre-RFI boreholes. Each quarter, ten of these boreholes are selected for pore-gas monitoring. Since 1997, pore-gas monitoring has been aided and directed using soil-gas screening with a Bruel and Kjaar (B&K) Multigas Analyzer, Model 1302. Currently all ports in the monitoring boreholes selected for that quarter are screened using the B&K, and SUMMA™ canisters are collected as needed to evaluate changes in the VOC plume based on a defined quarterly sampling schedule presented in the prior year's annual report September RRES-RS quarterly technical report [LANL 2002, 73712). Pore-gas monitoring activities are described in Section B-2.3.3 of Appendix B and in Appendix G of this IWP.

2.6.3 Phase I RFI Results

Conclusions regarding the nature and extent of contamination at MDA L that can be drawn from the results of Phase I RFI activities are as follows.

- 1. Concentrations of certain metals (barium, chromium, cobalt, copper, manganese nickel, uranium, and zinc) in tuff, beneath the pit, impoundments, and shafts, indicate that contamination has leached from the disposal units. The vertical extent of subsurface contamination beneath the three impoundments and shaft field has not been defined.
- 2. Concentrations of tritium beneath the disposal units indicate that it has migrated into the tuff. The extent of contamination has not been defined.
- 3. VOCs (primarily trichloroethylene [TCE], tetrachlorethane [PCA], and TCA) were detected in subsurface pore gas indicating a release. The vertical and horizontal extent of this contamination is defined.
- 4. Surface flux and ambient-air sampling results indicate that VOCs and tritium are being released into the atmosphere from the subsurface vapor plume residing in the vadose zone beneath MDA L.
- 5. Channel sediments contain low concentrations of methoxychlor and plutonium-238.

A detailed review of the Phase I RFI data is presented in Section B-3 of Appendix B. Phase I RFI data is presented in Appendix D of this IWP (CD on inside back cover).

3.0 SITE CONDITIONS

This section discusses aspects of the environmental setting at MDA L that are important to assessing the potential impacts of contaminated surface and subsurface media, including

- the semiarid climate with low precipitation and a high evapotranspiration rate that limits the amount of moisture percolating into the disposal units and subsequently limits the amount of moisture available to leach radionuclides or hazardous waste constituents;
- the thick, relatively dry unsaturated zone that greatly restricts or prevents downward migration of contaminants in the liquid phase through the vadose zone to the regional aquifer; and
- the canyon-mesa terrain that affects atmospheric conditions and ecological habitats.

3.1 Surface Conditions

MDA L is located in the central area of Mesita del Buey northwest of MDA G at TA-54 (Figure 4). Mesita del Buey is a 100- to 140-ft-high finger-shaped mesa that trends southeast. The elevation of Mesita del Buey ranges from 6775 to 6800 ft at MDA L. The mesa is approximately 500 ft wide and is bounded by

Cañada del Buey (450 ft to the north) and Pajarito Canyon (360 ft to the south). The topography at MDA L slopes gently from west to northeast, gradually steepening in the northeast quadrant of MDA L towards Cañada del Buey. The surface of MDA L is covered with a layer of asphalt.

3.1.1 Soils

The soils of Mesita del Buey are derived from the weathering of the Tshirege Member tuffs (phenocrysts and phenocryst fragments, devitrified glass, and minor lithic fragments) and from wind-blown sources. Soils on the flanks of the mesa are developed on Tshirege Member tuffs and colluvium with additions from wind-blown and water-transported sources. Native soils have been disturbed by waste management operations over much of the surface of Mesita del Buey, but when present, native soils are generally thickest near the center of the mesa and thinner toward the edges.

In general, soils on the mesa surface are thin and poorly developed; they tend to be sandy near the surface and more clay-like beneath the surface. More highly developed soil profiles exist on the northfacing slopes; they tend to be richer in organic matter. Soil profiles on the south-facing slopes tend to be poorly developed. Soil-forming processes have been identified along fractures in the upper part of the mesa, and the translocation of clay minerals from surface soils into fractures has been described at Mesita del Buey (Reneau and Vaniman 1998, 63135). A discussion of soils in the Los Alamos area can be found in Section 2.5.1.3 of the installation work plan (LANL 1998, 62060).

The original soils near MDA L were poorly developed, as is typical of soils derived from Bandelier Tuff and formed under semiarid climate conditions (Nyhan et al. 1978, 5702). In general, undisturbed soils on the mesa tops are comprised of the Carjo loam, the Hackroy loam, and the Seaby loam (Nyhan et al. 1978, 5702). At MDA L, natural or undisturbed surficial soil cover is limited as a result of disposal unit and cover construction. The present-day surface of MDA L is crushed tuff covered with an asphalt pad.

Canyon bottoms (Cañada del Buey and Pajarito Canyon) near MDA L are covered with colluvium and alluvium that has eroded from the tuff and soils on the mesa top and canyon walls. The canyon rims and slopes are composed of soils from the Hackroy-Rock outcrop complex; canyon bottoms are composed of the Tocal, a very fine, sandy loam. Since disposal activities began at MDA L, Cañada del Buey has experienced a period of accretion, and eroded soils from MDA L as well as other areas at TA-54 have been deposited on the canyon bottom and stream banks (Nyhan et al. 1978, 5702). Potentially, these soils can be redistributed downstream during storm runoff events. The drainages between the mesa and canyon bottoms were sampled during the Phase I RFI; the canyon bottoms will be investigated under separate canyon work plans.

3.1.2 Surface Water

There are no streams on Mesita del Buey; water flows only as storm water and snowmelt runoff on the mesa and in small drainages off the mesa to the north and the south. Storm water flows at a number of points along the perimeter of TA-54, as identified and characterized in the "Stormwater Pollution Prevention Plan" (LANL 2002, 74009), prepared for the Laboratory's National Pollutant Discharge Elimination System Storm Water Multi-Sector General Permit. Therefore, flooding at the site facility is not a concern. As a result of runoff, surface erosion occurs primarily as shallow sheet erosion on the relatively flat parts of the mesa and as channel erosion in major drainages from the mesa top. Runoff from summer storms reaches a maximum in less than 2 hr and lasts less than 24 hr. In contrast, runoff from spring snowmelt occurs over a period of several weeks at a low discharge rate. The amount of eroded material transported in runoff waters is generally higher during summer rainfall events than during snowmelt (LANL 1997, 63131, pp. 2–33).

In 2001, RRES-RS conducted a surface water assessment of the surface of MDA L, which is paved and is used as an active RCRA-permitted hazardous waste management unit. The area received a score of 10.6, indicating low erosion potential. The calculated erosion matrix score includes 3.6 for site setting, an erosion runoff score of 0.0, and a run-on score of 7.0 (Appendix K of this IWP).

3.2 Subsurface Conditions

3.2.1 Stratigraphy

The RRES-RS Project drilled and cored 18 boreholes (Figure 5), and sampled 16 of the boreholes at MDA L to characterize potential contaminant releases and transport in the subsurface. Borehole logs from the site (Figure 6; Appendix H) provide details on the stratigraphy to a depth of approximately 607 ft bgs (borehole 54-01015) and are included in Appendix H. The locations and depths of regional wells (R-20, R-21, R-22), were also used to infer the stratigraphy beneath MDA L (Figure 7). Figure 7 shows east-west cross sections beneath and near MDA L. The stratigraphy beneath MDA L includes the Bandelier Tuff and the Cerros del Rio basalt. The regional aquifer is primarily Santa Fe Group, Puye Formation, and Cerros del Rio basalts. Descriptions of the stratigraphic units beneath MDA L are included in Appendix K.

3.2.2 Hydrogeology

The proposed hydrogeologic conceptual model for the Pajarito Plateau (LANL 1998, 59599) is presented in Figure 8. The model predicts that infiltration of water into the subsurface and subsequent transport of water, vapor, and solutes through the upper regions of the vadose zone is heavily influenced by surface conditions such as topography, surface water flow, and microclimate. According to model predictions, movement through deeper layers, including the regional aquifer, is only weakly influenced by surface conditions and is influenced more by the hydraulic characteristics of aquifer rocks, regional groundwater flow patterns, and stresses induced by water-supply production. The following sections provide an overview of infiltration rates, groundwater, and stratigraphy in the vicinity of MDA L.

Infiltration

Surface and near-surface conditions (topography, precipitation, surface runoff) control the infiltration of water and the transport of contaminants into the shallow subsurface. In this respect, the behavior of mesas and canyons forming the plateau differ from one another (LANL 1998, 59599). Mesas are generally quite dry, both on the surface and within the rock forming the mesa. Canyons range from wet to relatively dry; the wettest canyons contain continuous streams and perennial groundwater in the canyonbottom alluvium. Dry canyons have only occasional stream flow and may lack alluvial groundwater.

Relatively small volumes of water move beneath mesa tops under natural conditions because of low rainfall, run-off into canyons, high evaporation, and efficient water use by vegetation. Liquid water generally infiltrates into the mesa, and water vapor generally moves upward, undergoing evapotranspiration along the top and sides of the mesa. Air readily circulates through the mesa-top units because of the relatively dry pore spaces and the topographic relief. Air circulation may be driven by temperature variations, barometric pumping, or surface winds. This process promotes atmospheric evaporation, which may extend deep within the mesa and further inhibit the downward liquid-water flow.

Mesita del Buey is one of the drier mesas at the Laboratory and the Pajarito Plateau. Infiltration into the mesa appears to be very low, possibly only 0.04 in./yr (LANL 1997, 63131), and occurs during snowmelts or intense summer thunderstorms, which leads to slightly higher moisture contents within the uppermost few meters of the mesa surface. During dry periods, evapotranspiration removes moisture from the

surface of the mesa; permeable zones such as fractures and surge beds act as conduits for air and aid in drying the mesa (Turin and Rosenberg 1996, 63559).

3.2.3 Groundwater

Groundwater beneath the Laboratory occurs in the regional aquifer (at depths ranging from 600 to 1200 ft bgs) and in perched, intermediate and shallow aquifers. Except under TA-16, perched groundwater has been detected only in wells beneath relatively wet canyons (e.g., Los Alamos Canyon). It exists as two types: (1) shallow alluvial groundwater that occurs in some wet canyons (generally at depths less than 100 ft), and (2) deeper "intermediate" perched groundwater that occurs in zones separated from both alluvial and regional groundwater by unsaturated rock. To date, data obtained indicate that dry mesas such as Mesita del Buey show no evidence of perched groundwater beneath the mesa. However, alluvial groundwater in Pajarito Canyon may cause increased moisture contents within the vadose zone at the base of the mesa (Nylander et al. 2003, 76059).

3.2.3.1 Perched Intermediate Waters

Perched intermediate groundwater is rarely observed on the Pajarito Plateau, and the causes for perching have not been fully determined (Nylander et al. 2003, 76059). Perched waters are thought to form mainly at horizons where medium properties change dramatically, such as at paleosol horizons containing clay or caliche. It is not known whether perched water bodies are isolated or connected and to what degree they may influence travel times and pathways for contaminants in the vadose zone. Although perched intermediate groundwater has been observed in some locations elsewhere on the plateau, none has been observed in the regional wells in the vicinity of MDA L (R-22, R-21, R-20, R-16) (LANL 1998, 59599). No perched groundwater was observed in 340 ft of drilling (to 6448 ft) in the deepest vertical borehole drilled to date (borehole 54-01004) at MDA L.

3.2.3.2 Regional Aquifer

The regional aquifer of the Pajarito Plateau is the only aquifer capable of supplying large-scale municipal water (Purtymun 1984, 6513). The regional aquifer extends throughout the Española Basin (an area roughly 2300 mi² [6000 km²]) and reaches its maximum thickness beneath the Pajarito Plateau (over 9800 ft thick; Cordell 1979, 76049).

Depths to the regional aquifer range between about 1200 ft along the western edge of the plateau and about 600 ft east. Beneath MDA L, the water table elevation is approximately 5810 ft (5767 ft at R-22; 5860 ft at R-32 or approximately 930 ft bgs). Figure 9 depicts water table elevations across the plateau, i.e., a cross section of hydraulic head data (water table elevations) collected in the regional aquifer.

Groundwater flow in the regional aquifer between TA-54 and the Rio Grande (approximately 4 mi) occurs primarily in the Santa Fe Group (see Figure 7). Pump test results in individual water supply wells throughout the plateau indicate that the hydraulic conductivity (K) of the Santa Fe Group along the eastern edge of the plateau is the lowest of any aquifer unit ([average K for LA well field = 0.7 ft/day]; Purtymun 1995, 45344). More recent analysis of water-level trends over a 55-yr span indicate that these K estimates, although accurate locally, may be higher than the large-scale, effective permeability of the Santa Fe Group (0.2 ft/day) because of the flow impedance of north-south trending faults. Assuming a porosity of 0.2 (typical of sedimentary rocks [Freeze and Cherry 1979, 64057]) and the measured gradient of 0.02, pore water velocities in this portion of the aquifer would be slow (approximately 0.02-0.07 m/yr [Nylander et al. 2003, 76059]). This result indicates that travel times within the regional aquifer (Santa Fe Group rocks) from TA-54 to the Rio Grande would be, on an average, over 1000 yr.

3.2.3.3 Vadose Zone

The region beneath the ground surface and above the regional aquifer is called the vadose (unsaturated) zone. The source of moisture in the vadose zone beneath TA-54 is infiltrating precipitation, but most of the precipitation is removed as runoff or evaporation and transpiration in the upper region of the vadose zone (LANL 1997, 63131). The subsurface movement of the remaining water (often referred to as recharge) is predominantly vertical and is influenced by properties and conditions of the vadose zone.

Two geologic properties of the Bandelier Tuff that influence the fluid flow in the unsaturated zone are the degree of welding and the devitrification, both effects of prolonged presence of residual gases and high temperatures when the rock was deposited. Because different tuff units were deposited at different temperatures, and because individual units were laid out in variable thicknesses over different landscapes, cooling was not uniform. Consequently, welding varies spatially, both between and within separate depositional layers. Welded tuffs tend to be more fractured than nonwelded tuffs.

Several competing effects determine moisture content and fluid flux in welded, devitrified tuff. While water moves slowly through the unsaturated tuff matrix, it can move relatively rapidly through fractures if nearly saturated conditions exist (LANL 1997, 63131). The saturation levels measured at MDA L are relatively low (1% to 13% gravimetric moisture content [LANL 1994, 76071]). At these saturation levels, most of the fractures beneath MDA L are completely dry and water is found only in the tuff matrix. Only in situations when substantial infiltration occurs from the ground surface do the fractures become wet and conduct water. However, modeling studies at MDA G predict that when fractures disappear at contacts between stratigraphic subunits, if fracture fills are encountered, or if coatings are interrupted, fracture moisture is absorbed into the tuff matrix (LANL 1997, 63131).

In summary, the groundwater flow and contaminant transport in the vadose zone is difficult to characterize. The flow rates and transport velocities/directions can be expected to be variable in both time and space. Between the ground surface and regional aquifer, the flow is predominantly vertical. Nevertheless, the groundwater transport velocities through the vadose zone in the region of TA-54 are slow, likely in the order of several centimeters per year (Birdsell et al. 1995, 70012; Birdsell et al. 1999, 69791).

4.0 SCOPE OF ACTIVITIES

Phase I RFI data for MDA L, evaluated in Section B-4 of Appendix B, identified several data gaps to be addressed to establish the nature and extent of environmental contamination that will be used to evaluate potential risks to human and ecological receptors. Data interpretation and the associated data gaps are summarized in Section 4.1.

4.1 Data Gaps

Seven data gaps were identified based on evaluation of the Phase I RFI data presented in Appendix B and supporting statistical evaluation in Appendix E. The rationale for identifying these data gaps is described in Sections 4.1.1 and 4.1.2 and includes

- 1. vertical extent of subsurface metal contamination;
- 2. lateral extent of tritium in the vapor phase in subsurface tuff;
- 3. nature and extent of perchlorate, nitrate, and high-explosive (HE) contamination in tuff beneath MDA L;
- 4. presence of perched groundwater beneath MDA L;
- 5. information on hydrogeologic properties and fracture characteristics of the vadose zone to support contaminant transport modeling for the future MDA L CMS;
- 6. information on vapor-phase VOC plume stability: continued monitoring is necessary to track plume stability, migration, or a release from the source areas, although the concentrations and the spatial extent of the vapor-phase VOC plume have been identified; and
- 7. collection of a supplemental channel sediment sample.

4.1.1 Extent of Metals Contamination Beneath the Pit, Shafts, and Impoundments

Subsurface data from the Phase I RFI investigation indicate that a release of metals has occurred beneath the pit, shafts, and impoundments at MDA L. Barium, chromium, cobalt, copper, manganese, nickel, uranium, and zinc were detected at concentrations above background values (BVs) in one or more boreholes in two out of three consecutive sampling depths (Appendix B). Other inorganic chemicals detected at concentrations above BV at discrete locations (i.e., in single samples taken from two or three different boreholes at different sampling depths) provided insufficient evidence of a release. The nature and extent of contamination is reviewed in the following subsections by specific impoundments, a pit, and shafts.

Impoundments B, C, and D. Boreholes 54-01012, 54-01013, and 54-01014 were drilled to angle beneath Impoundments B, C, and D, respectively. Concentrations of chromium and copper above their respective BV were detected at three consecutive sampling depths in core samples beneath Impoundment B. Beneath Impoundment C, concentrations of copper were above BV at three consecutive sampling depths, and nickel concentrations exceeded the BV at two out of three consecutive sampling depths. Based on these results, it was concluded that copper and chromium have been released from Impoundment B, and copper and nickel have been released from Impoundment C. In borehole 54-01014, uranium was the only inorganic chemical detected at several consecutive sampling depths. Samples were collected from the unit 2/unit 1v interface and uranium was detected in concentrations slightly above the unit 2 BV (2.40 mg/kg) but below the unit 1v BV (6.22 mg/kg [see Appendix L for a description of the stratigraphy of the area]). The pattern indicates that a release of uranium may have occurred from Impoundment D to the surrounding subsurface tuff. The vertical extent of inorganic chemical contamination is not completely bounded beneath the impoundments.

Pit A. Boreholes 54-01010 and 54-01011 were drilled at an angle to pass beneath the eastern and western portions of Pit A, respectively. In borehole 54-01011, barium was detected in one sample at approximately twice the BV (LANL 1998, 59730). In borehole 54-01010, cadmium, mercury, and uranium were detected above their respective BVs in one sample each, and chromium was detected above the BV in two samples separated by four sampling depths (LANL 1998, 59730). The results from the angled boreholes drilled beneath Pit A do not provide evidence of a release (no consecutive depths with detects greater than BV), and the vertical extent of the release is defined beneath Pit A.

Shafts 1 through 28. This shaft field is located on the east end of MDA L and was evaluated by samples collected from boreholes 54-01007 and 54-01009. The pattern of metal concentrations in these boreholes provided evidence of a release. The primary component of the release was copper, with smaller contributions from chromium, barium, and zinc. Nickel was also detected above BV in the lower tuff strata (units 1v and 1g [see Appendix L for a description of the stratigraphy of the area]).

Copper, chromium, barium, and zinc were detected in borehole 54-01007 at concentrations above their respective BVs at 146 ft (Appendix B). Copper concentrations were greater than BV in 10 of 13 core

samples, often by more than a factor of 10. Chromium concentrations were greater than BV (LANL 1998, 59730) in 5 of 13 samples but did not exceed BV by more than a factor of 2. Copper and chromium remained elevated at the deepest sampling location (146 ft). Barium and zinc concentrations were more than twice their respective BVs in a single core sample and at concentrations marginally above their BVs at two and four sampling depths (some consecutive depths), respectively. Concentrations of barium and zinc decreased to less than their respective BVs at the deeper sampling intervals. Distributions of copper, barium, and zinc in samples taken from borehole 54-01009 were similar to those noted for borehole 54-01007. Based on this analysis, the vertical extent of copper, chromium, and zinc has not been established.

Shafts 29 through 34. This shaft field is located on the west end of MDA L and was evaluated using data from borehole 54-01008, a vertical 150-ft borehole located about 20 ft to the southeast of Shafts 29 through 34. The inorganic chemicals measured at concentrations above background included copper, zinc, and chromium. Copper concentrations exceeded the BVs in a majority of the samples (10 of 12); concentrations detected were more than 10 times the BV. Zinc and chromium were detected at three or more consecutive sampling depths at concentrations exceeding their BVs by a factor of two or less. Manganese and cobalt concentrations above their BVs were reported at two consecutive sampling depths: manganese was marginally above its BV, and one cobalt concentration was more than twice the BV. Based on this analysis, it was concluded the vertical extent of chromium, cobalt, copper, manganese, and zinc have not been established beneath the western shaft group (Shafts 29 through 34). Figures 10, 11, and 12 show the concentrations for chromium, copper, and zinc.

4.1.2 Nature and Extent of Tritium Vapor Plume

Core samples from seven boreholes were analyzed for tritium. Five shallow boreholes (up to 60 ft bgs) were angled beneath Pit A and Impoundments B, C, and D (Figure 5). Two deep angled boreholes (54-01015 and 54-01016) were drilled beneath Shafts 1 through 34 and Pit A (Figure 5). The tritium sample results for the shallow boreholes beneath Pit A ranged from 0.03 pCi/g to 11.6 pCi/g, and concentrations decreased with depth. Tritium was detected twice at very low concentrations in the deep, angled boreholes. Tritium was detected at 0.13 pCi/g at approximately 524 ft in borehole 54-01015, and detected at 0.001 pCi/g at approximately 593 ft in borehole 54-01016. A tritium release beneath MDA L was evident from the sampling results (Figure 13). The data from the deep angled borehole indicates that the vertical extent of the tritium contamination is bounded.

4.1.3 Extent of Perchlorate, Nitrate, and High-Explosive Contamination in Tuff at MDA L

Tuff samples collected from MDA L during the Phase I RFI were not analyzed for perchlorate, nitrates, and HE. Nitrates and perchlorate are very soluble and, therefore, susceptible to migration with infiltrating surface water. Nitrates are associated with fertilizers and are a common breakdown product of most nitrogen-containing organic materials. Perchlorate-containing chemicals have been widely used as oxidizers in a variety of chemical processes, and perchloric acid is a common strong acid used in laboratories. Hence, from the perspectives of potential occurrence in disposed waste at MDA L and mobility of contaminants, analysis for nitrates and perchlorate in core samples collected from new boreholes is appropriate.

Some HE compounds are also relatively soluble in water and subject to transport from the disposed waste. However, the presence of HE in appreciable quantities in the disposed waste at MDA L is unlikely because it has always been Laboratory policy to "flash" (burn) HE-contaminated material prior to disposal. However, because disposal records at MDA L are incomplete and because certain HE compounds are relatively soluble, samples collected from the new boreholes should be analyzed for HE.

4.1.4 Potential Presence of Perched Groundwater Beneath MDA L

There is no site-specific information on intermediate-depth groundwater to determine whether perched groundwater exists beneath MDA L. The deepest Phase I RFI borehole sited on Mesita del Buey is 54-01004, located approximately 150 ft southeast of MDA L; it extends to a depth of approximately 340 ft bgs. The nearest well completed in the regional aquifer, R-22, is approximately 1 mi east of MDA L (Figure 4). No evidence of a zone of saturation (i.e., perched water) was found in borehole 54-01004 or in R-22. However, perched groundwater may be highly localized and the presence of groundwater beneath MDA L at depths below 340 ft has not been definitively determined.

4.1.5 Hydrogeologic Properties and Fracture Characteristics of the Vadose Zone at MDA L

Information relating to hydrogeologic properties and fracture characteristics is necessary for evaluating the potential transport of contaminants in the vadose zone tuff beneath MDA L. The Bandelier Tuff consists of several units with differing hydrogeologic properties and different fracture characteristics. Fractures in the tuff are evident only in the Tshirege Member, which consists of units 2 and 1 at MDA L, as described in Appendix L. Within these units, information relating to whether contamination is primarily associated with fractures or the tuff matrix is needed to evaluate the potential extent of past or future liquid-phase transport in the tuff. Additional information pertaining to the fractures needed to validate transport modeling in the tuff includes fracture density, fracture orientation and angle, fracture aperture, and fracture coatings or fill. Information on hydrogeologic properties of the vadose zone, including parameters such as saturated and unsaturated hydraulic conductivity, chloride-ion concentration, porosity, bulk density, matric potential, and moisture content, is also critical for modeling the potential transport of contaminants from the disposal units via liquid- or vapor-phase migration.

4.1.6 Information on Vapor-Phase VOC Plume Stability

Several organic chemicals were detected in subsurface tuff samples near Pit A and Shafts 1 through 28. The organic chemicals detected at concentrations near the estimated quantification levels (EQLs) are not reliably quantified. These measurements do not represent the extent of VOCs in the subsurface because the subsurface media (volcanic tuff) at MDA L contains almost no organic carbon, has a low moisture content, and has a low specific surface area. Therefore, the nature and extent of the vapor phase VOC plume at MDA L is best defined by sampling and analyzing pore-gas rather than by analyzing core samples.

The following statements can be made about to the nature and extent of the VOC release from MDA L:

- VOCs are transported from source areas mainly in the vapor phase;
- TCA is the dominant contaminant, followed by TCE;
- vertically, the plume extends between ground surface and the top of the basalt (approximately 320 ft bgs);
- laterally, the plume extends north-south about 1000 ft in diameter, and east-west it extends the width of the mesa (approximately 450 ft);
- the ratio of the major contaminants (TCA, TCE, and R-113 [Freon 113]) is approximately 1:0.3:0.2;
- the plume is changing very little in location or content with time; and
- vapor diffusion modeling fits the measured geographic distribution of TCA concentration.

Both field-screening results and analytical results indicate that the highest concentrations of vapor-phase VOCs exist nearest the two source areas (east side and west side of MDA L). Concentrations of vaporphase VOCs decrease in all directions from the two source areas.

The analytical data for VOCs in pore gas define the organic chemicals present in the vapor phase plume. The suite of organic chemicals detected has remained consistent over time and the concentrations of the chemicals have decreased over time (Appendix B). Furthermore, the relative concentrations among the major organic chemicals have remained constant over time. Measurements prior to 1993 detected much higher concentrations of VOCs within the plume than those detected today, especially in the source area. However, historical screening and analytical methods did not produce consistent results and the methodologies were not well developed; therefore, the pre-1993 data are of limited use. A discussion of historical and present pore-gas sampling methodologies is provided in Appendix G. Sampling and analytical methods have greatly improved since the late 1990s, resulting in consistent, good quality data from both the analytical chemistry and B&K screening. These data allow for evaluation of trends within the plume.

Field-screening results using a B&K multigas analyzer show a VOC plume that is stable or decreasing in concentration (Figures 14, 15, and 16). Figures 14 and 15 show the lateral and vertical extent by the 10-ppm concentration contour. Outside this contour, concentrations drop rapidly to below the quantification capability of the B&K instrument; analytical samples from this region indicate TCA concentrations in the part per million (ppm) range. Since 1999, the long-axis plume aerial extent, defined by the 10-ppm contour, has varied between 700 and 1000 ft. The short-axis extent has not varied considerably because of the physical constraint of the mesa walls. Vertically, the maximum extent of the 10-ppm TCA contour is approximately 300 ft below the mesa top and has not varied noticeably since 1999. The 10-ppm TCA contour is approximately 650 ft above the regional aquifer. Analytical results and screening results from pore-gas monitoring boreholes with ports in the basalt located between the lower plume boundary and the regional aquifer have not consistently detected VOCs. The deepest TCA concentration measured in a SUMMA™ canister sample (MD54-99-0025) analyzed by an off-site contract laboratory is 0.083 ppm in borehole 54-01016 at a depth of 390 ft. Figure 16 shows the two-dimensional characteristic profile of the plume. Concentrations increase to a depth of approximately 85 ft below the surface of MDA L, followed by a decrease in concentrations through the total depth of the plume.

Figures 17, 18 and 19 present SUMMA™ canister data for the VOCs with the highest concentrations in the plume. These samples were collected each quarter from the same borehole locations. Figure 17 presents data from borehole 54-02002, which is representative of the eastern shaft field. Figure 18 presents data from borehole 54-02023, which is representative of a medium to low concentration zone of the plume. Figure 19 presents data from borehole 54-01015, which is representative of the plume at a greater depth (approximately 400 ft bgs). As illustrated in these figures, the concentrations of the top 11 detected VOCs have remained relatively constant over time or have decreased slightly. Therefore, it is concluded that the plume is in a near steady-state condition.

Stauffer et al. (2002, 69794) modeled the evolution of the vapor-phase VOC plume using a threedimensional finite element program; the report is provided in Appendix I. An independent review of the report conducted by the Innovative Technology and Remediation Demonstration Program and studies of passive and active venting are provided in Appendix J. The model assumed vapor diffusion emanating from two source areas located at the two shaft fields at MDA L. It was calibrated using the quarterly poregas monitoring data. The resulting model closely matches the shape, concentration gradients, and extent of the plume as measured by existing data. In addition, the model predicts that the plume should be at or near steady state. This modeling supports the conclusion that the VOC plume exists predominantly in the vapor phase, the VOCs move by diffusion, and the plume is stable. Stauffer et al. (2002, 69794) also

predicted the evolution of the plume over a 50-yr period. If the assumed source remains constant, the plume should not change in size and concentration appreciably during the simulation period, which further verifies the stability of the plume. If a constant source were not assumed, the plume would gradually decrease in size and concentration over time.

Any remaining intact drums may rupture and add to the source of the plume. Since it is not possible to determine how many drums of liquid hazardous constituents remain intact in the shafts at MDA L, it is not possible to assume a constant or decreasing source term. Therefore, it will be necessary to monitor the stability of the vapor-phase VOC plume over time.

4.1.7 Channel Sediments

Phase I RFI analytical data showed that channel sediment samples at MDA L contained low concentrations of methoxyclor and plutonium-238. A location near previous Phase I RFI sediment sample location 54-05148 will be selected to collection a supplemental channel sediment sample to complete the characterization of the channel that drained storm water from the surface of MDA L before it was paved.

4.2 Proposed Sampling and Analysis Activities to Address Data Gaps

Acquisition of data to address the gaps described in Section 4.1 require drilling four additional boreholes to collect subsurface core, VOC pore-gas, and tritium samples. The key components of the drilling and sampling program are the location, depth, and angle of boreholes, sample collection methods and frequency of sampling, and the analytical suites requested. The proposed drilling and sampling program uses information from the existing Phase I RFI boreholes, surface flux, and pore-gas sampling results to delineate these components. The borehole locations were selected to provide the additional data required to determine the nature and extent of contamination in the subsurface of MDA L.

The technical approach and rationale for the drilling and sampling activities related to the seven data gaps described in Section 4.1 are discussed below. A summary of these drilling and sampling activities is provided in Table 2. The locations and cross sections of the proposed boreholes in relation to the disposal units at MDA L and the existing boreholes are shown in Figure 20. Figures 21 through 24 illustrate profiles of the four proposed characterization boreholes with planned sample locations and depths.

4.2.1 Proposed Drilling and Sampling to Address Data Gap 1

Impoundment D. One angled borehole (borehole A, Figure 21) will be advanced beneath Impoundment D to determine the vertical extent of metal contamination. Borehole A will be sited to the south of Impoundment D and will be advanced towards the northeast beneath the long axis of the impoundment. This siting is proposed because of the limited space between surface structures and fencing at MDA L. Borehole A will also be angled so that samples can be collected beneath locations in RFI borehole 54-01014 to determine the vertical extent of metals contamination.

Impoundments B and C. One angled borehole (borehole B, Figure 22) will be advanced beneath these impoundments to determine the vertical extent of metal contamination. It will be sited to the southeast of Impoundment B and advanced towards the northwest, passing beneath Impoundments B and C. This siting is proposed because of the limited space between surface structures and fencing at MDA L. This borehole will also be angled to allow for collection of samples from depths beneath the Phase I sample collection depths in RFI boreholes 54-01012 and 54-01013 to determine the vertical extent of metals contamination.

Shafts 29 through 34. One steeply angled borehole (borehole C, Figure 23) will be advanced beneath these shafts to determine the vertical extent of metals contamination. Borehole C will be sited between Shafts 30 and 34 and advanced northwest towards Shaft 29. A FLUTe™ liner will also be installed in this borehole for monitoring of pore gas in the northwest shaft field.

Shafts 1 through 28. One vertical borehole (borehole D, Figure 24) will be drilled immediately east of these shafts. Samples will be collected from the augured portion (approximately 300 ft) of this borehole to determine the vertical extent of metal contamination. The borehole is located within 50 ft of Shafts 1 through 5 and at the down-slope end of the shaft group (Figure 20).

All angled boreholes will pass no closer than 15 ft from any disposal unit. Before final siting of these boreholes, historical disposal records and RFI borehole logs will be examined to ensure that boreholes will not be advanced through the disposal units.

Tuff samples will be collected approximately every 30 linear ft down the boreholes, once the borehole passes beneath an impoundment or shaft. However, actual sampling will be biased according to the presence of fractures and/or the results of radiation field screening. Fractures will be used to bias sampling because they may play a role as conduits for liquid transport. Where fractures are encountered, paired samples of the fracture and the tuff matrix near the fracture will be obtained to evaluate whether potential contamination has migrated predominantly in fractures. This paired sampling is described in Section 5.3.

Tuff samples collected from boreholes A, B, and C will be submitted to an off-site contract laboratory for analysis of isotopic uranium, isotopic plutonium, americium-241, strontium-90, radionuclides by gamma spectroscopy (including cesium-134, cesium-137, cobalt-60, europium-152, ruthenium-106, and sodium-22), TAL metals and cyanide, HE (a subset of samples; see Section 4.2.3), nitrates, and perchlorate. Protocols for collecting tuff samples from boreholes A, B, and C are described in Section 5.1.2.

Required analytical detection limits for metals, cyanide, radionuclides, nitrates, perchlorate, and HE compounds are driven by the need to measure concentrations below BVs accurately, if these values are available. Detection limits for analytical methods specified by contract requirements of the Laboratory's analytical statement of work (SOW) are adequate for this purpose (LANL 2000, 71233).

4.2.2 Proposed Drilling and Sampling to Address Data Gap 2

In situ subsurface samples will be collected from pore gas to determine the lateral extent of the subsurface tritium release at MDA L. Samples will be collected as water vapor by pulling pore gas through columns filled with absorbent silica gel. A minimum of two tritium pore-gas samples will be collected in the following boreholes: 54-02002, 54-02014, 54-02016, 54-02020, 54-02021, 54-02022, 54-02023, 54-02025 and proposed boreholes A, B, and C to sample the center and boundaries of the potential plume.

Tritium in water extracted from the core sample will be measured by EPA Method 906.0. At gravimetric moisture contents less than 10%, a 3-in. length of 2-in.-diameter core will yield less water than the minimum required volume of 5 mL. To reach the necessary volume, the analytical laboratory adds deionized water to the extracted water. The analytical laboratory then corrects the reported activity and uncertainty resulting from the dilution. Therefore, any moisture from a core sample lost before analysis may substantially increase the uncertainty of the measurement. In addition, the method requires grinding the core material to a fine mesh before the water is extracted; thus, moisture loss is inevitable. Given these concerns, RRES-RS has concluded that tritium is best characterized in low moisture content

environments using sorbent materials to extract and retain in situ subsurface water samples from pore gas.

4.2.3 Proposed Sampling to Address Data Gap 3

The NMED has requested additional analytical suites for subsurface tuff samples because certain analytes were not included in the Phase I RFI analytical suites. These analytes include HE, dioxins/furans, nitrates, and perchlorate. The rationale for analyzing HE, nitrates, and perchlorate is presented in Section 4.1.3. PCBs and semivolatile organic compounds (SVOCs), which were not detected in Phase I RFI tuff samples, are characterized by low solubilities in water. To an even greater extent, low solubility is also characteristic of dioxins and furans. Hence, the presence of these four classes of chemicals in subsurface tuff in appreciable quantities as a consequence of dissolution in water is highly unlikely. A review of waste inventory records does not indicate the presence of dioxins or furans in the disposed waste or provide evidence that chemicals had been burned (Appendix K). Therefore, dioxins and furans will not be included the analytical suite. All tuff samples collected from boreholes A through C will be analyzed for nitrates and perchlorate.

Core collected from 30-ft intervals will be screened using immunoassay test kits for nitroaromatics (e.g., trinitrotoluene [TNT]) and nitrosamines (e.g., 1,3,5-trinitro-1, 3,5-triazacyclohexane [RDX]). Screening samples will be biased toward fractures, visibly stained media, paleosols, and core with elevated radioactivity field-screening results. These test kits (D-Tech) have a low detection limit (ppm range in soil) and have proven effective in biasing samples for laboratory analysis (LANL 1997, 55653). Of the tuff samples to be collected from boreholes A through C, at least three samples will be screened for HE. Because real-time qualitative results will be obtained in the field with the immunoassay test kits, 20% of the core samples will be submitted to an off-site contract laboratory for analysis of HE to verify immunoassay field-screening results and define the nature and extent of contamination. The lower sampling frequency reflects the low probability of encountering HE at MDA L.

4.2.4 Proposed Sampling to Address Data Gap 4

A single, vertical borehole (borehole D, Figure 24) will be drilled to a depth of 700 ft in the area immediately outside of the eastern boundary of MDA L to determine whether perched groundwater is present beneath MDA L. Borehole D is proposed for an area immediately east of MDA L within 100 ft of the eastern shaft field. The borehole site is adjacent to the eastern storm water discharge channel and downgradient of MDA L to provide the best chance of encountering perched water. Sampling of this borehole is described in Section 4.2.5 of this IWP.

4.2.5 Proposed Sampling to Address Data Gap 5

Geotechnical samples will be collected from borehole D to support transport modeling by characterizing site-specific hydrogeologic properties at MDA L. The geotechnical properties to be analyzed include saturated and unsaturated hydraulic conductivity, chloride-ion concentration, porosity, bulk density, matric potential, and moisture content. After drilling, borehole D will be logged for moisture content using a neutron probe. Logging will be conducted at 1-ft intervals to total depth following the applicable standard operating procedures (SOPs). A detailed profile of moisture content will ensure an adequate data set for calibrating a neutron probe for moisture logging. A profile of matric potential, in combination with the moisture content, will provide data on the likely direction of moisture movement in the subsurface. Estimates of saturated and unsaturated hydraulic conductivity will also support modeling of liquid migration in the vadose zone. Tuff samples for analysis of chloride-ion concentration will support evaluation of the rates of water infiltration and evaporation.

4.2.6 Proposed Sampling to Address Data Gap 6

As discussed in Section 4.1.5, the continued monitoring of the vadose zone VOC plume beneath MDA L is required. To supplement the current pore-gas monitoring program, borehole C will be completed as a vapor monitoring well by installing a FLUTe™ soil-gas sampling positive-pressure membrane. This borehole will then be incorporated into the proposed pore-gas monitoring program at MDA L (Section 6).

4.2.7 Proposed Sampling to Address Data Gap 7

To complete the characterization of the drainage channel, one sediment sample will be collected at the interface of the alluvial sediments and bedrock (Figure B-2) and submitted to an off-site contract laboratory for analysis of TAL metals and cyanide, pesticides/PCBs, nitrates, perchlorate, americium-241, isotopic plutonium, isotopic uranium, strontium-90, and tritium.

5.0 INVESTIGATION METHODS

The following RRES-RS SOPs are applicable to the investigation methods proposed in this plan:

- LANL-ER-SOP-1.01, Rev. 1, General Instructions for Field Investigations
- LANL-ER-SOP-1.02, Rev. 1, Sample Containers and Preservation
- LANL-ER-SOP-1.03, Rev. 2, Handling, Packaging, and Transporting Field Samples
- LANL-ER-SOP-1.04, Rev 4, Sample Control and Field Documentation
- LANL-ER-SOP-1.05, Rev. 0, Field Quality Control Samples
- LANL-ER-SOP-1.08, Rev. 1, Field Documentation of Drilling and Sampling Equipment
- LANL-ER-SOP-3.11, Rev 1, Geodetic Surveys
- LANL-ER-SOP-4.01, Rev. 1, Drilling Methods and Drill Site Management
- LANL-ER-SOP-5.07, Rev. 0, Operation of LANL Owned Borehole Logging Trailer
- LANL-ER-SOP-5.03, Rev. 2, Monitoring Well and RFI Borehole Abandonment
- LANL-ER-SOP-6.09, Rev. 1, Spade and Scoop Method for Collection of Soil Samples
- LANL-ER-SOP-6.14, Rev. 0, Sediment Material Collection
- LANL-ER-SOP-6.26, Rev. 1, Core Barrel Sampling for Subsurface Earth Materials
- LANL-ER-SOP-6.31, Rev. 1, Atmospheric and Sub-Atmospheric Air Sampling
- LANL-ER-SOP-7.05, Rev. 1, Subsurface Moisture Measurements Using a Neutron Probe
- LANL-ER-SOP-12.01, Rev. 4, Field Logging, Handling, and Documentation of Borehole Material

Additional procedures may be added as necessary to describe and document quality-affecting activities.

5.1 Methods for Drilling and Sampling Boreholes A through C

5.1.1 Drilling Protocol

Boreholes A through C will be drilled using the hollow-stem auger method because it allows for collecting undisturbed samples of core and subsurface vapors within the Tshirege Member of the Bandelier Tuff.

Borehole profiles for boreholes A through C illustrate their location relative to disposal units in Figures 20 through 23. The depth, angle, and sampling protocol for each borehole are described in Table 2. Each borehole will be continuously cored using a split-barrel sampler to total depth. Core will be screened for radiation and organic vapors, visually inspected, and geologically logged. The total depth of boreholes may increase if field screening indicates elevated readings of radionuclides and organic vapors. The boreholes will be located in the approximate areas shown in Figure 20. The proposed location of each borehole has been determined by best estimates of impoundment and shaft boundaries from historical documents and RFI borehole logs. Other factors such as the presence of utilities and access restrictions will also affect the exact location of each borehole.

5.1.2 Collection of Core Samples

Subsurface core samples will be collected from the split-barrel sampler into sealed sleeves or coreprotect bags to preserve the moisture content of the core. The analytical suites for samples to be collected from each borehole are listed in Table 2. The frequency of sampling and orientation to disposal units is displayed in Figures 21 through 23.

Tuff samples will be collected at least every 30 ft in boreholes A, B, and C; the first samples will be collected at the depth of the target disposal unit, and the last sample will be collected at total depth of each borehole. Samples will be collected from intervals where contamination is suspected because of elevated field screening measurements and/or fractures or staining identified by visual inspection.

Field documentation of samples collected from fractures will include a detailed physical description of the fracture-fill material and rock matrix sampled. The volumes of fracture fill and rock-matrix material included in the sample will be estimated from field measurements. An additional sample will be collected from the rock matrix adjacent to the fracture sample material to allow for comparison. A discussion of paired fracture sampling is in Section 5.3.

Tuff samples from boreholes A through C will be analyzed for TAL metals and cyanide, HE, nitrates, perchlorate, and radionuclides (americium-241, strontium-90, isotopic uranium, isotopic plutonium, and gamma spectroscopy radionuclides) using analytical methods specified by contract requirements of the Laboratory's Analytical SOW (LANL 2000, 71233).

QA/QC samples will include field duplicate samples collected following the applicable SOPs listed in Section 5.1. To confirm decontamination procedures, rinsate blanks will also be collected.

5.1.3 Collection of Pore-Gas Samples

Subsurface vapor samples will be collected from boreholes A through C at the depth of the nearest adjacent disposal units and from the bottom of the borehole for analysis of VOCs and tritium. Vapor samples will be collected using a straddle packer to isolate discrete depths of the borehole. Each interval will be purged prior to sampling until measurements of carbon dioxide and oxygen are stable. Subsurface vapor samples will be collected in SUMMA™ canisters and submitted for analysis using EPA Method TO-14 for VOCs. In situ subsurface water samples will be collected on silica gel in sealed columns and submitted for analysis using EPA Method 906.0 for tritium.

QA/QC samples for VOCs and tritium in pore gas will consist of an equipment blank and a field duplicate. The equipment blank will be collected through the packer sampling apparatus, after sampling and purge decontamination, to observe potential cross contamination. The field duplicate sample will indicate the precision of collection and analysis.

5.1.4 Borehole Completion

Once borehole C is drilled and sampled and core and initial pore-gas samples are collected, the borehole will be completed as a vapor-monitoring borehole. A FLUTe™ soil-gas sampling positive-pressure membrane will be installed, and the borehole will be incorporated into the pore-gas monitoring network.

Boreholes A and B will remain open at depth and sealed at the surface with a capped steel casing. These boreholes will remain available for vapor extraction or monitoring as necessary beneath Impoundments B, C, and D.

5.2 Methods for Drilling and Sampling Borehole D

5.2.1 Drilling Protocol

A single, vertical borehole will be drilled to a depth of 700 ft just east of the MDA L boundary. The location and depth of the borehole were selected to determine whether perched groundwater is present below MDA L.

Hollow-stem auger drilling will be used until refusal (at least 280 ft bgs) because auger drilling results in collecting undisturbed samples of core within the Tshirege Member of the Bandelier Tuff. Upon drill refusal, air-rotary drilling will be deployed to complete the borehole. The coupling of these drill methods is practical and allows the objectives of the sampling for this borehole to be met. The vertical borehole will be continuously cored with a split-barrel sampler to 700 ft bgs. Core will be radiologically screened, visually inspected, and geologically logged. The borehole will be located in the approximate location shown in Figure 20. The proposed location of this borehole has been determined by best estimates of impoundment and shaft boundaries and RFI borehole logs. Other factors such as the presence of utilities and access restrictions will also affect the exact location of each borehole.

5.2.2 Collection of Tuff Samples

Subsurface tuff samples will be collected from the split-barrel sampler into sealed sleeves or core-protect bags to preserve the core moisture content. The analytical suites for the borehole samples are listed in Table 2. The frequency of sampling and orientation to disposal units is shown in Figure 24.

Tuff samples will be collected at the depth of the target disposal unit and from the Cerro Toledo interval, approximately 280 ft below MDA L. Samples will also be collected from intervals where contamination is suspected because of elevated field screening and/or identification of fractures, staining or paleosols. Field documentation of samples collected from fractures will include a detailed physical description of the fracture fill material and rock matrix sampled. The volumes of fracture fill and rock-matrix material included in the sample will be estimated from field measurements. An additional sample will be collected from the rock matrix adjacent to the fracture sample material to allow for comparison. Section 5.3 discusses the paired fracture sampling method.

Two tuff samples from borehole D will be analyzed for TAL metals and cyanide, HE compounds, nitrates, perchlorate, and radionuclides (americium-241, strontium-90, isotopic uranium, isotopic plutonium, and gamma spectroscopy radionuclides) using analytical methods specified by contract requirements of the Laboratory's analytical SOW (LANL 2000, 71233). QA/QC samples will include field duplicate samples that will be collected following the applicable SOPs listed in Section 5.1. To confirm decontamination procedures, rinsate blanks also will be collected.

5.2.3 Collection of Geotechnical and Hydrogeological Samples

Moisture content and matric potential samples will be collected every 5 ft from borehole D and samples for chloride analysis will be collected every 10 ft. Samples for saturated and unsaturated hydraulic conductivity, porosity, and bulk density analyses will be collected once in each tuff unit and twice from the Cerro Toledo interval, and at five depths in the Otowi Member. Five samples will also be collected from the Puye Formation. The samples collected from the Cerro Toledo interval, Otowi Member, and Puye Formation will be selected from core to be representative of all the textural intervals encountered. Analyses for saturated and unsaturated hydraulic conductivity, porosity, and bulk density will be performed using the methods specified by contract requirements of the Laboratory's analytical SOW (LANL 2000, 71233). One field duplicate sample will be collected and analyzed. Samples will be collected, handled, packaged, and analyzed in accordance with applicable Laboratory SOPs.

5.3 Collection of Paired Fracture Samples

Empirical evidence of the role of fractures in facilitating contaminant transport in tuff will be obtained by collecting paired samples of fracture material and tuff matrix when tuff fractures are encountered during drilling. Because fracture fill may not be present, or may exist in minute quantities, fracture samples will include 3 in. of tuff both above and below the fracture. Detailed descriptions and photographs will be made for each fracture sample. To compare contaminant concentrations between fractured and unfractured tuff, a second sample of unfractured tuff will be collected 24 in. above the fracture sample (Figure 25). These paired samples collected from boreholes A, B, C, and D will be submitted to an offsite contract laboratory for analysis of isotopic uranium, isotopic plutonium, americium-241, strontium-90, radionuclides by gamma spectroscopy (including cesium-134, cesium-137, cobalt-60, europium-152, ruthenium-106, and sodium-22), TAL metals and cyanide using analytical methods specified by contract requirements of the Laboratory's analytical SOW (LANL 2000, 71233). This method of fracture collection and analyses provides information about potential preferred pathways of contaminant transport beneath MDA L.

5.4 Collection of Pore Gas for Tritium Analyses

Pore-gas samples for tritium analyses will be collected from ports in boreholes 54-02002, 54-02014, 54-02016, 54-02020, 54-02022, 54-02023, 54-02025, and proposed boreholes A, B, and C. These samples will be collected by pulling pore gas through columns filled with absorbent silica gel according to LANL-ER-SOP 6.31, Revision 1, and analyzed at an off-site fixed laboratory by EPA Method 906.0. QA/QC samples will be collected per applicable SOPs.

5.5 Collection of Sediment Sample

The sediment sample will be collected in accordance with LANL-ER-SOP-6.09, Rev. 1, Spade and Scoop Method for Collection of Soil Samples.

6.0 MONITORING AND SAMPLING PROGRAM

An investigation report will be prepared following implementation of this work plan. The investigation report will contain recommendations for future activities at MDA L, including any monitoring and sampling program beyond those described in Sections 4 and 5 of this IWP.

An interim monitoring program is recommended for MDA L to replace the current quarterly pore-gas monitoring program required by Module VIII of the Laboratory's Hazardous Waste Facility permit. The current quarterly pore-gas monitoring program focuses on defining the nature and extent of the vapor phase VOC plume for the RFI. While the historic investigation report concludes that the nature and extent of the VOC vapor phase plume has been defined, the plume will continue to be monitored to ensure that it behaves as predicted and to detect any potential release from the source area.

For the last two years, the quarterly pore-gas monitoring program has focused on collecting samples from the same locations and depths during each event. This data set will allow for statistical trend analysis of concentration and analyte through time from locations within the MDA L plume. Results for these samples have been reported in the RRES-RS quarterly technical reports (LANL 2002, 73712). A summary of the trend analysis will be included in the fiscal year (FY) 2003 annual report in October 2003.

The proposed interim pore-gas monitoring program will monitor the source areas and the vertical extent of the VOC vapor plume annually; the lateral extent of the plume will be monitored biannually. Sampling on an annual basis versus quarterly monitoring is adequate to detect changes in extent and identify potential new releases. Biannual sampling at the lateral perimeter of the plume is sufficient to confirm estimates of long-term extent. Boreholes 54-02002, 54-02014, and proposed borehole C will be used to monitor the source areas and the vertical extent of the plume. Boreholes 54-02021, 54-02022, and 54-02034 will be used to monitor the western extent of the plume, while boreholes 54-02020, 54-0024, and 54-02027 will be used to monitor the eastern extent of the plume. Figure 26 shows the locations of the current and proposed boreholes at MDA L, and Table 3 contains a summary of monitoring borehole vapor port depths, and the frequency of sampling. Samples will be collected using SUMMA™ canisters from all available ports in the monitoring boreholes, and will be completed using the latest revision of LANL-ER-SOP 6.31, Sampling of Sub-Atmospheric Air. The laboratory analysis method for the SUMMA™ samples is EPA TO-14. Once NMED approves a revised vapor-monitoring plan, the Laboratory will submit a Class III permit modification request.

Data collected from the monitoring boreholes will be evaluated for plume changes that are not consistent with the conceptual and computer models for new releases and will provide data for evaluating alternatives for plume remediation/containment in the CMS. A new release could be identified by changes in long-term trends, changes in the relative concentration of contaminants (e.g., ratio of TCA to PCE), or the appearance of a new contaminant.

7.0 SCHEDULE

The MDA L IWP will be submitted to NMED on August 29, 2003. Assuming a 90-day NMED review period, and 45 days to resolve comments between NMED and the Laboratory, field activities will start on February 1, 2004. Field activities, including drilling and sampling, will take approximately four weeks. Pore-gas monitoring borehole C will be instrumented during week 5 and samples will be collected in week 6.

The investigation report is scheduled for submittal to NMED on December 23, 2004.

8.0 REFERENCES

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Turin, H., and N. Rosenberg, January 1996. "A Conceptual Model for Flow in the Vadose Zone Beneath the Finger Mesas of the Pajarito Plateau," in New Mexico Geological Society 48th Annual Field Conference, September 25–28, 1996, F. Goff, et al. eds., Santa Fe, New Mexico. (Turin and Rosenberg 1996, 63559)

Figure 1. Location of MDA L within TA-54 with respect to other Laboratory TAs and surrounding land holdings

Figure 2. Location of MDA L within TA-54

Source: RRES-RS map R03074, 082003, MO_Rev. for F3, MDA L IWP, 082503, cf

Figure 3. Locations of subsurface disposal units at MDA L

Source: GIS Lab m200714, REK, 061703_Rev. for F9, MDA L IWP, 082503, cf

Figure 9. Water table elevations at the Laboratory

F6.1-16, TA-54 RFI RPT, 020100, PTM_Rev. for F12, MDA L IWP, 082203, cf

Figure 10. Chromium concentrations (mg/kg) in Phase I RFI tuff samples at MDA L. Concentrations are proportional to the area enclosed by the oval and plotted at sampled depths (ft bgs) from the borehole. Symbol × **indicates that the sample concentration is greater than the maximum concentration observed in tuff (all strata) at Laboratory background locations (13 mg/kg).**

F6.1-17, TA-54 RFI RPT, 020100, PTM_Rev. for F12, MDA L IWP, 082203, cf

Figure 11. Copper concentrations (mg/kg) in Phase I RFI tuff samples at MDA L. Concentrations are proportional to the area enclosed by the oval and plotted at sampled depths (ft bgs) within the borehole. Symbol × **indicates that the sample concentration is greater than the maximum concentration observed in tuff (all strata) at Laboratory background locations (6.2 mg/kg).**

F6.1-18, TA-54 RFI RPT, 020100, PTM_Rev. for F12, MDA L IWP, 082503, cf

Figure 12. Zinc concentrations (mg/kg) in Phase I RFI tuff samples at MDA L. Concentrations are proportional to the area enclosed by the oval and plotted at sampled depths (ft bgs) within the borehole. Symbol × **indicates that the sample concentration is greater than the maximum concentration observed in tuff (all strata) at Laboratory background locations (74 mg/kg).**

54-2022, TCA Concentration

Figure 16. Pore-gas monitoring borehole 54-02022—TCA concentration vs. depth. Note the characteristic increase in concentration to approximately 100 ft bgs at MDA L, followed by decreasing concentrations to the total depth of the borehole.

Figure 24. Profile of borehole D showing contaminant and geotechnical sample locations

Figure 25. Paired fracture sampling diagram

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Table 1 (continued) **Table 1 (continued)**

Table 1 (continued) **Table 1 (continued)**

b

n/a = Not applicable.

Proposed Borehole Locations and Analytical Suites for MDA L **Proposed Borehole Locations and Analytical Suites for MDA L Table 2**

Monitoring Well ID	Depths of Screened Ports (ft bgs)	Monitoring Purpose	Monitoring Frequency
54-2002	20, 40, 60, 80, 100, 120, 140, 157, 180, 200	Southeast source area, vertical extent	Annual
54-2014	13, 31, 46, 86	Southeast source area, vertical extent	Annual
Proposed borehole C	TBD*	Northwest source area, vertical extent	Annual
54-2021	20, 40, 60, 80, 100, 120, 140, 160, 180, 200	Western extent of plume	Biannual
54-2022	20, 40, 60, 80, 100, 120, 140, 160, 180, 200	Western extent of plume	Biannual
54-2034	20, 40, 60, 80, 100, 160, 200, 220, 260	Western extent of plume	Biannual
54-2020	20, 40, 60, 80, 95, 120, 140, 160, 180, 200	Eastern extent of plume	Biannual
54-2024	20, 40, 60, 80, 100, 120, 140, 160, 180, 200	Eastern extent of plume	Biannual

Table 3 Proposed Monitoring Boreholes for Long-Term Monitoring Network

*TBD = To be determined based on field data.

Appendix A

Acronyms, Glossary, and Metric Conversion Table

APPENDIX A ACRONYMS, GLOSSARY, AND METRIC CONVERSION TABLE

A-1.0 ACRONYMS

A-2.0 GLOSSARY

- **Background value (BV).** The upper tolerance limits (UTLs) of background sample results, calculated as the upper 95% confidence limit for the 95th percentile. When a UTL cannot be calculated, either the detection limit or the maximum reported value is used as a BV; BVs are used as simple threshold numbers to identify potentially contaminated site sample results that are greater than background levels in that geological sample medium (or group of media). Most inorganic chemicals and radionuclides have BVs.
- **Baseline risk assessment (also known as risk assessment).** A site-specific analysis of the potential adverse effects of hazardous substances that are released from a site in the absence of any control or mitigation actions. A baseline risk assessment consists of four steps: data collection and analysis, exposure assessment, toxicity assessment, and risk characterization.
- **Calibration**. Process used to identify the relationship between the true (reference) analyte concentration or other variable and the response of a measurement instrument, chemical analysis method, or other measurement systems.
- **Chemical of potential concern (COPC).** A chemical detected at a site that has the potential to adversely affect human *receptors* because of its concentration, distribution, and mechanism of toxicity. A COPC remains a concern until *exposure* pathways and receptors are evaluated in a site-specific human health risk assessment.
- **Chemical of potential ecological concern (COPEC).** A chemical detected at a site that has the potential to adversely affect ecological *receptors* because of its concentration, distribution, and mechanism of toxicity.
- **Data validation.** Systematic process that applies a defined set of performance-based criteria to a body of data and may result in qualification of the data. The data validation process is performed independently of the analytical laboratory that generates the data set and occurs before conclusions are drawn from the data. The process may comprise a standardized data review (routine data validation) and/or a problem-specific data review (focused data validation).
- **Department of Energy (DOE)**. Federal agency that sponsors energy research and regulates nuclear materials for weapons production.
- **Detection limit (DL).** Minimum concentration that can be determined by a single measurement by an instrument; it implies a specified statistical confidence that the analytical concentration is greater than zero.
- **Dose.** Quantity of radiation that is absorbed, per unit of mass, by the body or by any portion of the body.
- **Ecological screening level (ESL).** An organism's exposure-response threshold for a given chemical constituent. The concentration of a substance in a particular medium corresponds to a hazard quotient (HQ) of 1.0 for a given organism below which no risk is indicated.
- **Environmental Protection Agency (EPA)**. Federal agency responsible for enforcing environmental laws. While state regulatory agencies may be authorized to administer some of this responsibility, the EPA retains oversight authority to ensure protection of human health and the environment.
- **Groundwater.** Water in a subsurface saturated zone; water beneath the regional water table.
- **Migration.** The movement of inorganic and organic species through unsaturated or saturated materials.
- **Model.** A mathematical approximation of a physical, biological, or social system.
- **National Pollutant Discharge Elimination System (NPDES).** The national program for both issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits and imposing requirements under Sections 307, 318, 402, and 405 of the Clean Water Act.
- **Polychlorinated biphenyls (PCBs).** Any chemical substance that is limited to the biphenyl molecule that has been chlorinated to varying degrees or any combination of substances containing such substances. PCBs are colorless, odorless compounds that are chemically, electrically, and thermally stable and have proven to be toxic to both humans and animals.
- **Quality assurance (QA).** All those planned and systematic actions necessary to provide adequate confidence that a facility, structure, system, or component will perform satisfactorily in service.
- **Quality control (QC).** (1) All those actions necessary to control and verify the features and characteristics of a material, process, product, or service to specified requirements. QC is the process through which actual quality performance is measured and compared with standards. (2) All methods and procedures used to obtain accurate and reliable results from environmental sampling and analysis. Includes rules for when, where, and how samples are taken; sample storage, preservation and transport; and the use of blanks, duplicates, and split samples during the analysis.
- **Radionuclide.** A nuclide (species of atom) that exhibits radioactivity.
- **RCRA facility investigation (RFI).** The investigation that determines if a *release* has occurred and the nature and extent of the contamination from such a release at a hazardous waste facility. The RFI is generally equivalent to the remedial investigation portion of the Comprehensive Environment Response, Compensation, and Liability Act (CERCLA) process.
- **Receptor.** A person, plant, animal, or geographical location that is exposed to a chemical or physical agent released to the environment by human activities**.**
- **Regional aquifer.** Geologic material(s) or unit(s) of regional extent whose saturated portion yields significant quantities of water to wells, contains the regional zone of saturation, and is characterized by the regional water table or potentiometric surface.
- **Release.** Any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous waste or hazardous constituents into the environment (including the abandonment or discarding of barrels, containers, and other closed receptacles that contain any hazardous wastes or hazardous constituents).
- **Resource Conservation and Recovery Act (RCRA).** The Solid Waste Disposal Act as amended by the Resource Conservation and Recovery Act of 1976. (40 CFR 270.2)
- **Sample.** A portion of a material (e.g., rock, soil, water, air), which, alone or in combination with other samples, is expected to be representative of the material or area from which it is taken. Samples are typically sent to a laboratory for analysis or inspection or are analyzed in the field. When referring to samples of environmental media, the term "field sample" may be used.
- **Screening action level (SAL).** Medium-specific concentration level for a chemical derived using conservative criteria below which it is generally assumed that there is no potential for unacceptable *risk* to human health. The derivation of a SAL is based on conservative exposure and land-use assumptions. However, if an applicable regulatory standard exists that is less than the value derived by risk-based computations, it will be used for the SAL.
- **Screening assessment.** A process designed to determine whether contamination detected in a particular medium at a site may present a potentially unacceptable human-health and /or ecological risk. The assessment utilizes screening levels that are either human-health or ecologically based concentrations

derived by using chemical-specific toxicity information and standardized exposure assumptions below which no additional actions are generally warranted.

- **Sediment.** (1) A mass of fragmented inorganic solid that comes from the weathering of rock and is carried or dropped by air, water, gravity, or ice; or a mass that is accumulated by any other natural agent and that forms in layers on the earth's surface such as sand, gravel, silt, mud, fill, or loess. (2) A solid material that is not in solution and either is distributed through the liquid or has settled out of the liquid.
- **Site conceptual model.** A qualitative or quantitative description of sources of contamination, environmental transport pathways for contamination, and biota that may be impacted by contamination (called receptors) and whose relationships describe qualitatively or quantitatively the release of contamination from the sources, the movement of contamination along the pathways to the exposure points, and the uptake of contaminant by the receptors.
- **Standard operating procedure (SOP).** A document that details the method for an operation, *analysi*s, or action with thoroughly prescribed techniques and steps, and is officially approved as the method for performing certain routine or repetitive tasks.
- **Target analyte.** An element, chemical, or parameter, the concentration, mass, or magnitude of which is designed to be quantified by use of a particular test method.
- **Technical area (TA).** The Laboratory established technical areas as administrative units for all its operations.
- **Topography.** The physical configuration of the land surface in an area.
- **Tuff.** A compacted deposit of volcanic ash and dust that contains rock and mineral fragments accumulated during an eruption.
- **US Department of Energy (DOE).** Federal agency that sponsors energy research and regulates nuclear materials for weapons production. [Already listed under DOE]
- **US Environmental Protection Agency (EPA).** Federal agency responsible for enforcing environmental laws. While state regulatory agencies may be authorized to administer some of this responsibility, the EPA retains oversight authority to ensure protection of human health and the environment.[Already listed above]
- **Vadose zone.** The unsaturated zone. Portion of the subsurface above the water table in which pores are not fully saturated.

A-3.0 METRIC CONVERSION TABLE

Appendix B

Historical Investigation Report

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APPENDIX B HISTORICAL INVESTIGATION REPORT

This historical investigation report (HIR) provides a summary of the field investigations and associated environmental data collected to date for material disposal area (MDA) L. This HIR provides supporting information for identifying data gaps and the proposed sampling design necessary to complete the MDA L investigation as presented in Section 4 of the investigation work plan (IWP).

B-1.0 MDA L DISPOSAL UNIT INFORMATION (OPERATIONAL HISTORY)

The Los Alamos National Laboratory (LANL or the Laboratory) used MDA L from the early 1960s until 1986 as the designated disposal area for nonradiological liquid chemical wastes, including containerized and uncontainerized liquid wastes; bulk quantities of treated aqueous waste; batch-treated salt solutions and electroplating wastes, including precipitated heavy metals; and small batch quantities of treated lithium hydride. MDA L consists of an elongated pit (Pit A), three impoundments (Impoundments B, C, and D) and 34 shafts (Shafts 1 through 34) (Figure B-1). The pit, impoundments, and shafts were unlined. The dimensions, period of operation, and the capacity of the pit, impoundments, and shafts are listed in Tables B-1 through B-3. Laboratory drawings AB113 (LANL 1993, 76052) and ENG-C-45259 (DOE 1987, 25606) have been used to identify the locations of the pit, impoundments, and shafts at MDA L.

Pit A was excavated into native tuff, filled with waste to within three ft of the surface, and then decommissioned and covered with clean, crushed, consolidated tuff. Impoundments B, C, and D were excavated into native tuff and covered with clean, crushed, consolidated tuff after they were decommissioned. Thirty-four disposal shafts were dry-drilled directly into the subsurface tuff at MDA L. The shafts range in diameter from 3 ft to 8 ft and range in depth from 15 to 65 ft. Three feet of crushed tuff were placed in the bottom of each shaft to fill cracks and joints. When in use, the shafts were covered with a heavy steel cap, which could be opened or removed, depending on design, to place the wastes. When filled to within approximately 3 ft of the surface, the area below the steel plate was capped with a 3-ft concrete plug (Rogers 1977, 5707; 5708). When MDA L was decommissioned in 1986, the surface was paved with asphalt to accommodate waste management activities (permitted storage of hazardous and mixed waste).

B-1.1 Waste Inventory and Disposal History

Waste disposal records for MDA L are found in un-numbered disposal logbooks used to record information on the type, date, location, and volume of waste placed in MDA L (LANL 2003, 76036). Records prior to 1974 are incomplete, and many logbook entries contain only brief descriptions of wastes disposed at MDA L (i.e., waste types, volumes, and disposal locations are not always provided).

An estimate of the types and quantities of waste disposed of at MDA L was compiled in the operable unit (OU) 1148 data report (LANL 1992, 11729) and in the approved Resource Conservation and Recovery Act (RCRA) field investigation (RFI) work plan for OU 1148 (LANL 1992, 07669). Two waste inventory databases were developed based on original logbook entries for MDA L. The Source Term Database contains information on untreated waste, and the Batch Waste Source Term Database lists wastes that underwent batch treatment prior to disposal.

B-1.1.1 Source Term Database

The Source Term Database includes the following categories of information for untreated waste disposed at MDA L: date of disposal; waste volume or weight; number of cylinders or waste items disposed of; specific location of disposal (shaft, pit, or impoundment), if known; and a description of the untreated

waste. Many of the entries do not include a specific location of disposal within MDA L. An example of potential volume discrepancies in this database occurs within the inventory of beryllium waste. One entry described as "chemicals and beryllium-contaminated wood" lists the volume of waste as five cubic ft. The actual quantity of beryllium or beryllium-contaminated wood is not accurately represented by this volume. The Source-Term Database is included in Appendix L. The assumptions used to create the database are listed on pages 3-1 and 3-2 of Appendix L.

B-1.1.2 Batch Waste Source Term Database

The Batch Waste Source Term Database includes the following categories of information for waste treated at MDA L: date of treatment; waste volume; source area where material originated; waste type (inorganic and organic); impoundment or pit location if known; treatment method; and the physical form of the waste. The records document only the wastes that were disposed of without treatment or following treatment in Pit A and Impoundment B. The Batch Waste Source Term Database is presented in Appendix L. The assumptions used to create the database are listed on pages 3-3 and 3-4 of Appendix L.

B-1.1.3 Uncertainties in the MDA L Inventory

There are no logbook entries for the waste disposed prior to 1974/1975, and there are no logbook entries for treatment in Impoundments C and D. It is possible that these impoundments were used for waste treatment and the residues were removed and placed elsewhere at MDA L, or the residues were left in situ and not accounted for in the logbooks. Operating dates for each disposal unit and a summary of the waste inventory compiled from disposal records and the databases for MDA L follows (LANL 1992, 07669).

Pit A (Late 1950s to December 1978)

Pit A received liquid chemical wastes, including containerized and uncontainerized liquid wastes, and functioned as an evaporation pit where bulk quantities of treated aqueous waste from throughout the Laboratory were discharged, pooled, and allowed to evaporate. Disposal records provided in Appendix L indicate that 5123 cubic ft of material were discharged to Pit A. After the aqueous phase evaporated, a salt layer remained on the floor of the disposal pit. When Pit A was decommissioned in 1978, it was covered with crushed tuff.

Impoundments B (January 1979 to June 1985) and C (July 1985 to December 1985)

Impoundments B and C were used for evaporating batch-treated salt solutions and electroplating wastes. Disposal records provided in Appendix L indicate that 2622 cubic ft of aqueous waste were discharged into Impoundment B, pooled, and allowed to evaporate. The four processes that contributed to the wastes disposed of in Impoundments B and C are the same as the aqueous waste treatment processes described previously for Pit A. Upon decommissioning, Impoundments B and C were covered with a minimum of 3 ft of crushed tuff.

Treated solutions resulting from the following four aqueous waste treatment processes contributed to the waste streams discharged into Pit A and Impoundments B and C (LANL 1992, 11729).

• Ammonium bifluoride waste was neutralized with calcium chloride and calcium hydroxide. The end product was an aqueous solution consisting of ammonium chloride, calcium fluoride, and water.

- Acids and caustics in quantities greater than 55 gal. were diluted to 15% or less and neutralized. Acid solutions were neutralized with sodium hydroxide; base solutions were neutralized with mineral acids. Heavy metals were precipitated and removed prior to disposal. Heavy metals precipitated from acid solutions were packaged in 15-gal. drums and disposed of in the same shaft(s) as the neutralized acid solutions, while heavy metals precipitated from caustic solutions were also packaged in 15-gal. drums and disposed of in the same shaft(s) as the neutralized caustic solutions (LANL 2003, 76078).
- Cyanide solutions were treated with calcium hypochlorite or calcium chloride and calcium hydroxide at technical area (TA) 50. The end products of both processes are cyanate, carbon dioxide, and nitrogen. The resulting aqueous solution was tested to ensure complete cyanide treatment. After treatment, the aqueous solution was discharged primarily to Pit A or to one of the evaporation impoundments (B, C, or D). Solids from the process were placed in metal drums, mixed with cement, and disposed of in shafts at MDA L.
- Chromium waste was treated with sodium hydroxide and one of two reducing agents: sulfur dioxide or sodium bisulfate. The end-products of this process were sodium sulfate and chromium hydroxide. The treated chromium waste was disposed of in the same shaft(s) as the neutralized acid solutions.

Impoundment D (1972 to 1984)

Impoundment D was used exclusively for treating small batch quantities of lithium hydride by reacting lithium hydride with water and allowing the neutralized liquid to evaporate. Based on the results of a safety review, this treatment process was discontinued in 1984 because of the reactivity of the lithium hydride, and disposal activities in Impoundment D ceased. Impoundment D was partially filled with crushed tuff in 1985 and completely filled in 1989. Between 1984 and 1989, six aboveground fiberglass used-oil storage tanks (area of concern [AOC] 54-021) were located within a soil-containment berm adjacent to Impoundment D. The tanks, which stored waste oil, were pumped out in 1985 and moved from MDA L to MDA G in 1989 to make room for new waste management facilities on the surface of MDA L. The tanks themselves were subsequently closed in 1990 under RCRA regulations and a closure report was submitted to the New Mexico Environment Department (NMED) in 1991. Any associated contaminated soil from the tanks will be addressed during closure of the RCRA-permitted surface treatment and storage units currently located on the surface of MDA L.

Disposal Shafts 1 through 34 (February 1975 to February 1985)

Disposal Shafts 1 through 34 were used for disposing of containerized and uncontainerized liquid chemical wastes and precipitated solids from the treatment of aqueous wastes. Before 1982, containerized liquids were disposed of without adding absorbents to the containers in which they were placed. Frequently, small containers were simply dropped into a shaft. Larger drums were lowered by crane and arranged in layers of one drum in a 3-ft- or 4-ft-diameter shaft, four to five drums in a 6-ftdiameter shaft, or 6 drums in an 8-ft-diameter shaft. The space around the drums was filled with crushed tuff, and a 6-in. layer of crushed tuff was placed between each layer of drums. Uncontainerized liquid wastes were also disposed of in the shafts.

Between 1982 and 1985, only containerized wastes (including liquids, precipitated heavy metals, and stabilized heavy metals) were disposed of in the shafts. Wastes were accumulated on the site and packaged in drums until sufficient quantities had accumulated for emplacing them in a shaft.

B-1.2 Previous Field Investigations

On May 7, 1985, the Laboratory received a compliance order from the New Mexico Environmental Improvement Division (NMEID, now NMED) that addressed numerous waste management issues at the Laboratory (NMEID 1985, 75885). The 1985 order specified the following six tasks that involved site investigation activities in and around MDA L:

- Task 1 required measuring the intrinsic permeability of the tuff,
- Task 2 required determining the soil-moisture characteristic curves,
- Task 3 required determining the unsaturated hydraulic conductivity of the Bandelier Tuff,
- Task 4 required analyzing the infiltration and redistribution of meteoric water into the tuff,
- Task 5 required characterizing the core and pore gas in the vadose zone, and
- Task 6 required analyzing the potential presence of perched water.

The results and outcomes of the above six tasks are described in a report entitled "Hydrogeologic Assessment of Technical Area 54, Areas G and L" (LANL 1987, 76068), which was submitted in 1987 to the NMEID in response to the 1985 compliance order/schedule.

Task 1: In 1986, five boreholes (three at MDA L and two at MDA G) were advanced to 125 ft below ground surface (bgs) to measure air permeability in units 2 and 1v of the Tshirege Member of the Bandelier Tuff. Field methods included air injection and vacuum testing of five boreholes. Water injection permeability tests conducted in one borehole validated the results of air tests. The intrinsic permeability of four core samples from each borehole was determined in the laboratory via the Klinkenberg Method and the Dynamic Method. Field methods yielded intrinsic permeability in the range of 10⁻⁸ to 10⁻⁹ cm² and laboratory methods yielded values of 10⁻⁹ cm².

Task 2: According to field and laboratory analyses, the moisture content of the core ranges from 2% to 4%, with isolated intervals ranging from 10% to 28%. Soil moisture characteristic curves were difficult to develop because the samples disaggregated under simulated low-capillary pressures; however, curves were developed for 20 samples. The analyses of these samples showed that high moisture retention values and low moisture content measurements result in vapor transport as the major mechanism of water transport.

Task 3: Five samples from each of four horizons were used to determine unsaturated hydraulic conductivity using both theoretical and laboratory methods. Theoretical methods yielded an average of 2.64 x 10⁻⁴ ft/day and measured values averaged 1.32 x 10⁻⁴ ft/day.

Task 4: Analysis of infiltration and redistribution of meteoric water into the core was conducted by neutron-moisture monitoring and measuring matric potential with thermocouple psychrometers. Neutron moisture monitoring and gravimetric moisture measurements indicated that the volumetric moisture content of the tuff below 10 ft is approximately 2% to 4%. In addition, analysis of daily moisture logs after autumn preciptitation indicated the depth of infiltration of meteoric water was approximately 10 ft. Moisture was not observed to move deeper than 10 ft and was assumed to be returned to the surface through evapotranspiration. Psychrometers indicate soil tensions range from slightly less than 1 bar to approximately 15 bars. Vertical hydraulic gradients, as determined by psychrometers, ranged from a downward gradient of 10.2 ft/ft to an upward gradient of 4.12 ft/ft.

Calculation of moisture flux rates through porous media using field-derived hydraulic gradients and laboratory-derived unsaturated hydraulic conductivities yielded mean flux rates of 0.036 and 0.211 ft/yr for MDAs L and G, respectively. However, because the moisture content used in calculating unsaturated

hydraulic conductivity was greater than that observed in the field, the flux rates calculated were also higher than actual rates.

Task 5: In 1985, four boreholes were drilled at MDA L and two at MDA G; additionally, one background borehole was drilled on the western end of Mesita del Buey for core and pore-gas analyses of the Bandelier Tuff. Core samples collected from each 10-ft interval in all 7 boreholes were analyzed for extraction procedure (EP) toxicity and volatile organic compounds (VOCs). No EP toxic metals were detected in core samples beneath a depth of 20 ft. Part per million (ppm) concentrations of VOCs were detected in core samples from MDA L to depths of 100 ft (maximum depth sampled), and none was detected at MDA G.

A total of 23 sampling ports were installed in the 7 boreholes to collect pore-gas samples to 100-ft depths. Analysis of samples collected by pumping the pore gas through charcoal adsorption tubes showed that VOCs were detected in MDA L in ppm concentrations at all depths sampled and in the part per billion (ppb) range at all depths sampled at MDA G.

Task 6: Four test holes drilled in Cañada del Buey were converted to monitoring wells. Seven test holes were drilled in Pajarito Canyon, and three were converted to monitoring wells to investigate the alluvial, perched water systems potentially present in these canyons. The alluvium in Cañada del Buey was found to be confined to the canyon, and all test holes in the alluvium were dry. In Pajarito Canyon, the boreholes intersected a perched water system. The top of the perched water was about one to five ft below the surface of the alluvium, and the water level fluctuated significantly over short periods of time. It was concluded that perched water in Pajarito Canyon was confined to alluvium within the canyon and did not extend vertically or horizontally into the Bandelier Tuff, which forms Mesita del Buey. No perched water was found in Cañada del Buey. No perched bodies of water, which could be hydraulically connected to the regional aquifer, were found beneath MDAs G and L.

Between 1986 and 1990, the Laboratory voluntarily drilled and instrumented two additional boreholes at MDA G and 20 boreholes in and around MDA L to begin characterizing the nature and extent of the vapor-phase VOC plume. Analytical results from pore-gas samples collected between 1985 and 1990 were reported in "Analysis of the Pore-Gas Monitoring at Area L, TA-54" (Trent 1992, 11881) and "Review of Soil-Vapor Sampling Wells and Data from TA-54 Areas G and L" (LANL 1992, 11729).

A review of analytical data presented in these two reports for MDA L indicates

- releases from MDA L resulted in a subsurface vapor-phase VOC plume extending beneath the site and beyond the boundary of MDA L,
- 1,1,1-trichloroethane (TCA) is the primary constituent of the VOC plume,
- TCA is present to a depth of at least 200 ft below the surface of the mesa, and
- TCA concentrations vary across the plume.

A review of analytical results for pore-gas samples collected in 19 of the boreholes at MDA L between 1988 and 1992 is presented in a report entitled "Pilot Extraction Study Plan for the Organic Vapor Plume at MDA L" (LANL 1993, 22430). This report describes the VOC plume at MDA L as follows: "the principal vapor phase organic compounds, listed in descending order of concentration were TCA, trichloroethene (TCE), carbon tetrachloride, chloroform, tetrachloroethene (PCE), toluene, and benzene. Other contaminants that have been detected, but at much lower concentrations, include chlorobenzene, xylenes, and 1,2,4-trimethylbenzene. TCA was found in the greatest concentration, and it also exhibits the greatest lateral and vertical extent in the organic vapor plume. The measured concentrations of TCA are almost an order of magnitude greater than values measured for TCE, the contaminant of second highest concentration."

B-2.0 PHASE I RFI FIELD INVESTIGATIONS

Phase I RFI fieldwork was conducted at MDA L from 1993 through 2002. The approved RFI work plan for OU 1148 specified sampling surface soil/sediment, subsurface tuff, surface flux, ambient air, and pore gas. Surface water, soil/sediment, core, and particulates from ambient air samples were to be analyzed for inorganic chemicals (target analyte list [TAL] metals and cyanide), organic chemicals (VOCs, semivolatile organic compounds [SVOCs], pesticides, polychlorinated biphenyls [PCBs]), and radionuclides (LANL 1992, 07669). The objectives of the Phase I RFI were to better define the source term and the nature of contaminants released from MDA L, to define the extent of the VOC plume and any other identified contaminant releases, to collect data to support and supplement existing data, and to collect data to be used in a risk assessment. Phase I RFI fieldwork conducted at MDA L included

- collecting and analyzing four surface drainage sediment samples,
- drilling seven vertical boreholes and 11 angled boreholes,
- collecting and analyzing 184 core samples,
- collecting and analyzing 207 subsurface pore-gas samples for VOCs,
- collecting and analyzing 102 surface flux samples plus nine duplicates for VOCs, and
- colleting and analyzing 102 ambient air samples for VOCs.

A summary of work plan specifications, the fieldwork performed, and the rationale for deviations from the work plan are provided in Table B-4.

B-2.1 Surface Investigation

B-2.1.1 Channel Sediment Sampling

Runoff from MDA L is concentrated into a single drainage channel that carries surface runoff to the northnortheast into Cañada del Buey (Figure B-2). This drainage includes multiple braided channels traversing a 50-ft- to 65-ft-wide area of a colluvial slope to the floor of a tributary of Cañada del Buey. The channels begin along the eastern fence of MDA L and diverge below the cliffs on the north side of Mesita del Buey.

In July 1994, eight locations from within the drainage were selected for sediment sampling to determine if contaminants had migrated from MDA L; the most likely depositional areas (e.g., low areas behind obstructions) for the channel were determined by an on-site geomorphic survey. These locations included areas with coarse sediment deposition on the upper slope and areas with finer sediment deposition on the lower slope. Sample depth ranged from 0 to 4 in. to 0 to 8 in. Eight sediment samples (along with a field duplicate sample and rinsate blank) were collected and field-screened for gross alpha, beta, and gamma radiation to bias sample selection. The sample with the highest gross alpha and gross beta, the sample with the highest gross gamma, and two other samples selected at random (four total) were submitted to an off-site contract laboratory for analysis of TAL metals, PCBs, pesticides, herbicides, gamma spectroscopy radionuclides, americium-241, tritium, isotopic thorium, strontium-90, isotopic uranium, and isotopic plutonium (LANL 1996, 54462.7). Table B-5 lists the sediment sample locations, sample IDs, and requested analyses.

B-2.1.2 Ambient-Air Sampling

During the summer of 1994, ambient air samples were collected in SUMMA™ canisters for VOC analysis on eight days at two sampling locations (locations 4 and 5 in Figure B-3) on the northern perimeter of MDA L (Mischler and Anderson 1994, 63525). Samples were also collected at a background location

adjacent to Bandelier National Monument (location 3). Sampling dates included June 16, 17, 29, and 30; July 28; and August 1, 2, and 3, 1994. Duplicate samples were collected on three of the sampling days. The June samples were collected at the height of the dry season on the Pajarito Plateau, while the July and August samples were taken during the rainy season. Samples were collected over an 8-hr period beginning at 8:00 am. Meteorological data (i.e., ambient temperature and wind speed) were also recorded. Samples were analyzed by the US Environmental Protection Agency (EPA) Method TO-14. Ambient air data from these sampling events were used to evaluate potential air contamination from MDA L. A more detailed discussion of this sampling activity is presented in Mischler and Anderson (1994, 63525).

B-2.2 Surface Flux Measurements

B-2.2.1 Tritium Surface Flux (Chamber) Measurements

Tritium flux was measured using a flux chamber at five locations near MDA L during the summer of 1993 (locations T1, T2, C11, C29, and C30) and three locations during the summer of 1994 (locations S1, S2, and S3). Tritium flux chamber locations are shown in Figure B-4 and results are presented in Table B-6 (Eklund 1995, 56033). The flux chamber sampling apparatus consisted of a 1300 cm² Plexiglas flux chamber pressed about 1 in. into the soil through which a sweep gas was fed at a constant rate. Air was pulled through the chamber with a pump at a rate slightly less than the sweep gas rate to avoid dilution with ambient air. Tritium samples were collected on primary and secondary gel tubes.

B-2.2.2 VOC Surface Flux (EMFLUX®) Measurements

VOC surface flux was measured across MDA L in two surveys conducted in August 1993 and August 1994. The purpose of the surveys was to identify the nature and extent of potential subsurface VOC contamination. EMFLUX[®] collectors, consisting of an adsorbent cartridge suspended on a stake beneath a protective shell for a 72-hr period, were used in the survey. Details of the investigation are reported in Quadrel Services reports (Quadrel 1993, 63868). Trujillo et al. (1998, 58242) issued a report summarizing the results of the surface flux VOC measurement investigations.

In the first survey in August 1993, 70 sample locations were identified and an additional 32 locations were selected in the August 1994 survey. The majority of the 1993 sample locations were on the mesa top at MDA L, while most of the 1994 sample locations were in the slopes and drainages on the sides of the mesa. The EMFLUX[®] surface flux measurement locations are shown in Figure B-5. Four field duplicate samples also were collected during the first survey, and three field duplicates were collected during the second survey.

B-2.3 Subsurface Investigations

B-2.3.1 Core Sampling

From September 9, 1993, to May 8, 1995, 7 vertical boreholes and 11 angled boreholes were advanced at MDA L during the Phase I RFI. Detailed borehole logs, including lithologies and a diagram showing pore-gas sampling port construction for the monitoring borehole are presented in Appendix H. Borehole locations and trajectories are shown on Figure B-6. The RFI boreholes are described by depth, declination, and adjacent disposal unit in Table B-7. Table B-7 lists similar information for the pre-RFI boreholes. The exterior and ends of each core barrel and each 5-ft. interval of core were screened for VOCs using a photoionization detector (PID). Each 5-ft interval of core was inspected for fractures or stains, and the results were noted in borehole logs (Appendix H).

During the Phase I RFI at MDA L, 89 core samples were collected from 10 boreholes and submitted to an off-site contract laboratory for analysis. Depth intervals for sample collection and analytical suites varied by borehole and are described below. A total of 18 boreholes were drilled during the Phase I RFI; however, core samples were not collected from boreholes 54-01017 and 54-01018. Core samples collected from boreholes 54-01001 through 54-01006 were collected for screening only. Both screening and off-site contract laboratory core samples were submitted from borehole 54-01009. Borehole 54-01017 was designed as the extraction well for the pilot vapor extraction test, and borehole 54-01018 was drilled as an additional pore-gas monitoring borehole located 20 ft from borehole 54-01017. Table B-8 lists the core sample locations, sample IDs, depths, media sampled, and requested analyses.

In 1993, boreholes 54-01001 through 54-01006 were drilled immediately east of MDA L (Figure 6). These two vertical and four angled boreholes were drilled to depths ranging between 291 and 340 ft bgs using an 8-in.-diameter hollow-stem auger and a continuous-coring technique. These six boreholes were instrumented with vapor-monitoring systems using SEAMist™ positive-pressure borehole liners. A total of 94 core samples were collected at 20-ft intervals from boreholes 54-01001 through 54-01006 and submitted to an on-site mobile chemical laboratory for VOCs.

Vertical boreholes 54-01007, 54-01008, and 54-01009 were also drilled in 1993 adjacent to numerous shafts and Pit A. Twenty-six core samples were collected at 10-ft intervals and submitted for off-site contract laboratory for analysis of TAL metals, cyanide, pesticides/PCBs, herbicides, SVOCs, and VOCs. Five core samples from borehole 54-01009 were also submitted to an off-site contract laboratory for isotopic plutonium and isotopic uranium analysis. Twelve samples from 54-01009 were submitted to an on-site mobile chemical laboratory for VOC and SVOC analysis. Boreholes 54-01007, 54-01008, and 54-01009 were subsequently backfilled.

In 1994, angled boreholes 54-01010 through 54-01014 were advanced using an 8-in.-diameter hollowstem auger and a continuous-coring technique beneath Pit A and Impoundments B, C, and D at MDA L (Figure B-6). In 1996, the surface casings were removed, and each borehole was backfilled and grouted closed, ensuring that the borehole did not provide a conduit for surface runoff to enter the subsurface. A total of 29 core samples were collected at 10-ft intervals and submitted to an off-site contract laboratory for analysis of TAL metals, pesticides/PCBs, SVOCs, VOCs, and tritium. Additional core samples submitted for off-site contract laboratory analyses included all 24 core samples from boreholes 54-01010, 54-01011, 54-01012, and 54-01014 for cyanide; and 11 core samples from boreholes 54-01010, 54-01013, and 54-01014 for total uranium.

In 1994 and 1995, two deep-angled boreholes, designated as 54-01015 and 54-01016, were drilled from the adjacent canyon slope northeast of MDA L (Figure B-6) within Cañada del Buey to investigate the possible presence of vapor-phase contaminants at depth beneath MDA L. These boreholes were drilled to depths of 530 ft and 607 ft bgs, respectively, below MDA L using air-rotary installation of 8-in.-diameter STRATEX® casing to the bottom of each borehole. The boreholes were selectively cored for approximately 10 ft within every 40-ft interval below a depth of 260 ft bgs. From discontinuous core, 22 samples were collected at 50-ft intervals and analyzed at an off-site contract laboratory for VOCs and tritium. Following the installation of a Solinst multiport vapor and lysimeter-coupled systems in each borehole, the STRATEX® casing was withdrawn while annular well completion materials were emplaced to complete the vapor monitoring borehole. Both boreholes are maintained as vapor-monitoring wells.

In 1995, boreholes 54-01017 and 54-01018 were advanced east of MDA L (Figure B-6). Borehole 54-01017 was designed as the extraction well for the pilot vapor extraction test, and borehole 54-01018, located 20 ft south-southeast of borehole 54-01017, was used to monitor pore gas during extractor tests. Borehole 54-01017 was drilled to a depth of 159 ft bgs using an 8-in.-diameter hollow-stem auger and reamed to a 10-in. diameter. The top 75 ft of borehole 54-01017 is cased with 10-in.-diameter steel

casing and is open below the casing to a depth of 150 ft. Borehole 54-01018 was drilled to a depth of 328 ft bgs using an 8-in.-diameter hollow-stem auger and a continuous-coring technique. The top 30 ft of borehole 54-01018 is cased 8-in.-diameter steel. No core samples were collected from boreholes 54-01017 and 54-01018 for screening or analysis during the Phase I RFI. Both boreholes are capped at the ground surface.

Results of geologic logging were recorded in the borehole logs (Appendix H). Saturation was not encountered in any of the Phase I RFI boreholes at MDA L; however, intervals of cuttings and core with elevated moisture content were encountered in RFI boreholes 54-01015 and 54-01016 drilled in 1994 and 1995. Borehole logs provided in Appendix H document that elevated moisture was observed in the form of moist to wet cuttings and core at depths of 390 ft bgs (Puye Formation paleosol), 511 ft bgs (basalt), and 540 ft bgs (basalt) in borehole 54-01015. Similarly, the borehole log for borehole 54-01016 shows that elevated moisture was observed in cuttings and core at a depth of 254 ft bgs (Cerro Toledo interval) and at multiple depths within the basalt (362, 429, 430, 461, 533, 556, 577, and 592 ft bgs) beneath MDA L. Instruments to collect both pore vapor and water were installed where moist-to-wet conditions were found at two depths (350.8 and 525 ft bgs) in borehole 54-01015 and at four depths (188.3, 318.8, 480.8, and 600.7 ft bgs) in borehole 54-01016. During quarterly pore-gas monitoring conducted from 1996 through 1999, sampling of the water ports to target zones of potential perched zones was attempted; however, no water was recovered.

B-2.3.2 Borehole Airflow Velocity (Passive VOC Extraction)

In 1997 and 1998, the former Environmental Restoration Project (now called Risk Reduction and Environmental Stewardship–Remediation Services [RRES-RS]) evaluated the effectiveness of passive vapor extraction of subsurface vapor-phase VOCs at MDA L as specified in Appendix A of the approved RFI work plan for OU 1148 (LANL 1992, 07669). Passive vapor extraction uses natural changes in atmospheric barometric pressure as a pump to exhaust VOCs through the open boreholes. The volume of air flowing out of a borehole and the concentration of VOCs in this air are used to calculate the annual emission rate of VOCs from a borehole.

In 1997, airflow volume and VOC concentrations were measured with a Brϋel and Kjaer (B&K) Multigas Analyzer, Model 1302 at borehole 54-01006 and reported in Neeper and Kisiel (1998, 63999). In 1998, the tests were repeated using a one-way valve on borehole 54-01006 to allow only the exhalation of subsurface air during periods of relatively high atmospheric pressure. During the 1998 study, vapor concentrations and pressure were measured at several subsurface ports in boreholes 54-01004, 54-01006, and 54-01018 and in atmospheric air. The 1998 results are presented in Kisiel and Mason (1998, 63526). These data were not used for evaluating the nature and extent of contamination at MDA L.

B-2.3.3 Pore-Gas Sampling

Subsurface pore gas sampling at MDA L is required by Section C.5 of Module VIII of the Laboratory's Hazardous Waste Facility Permit, "Unsaturated Zone Monitoring" (EPA 1990, 1585; EPA 1994, 44146). The approved sampling and analysis plan (Davis 1993, 38812) requiring collecting pore-gas samples from 12 of 28 available boreholes at MDAs G (4) and L (24) on a quarterly basis is described in the Laboratory's response (Glatzmaier 1993, 30987) to an EPA notice of deficiency ([NOD] Driscoll 1992, 3849.3). Of the 12 boreholes, 10 boreholes are to be selected every quarter from the available 24 poregas monitoring boreholes located at MDA L (Figure B-6).

The depths of pore-gas sampling ports in the 24 operational boreholes currently sampled at MDA L are listed in Table B-9. Detailed borehole logs, including lithologies for boreholes 54-01015 and 54-01016,

are presented in Appendix H. Pore-gas monitoring methods have changed over the years in response to more sensitive detection capabilities. A summary of pore-gas sampling from 1995 through 2001 is included in Appendix G.

The pilot extraction study plan, as originally described in the approved RFI work plan for OU 1148 (LANL 1992, 07669), was modified in 1996 (LANL 1996, 55574) to include the installation of two angled boreholes instead of two vertical boreholes to allow for data collection beneath multiple disposal units and from deep geologic formations. The angled boreholes (54-01015 and 54-01016) were drilled into the basalt underlying the Bandelier Tuff between November 1994 and March 1995. The two angled boreholes were advanced from Cañada del Buey to vertical depths of 400 and 600 ft, respectively, below the surface of MDA L. Borehole 54-01015 was drilled to intersect the region below the closed disposal shafts located in the western part of MDA L. Borehole 54-01016 was drilled to intersect the region below the closed pit, impoundments, and shafts located in the eastern part of MDA L (Figure B-6).

Since 1997, pore-gas sampling has been aided and directed using soil-gas screening with a B&K Multigas Analyzer, Model 1302. The gas analyzer is capable of measuring up to five analytes and is used to screen for TCA, TCE, PCE, Freon 11 and Freon 13. These five analytes are used for screening because they are the most prominent VOCs in the MDA L vapor plume. The gas analyzer is integrated into a gas-sampling train that allows for subsurface soil-gas purging, screening, and SUMMA™ canister sampling. Soil-gas ports are purged until subsurface carbon dioxide levels have stabilized to representative soil-gas levels prior to screening and sampling. All sampling ports in all boreholes are screened using the B&K.

Until fiscal year (FY) 2000, the pore-gas procedure called for screening of well ports using the B&K, followed by SUMMA™ sampling at the highest concentration port of selected wells. This procedure provided a good data set for a limited number of ports in a limited number of boreholes. To address data gaps associated with nature and extent of contamination, the procedure was modified in FY 2000 at the request of NMED. All ports in all wells are still screened using the B&K to provide data regarding changes in the concentrations of VOCs in the plume; however, the screening results are not used to direct SUMMA™ sampling. Instead, ports are sampled with SUMMA™ canisters as needed to evaluate changes in the plume stability based on a defined quarterly sampling schedule presented in the July through September quarterly report (LANL 2002, 73712).

B-3.0 REVIEW OF PHASE I RFI FIELD SCREENING AND LABORATORY ANALYTICAL RESULTS

B-3.1 Data Review

The Phase I RFI data set for MDA L includes analytical data from four surface channel sediment samples, 184 core samples collected from 16 boreholes, 8 surface tritium flux samples, 102 surface VOC $EMFLUX^{\circledast}$ survey samples, as well as 7 field duplicates, 16 ambient air samples, and 207 subsurface pore-gas samples. All data used quantitatively to identify chemicals of potential concern (COPCs) at MDA L were subjected to RRES-RS quality assurance and quality control (QA/QC) procedures. The data review process for identifying COPCs begins with a comparison of site data with

- naturally occurring background concentrations for inorganic chemicals,
- naturally occurring background or fallout concentrations for radionuclides, and
- analytical estimated quantitation limits (EQLs) for organic chemicals.

Organic chemical data are evaluated based on detection status only. Background comparisons and a variety of statistical and graphical methods are used to compare site inorganic chemical and radionuclide data with Laboratory-wide background data (LANL 1998, 59730). For background comparisons, the first step is to compare the site data with a background value (BV), which is a calculated value that represents the background data set (upper tolerance limit [95, 95] or the 95% upper confidence bound on the 95th quantile).

If a site-specific datum exceeds its BV, additional evaluation of the datum may be performed by comparing the range of values in the site data set for that chemical to the range of values for that chemical in the background data set. Graphical analyses (e.g., box plots) may be used, or if adequate data are available, statistical tests that evaluate differences in distribution may be used. Nonparametric tests commonly used to assess data distributions include the Gehan, quantile, and slippage tests. Together these tests assess complete shifts in distributions, shifts of a subset of the data, and the potential for site data to be greater than the background data set. Observed significance levels (p-values) are obtained; these values indicate whether a difference exists between the data sets. A p-value of less than 0.05 indicates a difference between the distributions (i.e., the site data are different from the background data) exists, while a p-value greater than 0.05 indicates the distributions (i.e., site and background data) are similar. The results of these statistical analyses for MDA L are discussed in Appendix E.

Graphical analyses of the data sets provide a visual representation of the data and allow a visual comparison among concentration distributions. The observed differences may include an overall shift in concentration or, when centers are nearly equal, a difference between the upper tails of the two distributions. The plots may either be used alone to describe the relationship of the two distributions or may be used in conjunction with the statistical tests described above. Box plots and borehole profiles were used to assess the Phase I RFI inorganic chemical and radionuclide data from MDA L (Appendix E).

Only data that are relevant for identifying COPCs are included in this section; these data include measurements that are above applicable thresholds or whose detection limits (DLs) are greater than an applicable threshold. Tables D-8 through D-15 in Appendix D include the data for all analytes (detected and undetected).

B-3.1.1 Channel Sediment Samples

Channel sediments at MDA L are derived from the mesa-top materials, the tuff on the sides of the mesa, and colluvium and soils on the mesa slopes (LANL 1996, 54462). The samples were described in the field summary report as soil samples and in the channel sediment report as silt, sand, and gravel mixtures. Sample concentrations were compared with the Laboratory sediment background data set (LANL 1998, 59730), which was derived from sediment samples collected in Indio, Ancho, Los Alamos, Pueblo, and Guaje Canyons. Because these deposits are young alluvium in or near stream channels (LANL 1998, 59730), the Laboratory background data set for sediments might represent a different matrix than the channel sediment samples collected at MDA L.

Channel sediment samples collected at MDA L were analyzed for TAL metals, pesticides/PCBs, herbicides, gamma spectroscopy, isotopic plutonium, isotopic uranium, isotopic thorium, strontium-90, and tritium. Table B-5 includes the surface channel sediment samples collected during the Phase I RFI and the requested analyses for each sample.

Inorganic Chemical Comparison with Background

No inorganic chemicals were detected at concentrations above the sediment BVs in any of the channel sediment samples (Table B-10). Although cadmium, selenium, and silver were not detected, the DLs for these inorganic chemicals exceeded their respective BVs. The sediment BVs for cadmium, selenium, and silver were based on nominal DLs. The sample DLs were reported at approximately twice the BV or less. These metals data are evaluated further in Appendix E. Figures E-1 and E-2 in Appendix E provide more details on the inorganic chemical comparisons. There were no QA/QC issues associated with the channel sediment inorganic chemical results at MDA L. Overall, the sediment inorganic chemical data for MDA L were of good quality and suitable for data assessment. Table D-8 in Appendix D presents the complete data set.

Radionuclide Comparison with BVs and Fallout Values

Except for tritium, there were no QA/QC issues associated with the radionuclide results for samples collected at MDA L. Tritium results were qualified J (estimated) because the results from a blind QC sample fell outside sample recovery limits. Overall, the sediment radionuclide data for MDA L are of good quality and suitable for data assessments. Table D-9 in Appendix D provides the complete data set.

Detected concentrations of radionuclides were compared with the sediment BV or the sediment fallout values (FVs), depending on whether the radionuclide is naturally occurring or a fallout radionuclide (LANL 1998, 59730). Americium-241, cesium-137, cobalt-60, tritium, plutonium-238, plutonium-239, and strontium-90 were compared with sediment FVs. Isotopes of uranium and thorium, which are naturally occurring radionuclides, were compared with sediment BVs (Table B-11).

The channel sediment report (LANL 1996, 54462) listed americium-241, polonium-210, technetium-99, and yttrium-90 as COPCs because no BVs and FVs for those radionuclides were available at that time. Currently, americium-241 has a sediment BV of 0.04 pCi/g, which is greater than the detected concentrations in the channel sediment (Table B-11). Polonium-210 and yttrium-90 both have short halflives (approximately 138 days and 60 hours, respectively), so they are no longer present in the channel sediment and are, therefore, not evaluated in this HIR.

A detected concentration for plutonium-238 (0.011 pCi/g) exceeded the associated sediment BV of 0.006 pCi/g (Table B-11). Figure B-7 shows the sample location and detected plutonium-238 concentration. No other radionuclides were detected above their respective BVs or FVs. Table E-2 in Appendix E discusses the radionuclide background comparisons in more detail. Plutonium-238 is retained as a COPC in channel sediments at MDA L.

Evaluation of Organic Chemicals

There are no QA/QC issues associated with the analytical data, and the data are of good quality and suitable for data assessment. Table D-10 in Appendix D provides the complete data set.

Methoxychlor was detected in three samples at concentrations of 0.027 mg/kg (location 54-05148), 0.028 mg/kg (location 54-05143), and 0.063 mg/kg (location 54-05145) (Figure B-8). The concentrations detected are approximately one to three times the EQL (0.02 mg/kg). No other organic chemicals were detected in the sediment samples. Table E-3 in Appendix E provides more details on the organic chemical analyses. Methoxychlor was retained as a COPC in channel sediments at MDA L.

B-3.1.2 Subsurface Core Samples

A total of 96 subsurface core samples were collected from 10 boreholes at MDA L (Figure B-6). These samples were analyzed for TAL metals and cyanide, pesticides/PCBs, herbicides, VOCs, SVOCs, and radionuclides. Not every sample was analyzed for every constituent, as described below. Core samples from six boreholes (54-01001 through 54-01006) were drilled to investigate the vapor plume east of MDA L; 94 core samples from these boreholes were screened only for VOCs and moisture by an on-site mobile chemical laboratory. Two deep characterization boreholes (54-01015 and 54-01016) were drilled at an angle to investigate the potential presence of vapor-phase contaminants at depth below MDA L; the core samples from these boreholes were analyzed for moisture, VOCs, and tritium. The remaining eight boreholes (54-01007 through 54-01014) were drilled in the vicinity of the disposal units (i.e., pit, impoundments, and shafts) and were analyzed for all constituents, except herbicides in core samples from boreholes 54-01010 through 54-01014. Core samples were not collected from two additional boreholes drilled in 1995. Borehole 54-01017 was designed as the extraction well for the pilot vapor extraction test, and borehole 54-01018 was an additional pore-gas monitoring borehole. Table B-8 summarizes the subsurface core samples collected during the Phase I RFI and the requested analyses for each sample.

Inorganic Chemical Comparison with Background

Subsurface core sample data for inorganic chemicals (Table B-8) were obtained from the eight boreholes (54-01007 through 54-01014) in the vicinity of the disposal shafts, impoundments, and pit at MDA L (Figure B-6). Five (out of 67) mercury and cyanide analyses were rejected because the holding times had been exceeded, and four out of 67 arsenic and selenium results were rejected because of low analyte recovery from a QC sample. The low recovery indicates potentially unacceptable accuracy in the results for arsenic and selenium. Many results for the inorganic chemicals were qualified J (estimated) because of evidence of variable efficiencies of extraction from the soil matrix or very low reported concentrations relative to DLs. J-qualified data are usable for decision making but carry higher analytical uncertainty than unqualified data. Overall, except for the rejected data, the data are of good quality and are sufficient for data assessment.

Analytical results for the samples collected from Qbt 2 were compared with BVs for Qbts 2, 3, and 4, and samples from Qbt 1v and Qbt 1g were compared with BVs for those units (LANL 1998, 59730). Table B-12 provides a summary of the frequency of detected inorganic chemicals above background. Figure B-9 shows the locations and concentrations of inorganic chemicals detected above BVs in subsurface tuff at MDA L. Analytical results were plotted by depth in each borehole to identify patterns potentially associated with a release and migration through a fractured medium (Appendix E, Table E-4, Figures E-3 and E-4). Table D-11 in Appendix D provides the complete data set.

The data review indicates that barium, chromium, cobalt, copper, manganese, nickel, uranium, and zinc are elevated compared with Laboratory BVs and are retained as COPCs in subsurface tuff at MDA L.

Radionuclide Comparison with BVs or FVs

Core samples from seven boreholes (54-01010 through 54-01016) were analyzed for tritium, and five core samples from borehole 54-01009 were analyzed for isotopic plutonium and isotopic uranium (Table B-8). The analytical result from one of 48 core samples analyzed for tritium was rejected because of a laboratory error. A number of the analytical results are J qualified (estimated) because laboratory QC indicators identified more variability in the analytical results than normally expected. With the exception of one (of 48) rejected sample, the radionuclide results from subsurface tuff at MDA L are of good quality and sufficient for data assessment. Naturally occurring uranium isotopes were compared to Laboratory sitewide BVs from the appropriate tuff strata (LANL 1998, 59730). Fallout radionuclides (plutonium-238, plutonium-239, and tritium) were evaluated on the basis of detection status (i.e., if a fallout radionuclide is detected, it is evaluated further).

Data indicate that tritium was detected in 22 of 48 core samples and at several depths in boreholes 54-01010, 54 -01011, 54-01013, and 54-01015. The concentrations ranged from nondetect to 11.6 $pCi/g¹$ (196 pCi/mL) in borehole 54-01010. Uranium-234 and -238 were detected at low concentrations less than or equal to the BVs of 0.14 pCi/g and 1.93 pCi/g, respectively. Therefore, tritium is the only radionuclide identified as a COPC in the core samples. Table B-13 summarizes the frequency of detected radionuclides above BVs for the subsurface core samples. Table B-14 presents the detected tritium concentrations by subsurface sample. Figure B-7 presents the sample locations and results for the radionuclides detected above BV/FV concentrations in sediment and tuff.

Evaluation of Organic Chemicals

A total of 96 core samples collected from 10 boreholes were analyzed for VOCs. Sixty-seven core samples collected from the eight boreholes drilled in the vicinity of the disposal shafts and pits (54-01007 through 54-01014) were also analyzed for SVOCs, pesticides, and PCBs. Thirty-eight core samples collected from three boreholes (54-01007 through 54-01009) in closest proximity to the disposal shafts were also analyzed for herbicides.

Forty VOC results were qualified as not detected (U) because the results were less than 5 or 10 times the concentrations detected in the method blank. Six results were qualified as estimated (J or UJ) because the surrogate recoveries associated with these analytes were low. Eleven results were qualified as estimated (J) for acetone and 2-butanone because the results were less than the practical quantitation limit (PQL) but greater than the method detection limit (MDL). Two results were qualified as estimated (J) because the holding time was exceeded. Overall, the data are of good quality and sufficient for data assessments.

Six SVOC results were qualified as estimated (J or UJ) because the holding time had been exceeded. Two results were qualified as estimated (J) because the results were less than the PQL, but greater than the MDL. Three results were rejected (R) and could not be used for data assessment because the surrogate recoveries associated with the analytes were low (10%). Overall, except for the rejected data, the data are of good quality and are sufficient for data assessment.

Herbicides were not detected in any of the subsurface core samples from MDA L. Fifteen VOCs were detected in core, most at trace concentrations (i.e., less than or slightly above the EQLs). Concentrations greater than EQLs were detected at boreholes beneath Pit A (54-01010 and 54-01011), between Pit A and Shafts 1 through 28 (54-01009), and at the east end of the array of Shafts 1 through 28 (54-01007 [Figure B-10]).

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¹ The accuracy of the tritium values is questionable. Tritium in core is measured by EPA Method 906.0, which is performed on the water extracted from the core sample. At gravimetric moisture content less than 10%, a 3-in. length of 2-in.-diameter core will yield less water than the minimum required volume of 5 mL. To reach the necessary volume, de-ionized water is added to the extracted water. The reported activity and uncertainty are corrected for the dilution. Therefore, any moisture loss from a core sample prior to analysis at low moisture contents may substantially increase the uncertainty of the measurement. Moreover, the EPA method requires that the core material be ground to a fine mesh before the water is extracted, such that significant moisture loss is inevitable. Given these issues, RRES-RS concluded that tritium contamination is best characterized in low moisture content at MDA environments by using sorbent materials to extract and retain in situ subsurface water samples from pore gas. Disposal of tritium per se is not recorded in the disposal logbooks; however, chemicals containing hydrogen disposed of at MDA L could have contained tritium. Vacuum pump oils would be a likely source. The activity of tritium is low, indicating tritium-contaminated material may have gone into MDA L and not sent to MDA G as radioactive material.

Two pesticides, Aroclor-1260, and three SVOCs were detected in one to four samples at several sampling depths in tuff. Aroclor-1260 was reported in one sample from borehole 54-01010 at a concentration (0.313 mg/kg) about 70 times greater than the sample EQL (0.0044 mg/kg). Methoxychlor was detected above the EQL in one sample in borehole 54-01010 (0.0756 mg/kg versus the EQL of 0.0226 mg/kg), and the pesticide dichlorodiphyldichloroethane (DDD) was detected in two samples at concentrations marginally above to approximately three times the EQL (0.0044 mg/kg) in borehole 54-01011. In borehole 54-01009, bis(2-ethylhexyl)phthalate was detected at one sampling depth beneath Pit A at a concentration of 0.8 mg/kg compared to its EQL of 0.6 mg/kg. Di-n-butyl phthalate was reported at concentrations one to three times its EQL (0.44 mg/kg) at three nonconsecutive sampling depths. Pentachlorophenol was detected at concentrations three to ten times the EQL (1.2 mg/kg) at two sampling depths below Impoundment B (Figure B-10).

In summary, several organic chemicals were reported in the subsurface media near Pit A and Shafts 1 through 28. The organic chemicals were detected primarily at concentrations near or below the EQLs at only a few depths. Although some VOCs were detected in the core samples at concentrations approximating EQL values, these measurements were unreliable because VOCs do not adsorb to tuff. Therefore, the nature and extent of the VOC plume at MDA L was better defined using the pore-gas sampling results (see below) than the core results. The sporadic nature of the detections of SVOCs, Aroclor-1260, and pesticides does not indicate a release and has not been evaluated further.

The frequency and range of concentrations for the detected organic chemicals is given in Table B-15. Figure B-10 presents the sample locations for the detected organic chemicals. Table D-14 in Appendix D presents the complete data set.

B-3.1.3 Pore-Gas Samples

VOC Flux Measurements (EMFLUX®)

Twenty VOCs were detected in 102 EMFLUX[®] samples collected in 1993 and 1994 (Trujillo et al. 1998, 58242). Flux measurements were taken only in areas not covered by asphalt, which include perimeter and hillside locations. The detected VOCs include acetone, benzene, bromobenzene, 2-butanone, carbon tetrachloride, chlorobenzene, chloroform, chloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethene, 1,2-dichloropropane, ethylbenzene, n-propylbenzene, PCE, toluene, TCA, TCE, Freon 113, and xylene. Fewer VOCs were detected in the 1994 samples from the hillsides and were limited to acetone, chlorobenzene, chloroform, 1,1-dichloroethane, 1,1-dichloroethene, methylene chloride, PCE, toluene, TCA, TCE, Freon 113, and xylene. The highest surface flux measurements were found in samples collected in 1993 from the mesa top for TCA, PCE, and TCE. Freon 113 and acetone were also detected in many samples at relatively low levels compared to the three main VOCs: TCA, TCE, and PCE. The 1994 EMFLUX[®] data from the hillsides indicate much lower surface flux than those measured on top of the mesa in 1993; the most prevalent VOCs in the 1994 data were also TCA, PCE, and TCE. The compound 1,1-dichloroethene was also detected at a relatively high frequency in the 1994 samples on the north slope of the mesa. Freon 113 was detected frequently in the 1994 data set, although at low levels in samples collected on the southern slope of the mesa.

A plot showing the TCA surface flux results at MDA L is provided in Figure B-11. Flux measurements with values less than or equal to 3.1 ng/m²/min are represented as a small triangle. These are very near the detection limit of the method.

VOCs in Pore Gas

Pore-gas monitoring methodologies have evolved over time. Appendix G provides a history of the monitoring methodologies, including the current monitoring program. In general, the methods and resulting data quality have improved steadily. For this HIR, the pore-gas monitoring data collected prior to and during 1996 are used only semi-quantitatively to assess the history of MDA L's subsurface vaporphase VOC plume. The data collected from 1997 to the present have been subjected to rigorous QA/QC, both in field collection and in laboratory analysis. During each round of quarterly sampling, an equipment blank is collected to identify whether laboratory contamination has affected analytical results, a field duplicate is collected to determine if the analytical instrument is within precision limits, and a performance evaluation sample of calibration gases is collected to determine if calibration gases used for the B&K instrument are at the concentration listed on the gas cylinder.

The pore-gas monitoring data for MDA L indicate TCA is the primary VOC, followed consistently in abundance by TCE. The complete pore-gas data set is included in Appendix D, Table D-11. The frequency of detection and range of concentrations for sampling from 1997 through 2001 are presented in Table B-16. VOCs are retained as COPCs in subsurface pore gas at MDA L.

Table B-17 presents the maximum detected concentration for each VOC from the fourth quarter FY 1999 SUMMA™ canister sampling results, and the location of that sample (borehole and port depth). This data set is representative of the results from the sampling protocol in place prior to FY 2000 when the purpose of sampling was to determine the nature and extent of the VOC plume. Table B-18 provides similar information from the first quarter FY 2002 SUMMA™ canister sampling results, which are representative of the post-2000 pore-gas sampling protocol where the purpose of the sampling is to determine trends in plume concentration in the source area and at the boundaries of the plume.

Analysis of the pore-gas monitoring data indicates vapors from the two shaft fields (1 through 28 and 29 through 34) are compositionally different, indicating two unique sources. The two sources consist largely of TCA, but the relative concentrations of lesser compounds are different. The two source areas are referred to as the northwest source area and the southeast source area.

Tritium Surface Flux Chamber Measurements

The 1993 and 1994 tritium flux chamber data indicate that vapor-phase tritium contamination in ambient air is widespread near MDA L (Eklund 1995, 56033). However, these locations (Figure B-4) are not in close proximity to any known subsurface tritium sources. The tritium fluxes calculated from these samples are provided in Table B-6. Tritium is identified as a COPC in ambient air.

B-3.1.4 Ambient Air

Measured concentrations of selected aromatic and halogenated hydrocarbons at ambient air sampling locations 4 and 5 (Figure B-3) are shown in Tables B-19 and B-20. Only organic chemicals that were consistently detected in four or more samples are presented. The data set collected at the Bandelier National Monument for the analytes listed in these tables is shown in Table B-21. VOCs are identified as COPCs in ambient air.

B-3.1.5 Summary of COPCs at MDA L

Table B-22 summarizes the results of the data review and lists all COPCs at MDA L for channel sediments, ambient air, subsurface tuff, and pore-gas samples. For each COPC, or group of COPCs, the table identifies the analytes retained and the ones eliminated from further consideration in the HIR, and the rationale for the decision.

B-4.0 DATA INTERPRETATION AND IDENTIFICATION OF DATA GAPS

Information presented in Sections B-1.0, B-2.0, and B-3.0 is summarized and interpreted in this section to describe the current understanding of the nature and extent of environmental contamination at MDA L. Based on this interpretation, data gaps related to the nature and extent of environmental contamination at MDA L are identified. The information provided here is summarized in Section 4.1 of the IWP where it forms the basis for the proposed sampling activities in Section 4.2 of the IWP.

B-4.1 Nature and Extent of Contamination in Channel Sediments

Inorganic chemicals: No inorganic chemicals were detected above sediment BVs in the drainage channel at MDA L (Figures B-2, E-1, and E-2). However, the analytical detection limits for cadmium, selenium, and silver exceeded the sediment BVs (Table B-10; LANL 1998, 59730), and these inorganic chemicals are retained as COPCs. The analytical DLs were approximately twice the BVs, and there are no known historical surface releases of metals at MDA L.

Radionuclides: Plutonium-238 was the only radionuclide detected above BV/FV concentrations in the four channel sediment samples collected downgradient from MDA L (Table B-11). Although the detected concentration (0.011 pCi/g) is above the sediment FV of 0.006 pCi/g, there is no historical documentation of a surface release at MDA L.

Organic chemicals: Methoxychlor was detected in three of four sediment samples (locations 54-05143, 54-05145, and 54-05148) with a maximum concentration of 0.063 mg/kg (Figure B-8), which is approximately three times the EQL of 0.02 mg/kg. Similar to results of the MDA H RFI, the presence of methoxychlor is attributed to routine application of this pesticide at operating areas throughout TA-54 and not the result of past waste disposal practices (LANL 2002, 73270).

Data Gaps Related to Channel Sediments

Since Phase I RFI data showed that plutonium-238 and methoxychlor were detected in low concentrations, a supplemental channel sediment will be sampled at the interface of the alluvial sediments and bedrock to collect data where all the sediments accumulated over the years.

B-4.2 Nature and Extent of Contamination in Air

The data from ambient air samples near MDA L indicate that TCA and TCE are being emitted from the vadose zone plume. Other VOCs detected in MDA L ambient air samples but not detected in flux measurements include dichlorofluoromethane, chloromethane, n-hexane, trichlorofluoromethane, methylene chloride, benzene, toluene, and xylene.

Data Gaps Related to Air

An evaluation of the tritium and VOC Phase I RFI data for air at MDA L does not indicate any data gaps are present relative to identifying the nature and extent of contamination. Facility waste operations monitor the personnel who have been involved in ongoing waste management activities. These data are sufficient to assess for risk in a future report.

B-4.3 Nature and Extent of Contamination in Subsurface Core

Inorganic chemicals: Barium, chromium, cobalt, copper, manganese, nickel, uranium, and zinc were detected at concentrations above BVs in one or more borehole(s) in two out of three consecutive sampling depths (Figures B-12, B-13, and B-14 and E-4 through E-8). The data indicate that a release from subsurface waste disposal units occurred (Figure B-10). The nature and extent of the release is reviewed in the following subsections by the specific impoundments, pit, and shafts.

Impoundments B, C, and D: Boreholes 54-01012, 54-01013, and 54-01014 were drilled to angle beneath the three impoundments, respectively (Figure B-6). Concentrations of chromium and copper were detected above their respective BVs at three consecutive sampling depths in core samples beneath Impoundment B. Beneath Impoundment C, concentrations of copper were above BVs at three consecutive sampling depths, and nickel concentrations exceeded BV at two out of three consecutive sampling depths. Based on these results, it was concluded that copper and chromium have been released from Impoundment B, and copper and nickel have been released from Impoundment C. In borehole 54-01014, uranium was the only inorganic chemical detected at several consecutive sampling depths. Samples collected from the unit 2/unit 1v interface contain uranium concentrations that are slightly above the unit 2 BV (2.40 mg/kg) but below the unit 1v background value (6.22 mg/kg; see Appendix K). The pattern indicates that a release of uranium from Impoundment D to the surrounding subsurface tuff may have occurred. The vertical extent of inorganic chemical contamination is not completely bounded beneath the impoundments.

Pit A: Boreholes 54-01010 and 54-01011 were drilled at an angle to pass beneath the eastern and western portions of Pit A, respectively (Figure B-6). In borehole 54-01011, barium was detected in one sample (138 mg/kg at 29.5 ft bgs) at approximately twice the BV (LANL 1998, 59730). In borehole 54-01010, cadmium, mercury, and uranium were detected above their respective BVs (LANL 1998, 59730) in one sample each, and chromium was detected above BV in two samples separated by four sampling depths (Figure B-9). The results from the boreholes angled beneath Pit A show evidence of a release, but the vertical extent of the release is defined beneath Pit A.

Shafts 1 through 28: This shaft field is located on the east end of MDA L and was evaluated by core samples collected from boreholes 54-01007 and 54-01009. The pattern of inorganic chemical concentrations detected in these boreholes indicates that a release has occurred. The primary component of the release was copper, with smaller contributions from chromium, barium, and zinc. Nickel was also detected above the BV (LANL 1998, 59730) in the lower tuff strata (units 1v and 1g).

Copper, chromium, barium, and zinc were detected in borehole 54-01007 at concentrations above their respective BV values at 146 ft (LANL 1998, 59730) (Figure E-7, B-12, B-13, and B-14). Copper concentrations were greater than BV in 10 of 13 core samples, often by more than a factor of 10. Chromium concentrations were greater than BV (LANL 1998, 59730) in 5 of 13 samples but did not exceed BV by more than a factor of two. Copper and chromium remained elevated at the deepest sampling location (146 ft). Barium and zinc concentrations were more than twice their respective BVs in a single core sample and at concentrations marginally above their BVs at two and four sampling depths (some consecutive depths), respectively. Concentrations of barium and zinc decreased to less than their respective BVs at the deeper sampling intervals. Distributions of copper, barium, and zinc in samples taken from borehole 54-01009 were similar to those noted for borehole 54-01007. Based on this analysis, the vertical extent of copper, chromium, and zinc has not been established.

Shafts 29 through 34: This shaft field is located on the west end of MDA L and was evaluated using data from borehole 54-01008 (Figures B-12, B-13, and B-14), a vertical 150-ft borehole located about 20 ft to the southeast of Shafts 29 through 34. Inorganic chemicals detected at concentrations above BVs

included copper, zinc, and chromium. Copper concentrations exceeded the BV in a majority of the samples (10 out of 12); concentrations detected were more than 10 times the BV. Zinc and chromium were detected at three or more consecutive sampling depths at concentrations that exceeded their BVs by a factor of 2 or less. Manganese and cobalt concentrations above their BVs were reported at two consecutive sampling depths: manganese was marginally above its BV, and one cobalt concentration was more than twice the BV. Results from core samples collected in borehole 54-01008 indicated the release of inorganic chemicals from Shafts 29 to 34. The vertical extent of this release is not established.

Radionuclides: Core samples from seven boreholes were analyzed for tritium. Five shallow boreholes (up to 60 ft bgs) were angled beneath Pit A and Impoundments B, C, and D (Figure B-6). Two deep, angled boreholes (54-01015 and 54-01016) were drilled beneath Shafts 1 through 34 and Pit A (Figure B-6). The tritium data samples results from the shallow boreholes beneath Pit A ranged from 0.03 pCi/g to 11.6 pCi/g, and concentrations decreased with depth. Tritium was detected at low concentrations in two samples collected from the deep, angled boreholes; at 0.13 pCi/g at approximately 524 ft in borehole 54-01015; and at 0.001 pCi/g at approximately 593 ft in borehole 54-01016. These results indicate a tritium release from MDA L and indicate that the vertical extent of the tritium contamination is bounded. However, there are insufficient data to define the lateral extent of tritium contamination.

Organic chemicals: Twenty-two organic chemicals were detected in 127 core samples collected at MDA L, most at trace concentrations (i.e., less than or slightly above the EQLs). The higher concentrations (i.e., concentrations greater than EQLs) were detected in the boreholes beneath Pit A (boreholes 54-01010 and 54-01011), between Pit A and Shaft 28 (borehole 54-01009), and at the east end of the array of Shafts 1 through 7 (borehole 54-01007 [Figure B-6]).

Two pesticides, Aroclor-1260, and three SVOCs were detected in one to four samples at several sampling depths in tuff. Aroclor-1260 was reported in borehole 54-01010 at a concentration (0.313 mg/kg) at a depth of 30 ft and was not detected in deeper samples. Methoxychlor was detected above the EQL in a single sample collected at a depth of 59.5 ft in borehole 54-01010 at a concentration of 0.0756 mg/kg. The pesticide DDD was detected in two samples in borehole 54-01011; DDD was not detected in deeper samples from borehole 54-01011. In borehole 54-01010, bis(2-ethylhexyl)phthalate was detected in a single sample at a depth of 30 ft beneath Pit A but was not detected in deeper samples. Di-n-butyl phthalate was detected at four nonconsecutive sampling depths but was not detected at the bottom of the borehole. Pentachlorophenol was detected at concentrations (13.0 mg/kg and 3.3 mg/kg) at two sampling depths below Impoundment B and decreased with depth.

In summary, several organic chemicals were reported in the subsurface tuff near Pit A and Shafts 1 through 28. The SVOCs, pesticides, and Aroclor-1260 either decreased with depth or were detected at low concentration at the bottom of the borehole, with no detects at shallower depths in the borehole. VOCs were detected in the core samples at concentrations approximating EQL values; however, these measurements cannot be used to define the extent because VOCs do not adsorb readily to tuff and are transported mainly as vapor phase in the subsurface of MDA L. Therefore, the nature and extent of the VOC plume at MDA L is better defined using pore-gas sampling results (see below) than the core sample results. The nature and extent of the other organic chemicals detected do not indicate a release, have the extent defined, and are not evaluated further.

Data Gaps Related to Subsurface Core

Phase I RFI core data for inorganic chemicals and tritium indicate releases to subsurface tuff have occurred beneath Impoundments B, C and D and the two shaft fields, respectively. The number and locations of Phase I RFI samples of core are inadequate to support conclusions regarding the nature and extent of contamination beneath the impoundments and shaft fields.

In addition to the analytical suites required for Phase I RFI core samples, additional suites may be appropriate given the nature of the disposed waste at MDA L. Nitrates and perchlorate, which are very soluble and susceptible to migration with infiltrating surface water, were not analyzed in the Phase I RFI core samples. Nitrates are associated with fertilizers and are a common breakdown product of most nitrogen-containing organic materials. Perchlorate-containing chemicals have been widely used as oxidizers in a variety of chemical processes, and perchloric acid is a common strong acid used in laboratories. Because of their mobility and potential occurrence in disposed waste at MDA L, analysis of nitrates and perchlorate in core samples at MDA L is appropriate, and the absence of data for these chemicals is a data gap. Some high explosive (HE) compounds are also relatively soluble in water and subject to transport from the disposed waste. However, the presence of HE in appreciable quantities in the disposed waste is unlikely because it has always been Laboratory policy to "flash"' (burn) HEcontaminated material prior to disposal. However, inventory records for MDA L are incomplete, and with the absence of HE data for the Phase I RFI is a data gap.

Information on the hydrogeologic properties and other physical characteristics of the vadose zone at MDA L is minimal and is therefore identified as a data gap for completion of the future corrective measure study (CMS) for MDA L. During the Phase I RFI, information on the moisture content of core was collected only from a depth of approximately 271 ft bgs. Other relevant hydrogeologic information, as well as information on the water content of core at greater depths in the vadose zone, is presently inferred from data obtained elsewhere at TA-54. Hydrogeologic properties such as saturated and unsaturated hydraulic conductivity, porosity, bulk density, chloride-ion concentration, and matric potential are also important parameters for evaluating the migration of liquid- and vapor-phase contaminants in the vadose zone. Such an evaluation, usually performed using numerical models to simulate field conditions, provides support for conclusions regarding the current nature and extent of contamination. It will also be used in evaluating potential corrective measures to estimate possible future migration of contaminants from the waste disposal units.

The hydrogeologic properties described above pertain primarily to the rock matrices of the geologic strata at MDA L. Some strata, specifically units of the Tshirege Member of the Bandelier Tuff, also contain fractures that can act as conduits for migration of liquid- and vapor-phase contaminants in the vadose zone. Information from fractured rock that can be used to evaluate the potential role of fractures in contaminant migration includes fracture density, fracture apertures, the strike and dip of fractures, and information on the presence and characteristics of fracture coating and fill. Where fractures are encountered during coring of boreholes, a comparison of chemical concentration data from tuff immediately adjacent to a fracture and tuff further from the fracture can also provide valuable information on the role of fractures in contaminant transport at MDA L.

B-4.4 Nature and Extent of Contamination in Subsurface Pore-Gas and VOC and Tritium Surface Flux

Pore-gas analytical results indicate that the highest concentrations of vapor-phase VOCs exist in close proximity to the two source areas: the northwest source area and the southeast source area. Concentrations of vapor-phase VOCs decrease in all directions from the two source areas. TCA has consistently been the most prevalent VOC detected in pore-gas samples and is the best indicator of the extent of the plume.

The field-screening data obtained using the B&K multigas analyzer correlate well with the analytical laboratory SUMMA™ canister data for the four compounds screened for (TCA, TCE, PCE, and Freon 113) in the ppm concentration range. Figures B-15 and B-16 show the correlation of B&K screening results to EPA Method TO-14 analytical results (SUMMA™ canister samples) for TCA and TCE, respectively. The linear regression for SUMMA™ canister samples versus TCA indicates that the B&K reads to within approximately 70% of the EPA Method TO-14 analytical results with a correlation coefficient (r^2) of 0.87. For TCE, the B&K reads to within approximately 60% of the EPA Method TO-14 analytical results with an r^2 = 0.9. In summary, B&K screening is a good indicator of actual pore-gas concentrations in the ppm range and can be used to help define the extent of VOC contamination in the ppm concentration range.

Figure B-17 shows contours of TCA concentration at MDA L based on quarterly B&K screening data collected from FY 2000 through the first quarter of FY 2002. The figure shows projected 10, 100, and 500 parts per million by volume (ppmv) TCA contours, assuming a horizontal plane through the mesa at an elevation of 6736 ft. is equal to a depth of 100 ft bgs. Figure B-17 also shows the location of monitoring boreholes. Figure B-18 presents a cross section of the mesa, showing 10, 100, and 500 ppmv TCA contours based on quarterly B&K screening data collected since FY 1999. Figure B-19 shows a representative two-dimensional plot of the TCA concentration versus depth. Figure B-20 shows the extent of the TCA plume, in relation to White Rock and nearby domestic production wells.

Figures B-17 and B-18 show the lateral and vertical extent by the 10-ppmv concentration contour. Outside this contour, concentrations decrease noticeably to below the quantification capability of the B&K; analytical results for samples collected from this region show TCA concentrations in the part per billion by volume (ppbv) range. Since 1999, the long-axis plume aerial extent, defined by the 10 ppmv contour, has fluctuated between 700 and 1000 ft. The short axis extent has not fluctuated significantly because of the physical constraint of the mesa walls. Vertically, the maximum extent of the 10 ppmv TCA contour is approximately 300 ft below the mesa top (pore-gas samples are monitored to a depth of 607 ft bgs). The extent has not fluctuated significantly since 1999. The 10 ppmv TCA contour is approximately 650 ft above the regional aquifer. Concentrations increase to a depth of approximately 85 ft below the MDA L surface, followed by decreasing concentrations through the total depth of the plume.

A discussion of historical and current pore-gas sampling methodologies is provided in Appendix G. Sampling and analytical methods have greatly improved since the late 1990s, resulting in consistent, good quality data, from both the analytical chemistry and B&K screening. This allows some evaluation of trends within the plume. The B&K results indicate a stable plume (Figures B-21, B-22, and B-23). Figure B-20 shows the areal extent of the VOC plume with respect to surrounding facilities and the town of White Rock; the outer edge of the plume is approximately two miles from the town of White Rock. The SUMMA™ canister analytical results presented in Figures B-21, B-22, and B-23 show the organic chemicals present in the highest concentrations. Figure B-21 shows data from vapor-monitoring borehole 54-02002, which is representative of the source areas. Figure B-22 depicts data from vapor-monitoring borehole 54-02023, which is representative of a medium-to-low concentration zone of the plume. Figure B-23 shows data from vapor-monitoring borehole 54-01015, which is representative of the plume at a greater depth. As shown in the figures, the top 11 detected VOC concentrations have remained relatively constant over time or have decreased slightly. Therefore, it is concluded that the plume is in a near steady state.

Stauffer et al. (2002, 69794) modeled the plume evolution using a three-dimensional finite element program. The full report is provided in Appendix I, and an in-depth review of the report along with studies of passive and active venting is provided in Appendix J. The model assumed vapor diffusion emanating from two source areas located at the two shaft fields at MDA L. The model was calibrated using the

quarterly pore-gas monitoring data. The resulting modeled plume closely matches the shape, concentration gradients, and extent of the plume as measured. Also, the model predicts that the plume should be at or near steady state. This modeling supports the conclusion that the VOC plume exists predominantly in the vapor phase, that the VOCs move by diffusion, and that the plume is stable. Stauffer et al. (2002, 69794) also predicted plume evolution over a 50-yr period. If the assumed source remains constant, the plume does not change appreciably during the simulation period, which further verifies the stability of the plume. If a constant source were not assumed, the plume would gradually decrease in size and concentration over time.

The following statements can be made with respect to the nature and extent of the VOC vapor plume at MDA L based on pore-gas data:

- VOCs are transported from the source areas primarily in the vapor phase;
- TCA is the dominant contaminant, followed by TCE;
- the ratio of the major plume contaminants (TCA, TCE, and Freon 113) is 1:0.3:0.2;
- vertically, the plume extends between ground surface and the top of the basalt (approximately 300 ft bgs);
- laterally, the plume extends along the mesa about 1000 ft from the center of Area L, and perpendicular across the mesa (approximately 450 ft from the center of Area L);
- the plume is changing very little in area or contaminant concentrations over time (1999 to the present);
- the 11 VOCs detected most frequently have remained consistent over time, and the concentrations of these VOCs have remained relatively constant or have decreased slightly over time; and
- vapor diffusion modeling fits the measured geographic distribution of TCA concentration.

Based on this data set, the nature and extent of the VOC plume has been defined, and the current monitoring network adequately encompasses the plume to evaluate changes over time.

Results of the surface VOC flux study conducted in 1994 show the surface expression or "fingerprint" of the subsurface plume (Quadrel 1994, 63869; Figure B-11). The study was limited to non-asphalt covered locations; therefore, the VOC flux data only exists for the perimeter of MDA L. The flux study does show that the magnitude of surface flux is greatest near MDA L and decreases noticeably with distance from the sources. The lateral extent of the VOC plume as defined by the surface flux data closely matches the lateral extent defined by subsurface pore-gas measurements. The primary VOCs reported within the area closest to the source areas (the disposal shafts) were TCA, PCE, TCE, Freon 113, and acetone, which accounted for 33%, 30%, 27%, 6%, and 2% of the emissions, respectively.

Tritium flux data collected at MDA L indicate tritium transported in the vapor phase is diffusing from the subsurface into the atmosphere; however, the sample locations are not in close proximity to any known subsurface tritium sources. Tritium is a COPC. Because of the small number of samples and their poor geographic distribution, no determination can be made about the lateral extent of tritium contamination in the subsurface.

Data Gaps Related to Subsurface Pore Gas

The concentrations and spatial extent of VOC vapors in subsurface tuff have been identified; however, continued monitoring is required to track plume stability, migration, or the potential for a release from the source area. One additional pore-gas monitoring borehole is required for long-term monitoring of the western shaft fields. The extent of tritium is a data gap.

B-5.0 REFERENCES

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Figure B-1. Locations of subsurface disposal units at MDA L (PRS 54-006)

Figure B-2. Phase I RFI sediment sample locations at MDA L

Borehole

F6.1-16, TA-54 RFI RPT, 020100, PTM_Rev. for FB-12, MDA L IWP, 082503, cf

Figure B-12. Chromium concentrations (mg/kg) in borehole core samples at MDA L. Concentrations are proportional to the area enclosed by the oval and plotted at sampled depths (ft bgs) from the borehole. Symbol × **indicates that the sample concentration is greater than the maximum concentration observed in tuff (all strata) at Laboratory background locations (13 mg/kg).**

Borehole

F6.1-17, TA-54 RFI RPT, 020100, PTM_Rev. for FB-13, MDA L IWP, 082503, cf

Figure B-13. Copper concentrations (mg/kg) in borehole core samples at MDA L. Concentrations are proportional to the area enclosed by the oval and plotted at sampled depths (ft bgs) within the borehole. Symbol × **indicates that the sample concentration is greater than the maximum concentration observed in tuff (all strata) at Laboratory background locations (6.2 mg/kg).**

Borehole

F6.1-18, TA-54 RFI RPT, 020100, PTM_Rev. for FB-14, MDA L IWP, 082503, cf

Figure B-14. Zinc concentrations (mg/kg) in borehole core samples at MDA L. Concentrations are proportional to the area enclosed by the oval and plotted at sampled depths (ft bgs) within the borehole. Symbol × **indicates that the sample concentration is greater than the maximum concentration observed in tuff (all strata) at Laboratory background locations (74 mg/kg).**

1,1,1-Trichloroethane (TCA)

Figure B-15. Correlation of B&K screening data to SUMMA™ canister analytical results for TCA

Figure B-16. Correlation of B&K screening data to SUMMA™ canister analytical results for TCE

Borehole 54-02022, TCA Concentration

Figure B-19. Pore-gas monitoring borehole 54-02022, TCA concentration versus depth. Note the characteristic increase in concentration to approximately 100 ft below the MDA L surface, followed by decreasing concentrations to the total depth of the well.

Areal extent of the VOC plume, represented by TCA, with respect to White Rock and surrounding wells **Figure B-20. Areal extent of the VOC plume, represented by TCA, with respect to White Rock and surrounding wells** Figure B-20.

 frequently detected VOCs

Figure B-22. Pore-gas monitoring borehole 54-02023—160 ft bgs at MDA L: quarterly analytical results over time for the most

Dichlorodifluoromethane Dichlorodifluoromethane **X** Trichlorofluoromethane Trichlorofluoromethane o Trichloroethane[1,1,1-] Trichloroethane[1,1,1-] \blacksquare Trichloro-1,2,2-
trifluoroethane[1,1,2-] Carbon Tetrachloride trifluoroethane[1,1,2-] Carbon Tetrachloride **x Dichloroethene[1,1-]** Dichloroethane[1,1-] Dichloroethene[1,1-] Dichloroethane[1,1-] + Methylene Chloride Methylene Chloride Tetrachloroethene Tetrachloroethene Trichloroethene Trichloroethene Trichloro-1,2,2 o Chloroform Chloroform 01-Oct-00 $\ddot{}$ \blacksquare Ó \times 23-Jun-00 \circ 激 15-Mar-00 \circ ER2003-0504
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ER2003-0504**
 **ER2003-0504

ER2003-0504**
 **ER2003-0504

ER2003-0504**

 **ER2003-0504

ER2003-0** 06-Dec-99 28-Aug-99 **Date** 20-May-99 09-Feb-99 01-Nov-98 24-Jul-98 15-Apr-98 05-Jan-98 0.01 0.05 0.1 0.09 0.08 0.07 0.06 0.04 0.03 0.02 \circ **ppmv**

 frequently detected VOCs

Figure B-23. Pore-gas monitoring borehole 54-01015—400 ft bgs at MDA L: quarterly analytical results over time for most

MDA L Investigation Work Plan

Impoundment/Pit	Dimensions (ft) (width x length x depth)	Period of Use	Months Used	Total Capacity (ft ³)
A	200 x 12 x 12	1950s-12/78	>228	28,800
в	$60 \times 18 \times 10$	1/79-6/85	78	7560
С	$35 \times 12 \times 10$	7/85-12/86	18	2940
	75 x 18 x 10	1972-1984	156	9450

Table B-1 Dimensions, Dates of Operation, and Capacity of Pit and Impoundments at MDA L

Table B-2 Dimensions of Disposal Shafts at MDA L

Shaft	Diameter (f ^t)	Depth (f ^t)	Shaft	Diameter (f ^t)	Depth (f ^t)
1	$\mathsf 3$	60	18	$\bf 8$	60
$\overline{2}$	$\mathsf 3$	60	19	$\bf 8$	60
$\ensuremath{\mathsf{3}}$	$\mathsf 3$	60	20	$\ensuremath{\mathsf{3}}$	60
$\overline{\mathbf{4}}$	$\mathsf 3$	60	21	$\ensuremath{\mathsf{3}}$	60
5	$\mathsf 3$	60	22	$\mathsf 3$	60
$\,6\,$	$\overline{\mathbf{4}}$	60	23	$\overline{\mathbf{4}}$	60
$\overline{7}$	3	60	24	$\overline{\mathbf{4}}$	60
$\bf 8$	3	60	25	$\,6\,$	60
$\boldsymbol{9}$	$\ensuremath{\mathsf{3}}$	60	26	$\,6\,$	60
10	$\mathsf 3$	60	27	$\overline{\mathbf{4}}$	60
11	$\bf 8$	60	28	$\overline{\mathbf{4}}$	60
12	$\overline{\mathbf{4}}$	60	29	$\,6\,$	65
13	$\bf8$	60	$30\,$	$\,6\,$	65
14	$\mathsf 3$	60	31	$\,6\,$	61
15	$\ensuremath{\mathsf{3}}$	60	32	4	15
$16\,$	$\ensuremath{\mathsf{3}}$	60	33	$\,6\,$	65
17	$\ensuremath{\mathsf{3}}$	60	34	$\,6$	63

Shaft	Period of Use	Months Used	Total Capacity (ft ³)	Shaft	Period of Use	Months Used	Total Capacity (ft^3)
1	$4/80 - 8/83$	41	424	18	6/79-5/80	12	3016
$\overline{2}$	$2/75 - 6/79$	53	424	19	4/80-4/82	25	3016
3	2/75-10/78	45	424	20	$3/82 - 8/83$	18	424
4	$2/75 - 4/80$	63	424	21	3/82-12/84	46	424
5	$2/75 - 5/77$	28	424	22	$3/82 - 8/83$	18	424
6	$6/75 - 5/79$	48	754	23	$4/82 - 2/84$	23	754
$\overline{7}$	$6/75 - 5/79$	48	424	24	$4/82 - 3/84$	24	754
8	6/75-5/79	48	424	25	$9/82 - 4/85$	32	1696
9	$6/75 - 5/79$	48	424	26	$9/82 - 2/84$	18	1696
10	6/75-5/79	48	424	27	$1/83 - 1/85$	25	754
11	1/78-6/79	18	3016	28	1/82-4/85	40	754
12	1/78-6/79	18	754	29	12/83-7/84	8	1838
13	6/79-4/82	35	3016	30	12/83-4/84	5	1838
14	6/79-4/82	35	424	31	12/83-8/84	9	1725
15	6/79-4/82	36	424	32	$3/84 - 8/84$	6	188
16	6/79-4/82	35	424	33	$3/84 - 1/85$	11	1838
17	6/79-4/82	35	424	34	$2/85 - 4/85$	$\overline{2}$	1781

Table B-3 Dates of Operation and Capacity for Disposal Shafts at MDA L

Note: Information was taken from the OU 1148 work plan (LANL 1992, 07669, p. 5-106).

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Table B-4 (continued) **Table B-4 (continued)**

Table B-4 (continued) **Table B-4 (continued)**

b

n/a = Not applicable.

Table B-5
Summary of Phase I RFI Channel Sediment Samples Collected at MDA L **Summary of Phase I RFI Channel Sediment Samples Collected at MDA L Table B-5**

Table B-6 Calculated Tritium Surface Flux Concentration for Phase I RFI Samples Collected at MDA L

*Higher of two duplicate samples.

Table B-7 Borehole Information

Borehole ID	Year Installed	Depth (f ^t)	Declination (degrees from horizontal)	Adjacent Waste Disposal Unit	Current Status	
Pre-RFI						
54-02001	1986	200	Vertical	Lead stringer shafts; shaft 33	Buried	
54-02002	1986	200	Vertical	Shafts 7-11	Pore-gas monitoring borehole	
54-02012	1985	42	Vertical	Shafts 30-34	Pore-gas monitoring borehole	
54-02013	1985	63	Vertical	None	Pore-gas monitoring borehole	
54-02014	1985	86	Vertical	Shafts 17-18	Pore-gas monitoring borehole	
54-02015	1985	82	Vertical	Shafts 3-5	Pore-gas monitoring borehole	
54-02016	1985	82	Vertical	Pit A	Pore-gas monitoring borehole	
54-02020	1986	200	Vertical	None	Pore-gas monitoring borehole	
54-02021	1986	200	Vertical	None	Pore-gas monitoring borehole	
54-02022	1986	197	Vertical	None	Pore-gas monitoring borehole	
54-02023	1986	200	Vertical	None	Pore-gas monitoring borehole	
54-02024	1986	200	Vertical	None	Pore-gas monitoring borehole	
54-02025	1988	190	Vertical	None	Pore-gas monitoring borehole	
54-02026	1988	215	Vertical	None	Pore-gas monitoring borehole	
54-02027	1988	250	Vertical	None	Pore-gas monitoring borehole	
54-02028	1988	250	Vertical	None	Pore-gas monitoring borehole	
54-02029	1988	288	Vertical	None	Pore-gas monitoring borehole	
54-02030	1989	243	Vertical	None	Pore-gas monitoring borehole	
54-02031	1989	260	Vertical	None	Pore-gas monitoring borehole	
54-02034	1988	300	Vertical	None	Pore-gas monitoring borehole	
54-02087	1985?	86	Vertical	None	Pore-gas monitoring borehole	
54-02088	1985?	86	Vertical	None	Pore-gas monitoring borehole	
54-02089	1985?	86	Vertical	None	Pore-gas monitoring borehole	

Table B-7 (continued)

Note: The -01000 series boreholes are Phase I RFI characterization boreholes. The -02000 series boreholes are pre-RFI boreholes drilled for pore-gas monitoring.

Table B-8 (continued) **Table B-8 (continued)**

Table B-8 (continued) **Table B-8 (continued)**

Table B-8 (continued) **Table B-8 (continued)**

Note: Shaded values in cells indicate on-site mobile screening laboratory.

Note: Shaded values in cells indicate on-site mobile screening laboratory.

Borehole Number	Sample Port Depth (feet from surface)
54-01015	45, 187, 350, 385, 435, 485, 525
54-01016	36, 188, 318, 390, 481, 533, 601
54-02001	20, 40, 60, 80, 100, 130, 140, 160, 180, 200
54-02002	20, 40, 60, 80, 100, 120, 140, 160, 180, 200
54-02012	7, 27, 42
54-02014	13, 31, 46, 86
54-02015	8, 31, 82
54-02016	7, 8, 31, 82
54-02020	20, 40, 60, 80, 100, 130, 140, 160, 180, 200
54-02021	20, 40, 60, 80, 100, 130, 140, 160, 180, 200
54-02022	20, 40, 60, 80, 100, 120, 140, 160, 180, 197
54-02023	20, 40, 60, 80, 100, 120, 140, 160, 180, 200
54-02024	20, 40, 60, 80, 100, 120, 140, 160, 180, 200
54-02025	20, 60, 100, 160, 190
54-02026	20, 60, 100, 160, 200, 215
54-02027	20, 60, 100, 160, 200, 220, 250
24-02028	20, 60, 100, 160, 200, 220, 250
54-02029	20, 60, 100, 160, 200, 220, 260, 288
54-02030	20, 60, 100, 160, 200, 220, 243
54-02031	20, 60, 100, 160, 200, 220, 260
54-02034	60, 100, 160, 200, 220, 260, 300
54-02087	13, 31, 46, 86
54-02088	13, 31, 46, 86
54-02089	13, 31, 46, 86

Table B-9 Depths of Pore-Gas Sampling Ports in Boreholes at MDA L

Note: The -01000 series boreholes are Phase I RFI characterization boreholes. The -02000 series boreholes are pre-RFI boreholes drilled for pore-gas monitoring.

Analyte	Media	Number _{of} Analyses	Number _{of} Detects	Concentration Range ^a (mg/kg)	Background Valueb (mg/kg)	Frequency of Detects Above Background Value	Frequency of Nondetects Above Background Value
Aluminum	Sediment	$\overline{\mathbf{4}}$	4	2270 to 3940	15400	0/4	0/4
Antimony	Sediment	$\overline{4}$	$\mathbf{0}$	$[0.2 \text{ to } 0.21]$	0.83	0/4	0/4
Arsenic	Sediment	$\overline{\mathbf{4}}$	0	$[0.78 \text{ to } 1.5]$	3.98	0/4	0/4
Barium	Sediment	$\overline{\mathbf{4}}$	3	[37] to 65.7	127	0/4	0/4
Beryllium	Sediment	$\overline{4}$	0	$[0.25 \text{ to } 0.51]$	1.31	0/4	0/4
Cadmium	Sediment	$\overline{\mathbf{4}}$	0	$[0.4 \text{ to } 0.67]$	0.4	0/4	3/4
Calcium	Sediment	$\overline{\mathbf{4}}$	4	1130 to 1830	4420	0/4	0/4
Chromium	Sediment	$\overline{4}$	4	2 to 4.2	10.5	0/4	0/4
Cobalt	Sediment	$\overline{\mathbf{4}}$	0	$[1.4 \text{ to } 2.6]$	4.73	0/4	0/4
Copper	Sediment	4	0	$[3.6 \text{ to } 4.7]$	11.2	0/4	0/4
Iron	Sediment	$\overline{\mathbf{4}}$	4	3540 to 4870	13800	0/4	0/4
Lead	Sediment	4	4	7.3 to 15.3	19.7	0/4	0/4
Magnesium	Sediment	$\overline{4}$	0	[506 to 872]	2370	0/4	0/4
Manganese	Sediment	4	4	138 to 224	543	0/4	0/4
Mercury	Sediment	$\overline{\mathbf{4}}$	0	$[0.02 \text{ to } 0.02]$	0.1	0/4	0/4
Nickel	Sediment	$\overline{4}$	0	$[2.7 \text{ to } 3.8]$	9.38	0/4	0/4
Potassium	Sediment	$\overline{\mathbf{4}}$	0	[545 to 805]	2690	0/4	0/4
Selenium	Sediment	$\overline{4}$	0	$[0.6 \text{ to } 0.64]$	0.3	0/4	4/4
Silver	Sediment	$\overline{\mathbf{4}}$	0	[2 to 2.1]	1	0/4	4/4
Sodium	Sediment	$\overline{\mathbf{4}}$	0	[35.6 to 74]	1470	0/4	0/4
Thallium	Sediment	$\overline{4}$	0	[0.2 to 0.21]	0.73	0/4	0/4
Vanadium	Sediment	$\overline{\mathbf{4}}$	0	[4.7 to 7.7]	19.7	0/4	0/4
Zinc	Sediment	$\overline{4}$	$\overline{\mathbf{4}}$	20.7 to 30.3	60.2	0/4	0/4

Table B-10 Frequency of Detected Inorganic Chemicals Above the Background Value in Channel Sediment Samples at MDA L

b Sediment BVs obtained from LANL (1998, 59730).

Analyte	Media	Number of Analyses	Number of Detects	Concentration Range ^a (pCi/q)	Background Value ^b (pCi/q)	Frequency of Detects Above Background Value
Americium-241	Sediment	4	4	0.004 to 0.009	0.04	0/4
Cesium-137	Sediment	4	2	[0.09] to 0.38	0.9	0/4
Cobalt-60	Sediment	4	$\mathbf{0}$	[0.02 to 0.09]	na ^c	0/4
Plutonium-238	Sediment	4	4	0.003 to 0.011	0.006	1/4
Plutonium-239	Sediment	$\overline{4}$	4	0.01 to 0.017	0.068	0/4
Strontium-90	Sediment	4	4	-0.04 to 0.12	1.04	0/4
Technitium-99	Sediment	4	$\mathbf{0}$	$[0.2]$ to $[0.2]$	na	0/4
Thorium-228	Sediment	4	4	1.26 to 1.92	2.28	0/4
Thorium-230	Sediment	4	4	1.12 to 1.69	2.29	0/4
Thorium-232	Sediment	4	4	1.28 to 1.84	2.33	0/4
Tritium	Sediment	4	4	6.84E-03 to 3.30E-02	0.093	0/4
Uranium-234	Sediment	4	4	1.12 to 1.81	2.59	0/4
Uranium-235	Sediment	4	4	0.07 to 0.1	0.2	0/4
Uranium-238	Sediment	4	4	1.37 to 2.03	2.29	0/4

Table B-11 Frequency of Detected Radionuclides Above the Background Value in Channel Sediment Samples at MDA L

b Sediment background and fallout values obtained from LANL (1998, 59730).

 \rm{c} na = Not available.

Analyte	Geologic Unit	Number of Analyses	Number _{of} Detects	Concentration Background Range Value $(mg/kg)^a$ (mg/kg) Value		Frequency of Detects Above Background	Frequency of Nondetects Above Background Value
Aluminum	Qbt 2	34	34	130 to 10000	7340	1/34	0/34
Aluminum	Qbt 1g	4	$\overline{\mathbf{4}}$	563 to 1200	3560	0/4	0/4
Aluminum	Qbt 1v	29	29	270 to 4700	8170	0/29	0/29
Antimony	Qbt 2	34	1	$[0.1 \text{ to } 4.5]$	0.5	0/34	1/34
Antimony	Qbt 1g	4	$\mathbf{0}$	$[0.2 \text{ to } 0.3]$	0.5	0/4	0/4
Antimony	Qbt 1v	29	0	$[0.12 \text{ to } 0.3]$	0.5	0/29	0/29
Arsenic	Qbt 2	34	9	$[0.2 \text{ to } 1.6]$	2.79	0/34	0/34
Arsenic	Qbt 1g	4	1	$[0.2 \text{ to } 1.5]$	0.56	0/4	2/4
Arsenic	Qbt 1v	29	13	$[0.2]$ to 1.7	1.81	0/29	0/29
Barium	Qbt 2	34	11	3.5 to 138	46	3/34	0/34
Barium	Qbt 1g	4	$\overline{2}$	$[16.4]$ to 44	25.7	1/4	0/4
Barium	Qbt 1v	29	21	$[3.4]$ to 44	26.5	8/29	029
Beryllium	Qbt 2	34	$\overline{7}$	$[0.08]$ to 1.5	1.21	1/34	0/34
Beryllium	Qbt 1g	4	$\overline{2}$	$[0.42]$ to 1.6	1.44	1/4	0/4
Beryllium	Qbt 1v	29	18	[0.22] to 3.3	1.7	1/29	0/29
Boron	Qbt 2	27	1	$[1.7 \text{ to } 6.8]$	na ^b	1/27	na
Boron	Qbt 1g	3	$\pmb{0}$	[3 to 4.1]	na	0/3	na
Boron	Qbt 1v	20	0	$[1.7 \text{ to } 3.9]$	na	0/20	na
Cadmium	Qbt 2	34	$\overline{2}$	$[0.04]$ to 1.4	1.63	0/34	0/34
Cadmium	Qbt 1g	$\overline{4}$	$\pmb{0}$	$[0.3 \text{ to } 0.64]$	0.4	0/4	2/4
Cadmium	Qbt 1v	29	1	$[0.27]$ to 1.7	0.4	1/29	4/29
Calcium	Qbt 2	34	9	[203] to 79000	2200	1/34	3/34
Calcium	Qbt 1g	$\overline{4}$	1	[784 to 3100]	1900	0/4	1/4
Calcium	Qbt 1v	29	16	[565 to 3100]	3700	0/29	0/29
Chromium	Qbt 2	34	24	$[0.5]$ to 57.8	7.14	4/34	0/34
Chromium	Qbt 1g	$\overline{4}$	3	0.4 to 4.3	2.6	1/4	0/4
Chromium	Qbt 1v	29	27	0.6 to 4.8	2.24	14/29	0/29
Cobalt	Qbt 2	34	10	$[0.51 \text{ to } 3.9]$	3.14	1/34	1/34
Cobalt	Qbt 1g	4	$\overline{2}$	0.7 to 2.4	8.89	0/4	0/4
Cobalt	Qbt 1v	29	20	$[0.5]$ to 6.1	1.78	4/29	2/29
Copper	Qbt 2	34	16	[0.63] to 370	4.66	15/34	0/34
Copper	Qbt 1g	4	$\overline{4}$	17.3 to 180	3.96	4/4	0/4
Copper	Qbt 1v	29	24	[0.64] to 190	3.26	21/29	1/29
Cyanide (total)	Qbt 2	$30\,$	$\mathbf{1}$	$[0.00005]$ to 0.96	$0.5\,$	1/30	na

Table B-12 Frequency of Inorganic Chemicals Detected Above BV in Subsurface Core Samples at MDA L

Analyte	Geologic Unit	Number _{of} Analyses	Number _{of} Detects	Concentration Background Value Background Range (mg/kg) ^a (mg/kg)		Frequency of Detects Above Value	Frequency of Nondetects Above Background Value
Cyanide (Total)	Qbt 1g	$\overline{\mathbf{4}}$	0	[0.00005 to 0.21]	0.5	0/4	na
Cyanide (Total)	Qbt 1v	28	0	[0.00005 to 0.34]	0.5	0/28	na
Iron	Qbt 2	34	34	14500 1020 to 10000 0/34		0/34	
Iron	Qbt 1g	4	$\overline{4}$	1450 to 5000	3700	1/4	0/4
Iron	Qbt 1v	29	29	2550 to 9700	9900	0/29	0/29
Lead	Qbt 2	34	30	1.2 to 13	11.2	1/34	0/34
Lead	Qbt 1g	$\overline{4}$	3	3 to 7.1	13.5	0/4	0/4
Lead	Qbt 1v	29	27	3.5 to 20	18.4	1/29	0/29
Magnesium	Qbt 2	33	9	52 to 1300	1690	0/33	0/33
Magnesium	Qbt 1g	4	$\overline{2}$	[59 to 309]	739	0/4	0/4
Magnesium	Qbt 1v	28	21	[48.5] to 730	780	0/28	0/28
Manganese	Qbt 2	34	34	79 to 770	482	1/34	0/34
Manganese	Qbt 1g	4	4	149 to 210	189	1/4	0/4
Manganese	Qbt 1v	29	29	156 to 460	408	4/29	0/29
Mercury	Qbt 2	30	$\overline{2}$	$[0.02]$ to 0.16	0.1	2/30	0/230
Mercury	Qbt 1g	$\overline{4}$	0	$[0.02 \text{ to } 0.1]$	0.1	0/4	0/4
Mercury	Qbt 1v	28	$\pmb{0}$	$[0.02 \text{ to } 0.1]$	0.1	0/28	0/28
Molybdenum	Qbt 2	30	3	0.3 to $[5.9]$	na	3/30	na
Molybdenum	Qbt 1g	$\overline{4}$	1	0.7 to [6.2]	na	1/4	na
Molybdenum	Qbt 1v	28	9	0.3 to [5.9]	na	9/28	na
Nickel	Qbt 2	34	$\overline{7}$	$[1.3]$ to 17.3	6.58	3/34	0/34
Nickel	Qbt 1g	$\overline{4}$	$\mathbf{1}$	$[2]$ to 2.6	$\overline{2}$	1/4	2/4
Nickel	Qbt 1v	29	$\overline{7}$	$[1.3]$ to 22.4	$\overline{2}$	7/29	4/29
Potassium	Qbt 2	34	10	120 to 1000	3500	0/34	0/34
Potassium	Qbt 1g	4	$\overline{\mathbf{c}}$	[220 to 777]	2390	0/4	0/4
Potassium	Qbt 1v	29	22	140 to [754]	6670	0/29	0/29
Selenium	Qbt 2	24	3	$[0.2]$ to 1	0.3	1/24	14/24
Selenium	Qbt 1g	4	0	$[0.2 \text{ to } 0.43]$	0.3	0/4	2/4
Selenium	Qbt 1v	26	$\mathbf{1}$	$[0.2 \text{ to } 0.67]$	0.3	0/26	4/26
Silver	Qbt 2	34	0	$[0.06 \text{ to } 2.2]$	$\mathbf{1}$	0/34	1/34
Silver	Qbt 1g	4	0	$[0.3 \text{ to } 1.1]$	$\mathbf{1}$	0/4	1/4
Silver	Qbt 1v	29	0	$[0.3 \text{ to } 2.2]$	$\mathbf{1}$	0/29	1/29
Sodium	Qbt 2	34	13	[135] to 2100	2770	0/34	0/34
Sodium	Qbt 1g	4	$\overline{2}$	[256] to 720	4350	0/4	0/4
Sodium	Qbt 1v	29	23	150 to 1090	6330	0/29	0/29
Thallium	Qbt 2	34	$\mathbf{1}$	$[0.1 \text{ to } 0.62]$	1.1	0/34	0/34

Table B-12 (continued)

Analyte	Geologic Unit	Number Ωf Analyses	Number Ωf Detects	Concentration Range $(mg/kg)^a$	Background Value (mg/kg)	Frequency of Detects Above Background Value	Frequency of Nondetects Above Background Value
Thallium	Qbt 1g	4	$\mathbf{0}$	$[0.2 \text{ to } 0.3]$	1.22	0/4	0/4
Thallium	Qbt 1v	29	Ω	$[0.12 \text{ to } 0.4]$	1.24	0/29	0/29
Uranium	Qbt 2	24	24	0.601 to 9.54	2.4	12/24	0/24
Uranium	Qbt 1v	5	5	0.628 to 5.9	6.22	0/5	0/5
Vanadium	Qbt 2	34	9	$[0.8]$ to 9.5	17	0/34	0/34
Vanadium	Qbt 1g	4	$\overline{2}$	0.7 to 1.7	4.59	0/4	0/4
Vanadium	Qbt 1v	29	21	0.8 to 4.5	4.48	1/29	0/29
Zinc	Qbt 2	34	34	12 to 240	63.5	4/34	0/34
Zinc	Qbt 1g	4	4	34.3 to 140	40	3/4	0/4
Zinc	Qbt 1v	29	29	23.7 to 160	84.6	7/29	0/29

Table B-12 (continued)

b
na = Not available.

Table B-13 Frequency of Detected Radionuclides Above BV or Detects (for Fallout Radionuclides) in Subsurface Samples at MDA L

a
Values in brackets indicate detection limits for nondetects

b
n/a = Not applicable.

c
TCB = Tertiary Cerros del Rio basalts.

Sample ID	Location ID	Depth (ft)	Geologic Unit	Concentration (pCi/g)
AAB6794	54-01010	8.60-10.00	Qbt 2	0.16
AAB6797	54-01010	18.70-20.00	Qbt 2	0.17
AAB6808	54-01010	18.70-20.00	Qbt 2	0.33
AAB6798	54-01010	28.80-30.00	Qbt 2	11.63
AAB6802	54-01010	37.50-40.00	Qbt 2	0.71
AAB6787	54-01010	48.80-49.50	Qbt 2	0.14
AAB6800	54-01010	58.80-59.50	Qbt 1v	0.34
AAB6790	54-01011	8.80-9.60	Qbt 2	0.03
AAB6785	54-01011	18.50-19.80	Qbt 2	0.08
AAB6796	54-01011	28.80-29.50	Qbt 2	0.70
AAB6789	54-01011	38.80-40.00	Qbt 2	0.33
AAB6788	54-01011	49.40-50.00	Qbt 1v	0.32
AAB6809	54-01013	17.50-18.00	Qbt 2	0.09
AAB6799	54-01013	27.50-28.50	Qbt 2	0.12
AAB6810	54-01013	36.00-37.00	Qbt 2	0.09
AAB6792	54-01013	48.00-50.00	Qbt 1v	0.14
AAB6784	54-01014	28.60-29.40	Qbt 2	0.09
AAB6793	54-01014	41.20-42.10	Qbt 2	0.06
AAB6805	54-01014	41.20-42.10	Qbt 2	0.04
AAB6781	54-01014	49.00-50.00	Qbt 1v	0.05
AAC0721	54-01015	502-503	TCB*	0.13
AAC0777	54-01016	594.1-596.8	TCB	0.001

Table B-14 Summary of Tritium Concentrations in Subsurface Samples at MDA L

*TCB = Tertiary Cerros del Rio basalts.

Analyte	Geologic Unit	Number of Analyses	Number of Detects	Concentration Range^a (mg/kg)	EQL b (mg/kg)	Frequency of Detects
Acetone	Qbt 2	31	$\overline{7}$	[0.01] to 2.1	0.06	7/31
Acetone	Qbo	6	1	[0.022 to 0.043]	0.06	1/6
Acetone	Qbt 1v	21	6	$[0.01]$ to 0.7	0.06	6/21
Aroclor-1260	Qbt 2	34	1	[0.013] to 0.313	0.033	1/34
Bis(2-ethylhexyl)phthalate	Qbt 2	31	1	[0.14] to 0.8	0.59	1/31
Butanone ^[2-]	Qbt 2	31	$\overline{4}$	[0.01] to 4.8	0.027	4/31
Butanone ^[2-]	Qbt 1v	21	5	[0.01] to 0.88	0.027	5/21
DDD[4,4'-]	Qbt 2	34	2	[0.00067] to 0.0114	0.004	2/34
Dichloroethane[1,2-]	Qbt 2	31	3	[0.005] to 0.02	0.006	3/31
Dichloropropane[1,2-]	Qbt 2	31	1	$[0.005]$ to 0.01	0.006	1/31
Methoxychlor[4,4'-]	Sediment	4	2	[0.0171] to 0.063	0.022	2/4
Methoxychlor[4,4'-]	Qbt 1v	29	1	[0.00067] to 0.076	0.027	1/29
Methyl-2-pentanone[4-]	Qbt 1v	21	2	[0.01 to 0.022]	0.027	2/21
Methylene chloride	Qbt 2	31	3	[0.005] to 0.014	0.028	3/31
Pentachlorophenol	Qbt 2	31	$\overline{2}$	$[0.83]$ to 13	1.2	2/31
Tetrachloroethene	Qbt 2	31	1	[0.005] to 0.009	0.007	1/31
Trichloroethane[1,1,1-]	Qbt 2	31	2	[0.005] to 0.015	0.006	2/31
Trichloroethene	Qbt 2	31	3	[0.005] to 0.008	0.006	3/31

Table B-15 Frequency of Detected Organic Chemicals in the Subsurface Samples at MDA L

b
EQL is the maximum EQL reported for the organic chemical.

Second Quarter FY 1997 through First Quarter 2002									
Analyte	Media Type	Number of Analyses	Number of Detects	Concentration ^a (ppbv)	EQL (ppbv)	Frequency of Detects			
Acetone	Pore gas	197	34	$0.5 - [1100000]$	5	34/197			
Acetonitrile	Pore gas	153	3	1.8-[210000]	1	3/153			
Acetophenone	Pore gas	74	1	$[5]$ - $[10000]$	0.2	1/74			
Acrolein	Pore gas	153	0	$[1.2]$ - $[110000]$	0.5	0/153			
Acrylonitrile	Pore gas	153	$\overline{2}$	$[1.2]$ - $[110000]$	0.5	2/153			
Benzene	Pore gas	206	72	$0.13 - [42000]$	0.2	72/206			
Benzonitrile	Pore gas	74	5	$1.2 - [10000]$	0.5	5/74			
Benzyl chloride	Pore gas	170	0	$[0.47]$ - $[42000]$	0.2	0/170			
Bromodichloromethane	Pore gas	196	1	$[0.47]$ - $[42000]$	0.2	1/196			
Bromoform	Pore gas	197	$\overline{7}$	$[0.47]$ - $[42000]$	0.2	7/197			
Bromomethane	Pore gas	206	8	$[0.47]$ - $[42000]$	0.5	8/206			

Table B-16 Frequency of VOCs Detected in Pore Gas at MDA L

Analyte	Media Type	Number of Analyses	Number of Detects	Concentration ^a (ppbv)	EQL (ppbv)	Frequency of Detects
Butadiene[1,3-]	Pore gas	196	$\overline{2}$	$[0.47]$ - $[42000]$	0.2	2/196
Butane[n-]	Pore gas	153	65	$[0.48]$ - $[42000]$	0.2	65/153
Butanol[1-]	Pore gas	197	$\mathsf 3$	$[1.2]$ - $[110000]$	0.5	3/197
Butanone[2-]	Pore gas	197	1	$[1.2]$ - $[110000]$	0.5	1/197
Butene[1-]	Pore gas	74	39	$[1.6] - 2950$	0.2	39/74
Butene[cis-2-]	Pore gas	74	37	$[0.19] - 8550$	0.2	37/74
Butene[trans-2-]	Pore gas	74	28	$[0.15]$ - $[1000]$	0.2	28/74
Carbon disulfide	Pore gas	197	$\,6\,$	$[0.12]$ - $[42000]$	0.2	6/197
Carbon Tetrachloride	Pore gas	206	115	$0.47 - [42000]$	0.2	115/206
Chloro-1,3-butadiene[2-]	Pore gas	73	$\overline{2}$	$[0.5]$ - $[1000]$	0.2	2/73
Chloro-1-propene[3-]	Pore gas	152	$\mathbf 0$	$[0.47]$ - $[42000]$	0.2	0/152
Chlorobenzene	Pore gas	207	49	$0.04 - [42000]$	0.2	49/207
Chlorodibromomethane	Pore gas	196	3	$0.4 - [42000]$	0.2	3/196
Chlorodifluoromethane	Pore gas	189	31	$[0.47]$ - $[42000]$	0.2	31/189
Chloroethane	Pore gas	206	36	$[0.47]$ - $[42000]$	0.5	36/206
Chloroform	Pore gas	206	153	$[0.26] - 46700$	0.2	153/206
Chloromethane	Pore gas	206	16	$[0.82]$ - [110000]	0.5	16/206
Cyclohexane	Pore gas	197	66	$0.44 - [73000]$	0.5	66/197
Cyclohexanone	Pore gas	74	1	$[5]$ - $[10000]$	0.2	1/74
Cyclopentane	Pore gas	74	46	$0.12 - 1340$	0.2	46/74
Cyclopentene	Pore gas	74	13	$0.2 - [1000]$	0.2	13/74
Decane[n-]	Pore gas	78	$\pmb{0}$	$[0.47]$ - $[42000]$	na ^b	0/78
Dibromoethane[1,2-]	Pore gas	169	11	$[0.47]$ - $[42000]$	0.2	11/169
Dibromomethane	Pore gas	79	$\pmb{0}$	$[0.47]$ - $[42000]$	na	0/79
Dichloro-1, 1, 2, 2- tetrafluoroethane[1,2-]	Pore gas	169	3	$[0.47]$ - $[42000]$	0.2	3/169
Dichlorobenzene[1,2-]	Pore gas	207	$\overline{2}$	$0.2 - [42000]$	0.2	2/207
Dichlorobenzene[1,3-]	Pore gas	207	$\pmb{0}$	$[0.47]$ - $[42000]$	0.2	0/207
Dichlorobenzene[1,4-]	Pore gas	207	22	$[0.2]$ - $[42000]$	0.2	22/207
Dichlorodifluoromethane	Pore gas	169	117	$[2.4]$ - $[42000]$	0.2	117/169
Dichloroethane[1,1-]	Pore gas	205	171	0.81-287000	0.2	171/205
Dichloroethane[1,2-]	Pore gas	206	99	0.22-240000	0.2	99/206
Dichloroethene[1,1-]	Pore gas	206	195	3.4-49000	0.2	195/206
Dichloroethene[cis-1,2-]	Pore gas	206	24	$[0.47]$ - $[42000]$	0.2	24/206
Dichloroethene[trans-1,2-]	Pore gas	195	27	$[0.47]$ - $[42000]$	0.2	27/195
Dichloropropane[1,2-]	Pore gas	206	91	$[0.47] - 144000$	0.2	91/206
Dichloropropene[cis-1,3-]	Pore gas	206	$\boldsymbol{2}$	$[0.47]$ - $[42000]$	0.2	2/206
Dichloropropene[trans-1,3-]	Pore gas	205	$\mathbf{1}$	$[0.47]$ - $[42000]$	0.2	1/205

Table B-16 (continued)

Table B-16 (continued)

Table B-16 (continued)

a
Values in square brackets indicate detection limits for nondetects.

b
na = Not available.

a
Listed in order of decreasing concentration.

b
ppmv = Parts per million by volume.

Table B-18 Maximum Pore-Gas Concentrations in the First Quarter of FY 2002 (EPA Method TO-14) at MDA L

Compound ^a	Well Number	Port Depth (f ^t)	Maximum Concentration $(ppmv)^b$
1,1,1-Trichloroethane (TCA)	54-02002	100	390
Trichloroethene (TCE)	54-02002	100	78
Ethanol	54-02002	100	58
Trichloro-1,2,2-trifluoroethane(Freon 113)	54-02002	100	49
Methanol	54-02009	62	35
Methylene chloride	54-02002	100	23
Trichlorofluoromethane (Freon 11)	54-02002	100	18
1,2-Dichloropropane	54-02002	100	16
2-Propanol	54-02002	100	16
Tetrahydrofuran	54-02002	100	13
Chloroform	54-02002	100	9.4
Carbon tetrachloride	54-02030	100	8.9
Tetrachloroethene (PCE)	54-02002	100	7.4
1,1-Dichloroethane	54-02002	100	6.8
Toluene	54-02002	100	5.6
m,p-Xylene	54-02002	100	2.3
Dichlorodifluoromethane	54-02021	100	0.35
Tetrachloroethene (PCE)	54-02023	153	0.26
Benzene	54-01015	385	0.003

a
Listed in order of decreasing concentration.

b ppmv = parts per million by volume.

		Ambient Concentration (ppbv)						
VOC	6/16/94	6/17/94	6/29/94	6/30/94	7/28/94	8/01/94	8/02/94	8/03/94
Chlorodifluoromethane	0.6	0.2	0.3	0.6	ND^*	ND	ND	ND.
Chloromethane	0.3	0.3	ND.	0.6	ND	0.3	ND	ND.
Dichlorodifluoromethane	0.4	0.4	0.4	0.4	0.3	0.4	0.06	0.07
n-hexane	ND	ND.	ND.	ND	0.2	0.3	0.3	0.5
Trichlorofluoromethane	0.2	0.2	0.1	0.1	0.1	0.2	0.05	0.03
Freon 113	0.04	0.05	0.03	0.06	ND.	0.06	ND.	ND.
TCA	0.7	0.4	0.9	0.4	1.0	0.7	0.5	0.4
Benzene	0.2	0.1	0.2	0.2	0.2	0.4	0.4	0.6
Carbon tetrachloride	0.1	0.06	0.06	ND	0.06	0.07	0.05	0.08
Trichloroethene	ND	0.1	0.06	ND	0.3	0.1	0.07	ND.
Toluene	0.2	0.1	0.2	0.2	0.4	1.0	0.8	0.9

Table B-19 Air Concentrations of Selected VOCs at MDA L, Location 4

*ND = Not detected.

	Ambient Concentration (ppbv)								
VOC	6/16/94	6/17/94	6/29/94	6/30/94	7/28/94	8/01/94	8/02/94	8/03/94	
Chloromethane	0.3	0.3	ND^*	0.7	ND	0.7	ND	0.2	
Dichlorodifluoromethane	0.5	0.3	0.3	0.4	0.2	0.4	0.06	0.4	
Trichlorofluoromethane	0.2	0.2	0.2	0.2	0.09	0.3	0.08	0.2	
Methylene chloride	1.6	0.4	1.3	1.2	0.6	1.0	1.7	0.9	
Freon 113	0.2	0.1	0.1	0.3	0.07	0.4	0.2	ND.	
TCA	15.2	6.0	8.6	4.0	0.6	1.0	0.8	2.4	
Benzene	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	
Carbon tetrachloride	ND.	0.1	ND.	0.05	0.05	0.1	ND	0.07	
Trichloroethene	ND.	0.2	0.1	0.03	0.1	ND	0.06	0.1	
Toluene	0.3	0.2	0.3	0.6	0.3	0.2	0.3	0.2	
Xylene	ND	ND.	0.1	0.2	0.2	0.09	0.1	ND.	

Table B-20 Air Concentrations of Selected VOCs at MDA L, Location 5

*ND = Not detected.

Table B-21 Air Concentrations of Selected VOCs at Bandelier National Monument, Location 3 (Background)

*ND = not detected.

Analyte	Medium	COPC?	Rationale	Appendix D Table			
Inorganic chemicals (except cadmium, selenium, and silver)	Sediment	No	Inorganic chemical data were either less than the BVs or not different from background data sets	$D-2.0-1$			
Cadmium	Sediment	Yes	Elevated DLs > BV				
Selenium	Sediment	Yes	Elevated DLs > BV				
Silver	Sediment	Yes	Elevated DLs > BV				
Inorganic chemicals (except for barium, cobalt, copper, chromium, manganese, nickel, uranium, and zinc)	Tuff	No	Inorganic chemical data were either less than the BVs or not different from background data sets	$D-2.0-5$			
Barium	Tuff	Yes	Detected above BV in 11 samples				
Cobalt	Tuff	Yes	Detected above BV in 5 samples				
Copper	Tuff	Yes	Detected above BV in 40 samples				
Chromium	Tuff	Yes	Detected above BV in 19 samples				
Manganese	Tuff	Yes	Detected above BV in 6 samples				
Nickel	Tuff	Yes	Detected above BV in 11 samples				
Uranium	Tuff	Yes	Detected above BV in 12 samples				
Zinc	Tuff	Yes	Detected above BV in 14 samples				
Radionuclides (except tritium and plutonium)	Sediment, ambient air, pore gas, tuff	No	Radiological data were either less than the BVs or not detected	$D-2.02.$ $D-2.0-4,$ $D-2.0-6$			
Tritium	Ambient air, tuff	Yes	Tritium was detected in these media				
	Sediment	No	Not detected above sediment BV				
Plutonium-238	Sediment	Yes	Detected above sediment BV in one sample				
Organic chemicals				$D-2.0-4$			
VOCs	Tuff	Yes	Detected in the media				
	Ambient air	Yes	Detected in the media				
	Pore gas	Yes	Detected in the media				
SVOCs	Air/pore gas			$D-2.0-7$			
	Tuff	No	Detected but extent defined				
Pesticides							
Methoxychlor	Tuff	No	Detected but extent defined				
	Sediment	Yes	Detected in 3 sediment samples				
DDD	Tuff	No	Detected but extent defined				
PCBs				$D-2.0-3$			
Aroclor-1260	Tuff	No	Detected but extent defined				

Table B-22 Summary of Data Review Results

Appendix C

Quality Assurance/Quality Control Process

APPENDIX C QUALITY ASSURANCE/QUALITY CONTROL PROCESS

The data evaluation and qualification for the samples taken at Material Disposal Area (MDA) L are discussed below. Only samples qualified for various reasons are mentioned for inorganics, organics and radionuclides.

For inorganics, 68 samples were qualified. Forty-five samples were qualified as estimated (J/UJ) for the following reasons. All of the samples are usable for data assessment. In ten samples, the recoveries in the matrix spike were low. In 24 samples, recoveries for the internal analytical laboratory control samples (LCS) were low. In 6 samples the recoveries for silver were high in the LCS sample and for 5 samples the recoveries for copper in the matrix spike were high.

Twenty-three samples were qualified as rejected (R) and are not usable in risk assessment for the following reasons. Nine samples analyzed for selenium were rejected because the quality control (QC) sample results were high (>200%). Five samples for arsenic and selenium were rejected because the recoveries in the QC samples were low (<10%). The other 9 samples were rejected because the holding time had been exceeded.

The following discussion on VOCs and SVOCs applies to both analytical data and screening data. Data on VOCs and SVOCs from boreholes (locations) 54-01001 through 54-01006 and 54-01009 are screening level data from an on-site mobile chemical laboratory.

For organics, 59 samples for volatile organics (VOCs) were qualified and all qualified data are usable in data assessment. Forty samples were qualified as not detected (U) because the results were less than 5/10 times the analytes found in the method blank. Six samples were qualified as estimated (J/UJ) because the surrogate recoveries associated with these analytes were low. Eleven samples were qualified as estimated (J) for acetone and 2-butanone because the results were less than the practical quantitation limit (PQL) but greater than the method detection limit (MDL). Two were qualified as estimated (J) because the holding time had been exceeded.

Eleven semivolatile organic (SVOCs) samples were qualified, and eight samples can be used for data assessment. Six samples were qualified as estimated (J/UJ) because of the holding time had been exceeded. Two were qualified as estimated (J) because the results were less than the PQL but greater than the MDL. Three samples were rejected (R) and are not usable for data assessment because the surrogate recoveries associated with the analytes were low (10%).

For pesticides/polychlorinated biphenyls (pest/PCBs), two samples were qualified as estimated (J/UJ) because the holding time had been exceeded. These data can be used in data assessment.

For herbicides, four samples were qualified as rejected (R) because the recoveries for the analyte, Dicamba, in the QC samples were low (<10%). These data cannot be used in data assessment.

Appendix D

Phase I RFI Data (CD on inside back cover of this report)

Appendix E

Statistical Results for Chemical Analytical Data

APPENDIX E STATISTICAL RESULTS FOR CHEMICAL ANALYTICAL DATA

E-1.0 INTRODUCTION

This appendix provides detailed statistical evaluations to support Section B-4.0 (data review) and Section B-5.0 (nature and extent) To support the data review and nature and extent, the statistical analyses include summary statistics, exploratory data analyses, spatial plots, and background comparisons.

The plots and evaluation results for Material Disposal Area (MDA) L at Technical Area 54 of Los Alamos National Laboratory (the Laboratory or LANL) are presented in Section E-3.0. This section is organized by categories of sampling media and analytical suites. Separate sections are presented for each medium (channel sediments and subsurface tuff). The analytical data consist of inorganic chemicals (metals and cyanide), radionuclides, and organic chemicals (volatile organic compounds [VOCs], semivolatile organic compounds [SVOCs], polychlorinated biphenyls [PCBs], pesticides, and herbicides).

E-2.0 OVERVIEW OF STATISTICAL ANALYSES

A variety of statistical methods may be applied to each of the data sets. The use of any of these methods depends on how appropriate it is for the available data.

E-2.1 Summary Statistics

The summary statistics are calculated and presented as tables in Appendix B of this report. For values reported as detected, summary statistics include both the minimum and maximum reported concentrations, median, and arithmetic average concentrations. These values provide some indication of the central tendency and skew of the concentration distribution. For data sets containing values reported as undetected, the summary table includes the minimum and maximum reported detection limits (DLs) or estimated quantitation limits (EQLs).

E-2.2 Exploratory Data Analyses

The graphical analyses include box plots and borehole profiles. These analyses provide a visual representation of the data and aid in determining the presence of outliers or other anomalous data that might affect statistical results and interpretations. Specifically, the plots allow a visual comparison among distributions of concentrations for different analytes. The differences of interest may include an overall shift in concentration (shift of central location) or, when the centers are nearly equal, a difference between the upper tails of the two distributions (elevated concentrations in a small fraction of one distribution). The plots may be used in conjunction with the statistical tests (distributional comparisons) to evaluate the statistical results. Unless otherwise noted, the nondetects are included in plots at their reported DL or EQL.

Box plots. A box plot consists of a box, a line across the box, whiskers (lines extended beyond the box and terminated with a short perpendicular line), and points outside the whiskers. The box area of the plot is the region between the 25th percentile and the 75th percentile of the data, the interquartile range or middle half of the data. The horizontal line within the box represents the median (50th percentile) of the data. The whiskers give an interval of 1.5 times the interquartile range, outside of which the data may be evaluated for their potential to be outliers. When box plots are presented from more than two groups, the box representing the baseline or background set is the leftmost box; unless otherwise noted, the remaining boxes are arranged in ascending order by group medians. Often, the concentrations are plotted as points overlaying the box plot. When a data set contains both detected concentrations and

nondetected results, reported as DLs, the detected concentrations are plotted as x's and the nondetected results are reported as o's.

Borehole profile plots. Borehole profile plots depict the concentration results by depth in boreholes. They are used to evaluate evidence of release from the disposal structure associated with a given borehole and to determine if the extent of contamination has been bounded (decreasing trend).

E-2.3 Comparisons Between Distributions

Comparisons between data sets that might represent different concentration distributions, such as site data and Laboratory background data, are performed using a variety of statistical methods. For background comparisons, these methods begin with a simple screening comparison of site-specific data with an upper tolerance limit (UTL) estimated from the background data (UTL [95, 95] or the 95% upper confidence bound on the 95th quantile). UTLs are used to represent the upper end of concentration distribution and are also referred to as background values (BVs). When appropriate, BV comparisons are followed by statistical tests that evaluate potential differences between the distributions. These tests are used for testing hypotheses about data from two potentially different distributions. One specific example would be the test of the hypothesis that site concentrations are elevated above background levels.

E-3.0 MDA L ANALYTICAL DATA

E-3.1 Surface Soil and Sediments

Runoff from MDA L is concentrated into a single drainage to the north. The drainage includes multiple braided channels traversing a 50- to 65-ft-wide area of a colluvial slope on the floor of a tributary of Cañada del Buey. These channels begin in one area along the MDA L fence and diverge below the cliffs on the north side of Mesita del Buey. Eight locations were selected for sediment sampling; these locations included areas with coarse sediment deposition upslope and areas with finer sediment deposition on the lower slopes (LANL 1996, 54462, Figure 1-11). The samples were field screened for gross alpha, beta, and gamma radiation to bias sample selection. A total of four samples (the sample with the highest gross alpha and gross beta, the sample with the highest gross gamma, and two other samples) were submitted for analysis of target analyte list (TAL) metals, PCBs, pesticides, and radionuclides. All results from the sediments are used without qualification except for tritium, which was qualified J (estimated) because of results from the blind quality control (QC) sample were outside acceptance limits.

E-3.1.1 Inorganic Chemicals in Sediment

The concentrations of inorganic chemicals for the four channel sediment samples were compared to Laboratory-wide sediment BVs (LANL 1998, 59730). No inorganic chemical was detected above its sediment BV. Three inorganic chemicals (cadmium, selenium, and silver) were not detected but have DLs larger than their respective sediment BVs. The inorganic chemical results are summarized in Table B-10 in Appendix B.

Box plots comparing the distribution of inorganic chemical concentrations in MDA L channel sediment samples to the concentrations from Laboratory background sediment samples support the conclusion that inorganic chemicals do not differ from background (Figure E-1). The inorganic chemicals with elevated DLs (cadmium, selenium, and silver) are identified in Appendix B as COPCs in sediment.

E-3.1.2 Radionuclides in Sediment

The channel sediment samples were analyzed for radionuclides. The detected concentrations for americium-241, cesium-137, tritium, plutonium-238, plutionium-239, radium-226, and strontium-90 were compared to sediment fallout values (FVs); the isotopes in the uranium and thorium decay chains were compared to BVs for these naturally occurring radiochemicals (LANL 1998, 59730). A summary of the radionuclide activities is presented in Table B-11 in Appendix B, including a separate summary for detected results and DLs for nondetects, the frequency of detection, and the frequency at which detected radionuclides exceed BVs or FVs.

Plutonium-238 was the only detected radionuclide (0.011 pCi/g) above the sediment BV of 0.006 pCi/g. The background comparison tests concluded that the plutonium-238 concentration is above sediment background.

E-3.1.3 Organic Chemicals in Sediment

Channel sediment samples were analyzed for pesticides and PCBs. One pesticide (methoxychlor) was detected in two of the four samples at concentrations of 0.028 mg/kg (location 5405143) and 0.063 mg/kg (location 54-05145). The concentrations were about two to three times above the sample EQL of 0.017 mg/kg.

E-3.2 Subsurface Tuff

One hundred and eighty-four samples of subsurface core were collected from 16 (RFI boreholes at MDA L. The locations of the boreholes relative to the disposal structures are shown in Figure B-6, Appendix B. The core samples were analyzed for TAL metals, cyanide, pesticides/PCBs, herbicides, VOCs, SVOCs, and radionuclides. However, not all samples were analyzed for every suite. Six of the boreholes were drilled to investigate the vapor plume east of MDA L; the core samples from these boreholes were analyzed only for VOCs. Two deep characterization boreholes were drilled at an angle from pads on Mesita del Buey to investigate the possibility of vapor-phase contaminants at depth below MDA L; the core samples from these boreholes were analyzed only for VOCs and tritium.

The eight boreholes drilled in the vicinity of the disposal units (i.e., disposal pit, impoundments, and shafts) were analyzed for all, or a majority of, the suites depending on the location of the borehole. The subsurface tuff investigation was intended to support the characterization of releases from a local source term (waste structures) either through a relatively uniform, homogeneous substratum (general dispersal in a volume through a subsurface medium) or through a heterogeneous fractured substratum. Evidence of a release through a uniform medium would include the consistent presence of concentrations greater than BVs (i.e., at two or more consecutive sampling depths). Evidence of migration through a fractured medium might include intermittent detects of several analytes within a borehole, or across boreholes, as fractures were occasionally intersected.

E-3.2.1 Inorganic Chemicals in Tuff

Subsurface core data for inorganic chemicals were obtained from the eight boreholes in closest proximity to the disposal units. Some of these data were rejected. Five out of the 67 mercury and cyanide analyses were rejected because holding times were substantially exceeded, while 4 out of 67 arsenic and selenium results were rejected because of low analyte recovery from a QC sample in the batch. The analytical results for the inorganic chemicals were compared to the BVs from the appropriate tuff strata of Laboratory-wide background data (LANL 1998, 59730). Inorganic chemicals with detected concentrations

greater than the BVs were barium, copper, chromium, manganese, mercury, nickel, uranium, and zinc. Some inorganic chemicals had concentrations that were just greater than BVs, and a few inorganic chemicals were reported as nondetects with DLs larger than BVs. A summary of the results for the inorganic chemicals, separated by the tuff strata, is given in Table B-12 in Appendix B.

Sample concentrations were compared with BVs and evaluated by borehole. Barium, chromium, cobalt, copper, nickel, uranium, and zinc were detected at concentrations above their BVs in one or more borehole(s) at consecutive sampling depths or were detected above BVs in two out of three consecutive sampling depths. These data indicate a subsurface release from a disposal unit. Other inorganic chemicals that were detected at a single location or at random (i.e., in samples taken from two or three different boreholes at different sampling depths) with concentrations above BVs are less likely to indicate a release. This section discusses the releases of certain inorganic chemicals in some boreholes by disposal unit and by borehole.

All concentrations above their BV are discussed and shown in [Figures E-2 through E-7]. The figures show the borehole profile or pattern of concentrations by depth below ground surface (bgs) for the sampled cores within the individual boreholes. Detected concentrations (filled circles) and DLs for nondetects (open circles) are plotted at the midpoint of the sample depth interval (ft bgs). The unitspecific BVs are displayed in the figures as dotted lines.

Impoundments B, C, and D: Boreholes 54-01012, 54-01013, and 54-01014 were drilled at an angle beneath Impoundments B, C, and D, respectively. Analytical results were used to look for evidence of a release from these disposal units. The borehole locations relative to the impoundments are shown in Figure B-6 in Appendix B. Borehole profile plots show the angle of the boreholes and subsurface locations of the sampled cores relative to the disposal unit specified.

Impoundments B and C were used to dispose of liquid electroplating wastes. The analytical results for boreholes 54-01012 and 54-01013 are consistent with their operational records; inorganic chemicals detected above background in core samples include chromium, copper, and nickel. Concentrations of chromium and copper above their respective BVs were detected at three consecutive sampling depths in core samples from 54-01012 beneath Impoundment B (Figure E-2). Copper and nickel were similarly detected in 54-01013 beneath Impoundment C (Figure E-3, top row). In 54-01013, the detected concentrations for copper are above the BV at three consecutive sampling depths, while nickel concentrations exceeded the BV at two out of three consecutive sampling depths in borehole 54-01013. These results indicate that copper and chromium have been released from Impoundment B, and copper and nickel have been released from Impoundment C.

In borehole 54-01012 (Impoundment B) the patterns for other inorganic chemicals above their BVs were less indicative of a release. There were single detected concentrations of beryllium, cadmium, cyanide, mercury, and uranium, scattered among the different depth intervals (Figure E-2).

In borehole 54-01013 (Impoundment C), cadmium and chromium were detected above their BVs in a single sample at the deepest sampling interval. For both inorganic chemicals, the concentrations at this depth are similar to the concentrations (and reported DLs) of the samples at depths directly above it (i.e., sample concentrations do not represent an increase). The sampled core interval falls immediately below the Tshirege unit 2/unit 1v interface, but the BVs for these two units differ. In both cases, the sample concentrations at the interface fall between the BVs for the different units. The BV for cadmium in Qbt 1v is a nominal DL because there were no Laboratory background data for cadmium from that tuff unit. In contrast, cadmium was analyzed in background samples from Qbt 2 tuff, and had a BV of 1.63 mg/kg. The results for cadmium and chromium do not indicate a release from Impoundment C.

Borehole 54-01014 was drilled between Impoundments C and D at an angle to pass beneath Impoundment D. Uranium was the only inorganic chemical detected above its BV at several consecutive sampling depths (Figure E-3, bottom row). The concentrations of uranium are slightly above the Qbt 2 BV. The pattern may indicate natural variability, or it may indicate that a release of uranium at low concentrations to the surrounding subsurface tuff occurred from Impoundment D. There were also single detects of nickel and copper above their BVs at different sampling depths. Nickel was reported in the shallowest sampling depth between Impoundments C and D. The copper concentration above the BV was not replicated in the field duplicate sample (a second core taken from the same depth interval). The copper and nickel data do not indicate releases from Impoundment D.

Pit A: Boreholes 54-01009, 54-01010, and 54-01011 were drilled to characterize subsurface media near Pit A. Boreholes 54-01010 (at –45 degrees) and 54-01011 (at –55 degrees) were drilled at an angle to pass beneath the eastern and western portions of Pit A, respectively. Borehole 54-01009 was drilled vertically on the south side of Pit A near the west end. As shown in Figure B-6 of Appendix B, borehole 54-01009 is about 20 ft south of Pit A and is nearly equidistant between the pit and Shafts 1 through 28. If a release had occurred from Pit A, the placement of borehole 54-01009 could be used to bound the lateral extent of the release. Instead, the results from 54-01009 are different from those beneath Pit A but similar to results from borehole 54-01007 at the other end of Shafts 1 through 28. The similarity of borehole results from 54-01007 and 54-01009 might be expected based on the knowledge that Shafts 1 through 22 received uncontained liquid waste with no absorbents added. The results for borehole 54-01009 are discussed in the section on Shafts 1 through 28 below.

Analytical results from the boreholes angled beneath Pit A do not provide evidence of a release. Borehole 54-01011 had only one inorganic chemical (barium) detected in one sample at approximately twice the BV of 26.5 mg/kg for Qbt 1v (Figure E-4, bottom row). The detected concentrations of barium at all other sampling depths in this borehole were below BV. The analytical results for borehole 54-01010 indicate the presence of inorganic chemicals at concentrations above BVs at random depths (Figure E-4, top row). Three of the borehole 54-01010 sample concentrations (cadmium, uranium, and chromium) come from core samples collected just above or just below the unit 2/unit 1v interface, and the reported concentrations were between the BVs for the two strata. The chromium concentration in the sample collected from unit 2 was above the unit 2 BV but within the range of concentrations reported for the Laboratory background data (0.25 to 13.0 mg/kg [LANL 1998, 59730]).

Shafts 1 through 28: Both boreholes 54-01007 and 54-01009 are more than twice as deep as disposal Shafts 1 through 28. Both boreholes are vertical and are 25 to 30 ft from the nearest disposal shaft. The pattern of inorganic chemical concentrations in these boreholes provides evidence of a release. The most likely source of the release is the shafts. The primary component of the release is copper, with smaller contributions from chromium, barium, and zinc. Nickel was also detected above its BV in the lower tuff strata (Units 1v and 1g).

The distributions of copper, barium, and zinc in samples collected from borehole 54-01009 (Figure E-5) are similar to those noted for borehole 54-01007 (Figure E-6). The copper concentrations are much larger than the BVs in approximately half of the samples, while barium and zinc were reported at concentrations above the BVs in a few samples. Single samples had concentrations of beryllium, chromium, and manganese that were slightly above their BVs. The beryllium and manganese reported in a core sample were collected just below the unit 1v/unit 1g interface at concentrations between the BVs for the two tuff strata. Nickel was detected above its BV of 2 mg/kg, a nominal DL, in one of ten samples in borehole 54-01007 and in seven of nine samples in borehole 54-01009 in unit 1v or unit 1g samples, but all the results were below the unit 2 BV (6.58 mg/kg).

Borehole 54-01007 was drilled about 30 ft south of the southeastern corner of Shafts 1 through 28. Analysis of core samples detected copper, chromium, barium, and zinc at concentrations above their BVs (Figure E-6). Copper concentrations were greater than the BV in 10 of 13 samples, often by more than a factor of 10. Chromium concentrations were greater than its BV in 5 of 13 samples but did not exceed background by more than a factor of 2. Copper and chromium remained elevated at the deepest sampling depth (146 ft bgs). Barium and zinc concentrations were more than twice their BVs in a single sample and at concentrations slightly above their BVs in two and in four sampling depths (some consecutive depths), respectively. The concentrations of barium and zinc decreased to less than their BVs at the deeper sampling intervals.

Aluminum, lead, and manganese were detected in samples from borehole 54-01007 at concentrations that exceeded their BVs in a single sample or in two core samples at nonconsecutive sampling depths

Shafts 29 through 34. Borehole 54-01008 is a vertical 150-ft borehole located about 20 ft to the southeast of Shafts 29 through 34. The borehole was drilled to characterize the subsurface media in the vicinity of these shafts. The inorganic chemicals reported at concentrations above background include copper, zinc, and chromium (Figure E-7). Copper concentrations exceeded its BVs in the majority of the samples (10 out of 12); several concentrations were more than 10 times the BV for copper. Zinc and chromium were detected at three or more consecutive sampling depths at concentrations exceeding their BVs by a factor of two or less. Manganese and cobalt concentrations were also above their BVs at two consecutive sampling depths. Manganese was marginally above its BV; one of the five cobalt concentrations with values above its BV was more than double its BV. Other inorganic chemicals with single detected concentrations above the BVs include barium, beryllium, iron, and lead.

E-3.2.2 Radionuclides in Tuff

Tuff core samples from seven boreholes were analyzed for tritium. The seven boreholes included the five shallow (vertical depths to 60 ft) holes angled beneath the Pit A and Impoundments B, C, and D (boreholes 54-01010 through 54-01014) and two additional deep boreholes (54-01015 and 54-01016) drilled at an angle from Cañada del Buey to the north. Borehole 54-01015 passes beneath Pit A at a depth of about 470 ft and terminates beneath the array of Shafts 1 through 28 at a vertical depth of about 600 ft. Borehole 54-01016 terminates beneath Shafts 29 through 34 at a vertical depth of about 550 ft. Analytical results for 1 of 46 tritium samples were rejected because of a laboratory error. With the exception of the one rejected sample, the tritium results from the MDA L boreholes are useable.

The tritium results for the shallow boreholes (54-01010 through 54-01014) ranged between 0.1 pCi/mL and 196 pCi/mL. The samples with the highest concentrations (13.1 pCi/mL and 196 pCi/mL) were collected at depths between 20 and 25 ft below Pit A. The concentrations at deeper depths (35 to 45 ft) below Pit A decreased to approximately 5 pCi/ml. The tritium results in the deep boreholes (54-01015 and 54-01016) were variable primarily because of low (<2%) moisture content in the samples collected. Low moisture tends to increase analytical counting error and accuracy of the dilution factor that multiplies the final result. With the exception of a single detect of 1.5 pCi/mL, all the samples with moisture contents greater than about 2% for the deep boreholes were reported at low DLs (less than 0.5 pCi/mLl).

Figure E-8 shows the tritium results by borehole. The largest concentration (196 pCi/mL from borehole 54-01010) is omitted from the plot so as to better depict the differences in results at lower concentrations; the omitted concentration is more than 10 times greater than the largest concentration shown in the figure. The tritium results from samples with low moisture content are plotted as triangles, and the results from greater moisture content are plotted as circles. Low moisture content was reported only in samples from the deep boreholes. The results based on sample moisture content of greater than 2% (circles) are

clustered at the low end of the concentration range. The results based on samples with lower moisture content (triangles) are scattered across the full range of concentrations and include most of the largest results reported for the deep boreholes.

A tritium plume beneath MDA L is evident from the sampling results. The concentrations of tritium are highest (13 to 196 pCi/mL) at a depth between 20 and 25 ft beneath Pit A and are not detected or detected at concentrations of less than about 5 pCi/mL in all boreholes and all other sampling depths. The results from the deep boreholes provide some evidence that tritium contamination is restricted to the vicinity of MDA L.

Five core samples from borehole 54-01009 were analyzed for five radionuclides (plutonium-238, -239 and uranium-234, -235, and -238). The naturally occurring uranium isotopes were compared to Laboratorywide BVs from the appropriate tuff strata. Plutonium-238 and -239 were evaluated on the basis of detection status. Uranium-235 was detected in a single sample at a concentration that is essentially equal to its BV. The plutonium isotopes were detected at trace concentrations (below the minimum DL). The results are not indicative of a release from MDA L. A summary of the radionuclide concentrations is presented in Table B-13 in Appendix B.

E-3.2.3 Organic Chemicals in Tuff

Borehole core samples were analyzed for SVOCs, pesticides, PCBs, herbicides, and VOCs. Core from all 16 boreholes was analyzed for VOCs. The eight boreholes drilled in the vicinity of the disposal units (54-01007 through 54-01014) were analyzed for SVOCs, pesticides, and PCBs, in addition to the VOCs at an off-site contract laboratory. The exception is samples from borehole 54-01009. These samples were submitted to an on-site mobile chemical laboratory for VOC and SVOC analysis. The three boreholes closest to the disposal shafts (54-01007 through 54-01009) were also analyzed for herbicides.

No herbicides were detected in any samples. Detected organic chemicals included 4 SVOCs, 1 PCB, 2 pesticides, and 15 VOCs; most concentrations were less than or equal to three times their EQLs. The only notable exception was Aroclor-1260, which was detected at a concentration more than 10 times its EQL. The most frequently detected VOCs were acetone and 2-butanone, which are common laboratory contaminants. A summary of the detected organic chemicals is presented in Table B-15 in Appendix B.

Twenty-two organic chemicals were detected, most at negligible concentrations (i.e., less than or slightly above their EQLs). The larger concentrations (i.e., concentrations above their EQLs) were detected in borehole samples beneath Pit A (54-01010 and 54-01011), between Pit A and the array of Shafts 1 through 28 (54-01009), and at the east end of the array of Shafts 1 through 28 (54-01007).

Two pesticides, Aroclor-1260, and three SVOCs were detected at a few sampling depths. Only Aroclor-1260 was reported in borehole 54-1010 at a concentration (0.313 mg/kg) that was much greater than its sample EQL (0.0044 mg/kg). Methoxychlor was detected at different sampling depths in borehole 54-01010, and dichlorodiphenyldichloroethane (DDD) was detected in a single sample at a concentration (0.00588 mg/kg), marginally above the EQL (0.0044 mg/kg) in borehole 54-01011. Bis(2-ethylhexyl)phthalate was detected at a concentration (0.8 mg/kg), which was 25% greater than its EQL (0.6 mg/kg) at one sampling depth beneath Pit A. Pentachlorophenol was detected at concentrations that were more than three times the EQL at two sampling depths below Impoundment B (in borehole 54-01012).

Detected VOCs were more widespread but generally occurred at low concentrations (less than or near the EQLs). Six VOCs (bromobenzene, dibromomethane, 1,2-dichloropropane, 4-isopropyltoluene, tetrachloroethene) were reported as detected in a single sample (borehole 54-01003 on the mesa top outside the perimeter of MDA L) at concentrations less than or equal to their reported EQLs. One VOC

(1,3-dichloropropane) was detected below the EQL in two boreholes (54-01003, 54-01005) on the mesa to the east of MDA L. Acetone was detected at low concentrations in the majority of the boreholes (12 of 16) but was detected at concentrations more than 10 times its EQL (0.06 mg/kg) in four samples from 54-01007 (at the east end of Shafts 1 through 28). The VOCs below Pit A included trichloroethane (0.008 and 0.015 mg/kg) and trichloroethene (three samples at 0.008 mg/kg), methylene chloride at approximately twice its EQL (0.010 to 0.014 mg/kg) in two samples, and 1,2-dichloroethane at concentrations more than three times its EQL (0.018 and 0.020 mg/kg) in two samples. Between Pit A and Shafts 1 through 28 (borehole 54-01009), 1,2-dichloroethane was detected in a single sample at a concentration slightly above its EQL (0.0093 mg/kg) and 1,3-dichlorobenzene was detected once (at 0.011 above its EQL (0.005 mg/kg), and 4-methyl-2-pentanone was detected in two samples at concentrations that were up to three times its EQL (0.034 and 0.078 mg/kg) in two samples.

In summary, organic chemicals were reported in the subsurface media near Pit A and the array of Shafts 1 through 28. The organic chemicals detected at concentrations lower than the EQLs are less reliably quantified because VOCs may be lost in tuff media samples during sample and analysis.

REFERENCES

The following list includes all references cited in this appendix. Parenthetical information following each reference provides the author, publication date, and the RRES record identification (ER ID) number. This information also is included in the citations in the text. ER ID numbers are assigned by the Laboratory's RRES-RS Program (formerly the ER Project) to track records.

LANL (Los Alamos National Laboratory), February 1996. "RFI Report for Channel Sediment Pathways from MDAs G, H, J, and L, TA-54, (Located in Former Operable Unit 1148), Field Unit 5," Los Alamos National Laboratory document LA-UR-96-110, Los Alamos, New Mexico. (LANL 1996, 54462)

LANL (Los Alamos National Laboratory), September 1998. "Inorganic and Radionuclide Background Data for Soils, Canyon Sediments, and Bandelier Tuff at Los Alamos National Laboratory" Los Alamos National Laboratory document LA-UR-98-4847 (draft), Los Alamos, New Mexico. (LANL 1998, 59730)

FE-1 / MDA L IWP / 082503 / PTM

Figure E-1. Box plots of inorganic chemical concentrations from channel sediments at MDA L and from Laboratory background sediments

FE-1 (cont.) / MDA L IWP / 082503 / PTM

FE-2 / MDA L IWP / 082503 / PTM

Figure E-2. Inorganic chemical concentration profiles from borehole 54-01012 at MDA L

Figure E-4. Inorganic chemical concentration profiles from boreholes 54-01010 and 54-01011 at MDA L

FE-5 / MDA L IWP / 082503 / PTM

Figure E-5. Inorganic chemical concentration profiles from borehole 54-01009 at MDA L

FE-6 / MDA L IWP / 082503 / PTM

Figure E-6. Inorganic chemical concentration profiles from borehole 54-01007 at MDA L

Figure E-7. Inorganic chemical concentration profiles from borehole 54-01008 at MDA L

FE-8 / MDA L IWP / 082503 / PTM

Figure E-8. Box plots of tritium concentrations by borehole at MDA L. The concentration of 196 pCi/ml at 54-01010 is not shown. Triangles are used for samples with low (less than 2%) moisture content; circles are used when moisture content is greater than 2%. Solid symbols (filled triangles or circles) are used for detects; open symbols (outline of triangles or circles) are used for nondetects.

Appendix F

Regulatory History and Documents

APPENDIX F REGULATORY HISTORY AND DOCUMENTS

This appendix describes the regulatory history and status of solid waste management units (SWMUs) and areas of concern (AOCs) at Technical Area (TA-)54, Area L, one of which is addressed in this investigation work plan. This information is presented because TA-54, Area L, is comprised of a number of active and inactive waste management units, some of which are subject to corrective action while others are subject to other regulatory programs.

The operable unit (OU) 1148 Resource Conservation and Recovery Act (RCRA) facility investigation (RFI) work plan included five AOCs in TA-51 and 46 SWMUs and AOCs in TA-54 (LANL 1992, 7669). Most SWMUs and AOCs in TA-54 are associated with waste management Areas G, H, J, and L. Table F-1 identifies the SWMUS and AOCs associated with Area L, provides brief descriptions of the sites, and identifies the appropriate regulatory program for managing and closing the sites.

The 13 SWMUs and AOCS listed in Table F-1 can be placed into the following categories:

- sites for which no further action (NFA) was recommended and approved [SWMU 54-001(c), AOC 54-008, AOC 54-015(g), and AOC 54-015(i)];
- active sites that will be investigated and, if necessary, cleaned up by the Risk Reduction and Environmental Stewardship Division–Remediation Services (RRES-RS) in accordance with the corrective action requirements of the Hazardous and Solid Waste Amendments (HSWA) Module (Module VIII) of the Los Alamos National Laboratory (LANL or the Laboratory) Hazardous Waste Facility Permit [SWMU 54-006 and SWMU 54-012(b)];
- sites that will undergo RCRA closure under the Laboratory's Hazardous Waste Facility Permit [SWMU 54-001(a), SWMU 54-001(b), AOC 54-001(e), AOC 54-002, AOC 54-009, and AOC 54-014(a)]; and
- an active site that manages polychlorinated biphenyls (PCBs) will be closed in accordance with requirements of the Toxic Substances Control Act [(TSCA) AOC 54-001(d)].

SWMU 54-006 (in the second category) consists of inactive subsurface waste management units that are collectively referred to as material disposal area (MDA) L and are the subject of the investigation described in this investigation work plan. The other SWMU in the second category and the SWMUs and AOCs in the other three categories are not within the scope of this investigation work plan, and the disposition of these sites is presented in Table F-1.

The process for investigating MDA L was initially described in the OU 1148 RFI work plan (LANL 1992, 7669) and has been subsequently modified by other documents. The chronology of documents is presented below.

- 1. April 23, 1993. The US Environmental Protection Agency (EPA) issued a notice of deficiency (NOD) for the RFI work plan for OU 1148 (Reiter 1993, 6743).
- 2. July 27, 1993. The Laboratory submitted revised Appendix A to OU 1148 RFI work plan to the US Department of Energy-Los Alamos Area Office (DOE-LAAO) for transmittal to EPA (Tiedman 1993, 22430). This appendix consisted of a revised pilot extraction study plan for treatment of the volatile organic compound (VOC) plume beneath MDA L.
- 3. August 25, 1993. EPA approved the revised Appendix A to the OU 1148 RFI work plan (Honker 1993, 30522).
- 4. October 19, 1993. The the Laboratory held a conference call with the EPA Region 6 office to discuss proposed modifications to the OU 1148 RFI work plan. The Laboratory and EPA personnel discussed changes to the Laboratory-proposed drilling plan at MDA L and received verbal approval from EPA to drill boreholes 54-1007, 54-1008, and 54-1009 to 150 ft rather than to the 300-ft and 500-ft depths proposed in the RFI work plan. These changes and the approval were later referenced in a June 1994 proposal for work plan modifications (Item 10).
- 5. November 1, 1993. DOE-LAAO submitted proposed modifications to the approved pilot extraction study plan to EPA (Taylor 1993, 30249). These modifications addressed changes to drilling near MDA L.
- 6. November 15, 1993. The New Mexico Environment Department (NMED) submitted technical comment memorandum for the OU 1148 RFI work plan (Swanton 1993, 63981).
- 7. November 23, 1993. DOE-LAAO submitted responses to the NOD for the OU 1148 RFI work plan to EPA (Vozella 1993, 30327).
- 8. December 14, 1993. EPA approved the OU 1148 RFI work plan, as modified by the November 23, 1993, NOD response (Davis 1993, 38812). The approval concurred with the no further action (NFA) recommendations for potential release sites $(PRSS)$ 54-001 (c) , 54-008, 54-015 (g) , and 54-015(i), but indicated that a Class III permit modification would be necessary to remove SWMU 54-001(c) from the HSWA Module.
- 9. April 21, 1994. The Laboratory documented minutes of conference call discussions with EPA Region 6 on April 8, 1994, concerning proposed modifications to the OU 1148 RFI work plan (Glatzmaier 1994, 35207). These discussions related to channel sediment sampling at TA-54 MDAs, deep borehole drilling beneath MDA L, and passive air sampling using the EMFLUX® system. EPA concurred with proposed modifications except those addressing passive air sampling.
- 10. June 8, 1994. The Laboratory submitted proposed modifications to the OU 1148 RFI work plan to DOE-LAAO for transmittal to EPA. These modifications addressed channel sediment sampling, deep borehole sampling, passive air sampling, and existing vapor well sampling at MDA L. These modifications had been previously discussed with EPA, but the modification request was never formally transmitted to EPA by DOE-LAAO.
- 11. July 18, 1994. EPA approved use of EMFLUX® passive air-sampling method for estimating extent and semiqualitative nature of vapor-phase plumes. This approval was based on a draft report of passive soil gas sampling performed at OU 1148, dated May 3, 1994, that was submitted to EPA for review.
- 12. March 28, 1995. The Laboratory submitted a permit modification request to NMED for PRSs requested for NFA (LANL 1995, 45365). Request included SWMU 54-001(c), which was listed in the HSWA Module, and AOCs 54-008, 54-015(g), and 54-015(i), which were not listed in the HSWA module.
- 13. October 11, 1995. DOE-LAAO concurred with the NFA determination for non-HSWA units contained in the March 1995 permit modification request (Taylor 1995, 50023). This concurrence included AOCs 54-008, 54-015(g), and 54-015(i).
- 14. December 10, 1996. NMED submitted a notice of determination on permit modification requests for units proposed for NFA (Dinwiddie 1996, 55815). This notice concurred that SWMU 54-001(c) was suitable for a Class III permit modification.
- 15. February 27, 1996. The Laboratory submitted the "RFI Report for Channels Sediment Pathways from MDAs G, H, J, and L, TA-54" to the EPA (Jansen and Taylor 1996, 54462).
- 16. September 23, 1997. NMED approved the RFI report for channels sediment pathways from MDAs G, H, J, and L, TA-54 (Dinwiddie 1997, 63982).
- 17. December 23, 1998. NMED approved a Class III permit modification for removal of 99 SWMUs from HSWA Module (Kelley 1998, 63042). The permit modification included removal of SWMU 54-001(c).

REFERENCES

The following list includes all references cited in this appendix. Parenthetical information following each reference provides the author, publication date, and a record identification (ER ID) number, when available. These numbers can be used to locate copies of actual documents at the RRES-RS Records Processing Facility.

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Dinwiddie, R. S., September 23, 1997. "Approval of RCRA Investigation Report for Channel Sediment Pathways from Material Disposal Areas (MDAs) G, H, J, and L at Technical Area 54 (TA-54), Los Alamos National Laboratory NM0890010515," Los Alamos National Laboratory letter to S. Hecker and T. Todd, DOE-LAAO, from R. S. Dinwiddie, NMED-HRMB, Los Alamos, New Mexico. (Dinwiddie 1997, 63982)

Dinwiddie, R. S., December 10, 1996. "Notice of Determination Requests for Permit Modification Units Proposed for No Further Action, March and September 1995, Los Alamos National Laboratory NM0890010515," Los Alamos National Laboratory letter to T. Taylor and J. Jensen, EM/ER, from R. S. Dinwiddie, NMED-HRMB, Los Alamos, New Mexico. (Dinwiddie 1996, 55815)

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Honker, W. K., August 25, 1993. "Pilot Extraction Plan for the Organic Vapor Plume (MDA L), Los Alamos National Laboratory, NM0890010515," Los Alamos National Laboratory letter to J. Vozella, DOE, from W. K. Honker, EPA, Los Alamos, New Mexico. (Honker 1993, 30522)

Jansen, J., and T. Taylor, February 27, 1996. "Submittal of the Resource Conservation and Recovery Act Facility Investigation (RFI) Report for Channels from Material Disposal Areas (MDAs) G, H, J, and L in Technical Area (TA) 54," Los Alamos National Laboratory letter (EM/ER:96-007) to D. Neleigh, EPA, Los Alamos, New Mexico. (Jansen and Taylor 1996, 54462)

Kelley, E., December 21, 1998. "Approval: Class III Permit Modification to Remove Ninety-Nine (99) Solid Waste Management Units from the Department ff Energy/Los Alamos National Laboratory RCRA Permit," Los Alamos National Laboratory letter to T. Taylor, DOE-LAAO, and J. Browne, LANL, from E. Kelley, Los Alamos, New Mexico. (Kelley 1998, 63042)

LANL (Los Alamos National Laboratory), May 1992. "RFI Work Plan for Operable Unit 1148," Los Alamos National Laboratory document LA-UR-92-855, Los Alamos, New Mexico. (LANL 1992, 7669)

LANL (Los Alamos National Laboratory), March 1995. "Request for Permit Modification Units Proposed for NFA, March 1995," Los Alamos National Laboratory document LA-UR-95-767, Los Alamos, New Mexico. (LANL 1995, 45365)

Reiter, G., April 23, 1993. "RFI Work Plan for OU 1148 Notice of Deficiency, Los Alamos National Laboratory NM0890010515," Los Alamos National Laboratory letter to J. L. Bellows, DOE-LAAO, from G. Reiter, EPA, Region 6, Los Alamos, New Mexico. (Reiter 1993, 6743)

Swanton, B., November 15, 1995. "Review of LANL's May 1992 RCRA Facility Investigation (RFI) Work Plan for Operable Unit (OU) 1148 (Agreement in Principles [AIP] Technical Comments Attached)," Los Alamos National Laboratory letter to D. Webb, DOE-LAAO, from B. Swanton, NMED, Los Alamos, New Mexico. (Swanton 1993, 63981)

Taylor, T., November 1, 1993. "Cover Letter for the Modification to the EPA-Approved Pilot Study for MDA L at OU 1148," Los Alamos National Laboratory letter (LESH:7TT-004) to B. Driscoll, EPA, from T. Taylor, Program Manager, DOE-LAAO, Los Alamos, New Mexico. (Taylor 1993, 30249)

Taylor, T., October 11, 1995. "NFA Permit Modification, March 1995 (DOE Concurrence in Determination of NFA for AOCs Non-HSWA Units)," Los Alamos National Laboratory letter (LAAMEP:CGF:NFA Approval) to J. Jansen, EM/ER, from T. Taylor, DOE, Los Alamos, New Mexico. (Taylor 1995, 50023)

Tiedman, A., July 27, 1993. "Pilot Extraction Study Plan for the Organic Vapor Plume at Material Disposal Area (MDA) L," Los Alamos National Laboratory letter (ADO/93-614-U) to J. Bellows, DOE-LLAO, from A. Tiedman, ADO, Los Alamos, New Mexico. (Tiedman 1993, 22430)

Vozella, J. C., November 23, 1993. "Cover Letter for Response to Notice of Deficiency for Work Plan for Operable Unit 1148 for ER Program," Los Alamos National Laboratory letter to W. Honker, Chief, EPA Region 6, from J. C. Vozella, Chief, DOE, Los Alamos, New Mexico. (Vozella 1993, 30327)

PRS Number	Unit Type	HSWA PRS (Y/N)	Active Waste Management Areas (Y/N)	Regulatory Status
$54-001(a)$	Radioactive mixed waste storage area	Y	Y	Active mixed waste storage area currently operated under RCRA interim status. Unit will be permitted in next revision to the Laboratory's Hazardous Waste Facility Permit. Unit will be closed under RCRA closure requirements for permitted storage units.
$54-001(b)$	Hazardous waste storage area	N	Y	Active hazardous waste storage area currently operated under the Laboratory's Hazardous Waste Facility Permit. Unit will be closed under RCRA closure requirements for permitted storage units.
$54-001(c)$	Storage tank and containment berm	Y (Removed)	N (Removed)	Unit was never used for management of solid waste. Unit was recommended for NFA in RFI work plan and was removed from HSWA Module in December 1998.
$54-001(d)$	PCB waste storage area	N	Y	Active PCB waste storage area operated under EPA TSCA authorization. Unit will be closed under TSCA closure requirements for storage units.
$54-001(e)$	Hazardous waste storage area	N	Y	Active hazardous waste storage area currently operated under the Laboratory's Hazardous Waste Facility Permit. Unit will be closed under RCRA closure requirements for permitted storage units.
54-002	Hazardous waste storage area	N	Y	Active hazardous waste storage area currently operated under the Laboratory's Hazardous Waste Facility Permit. Unit will be closed under RCRA closure requirements for permitted storage units.
54-006	Subsurface waste disposal (pit, shafts, impoundments)	Y	N	Site is being addressed under RCRA corrective action.
54-008	Sanitary sewage holding tanks	N	Y	Tanks are permitted holding tanks operated under NMED Liquid Waste Disposal Regulations. Unit was recommended for NFA in RFI work plan. EPA and DOE concurred with NFA recommendation and unit has been administratively closed.
54-009	Hazardous waste storage/treatment tanks	N	N (Removed)	Tanks were operated under the Laboratory's Hazardous Waste Facility Permit and were closed at risk without approved closure plan. Unit will be formally closed under RCRA following submittal of RCRA closure plan.
54-012(b)	Former site of drum compactor	Υ	N	Site is being addressed under RCRA corrective action.

Table F-1 Status of Potential Release Sites at TA-54 Area L

Table F-1 (continued)

Appendix G

History of Monitoring for Subsurface Volatile Organic Compound Plumes at Material Disposal Area L

APPENDIX G HISTORY OF MONITORING FOR SUBSURFACE VOLATILE ORGANIC COMPOUND PLUMES AT MATERIAL DISPOSAL AREA L

G-1.0 PORE-GAS MONITORING WELL NETWORK

A total of 32 monitoring boreholes are available for pore-gas monitoring and sampling at Technical Area (TA) 54. Of these 32, 24 are available specifically for pore gas monitoring and sampling at MDA L. Details on the installation and locations of the boreholes currently used for vadose zone monitoring at material disposal area (MDA) L are described in Sections 2 and 3. Figure G-1 shows the location of the pore-gas monitoring wells at MDA L. Detailed borehole logs including lithologies and well construction are presented in Appendix H of this report. The depths of the pore-gas sampling ports are shown in Table G-1.

G-2.0 METHODS OF PORE-GAS COLLECTION AND ANALYSIS

Methods of pore-gas collection and analysis have changed during the years of monitoring the vaporphase plume. Each change was an improvement over the previous method in terms of number of analytes, precision, accuracy, and/or cost. A brief review is necessary to understand variations in sampling results. Table G-2 lists the sampling methods used from 1988 to the present. Table G-3 lists the analytical methods used for the different pore-gas analytes. Pore-gas sampling at the Laboratory is governed by LANL-ER-SOP-06.31, current version, Sampling Sub-Atmospheric Air. The following sections review the historic analytical methods used to measure volatile organic compounds (VOCs) in pore gas.

Solvent Desorption Gas Chromatograph/Mass Spectrometer

In the solvent desorption gas chromatograph/mass spectrometer (SDGCMS) method, a positivedisplacement pump purges the borehole sampling lines and draws a pore-gas sample through a singlesample ampule containing granulated activated charcoal as a sorbent. After the sampling line is purged of one volume, the ampule is opened and connected in series with the well; an additional 1.2 L of pore gas is pumped through the ampule. In the laboratory, the granulated charcoal is desorbed by solvent extraction using carbon disulfide. The solute obtained by this extraction is analyzed by gas chromatography/mass spectrometry (GCMS) for 12 analytes using the National Institute of Occupational Safety and Health Volatile Sample Train (NIOSH VOST) method. Results of the SDGCMS sampling are summarized in revised Appendix A of the operable unit (OU) 1148 work plan (LANL 1993, 22430).

Thermal Desorption Gas Chromatograph/Mass Spectrometer

Thermal desorption gas chromotograph/mass spectrometer (TDGCMS) is a method developed in 1993 because more precise results were needed for remediation designs (Neeper 1993, 55533). Forty-eight analytes were analyzed by TDGCMS. This method uses two glass sample tubes with three specified sorbent beds in each tube instead of the single ampules of granulated activated charcoal used in the SDGCMS method. The sorbents can be chosen to maximize absorption of the chemicals expected to be present. To obtain representative pore-gas samples, at least two headspace volumes are purged from the line to each monitor port before sampling. After purging, the gas line to the sampling port is never opened to the atmosphere but directed to the sampling unit by switching valves. The gas flow is split such that one sample tube receives 10 times more pore gas than the other. In addition to increasing the dynamic range of the measurement, the TDGCMS method uses an integrating mass flow meter to measure the volume accurately.

One tube was sampled at 10 mL/min, and the other tube was sampled at 100 mL/min. The method used for analysis was a modified US Environmental Protection Agency (EPA) Method TO-1/TO-2, which specifies a flow of 30- to 50-mL/min. At flow rates higher than 50-mL/min, light volatile compounds such as vinyl chloride will pass through the absorbent trap. The low flow-rate tube data (10 mL/min) can be used with greater confidence because even though the flow rate is not proper for collecting heavier compounds, breakthrough and loss of the lighter compounds does not occur.

For these results the laboratory used liquid injections for all gas chromotograph/mass spectrometer (GCMS) calibrations of gaseous samples. The EPA method requires dynamic calibration, that is, the calibration of an analytical system using gas standards introduced into the analytical system in the same manner as the samples. The calibration standards are identical or very similar to the samples to be analyzed.

Photoacoustic Radiometry

Beginning in the third quarter of calendar year 1993, the former ER Project, now Risk Reduction and Environmental Stewardship–Remediation Services (RRES-RS), adopted an infrared technique, called photoacoustic radiometer (PAR), as a screening method to monitor the vapor plume. Although specific ports in selected monitoring wells are still analyzed by GCMS, the PAR is used to monitor each sampling port in each borehole. Since the first quarter of 1998, PAR has been used to screen all wells at all depths. The PAR technique uses a Bruel & Kjaer (B&K) model 1302 infrared field-screening instrument to measure up to five analytes at a time at each port. The results are reliable and immediately available in the field. Through 1999, samples from the port in each well that has the highest total concentration of VOCs (using PAR) are then analyzed by the GCMS method. During this period, the sampling program targeted the maximum concentration of the plume. Beginning in 2000, samples were collected from a defined list for analysis by the GCMS method to address data gaps that remained for defining the nature and extent of contamination. The methodology and analyte list for the PAR screening has changed since 1993. The current procedure requires purging each sample port with a pump until carbon dioxide levels have stabilized at levels representative of subsurface pore gas. The carbon dioxide concentration is measured with an in-line carbon dioxide detector. The B&K gas analyzer is then used to measure the concentrations of 1,1,1-trichloroethane (TCA), trichloroethene (TCE), tetrachloroethene (PCA), and Freon 11. In addition, the B&K measures the pore gas carbon dioxide and water vapor concentration.

Tedlar Bag Sampling and GCMS Analysis

The multiple-port monitoring boreholes at MDA L have sampling ports located over a great range of depths. Consequently, the gas impedance in sampling lines to discrete ports varies over a factor of about 300. To sample and analyze those ports with high impedance, a lung box was employed to fill Tedlar sample bags with the pore gas. Using PAR, the pore gas was analyzed directly from the Tedlar bag. The same Tedlar bag (containing the pore gas) was submitted for GCMS analysis of 60 chemicals. Analysis was done within eight hours. The Tedlar bag GCMS method was used during the first quarter of 1996. Dynamic calibration was not employed for these samples. The quality assurance (QA) audit of this technique resulted in a shut down of the pore-gas program because of sampling and analytical deficiencies.

SUMMA™ Canisters and GCMS Analysis

Since 1997, pore-gas samples have been collected using SUMMA™ canisters with analysis by GCMS by EPA Method TO-14. Through fiscal year (FY) 2000, SUMMA™ canister samples were drawn from the port with the highest contaminant concentration (determined by field screening every port with the PAR

field instrument). Starting in FY 2001, a defined list of ports were sampled using SUMMA™ canisters for GCMS analysis by EPA Method TO-14. The defined list of ports is provided in the annual report at the end of each fiscal year. The 2001 list was defined at the end of the fourth quarter of 2000, and the 2002 list was defined at the end of the fourth quarter of 2001. The defined list of ports was based on an evaluation of past data for data needs with respect to nature and extent.

Currently samples are collected in SUMMA™ canisters from 12 boreholes each quarter. This protocol has been in place since the EPA approved amended Appendix A of the OU 1148 work plan. Of the 12 boreholes sampled, 7 are at MDA L (Figure G-1), 2 are located at MDA G, and 3 are discretionary samples collected from the remaining wells at either MDA L or MDA G. In addition to the required SUMMA sampling, all available ports in the available boreholes are screened with a B&K model 1302 infrared field-screening instrument.

Most recently, the quarterly pore-gas monitoring has focused on

- identifying changes in contaminant concentrations at the perimeter of the well-characterized plume at MDA L as an indicator of outward plume behavior,
- identifying changes in the source area as an indicator of new releases, and
- addressing data needs for estimating nature and extent.

Field quality assurance (QA) samples include a duplicate sample drawn from one well, an equipment blank of zero air or nitrogen drawn through the sampling apparatus in the working area, and a sample of a known calibration gas. Laboratory QA for the EPA Method TO-14 gas chromatography includes internal surrogates, replicates, blanks, laboratory control samples, and reference standards.

G-3.0 PORE-GAS MONITORING RESULTS

G-3.1 Quarterly Monitoring Results (Pre-1993)

Characterization and monitoring of the MDA L vapor plume began in the mid-1980s. Results of MDA L monitoring before the RFI began in 1993 are presented in this section.

Plume Composition as Determined by Pre-1993 Data

Analytical results on discrete pore-gas samples collected from the monitoring well network for MDA L from 1985 to 1988 are presented in a report by Trent (1990, 12557). Revised Appendix A to the OU 1148 work plan summarizes analytical results on pore-gas samples collected at MDA L during the period 1988 to 1992 and states that "the principal vapor phase organic compounds, listed in descending order of concentration, were 1,1,1-trichloroethane (TCA), trichloroethene (TCE), carbon tetrachloride, chloroform, tetrachloroethene (PCE), toluene, and benzene. Other contaminants that have been detected but at much lower concentrations include chlorobenzene, xylenes, and 1,2,4-trimethylbenzene. In addition to having the greatest concentration, TCA also exhibits the greatest lateral and vertical extent in the organic chemical vapor plume. The measured concentrations of TCA are almost an order of magnitude greater than values measured for TCE, the contaminant of second highest concentration." The SDGCMS method was used to measure 12 VOCs in the pore gas.

G-3.2 QUARTERLY MONITORING RESULTS (POST-1993)

Plume Composition as Determined by 1993–1996 Data

Before 1993, pore-gas samples for the MDA L plume were analyzed for only 12 chemicals. In the first quarter of 1996, using the Tedlar bag GCMS method, pore-gas samples were analyzed for 60 chemicals. In the first quarter of 1996, the total number of chemicals detected was 21. The compound TCA was the dominant analyte; PCE, and trichlorotrifluoroethane (Freon 113) were next in abundance. Prior to 1993, Freons had not been detected because they were not included in the analytical suite. QA deficiencies were identified in the analytical methods used during this period and the results should be used for comparison purposes only.

Plume Composition as Determined by 1997 – Present Data

Beginning in 1997, the pore-gas sampling and analyses methodology were greatly improved to provide quantitative analytical results that could be used to define nature and extent of contamination and track plume behavior over time. The pore-gas screening and sampling adhered to strict procedures, and stringent QA was required of analytical laboratories conducting the EPA Method TO-14 organic analysis.

The latest analytical data available for MDA L are the first quarter FY 2002 SUMMA™ canister analyses. Through the fourth quarter of 1999, the SUMMA™ samples were collected from ports with the highest detected concentrations based on field screening with the B&K. Beginning in 2000, the SUMMA™ samples were collected according to a predefined schedule developed to address data gaps regarding the nature and extent of contamination. The SUMMA™ samples after 1999 do not necessarily represent maximum plume concentrations. For maximum concentration comparison purposes, Table G-4 and G-5 show the maximum detected concentrations for each chemical and their locations for the first quarter of 1997 and fourth quarter of 1999, respectively. Table G-4 also includes a large number of compounds, whereas Table G-5 shows a fairly limited number of compounds. This difference results primarily from more rigorous data validation procedures since 1997, which limits the actual number of detected compounds. The entire set of the SUMMA™ canister data is included in Appendix D.

The SUMMA™ analytical data collected since 1997 are of sufficient quality to define the nature of the subsurface VOC contamination at MDA L. However, spatially, the SUMMA™ analytical data are limited and cannot be used to fully define extent. To define extent the pore-gas screening data are used. The pore-gas screening data have been collected from every functional port in every available pore-gas monitoring well since 1997 and provides a very extensive extent data set. As presented in Section 2 of this IWP, the B&K screening data correlates well with the SUMMA™ analytical data. Figure G-2 shows the lateral and vertical extent for TCA as defined by the B&K screening data for each quarter since 1999.

G-4.0 REFERENCES

The following list includes all references cited in this attachment. Parenthetical information following each reference provides the author, publication date, and a record identification (ER ID) number, when available. These numbers can be used to locate copies of the actual documents at the RRES-RS Records Processing Facility.

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Trent, B., November 1, 1990. "Update on Analysis of Area L," Los Alamos National Laboratory memorandum EES-5:90-718 to A. Barr, Los Alamos, New Mexico. (Trent 1990, 12557)

MDA L Pore Gas Sampling 1st Quarter - 1999

MDA L Pore Gas Sampling 3rd Quarter - 1999

MDA L Pore Gas Sampling 3rd Quarter - 2000

MDA L Pore Gas Sampling 3rd Quarter - 2001

Well Number	Sample Port Depth (ft from surface)	Well Number	Sample Port Depth (ft from surface)	
54-01015 54-01016 54-02001	45, 187, 350, 385, 435, 485, 525 36, 188, 318, 390, 481, 533, 601 20, 40, 60, 80, 100, 130, 140, 160, 180, 200	54-02025	20, 60, 100, 160, 190	
54-02002	20, 40, 60, 80, 100, 120, 140, 160, 180, 200	54-02026	20, 60, 100, 160, 200, 215	
54-02012	7, 27, 42,	54-02027	20, 60, 100, 160, 200, 220, 250	
54-02014	13, 31, 46, 86	54-02028	20, 60, 100, 160, 200, 220, 250	
54-02015	8, 31, 82	54-02029	20, 60, 100, 160, 200, 220, 260, 288	
54-02016	7, 8, 31, 82	54-02030	20, 60, 100, 160, 200, 220, 243	
54-02020	20, 40, 60, 80, 100, 130, 140, 160, 180, 200	54-02031	20, 60, 100, 160, 200, 220, 260	
54-02021	20, 40, 60, 80, 100, 130, 140, 160, 180, 200	54-02034	60, 100, 160, 200, 220, 260, 300	
54-02022	20, 40, 60, 80, 100, 120, 140, 160, 180, 197	54-02087	13, 31, 46, 86	
54-02023	20, 40, 60, 80, 100, 120, 140, 160, 180, 200	54-02088	13, 31, 46, 86	
54-02024	20, 40, 60, 80, 100, 120, 140, 160, 180, 200	54-02089	13, 31, 46, 86	

Table G-1 Sample Port Depths in 1000- and 2000-Series Boreholes

Table G-2 Chronology of Sampling and Analysis Methods

Time Frame	Sampling Method	Laboratory Method	Analysis Method	Analytes (number)
1988-1993	Single ampule GAC ^a	Fixed laboratory analytical method	SDGCMS ^b	12
1993-1996	Twin tube Tenax	Fixed laboratory analytical method	TDGCMS^c	48
1993-present	Directly in real time	Field screening method	PAR ^d	5
1996-1997	Tedlar Bag	Fixed laboratory analytical method (used only once)	GCMS	60
1997-present	SUMMA™	Fixed laboratory analytical methods	$EPAe$ TO-14	63

a
^a GAC = granulated activated charcoal.

b
SDGCMS = solvent desorption gas chromatograph/mass spectrometer.

c
TDGCMS = thermal desorption gas chromatograph/mass spectrometer.

d
PAR = photoacoustic radiometer.

e
EPA = Environmental Protection Agency.

Table G-3
Methods for Detecting Pore-Gas Analytes **Table G-3 Methods for Detecting Pore-Gas Analytes**

Table G-3 (continued) **Table G-3 (continued)**

Table G-3 (continued) **Table G-3 (continued)**

a NIOSH VOST = National Institute of Occupational Safety and Health Volatile Organic Sample Train.
b CST = Chemical Science and Technology (Laboratory division).
c ESE = Environmental Science Engineering. უ
თ b NIC/SH VOST ≡ National Institute or Occupational Safety and He
^b CST = Chemical Science and Technology (Laboratory division).
^C ESE = Environmental Science Engineering.

Table G-4 Maximum Contaminant Concentrations in the First Quarter of Fiscal Year 1997 (Tedlar Bag GCMS Method)

Table G-4 (continued)

Table G-5 Maximum Contaminant Concentrations in the Fourth Quarter of Fiscal Year 1999 (TO-14 Method) at MDA L

Appendix H

Borehole Profiles and Logs

APPENDIX H BOREHOLE PROFILES AND LOGS

This appendix presents logs of boreholes 54-01001 through 54-01018 and profiles of boreholes 54-01001 through 54-01016 (Figures H-1 to H-16) drilled at Material Disposal Area L. The profiles depict the subsurface trajectories of the boreholes relative to adjacent subsurface disposal units, the stratigraphic units encountered during drilling, the location of samples taken from the core, and the pore-gas sample and monitoring port locations, where applicable.

Footages on the logs are the length along each borehole.

Figure H-17 presents a diagram showing pore-gas sampling port construction.

REFERENCE

The following list includes all references cited in this document. Parenthetical information following each reference provides the author, publication date, and a record identification (ER ID) number, when available. These numbers can be used to locate copies of actual documents at the RRES-RS Records Processing Facility.

Broxton, D. E., and S. L. Reneau, August 1995. "Stratigraphic Nomenclature of the Bandelier Tuff for the Environmental Restoration Project at Los Alamos National Laboratory," Los Alamos National Laboratory report LA-13010-MS, Los Alamos, New Mexico. (Broxton and Reneau 1995, 49726)

View is N77°W

Figure H-2. Profile of borehole 54-01002 showing subsurface sample locations

Figure H-3. Profile of borehole 54-01003 showing subsurface sample locations

Figure H-6. Profile of borehole 54-01006 showing subsurface sample locations

View is N6°W

Figure H-11. Profile of borehole 54-01011 showing subsurface sample locations

View is N65°W

View is N67°W

View is S65°W

Figure H-15. Profile of borehole 54-01015 showing subsurface sample and monitoring port locations

Figure H-16. Profile of borehole 54-01016 showing subsurface sample and monitoring port locations

Figure H-17. Diagram showing pore-gas sampling port instrumentation **Figure H-17. Diagram showing pore-gas sampling port instrumentation**

Appendix I

Subsurface Vapor-Phase Transport of TCA at MDA L: Model Predictions, Revision 1

Subsurface Vapor-Phase Transport of TCA at MDA L: Model Predictions

Revision 1 LA-UR-02-2080

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and

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May, 2002
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1.0 - INTRODUCTION

TA-54 MDA L is a material disposal area (MDA) that received liquid chemical wastes from the late 1950's through 1986 [LANL, 2000]. From the late 1950's through 1975, bulk liquid waste was disposed of in an open pit at MDA L and allowed to evaporate. Due to the high vapor pressure of the organic liquids, most of the VOCs introduced to the open pit should have readily evaporated into the atmosphere. From 1975 through 1985, organic liquids were disposed of in a series of 20-m deep shafts. Some organic liquids were poured directly into the shafts while others were containerized in drums before being disposed of in the shafts. All of these disposal operations occurred beneath the surface of Mesita del Buey in the underlying unsaturated tuff units, some 300 meters above the regional aquifer.

The major chemicals of potential concern (COPC) measured at this site are found in poregas sampling and include a host of volatile organic compounds (VOCs) and tritium [LANL, 2000]. Although VOCs may percolate as liquids in the subsurface (especially in saturated systems), the dry subsurface environment at MDA L causes rapid volatilization. The organic vapors emanating from the liquid waste shafts must migrate through the subsurface before reaching the atmosphere. Large amounts of the liquid waste have volatilized to create the current plume of organic vapor in the subsurface. The vapor plume has migrated over 100 meters laterally from the shafts as demonstrated by pore-gas sampling, and it is estimated to contain nearly 1000 kg of vapor-phase VOCs [LANL, 1999]. Pore-gas sampling shows that VOCs disposed of at this site include 1,1,1 trichloroethane (TCA), trichloroethylene (TCE), trichlorotri-flouroethane (FREON), and lesser amounts of chloroform, toluene, benzene, cyclohexane, methyl chloride, and other similar solvents.

The purpose of this work is to develop a calibrated numerical model for the vapor plume beneath MDA L that can be used to analyze the current and future state of the plume. In this report, we initially develop a diffusion model for TCA transport at the site that predicts the migration of the vapor-phase plume from the shafts through the subsurface. This relatively simple model captures the first-order effects that control migration of the vapor-phase plume. For instance, it assumes that the movement of the vapor plume can be described through its most prevalent component, vapor-phase TCA. It also assumes that plume growth is controlled by diffusive processes rather than by air flow within the mesa top. The model is calibrated to pore-gas data collected at the site. Simulations of several different cases that use various diffusion coefficients, source-term concentrations, and boundary conditions are examined. The best-fit simulation is

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determined with a goodness-of-fit scheme that compares the different model results to the field data. We found that the predicted subsurface concentrations match observed pore-gas concentrations quite well for a few of the better simulations, indicating that this first-order diffusion model adequately describes plume behavior. The model is applied to predict plume growth over the next 50 years, to suggest monitoring frequency, and to estimate the possible system response to the bursting of a buried drum.

The simulations were revised to determine the effects of some second-order processes following an Innovative Treatment and Remediation Demonstration (ITRD) peer review . The reviewers commented on the original April, 2000 version of this report. The current report (Rev. 1) is a modification of the original report and considers the effects of the following processes, as recommended by the peer reviewers:

1) Henry's Law fractionation of TCA into porewater,

f2) Diffusion coefficient as a function of moisture content,

3) Higher source concentrations during disposal operations (pre-1985) caused by noncontainerized releases

4) Surface flux reduction due to boundary layer effects,

5) Fractures,

- 6) Non-Fickian behavior at low permeabilities, and
- 7) Sorption of TCA onto the tuff matrix.

To address the reviewers' concerns, the conceptual model (Section 2.3) was revised to discuss all the items above. Furthermore, new simulations were run that include the processes identified in items 1 through 4, and the results are reported at the end of the paper in Section 4.4 'Simulations in Response to the ITRD Peer Review'. The simulated surface flux results have been modified to more accurately calculate the emissions from the surface, and these results are reported in Section 4.1.2. In addition to the major conceptual/modeling concerns of the reviewers, many smaller items have been corrected to make this document more consistent with the TA-54 RFI (LANL 2000) and other supporting documents.

Although the initial goal of the site model was to determine if the first-order processes of pure diffusion of a vapor plume could explain the bulk of the data, the reviewers' ideas for improving the fit between model and data proved quite useful in showing that the conceptual model

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for TCA transport is valid, and that the numerical model should perform robustly in exploring the fate of the VOC plume at this site. In a future study, this revised model will be used to explore schemes for site corrective measures, such as passive venting.

2.0 - SITE DESCRIPTION

2.1 STRATIGRAPHY AND TOPOGRAPHY

The strata that immediately underlie MDA L are composed of nonwelded to moderately welded rhyolitic ash-flow and ash-fall tuffs interbedded with thin pumice beds. The rhyolitic units are underlain by a thick basalt unit, and a conglomerate formation [Krier, et al., 1997]. The tuff layers were deposited during violent eruptions of volcanic ash from the Valles Caldera between 1.2 and 1.6 million years ago [Smith and Bailey, 1966; Gardner et al., 1986]. Since then, the tuff has eroded to leave a system of alternating finger-shaped mesas and canyons. MDA L is located atop one such mesa, Mesita del Buey, with the waste disposed in shallow pits (4 m deep) and shafts (approximately 20 meters deep). The surrounding canyons, Canada del Buey and Pajarito Canyon, lie 30 m below the steep-sided mesa, and the regional aquifer is located approximately 300 meters below the disposal pits. There are no known perched aquifers below the mesa. Figure 2.1_1 shows the site topography and the locations of disposal pits, disposal shafts and monitoring wells.

Figure 2.1_2 shows a simplified stratigraphic column of the rocks underlying MDA L. The upper three stratigraphic units make up the Tshirege member of the Bandelier Tuff. Unit 2 and the lower half of the Unit 1v are fractured. The Cerro Toledo interval is comprised of volcanoclastic sediments interbedded with minor pyroclastic flows, and separates the Tshirege and Otowi Members of the Bandelier Tuff. The Otowi Member is nonwelded to poorly welded and is not fractured. The units comprising the Bandelier Tuff dip gently and thin toward the eastern end of the site [Vaniman et al., 1998].

The following subdivisions and thin units are not included in Figure 2.1_2 or in the numerical model domain. The Tshirege Unit 1v is generally subdivided into units 1v-u and 1v-c. Units 1v and 1g are separated by a thin horizon known as the vapor-phase notch, which is easily seen in outcrop, but is not necessarily continuous and additionally is too thin to include in a sitescale model. The Tsankawi Pumice, a thin (20-100cm) bed at the base of Unit 1g, is lumped into Unit 1g in the model. There are surge beds at the bases of both Tshirege Unit 2 and Unit 1 which are not included in Figure 2.1_2 or in the site-wide geologic model [Vaniman et al., 1998]. The Otowi is subdivided into an ash-flow component and a pumice fall that are not separated in Figure 2.1_2 or in the site-wide geologic model. Although these units can be hydrologically significant, their effect on the diffusion equation is minimal, as only the diffusion coefficient and the moisture content of a given unit affect the diffusion solution. As we show later, a uniform diffusion

coefficient is chosen for the modeling, and the site moisture content does not vary by more than an order of magnitude. Therefore, excluding these units should not strongly affect the solution.

The Cerros del Rio Basalts, which comprise nearly 50% of the unsaturated zone, display wide variability [Turin, 1995], ranging from extremely dense with no effective porosity, to highly fractured, to so vesicular as to appear foamy. The Puye Formation underlies the Cerros del Rio Basalts and extends from the of base of the unsaturated zone well into the saturated zone. The Puye Formation is an amalgamation of alluvial fan, river, and lake deposits containing cobbles and boulders of both volcanic and plutionic origin in a matrix of silts, clays, and sands. Interbedded basalt flows, dacite flows, and pumice lenses are also common [Purtymun, 1995].

Figure 2.1_1 Geographical information for MDA L and the surrounding area.

Figure 2.1_2 Simplified site stratigraphy.

2.2 CONTAMINANT SOURCE

MDA L was used as a disposal site for liquid chemical waste from the late 1950's until its closure in 1986 [LANL, 2000]. After passage of the Resource Conservation and Recovery Act (RCRA), regulations concerning the disposal and storage of hazardous waste caused the Laboratory to discontinue subsurface disposal of RCRA regulated chemical wastes. Both solid and liquid chemical wastes are currently stored above ground in facilities at MDA L that allow the waste to be inspected and monitored before removal to permanent disposal/treatment facilities.

2.2.1 Timing of waste disposal at MDA L

One pit, three surface disposal impoundments, and 34 disposal shafts are the Potential Release Sites (PRS) at MDA L (Figure 2_2.1) [LANL, 2000]. These PRSs had varying purposes and were used for different time periods. Disposal Pit A was the only disposal unit in operation before 1975. Dates of operation for Pit A were from 1964 until 1978. Surface impoundment B was established in 1979 and decommissioned in 1985. Impoundments C and D were in use from 1985 to 1986 and 1972 to 1984 respectively.

Figure 2.2₁ Location map for waste disposal shafts and pits at MDA L

Operation dates for the 34 disposal shafts ranged from 1975 to 1985. Shaft numbers 1 through 28 operated from 1975 through 1985, while shaft numbers 29 through 34 operated from 1983 through 1985. After decommissioning, most of the 2.5 acres comprising MDA L were covered with asphalt upon which were built temporary storage facilities for chemical waste. The asphalt covering affects the subsurface transport of the VOCs as discussed in Section 2.3.2.

2.2.2 Types of waste found at MDA L

 There is little information on specific chemicals, timing, or quantities of waste that were disposed of at MDA L. However, the major COPCs measured at this site are found in pore-gas sampling and include a host of volatile organic compounds (VOCs) and tritium [LANL, 2000]. Pit A received non-containerized bulk quantities of treated aqueous waste that was left to pool and evaporate without added absorbent material. This waste is not reported to contain VOCs. However, if some VOCs were disposed of in Pit A, their high vapor pressures would have led to quick evaporation into the atmosphere. Therefore our conceptual model of MDA L does not include Pit A as a source of VOC vapor in the subsurface.

Surface Impoundments B, C, and D were exclusively used as evaporative lagoons for treated salt solutions. Salt solutions such as ammonium biflouride and electroplating wastes were a source of copper, barium, chromium, and zinc contamination in the impoundments [LANL, 2000]. Records indicate that the majority of waste disposed of in the surface impoundments was inorganic, therefore these disposal units are not included as a source term in the simulations of the VOC vapor plume.

The 34 shafts received metal drums (55 gallon) containing chemical liquid waste. The waste drums were packed in lifts with one to six barrels per layer. In the shafts, layered waste was covered with crushed tuff to provide absorbent material as well as structural support for the drums. Additionally, unknown quantities of small containers and free product were dropped directly into the shafts. The locations of the pits and shafts can be seen on Figure 2.2_1. Shaft numbers 1 through 28 are located near Pit A, while shaft numbers 29 through 34 are located 60 m northwest of Pit A. The spatial distribution of the waste led to two main source regions for organic vapors, causing the development of the double-lobed plume seen in the site data (Figure 2.2_2). Records indicate that the majority of material placed in the shafts was organic waste. The records do not differentiate between pure liquid and organic contaminated solids (rags, paper, etc.). However, because MDA L is a designated liquid waste disposal area, contaminated solids were most likely disposed of at MDAs C and G. For these reasons, a source term for the organic liquids can only be roughly defined. The major long-term source for organic contamination in the disposal shafts is expected to be from potential future releases as a result of drum deterioration.

Sampling conducted to determine the existing VOC plume in rock core and pore gas from various boreholes on or near the site found a vapor-phase plume that consists primarily of TCA, TCE, carbon tetrachloride, and chloroform [LANL, 2000]. Although we cannot rule out the possibility that free product existed at some point in time, current vapor phase concentrations are well below the vapor pressure of TCA which implies that free product is not present near the sampling points. Peak concentrations of TCA vapor found below the bottom of the shafts suggests that some limited liquid transport of VOC may have occurred prior to the core studies [LANL, 2000].

The major vapor-phase contaminant measured in the second quarter of FY99 was TCA, which composed approximately 75% by volume of the spatially averaged plume. The second most prevalent contaminant found was TCE, comprising 12.5% by volume of the plume, while

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Freon 113 composed 11.2% by volume of the averaged plume. These values are averaged over 140 sampling locations measured using the B and K field-screening method, which detects only TCA, TCE, and Freon. Although these numbers are spatial averages, individual sampling ports show wide variation in the ratios of the most prevalent VOCs, and the more complete analytic laboratory analyses show some ports (for example, well 54-2032 at 47.5 m (156 ft) below the collar) have significant percentages of compounds such as napthalene (12%) and dichloroethene 1,1 (14%) [Smith et al., 1999b].

2.2.3 Pore-gas monitoring data

Quarterly pore-gas monitoring has been conducted at the site since 1985 in accordance with a compliance ordered issued by the state of New Mexico [LANL, 2000]. Continued monitoring of soil gas has shown that the organic vapor-plume source region is coincident with the disposal shafts, and that the plume does not appear to have grown at a detectable rate over the past three years [Smith et al., 1998, 1999a, 1999b]. In fact, the current maximum TCA pore-gas concentration is similar to the value of 3400 ppmv reported by Trent [1992] in data from June, 1988.

The individual shafts that have contributed the largest portion of the plume are not well defined, and the simulations we present are designed to capture the general behavior of the main source regions. Figure 2.2_2 shows the second quarter FY99 monitoring data of measured TCA concentration at a depth of 18.3 m (60 ft.) below the mesa top contoured in map view. The data have been clipped at 10 ppmv to represent the lower limit of data reliability, which is 5 to 10 ppmv.

2.3 CONCEPTUAL MODEL and MODEL ASSUMPTIONS

The conceptual model on which the numerical simulations are based contains several key features [Rogers, 2000]. During the initial version of this document, we assumed that VOC migration at the site can be described by the diffusive transport of TCA vapors. Although some advective processes, such as barometric pumping, may enhance plume migration, Auer et al. [1996] showed that this can be modeled as enhanced diffusion. The plumes, however, do not grow as ideal spherical plumes because several external factors influence their shape. These factors include nonideal boundary conditions such as the topography of the site, the asphalt cover, and the venting of the plume through the deep basalt unit. Disposal history and source location also contribute to nonspherical plumes.

As a result of the ITRD peer review and questions from the NMED, this document (Revision #1) has been updated to explore several other processes that are known to be important in subsurface transport of VOCs. In Section 4.4, we present results from modeling that includes Henry's Law fractionation of VOC between porewater and the vapor phase, reduction in the TCA diffusion coefficient as a function of moisture content, and reduction in diffusion across the land/ air interface due to boundary layer processes which may impede mass transfer.

2.3.1 Unsaturated-Zone Transport Processes

I

As suggested by the preliminary conceptual model [Rogers, 2000], the original version of this document assumes that diffusion is the fundamental process controlling migration rates of TCA vapors in this unsaturated environment. Diffusion moves chemicals from areas of high concentration to areas of low concentration [Fetter, 1999]. Diffusion is caused by random motion of molecules and is a function of both temperature and the chemical's molecular weight. Thus, chemicals with a low molecular weight diffuse more rapidly at a given temperature. The effect of diffusion is to homogenize an initially heterogeneous distribution of chemical concentrations. The speed at which a chemical diffuses is described by the diffusion coefficient, D. D is much larger in

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air than in water, thus a drop of dye in water spreads more slowly than, for example, perfume spreads in air. Also, diffusion is slower in a porous medium than in free space because of the tortuous nature of small pores. Typically, a porous medium diffusion coefficient D* is 1/2 to 1/100 the value in free space [Freeze and Cherry, 1979].

Several secondary processes may play a role in affecting the size and growth rate of the plume. Henry's Law fractionation would tend to buffer the vapor plume's growth relative to the pure diffusion case [Fetter, 1999], by storing some of the TCA mass in the porewater of the Bandelier tuff. This effect increases with increasing water content and may help to explain why transport is less pronounced in the vertical direction within the Cerro Toledo interval and the Otowi Member, which both have higher background saturations than the Tshirege Units (Figure 2.1_2). Section 4.4 examines this process.

The vapor-phase diffusion coefficient for TCE in the Bandelier Tuff was measured at two saturation intervals (1-3% and 13-15%,). As expected from the literature (Millington, 1959), the measured diffusion coefficient was about an order of magnitude lower in the higher saturation experiments (Fuentes et al., 1991). Lower diffusion at higher moisture content will also help to bring the base model into agreement with the measured data within the Otowi Member and the Cerro Toledo interval. Diffusion coefficients for TCA have not been measured in Bandelier Tuff, but because TCA and TCE have similar molecular weights, we assume their diffusion coefficients are in the same range. Section 4.4 examines the effect of saturation on the diffusion coefficient.

Observations of alluvium on the mesa top at MDA L and examples from the literature citing lowered surface flux due to boundary-layer effects (Jury, 1990) have prompted us to determine the sensitivity of the model to a decrease in the diffusion coefficient across the land/air interface. The need for this modification was also suggested by a large difference in the original predicted versus measured surface flux at the site. The estimated surface flux from the base model was much higher than that measured at and around MDA L. Section 4.4 examines this process as well.

Fractures can affect the mobility of vapor-phase contaminants. At this site, however, fractures are found predominantly in Unit 2 and the very top of Unit 1v with fracture spacing on the order of one meter (Reneau et al., 1998). Additionally, fractures on the Pajarito Plateau are often filled with clay/calcite mixtures in the near surface that would effectively limit thier ability to act as high flux pathways for organic vapors (Broxton and Reneau, 1995). Although fractures may play a secondary role in gross plume behavior, we do not explicitly address this issue numerically.

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At low permeabilities $\left($ <1e-14 m2) vapor-phase diffusion in porous media may be better modeled by equations such as the Dusty Gas Model. However, because permeabilities at this site are greater than $1x10^{-13}$, we do not invoke this theory.

Sorption of TCE onto unsaturated Bandelier tuff has been measured by Ong and Lions (1991). Results from their study show that at high vapor-phase concentrations (20,000 ppmv) and low moisture contents (<0.3%), some amount of TCE partitions onto the solid mineral surfaces. However, at moisture contents found in the mesa, their data shows a low Kd of < 0.5 mL/g. Thus, for Revision 1, we do not numerically address this issue.

2.3.2 The effect of system geometry on plume growth

Ι

Because MDA L is located on the edge of a narrow finger mesa, the interaction of the subsurface vapor-phase contamination with atmospheric air must be considered [Rogers, 2000]. The topographic relief of the mesa provides an atmospheric boundary condition of near zero concentration [Mishier and Anderson, 1994] where the plume intersects the mesa top and sides. Because diffusion occurs from areas of high concentration to low concentration, the atmospheric boundary provides a huge sink, or low concentration volume, that can accept the VOCs that diffuse from the subsurface. This boundary maintains a steep concentration gradient between the subsurface plume and the mesa sides, which limits plume growth along the axis of the mesa.

Additionally, Neeper [1997] reports that the air in the basalt appears to be much more connected to the atmosphere than the air in the Bandelier tuff. We hypothesize that a low concentration boundary, similar to the atmospheric boundary, exists in the basalt unit. We test the hypothesis by fixing the concentration in the basalt at an atmospheric (zero) concentration of TCA in some simulations during model calibration.

The presence of the asphalt at MDA L potentially affects the ability of TCA vapor to migrate upward into the atmosphere. For this reason we test the sensitivity of the system with sealed asphalt (choosing $D^* = 1x10^{-14}$ m²/s to effectively stop diffusion through the asphalt), leaky asphalt (choosing $D^* = 4x10^{-7}$ m²/s to allow limited communication of the source with the atmosphere above the asphalt), and no asphalt.

2.3.3 Release and mobility of TCA vapor

The migration of TCA vapor from the shafts is conceptualized as a time-release phenomenon. This is based on the idea that liquid will leak slowly from the buried drums and quickly volatilize in the subsurface. Once released from the shafts, we assume the mobility of TCA through the unsaturated zone is controlled by diffusion along concentration gradients. The steepest concentration gradients will form along pathways to the atmosphere [Fetter, 1999].

Migration of TCA in the liquid phase is not included in the model, because there are no observations at the site of saturated conditions in the subsurface. In fact, moisture monitoring shows that the current subsurface moisture profiles are near background conditions, despite the previous disposal of liquid waste at the site [LANL, 2000]. The pore-gas concentrations also clearly indicate that no migration of free product (pure TCA) occurs. If pure-phase TCA were in the pores, its vapor pressure would yield pore-gas concentrations from one to two orders of magnitude larger than the highest concentrations observed in the monitoring data.

2.4 HYDROGEOLOGIC DATA

This study deals strictly with vapor-phase diffusion in the subsurface of MDA L. Therefore, the subsurface flow of water and air is decoupled from the diffusive transport. The major parameters affecting diffusive vapor transport are porosity, saturation, and the porous medium diffusion coefficient (D^*) . The porosities and saturations are fairly well characterized for the six Bandelier Tuff units. Saturated permeabilities, porosities, and saturations for the tuff units [Rogers and Gallaher, 1995] and the Guaje Pumice were measured on core samples. Estimated values for the porosity and saturation of the Puye Formation are used. No hydrologic property data were available for the basalts at the time this study was performed. Therefore, the porosity of a vesicular basalt located beneath Idaho National Engineering Laboratory is used as an analog [Bishop, 1991]. The saturation of the basalt is based on previous modeling results [Birdsell et al., 1997]. Fortunately, the model of the contaminant plume is relatively insensitive to the properties of the Puye Formation and Cerros del Rio Basalts. Table 1 summarizes the hydrologic parameters used for all of the units in the unsaturated-zone flow and transport model.

Unit	Effective porosity	Saturated permeability m ²	In-situ saturation	Effective diffusion coefficient $(10^6 \text{xD* in m}^2/\text{s})$
Tsh ₂	0.48	7.48e-13	0.05	1, 2, 4, 8, 20
Tsh 1 v	0.51	1.96e-13	0.04	1, 2, 4, 8
Tsh $1 g$	0.48	3.68e-13	0.2	1, 2, 3, 4, 8

Table 1: Physical Parameters used in the numeric model, bold indicates the base simulation

Unit	Effective porosity	Saturated permeability m ²	In-situ saturation	Effective diffusion coefficient $(10^6 \text{xD* in m}^2/\text{s})$
Cerro Toledo	0.473	8.82e-13	0.3	1, 2, 4, 8
Otowi Member	0.435	$7.25e-13$	0.25	1, 2, 4, 8
Cerros del Rio basalt (matrix)	0.23	$2.96e-13$	0.25	1, 2, 4, 8, 20
Puye Formation	0.25	$4.73e-12$	0.25	1, 2, 4, 8
Shafts	0.5	7.48e-13	0.05	1, 2, 4, 8
Asphalt	0.5	$1e-21$	0.05	$1x10^{-8}$, 0.4, 4
Surface (not includ- ing asphalt)	0.48		0.05	1, 2, 4, 8, 20

Table 1: Physical Parameters used in the numeric model, bold indicates the base simulation

2.5 TRANSPORT PROPERTIES

The modeling uses an estimate for the subsurface, vapor diffusion coefficient (D^*) of the predominant vapor-phase contaminant, TCA. The initial estimate of the diffusion coefficient for TCA vapor $(D^*=4x10^{-6} \text{ m}^2/\text{s})$ is based on core-scale measurements of TCA diffusion in Bandelier Tuff from TA-54 [Fuentes et al., 1991]. The model is run with a range of diffusion coefficients centered on the core-scale results to determine which diffusion coefficient best fits the site data. Because the diffusion coefficient of TCA in asphalt is unknown, we examine the sensitivity of the system to two values of the diffusion coefficient through the asphalt. In the first case, we assume a diffusion coefficient of $1x10^{-14}$ m²/s in the asphalt, which essentially stops the contaminant from mixing with the atmosphere in asphalt-covered regions. In the second case, we assume the asphalt is leaky, with $D^* = 4x10^{-7}$ m²/s, allowing some mixing of the source with the atmosphere above the asphalt.

3.0 - NUMERICAL MODEL OF TCA TRANSPORT AT MDA L

The MDA L site model is a three-dimensional representation of the hydrogeologic system, including the surface topography. The numeric modeling is limited to diffusive transport in the subsurface and reduces the complexity of the problem by neglecting water flow (infiltration), air flow (barometric pumping and wind effects), Henry's law phenomenon (solubility of the vapor contamination in the aqueous phase), and dispersivity (increased mixing due to airflow). These simplifications are suggested by the preliminary conceptual model [Rogers, 2000].

The simulations are run with FEHM, a three-dimensional finite-volume heat and mass transfer code suitable for simulating systems with complex geometries [Zyvoloski et al., 1997]. The governing equations in FEHM arise from the principles of conservation of water mass, air mass, contaminant mass, and energy. Darcy's law is assumed to be valid for the momentum of the air and water phases. The advection-dispersion equation, which governs solute transport in FEHM [Fetter, 1999; Zyvoloski et al., 1997], becomes the diffusion equation under no-flow conditions. Water flow is restricted by using van Genuchten [1980] parameters that result in no appreciable water flux. Air convection is damped by fixing a horizontally stratified temperature gradient in the model domain. This results in air velocities that are negligible relative to the diffusivity of the contaminant and allows us to better understand the process of diffusion within the mesa.

3.1 MODEL DOMAIN AND COMPUTATIONAL GRID

The model domain covers a rectangular map area with the southwest corner at State Plane (SP) coordinate (1639275,1758825) and the northeast corner at SP coordinate (1640625,1759775). The model uses SI units, and the SP data (feet) were converted to meters for the simulation. The grid is 411 m (1350 ft.) wide in the x direction (east-west) and 290 m (950 ft.) in the y direction (north-south), as shown in Figure 3.1_1. The land surface in the model domain is based on Digital Elevation Model (DEM) data, which allow accurate representation of the major features of the mesa/canyon system. The grid uses a subset from the DEM data to approximate the surface with 15-m spacing. The model surface shown in Figure 3.1_1 compares favorably to the site topography seen in Figure 2.1_1. Node spacing is 15.24 m (50 ft.) in both the x and y directions, and is variable in the z direction from a minimum spacing of 1 m (3.3 ft.) to a maximum of 15.24 m (50 ft.). The node spacing was chosen to assure a final grid that will compute in a reasonable time frame (on the order of 1 hour for a 10 year simulation) while maintaining the basic site topography. Model

geometries of the subsurface hydrogeologic units are based on interpolated data from existing boreholes and outcrop, and are of a lower resolution than surface geometry.

Figure 3.1_1 Model topography and computational grid

The model domain extends vertically from the land surface to below the water table and delineates a rectangular volume of over 43 million cubic meters. The stratigraphic configuration used for the model (Figure 3.1_2) is derived from the LANL site-wide geologic model [Vaniman et al., 1998]. Surfaces and interfaces are loaded into the LaGrit grid generation software [Trease et al., 1996; George, 1997], and a computational grid is formulated that maintains positive definite coupling coefficients at all volume interfaces. Furthermore, the stratigraphic interfaces are given higher-resolution node spacing to allow for sharp gradients in material properties. The final grid contains 25,456 nodes and 147,438 tetrahedral volume elements.

Figure 3.1_2 Model stratigraphy for cross-section B-B' (see Figure 4.3.1_2).

3.2 BOUNDARY AND INITIAL CONDITIONS

 The bottom boundary of the domain is flat and lies below the water table. The presence of the water table within the model domain allows us to estimate travel times to this important horizon. No flow of water or vapor is permitted across the bottom boundary, and its temperature is held constant at 25^oC, based on well bore measurements [Griggs, 1955]. The atmosphere at the top of the model is held at a pressure of 0.078 MPa, and the temperature is fixed to the yearly average of 10° C [LANL weather website]. The atmosphere is represented by fixing the concentration at zero in the nodes above the land surface. The vertical side boundaries of the domain are no flow with respect to both mass and heat.

Before running the contaminant transport simulations, a static air pressure field is established by running the model until pressures and temperatures reach equilibrium. This ensures that the transport simulations are not affected by transient behavior associated with establishing a static air pressure field. The steady-state initial condition has no TCA present and is meant to represent the mesa before release of contaminants.

3.3 SHAFTS AND ASPHALT

The model node spacing is too coarse to explicitly include each shaft found at MDA L. Therefore, we group the shafts into two clusters, with cluster #1 containing shafts 1 through 28 and cluster #2 containing shafts 29 through 34. Each cluster is specified using three nodes which include a volume of the model domain (3520 m^3) extending from two meters below the surface to a depth of approximately 20 meters (60 ft.). The model shafts coincide spatially with the two actual shaft clusters shown in Figure 2.2_1. TCA is introduced to the model shafts based on a simplification of the available data. The shaft nodes are assigned fixed concentrations of TCA based on the highest measured concentrations from vapor ports near the shafts. Because maximum measured concentrations vary through time, we simulate both high (11,000 ppmv) and low (3000 ppmv) fixed concentration sources in the shafts.

The asphalt cover is modeled as having been laid down as one layer at the beginning of 1985. The timing of the asphalt cover is not well documented, and our approach is meant to capture the gross system behavior. The spatial location of the asphalt is based on the site map and personal communication from Dennis Newell that 98% of MDA L is paved. In addition to the extensive asphalt covering within the boundaries of the site, substantial portions of the mesa around MDA L have been paved for parking lots, trailer foundations, and roads [Site visit, Jan. 2000]. The modeling presented below includes only the asphalt within the boundaries of MDA L. The aerial extent of the asphalt covering is identical to the site boundaries and can be seen in Figure 4.1.2_1. The asphalt restricts surface flux to the atmosphere. Future modeling may include more detailed representation of the surrounding asphalt and structures as data become available.

The time-varying site model is run in three stages to capture the main events that occurred during the emplacement of waste at MDA L. We begin all the contaminant transport simulations in 1975 by fixing TCA concentrations in shaft cluster #1. The simulation is halted at 1983 to add shaft cluster #2, then restarted and run until 1985, at which time the asphalt is added to the mesa top. The simulations is again restarted and run to 2000 and beyond. The above simplification of the sequence of events at MDA L is justified based on the limited site data and the need to minimize the complexity of the simulations.

3.4 SUMMARY OF LOGIC FLOW FOR THE BASE SIMULATION

The first simulation we present uses our initial best estimate for the in-situ effective diffusion coefficient and other important hydrogeologic parameters. We refer to this initial model as the base simulation (Table 1). We create a set of results for the base simulation to which we compare results for simulations with variations in boundary conditions (asphalt vs. no asphalt), variations in the TCA effective diffusion coefficient (D*), and variations in source concentration.

The base simulation is initiated in 1975 when shaft cluster #1 (representing shafts 1-28) is fixed to a concentration of 3000 ppmv and held at this concentration throughout the simulation. This source is allowed to diffuse until 1983 when the model is halted to add shaft cluster #2 (representing shafts 29-34). The second shaft cluster is then also fixed at 3000 ppmv for the duration of the simulation. The model is restarted and run until 1985. Finally, the asphalt cover is added, and the model is run until the year 2000. The base simulation results in approximately 865 kg of TCA in the modeled plume at the year 2000. The method for modeling the TCA source is reasonable given the sparse data on disposal operations at the site. The TCA mass generated with this method also compares favorably to the integrated mass of the measured TCA vapor plume, which yields a value in the range of 1000 kg based on data from 1999 [LANL, 1999].

4.0 - RESULTS

4.1 BASE SIMULATION RESULTS

4.1.1 TCA concentrations through the model domain

 Figure 4.1.1_1 shows the predicted TCA concentration in the year 2000 for the base simulation with a TCA diffusion coefficient of 4×10^{-6} m²/s. The figure is a two-dimensional

Figure 4.1.1¹ TCA concentration (log scale) for the base simulation contoured on a plane 18 m (60 ft.) below the mesa top.

horizontal slice of the model domain at a depth of approximately 18 m (60 ft.) below the top of the mesa. The concentrations are shown in powers of ten (log scale) to allow regions of both high and low concentrations to be visualized. The maximum concentration (red) of 3000 ppmv TCA shows the locations of the shaft clusters. The edges of the mesa are clearly visible as areas where concentrations drop quickly to near zero (darkest blue). The plume at this depth is spreading along the axis of the mesa, while TCA is being removed from the system along the mesa edges. As discussed in the conceptual model, the atmospheric boundary at the mesa edge is expected to give rise to the high concentration gradient along Canada del Buey that is evident in the figure. This figure can be compared directly with the monitoring data shown in Figure 2.2_2. The most obvious similarities are the shape of the plume and the location of the highest concentrations near the two shaft clusters. The 10 ppmv contour outline in both figures covers approximately the same areal extent.

Several differences are evident as well between the data and the simulation. The first is that the two source areas are not as pronounced in the data as in the model results. The data are not gathered at regularly spaced intervals and therefore require interpolation for the visualization. The data presented here are interpolated with a nearest neighbor scheme. Monitoring data are gathered near the two shaft clusters but not near the center of MDA L (Figure 2.1_1). Because of this, the nearest neighbor interpolation scheme yields higher concentrations between the two concentrated source regions than calculated by the diffusion model. For this reason, visual interpretation in itself cannot be used to assess the quality of the calibration. In a later section, we present a goodness-offit analysis that is used to determine the best-fit simulation.

Another difference between the data and the simulation is seen on the north boundary of the model domain where the model's no-flow boundary becomes apparent. At this boundary, TCA is unable to leave the system, leading to higher concentrations than seen in the data. The effect of the no-flow boundary is explored later in simulations by fixing this boundary at zero concentration rather than as no flow.

Figure 4.1.1_2 is a comparison of TCA concentration for the data and the base simulation contoured on a horizontal plane at a depth of 49 m (160 ft.) below the mesa top. The extent of the 10 ppmv contour of the simulation matches the data very well over most of the domain. Again the source regions differ and the effect of the no-flow northern boundary is evident in the simulation results.

4.1.2 Surface flux

Figure 4.1.2_1 shows the predicted surface flux of TCA at the interface between the ground surface and the atmosphere. We present the surface flux from the best fit calculation of Revision #1, which is explained in more detail in section 4.4. The surface flux is calculated simply from Ficks Law using the modeled concentration at the surface, the distance from the surface node to the first air node (zero concentration), and the land surface diffusion coefficient (1.e-6 m2/s). The location of the simulated asphalt is seen as the dark blue patch overlying the outline of MDA L. Flux through the asphalt is very low because the asphalt is modeled with a very low diffusion

Figure 4.1.1₂ TCA Concentration for the data versus the base simulation on a plane 49 m (160 ft.) below the mesa top.

coefficient that forces the TCA to diffuse by an alternate path to the surface. The effects of the asphalt on surface flux are clearly seen by the high fluxes around the edge of the site. Because TCA flux is controlled by concentration gradients, the model predicts that the highest loss of TCA to the atmosphere occurs along the edges of the asphalt, the shortest path from the high concentration source to the atmosphere. The wall of Canada del Buey, immediately to the north of the site, also has high concentration gradients and is important in removing TCA from the subsurface. The high surface fluxes seen along the northern boundary of the model domain are artifacts of the no-flow boundary condition and should not be interpreted as physically significant.

In the base model, 1780 kg of TCA are lost to the atmosphere during the simulation. This loss represents nearly 70% of the 2645 kg of TCA mass input during the simulation. Our surface flux results compared qualitatively to surface flux chamber measurements performed in 1993 that show high fluxes around the edge of the site boundary and on the slopes of Canada del Buey to the north [Trujillo, 1998]. Quantitatively, however, the maximum computed surface flux from the model (4.7x10⁻² kg/(m² yr)) is more than 100 times higher than the maximum values reported for

Figure 4.1.2_1 Flux of TCA to the atmosphere for the base simulation.

the sampling (668 ng/(m² min) = $3.5x10^{-4}$ kg/(m² year)). Simulations in support of Revision #1, discussed further in section 4.4, show conclusively that reductions in surface flux of 10x or more cause the modeled plume geometry to diverge considerably from the observed plume. The best-fit simulation in Revision #1 was found to have a land-surface diffusion coefficient of 1.e-6 m2/s.

We also present a back-of-the-envelope calculation based on the observed near-surface concentrations of TCA (approx. 1000 ppmv) in well 54-2089 at a depth of 4 meters and assumed land-surface $D^* = 1x10^{-6}$ m²/s from Revision #1. One thousand ppmv is equivalent to 0.001 (moles TCA)/(mole air). One m³ of air is about 34.5 moles. Thus there are 0.034 moles TCA/(m³ air). TCA contains 133 g/mole yielding 4.6 grams of TCA per cubic meter of air. Calculating the flux to the surface using these numbers gives: Surface flux = D^* x (dC/dz) = 1x10⁻⁶ m²/s x (4.6 g/m³)/ $(4 \text{ m}) = 1.15 \text{ x } 10\text{-}6 \text{ g/(m}^2\text{s}) = 0.036 \text{ kg/(m}^2 \text{ yr})$, which agrees well with the maximum model surface flux of 0.047 kg/(m^2 yr). We believe that this discrepancy between the simulated and the measured surface flux may be affected by systematic measurement error. One source of possible

error in the measurements is that 5.4 centimeters of rain fell during the sampling period, which could decrease the ability of organic vapor to diffuse to the surface. Furthermore, nearly half of the 15 samples sent out for EPA review showed TCA concentrations in excess of the linear response range of the calibration [Trujillo, 1998]. These problems were noted in the TA-54 RFI report, and for this reason the surface flux data are used only qualitatively to describe the extent of the plumes at MDA L [LANL, 2000].

4.1.3 Goodness of fit of the base simulation

To analyze the goodness of fit between the model results and the monitoring data (Second quarter, FY99), we calculate the mean (μ) and standard deviation (R) of the relative error of the model as a percentage of the data ($PE = model/data$) [Boas, 1983]. Percent error is used instead of the more traditional absolute residual (model - data) to capture the three order of magnitude variation in the data. Using this scheme, values for PE are greater than 1 when the model is higher than the data, and less than 1 when to the model is less than the data. To generate meaningful statistics, the values less than 1 are renormalized as the negative of the inverse of the value which can be expressed as a logical statement: If $PE < 1$. then $PE = -1*(1/PE)$. Thus, when the model is higher than the data, PE ranges from 1 upward, and when the model is lower than the data, PE ranges from -1 downward. The values are then shifted to $PE = PE$ - abs(PE)/ PE . This results in an ideal mean that lies at zero and allows a standard deviation about the mean to be calculated consistently for the various simulations. To avoid infinite percentages when the data are very close or equal to zero, we choose a lower cut-off of 10 ppmv and consider the model to be in agreement with the data when both values are below the lower cut-off. The reliability of the data falls as values approach 5 to 10 ppmv and this fact provides further justification for the chosen cut-off.

We also employ a conditional statement that is designed to flag potentially spurious data points or sections of the model domain that are extremely different than the data. This condition states that if the ratio, model/data, is greater than 3 or lower than 0.33, the model/data pair is flagged and removed from the calculation of the mean and standard deviation. The number of points removed is counted and reported along with the statistical properties to determine goodness of fit for the base simulation as well as other simulations presented later. This gives us a consistent approach to differentiate simulations and find the model parameters that yield the best overall fit to the greatest number of monitoring points. Future fitting should include all relevant data sets, perhaps with quality control at the level of the data collectors to remove questionable data based

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on intimate knowledge of the sampling apparatus and site-specific problems. Such quality control would help tremendously in yielding meaningful results.

Using the logic outlined above, the base simulation gives a mean of -0.068 and a standard deviation of 0.72, with 29 of the 142 data points removed from the calculation [Table 2]. The mean model result is therefore only 6.4% below the data, with one standard deviation including values from $(1.72 \times data)$ on the high side to $(0.58 \times data)$ on the low side. This is a good fit considering the simple nature of the parameters used in the simulation.

4.2 MODEL BEHAVIOR WITH VARIATION FROM THE BASE SIMULATION

We next present a series of simulations that explore variations in the base model. Results are shown in Table 2 for several scenarios.

Changes from the Base simulation	mean	Standard Deviation	Points removed
None (Base simulation)	-0.068	0.72	29
no asphalt	-0.24	0.69	31
leaky asphalt	-0.13	0.69	28
$D^* = 1 \times 10^{-6}$ m ² /s	-0.23	0.52	44
$D^* = 8x10^{-6}$ m ² /s	0.0015	0.69	44
Basalt $C = 0$.	$-0.072%$	0.71	24
N, and W, $C = 0$.	0.089	0.68	18
N., W., and B.; $C = 0$.	$-0.093%$	0.67	15

Table 2: Goodness of Fit for various simulations

B. = basalt; N. = North boundary; W. = West boundary; CT = Cerro Toledo, S. = surface

First, we simulated the site with no asphalt. The number of points lying outside the cut-off for this case is slightly larger than the base case ($N = 31$ vs. 29), however the mean of -0.24 is much lower and implies that the simulated concentrations are lower than the measured concentrations at more points. The standard deviation is nearly the same implying that both simulations spread equally about their respective means. The results for the leaky asphalt ($D^* = 4x10^{-7}$ m²/s) are shifted similarly toward the model underestimating the data. Thus, the asphalt at MDA L appears to be

best fit as a non-diffusive barrier forcing VOC's to migrate downward and laterally to reach pathways that lead to the atmosphere.

We next explore the effect of varying the porous-medium, vapor diffusion coefficient. When D^{*} is doubled from the base case to $8x10^{-6}$ m²/s, 44 points fall outside the cut-off, and the mean is positive showing that the simulated concentrations overestimate the data. When D* is quartered from the base case to $1x10^{-6}$ m²/s, 44 points again fall outside the cut-off, and the mean lies well below zero, showing that the simulated concentrations are lower than measured concentrations. Because both of these simulations have more points lying outside of the cut-off, the base simulation is seen to be a better fit to the data.

We explore the effects of the no-flow boundary and of the potential of the basalt to rapidly exchange pore gas with the atmosphere by fixing these sections of the model domain to zero concentration. When the basalt is fixed to zero concentration, there are 24 points lying outside of the cut-off, whereas when the north and west boundaries are fixed to zero, there are only 18 points removed. Combining these two simulations results in only 15 points removed and a slightly improved standard deviation.

 Figure 4.2_1 shows the data versus model regressions for all simulations except the 'no asphalt' and 'leaky asphalt'. This series of plots helps to show differences between the individual simulations in a graphical manner. In an ideal model, the regression would plot exactly on the 1:1 line, which is shown in red on Figure 4.2_1.

Figure 4.2_2 shows another way of representing the data versus model regression. The regression is now in the form $log10$ (model) versus $log10$ (data). Log(10) is used to reduce the dominance of high values that occurs when a simple model versus data regression is performed. Most importantly, there have been 10 points deemed to be spurious data removed from each of the simulations and the data. These 10 points were found to lie outside the statistical cut-off used for most of the simulations, and the individual points removed were checked by hand to ensure that they meet criterion for being spurious data (i.e. values that change radically from one quarter to the next, or values that are unrealistically low or high for their position in the plume). This figure shows the same trend as seen in Figures 4.2_1 as well as in Table 2. The different simulations are clearly separated graphically and show that the best-fit simulation has the north and west boundaries and the basalt fixed to zero concentration (NWB; standard deviation $(R) = 0.94$, intercept $(I) = 0.095$; slope $(S) = 0.88$, in complete agreement with Table 2. The base simulation yields $R = 0.844$, $I = 0.44$, and $S = 0.72$ showing that the base simulation is overestimating

Figure 4.2 1 Regression plot of simulations presented, based on GOF statistics. Points flagged by the upper and lower cut-off in the statistical logic (N) have been removed from these plots.

concentration data at the low end while underestimating data at the high end. The $D^* = 1e-6$ simulation (labeled as 1D) intercept $(I = -0.19)$ lies well to the left of the 1:1 line and has $R = 0.88$ and $S = 0.82$, while the D^{*} = 8e-6 simulation yields I = 0.79, R = 0.80, and S = 0.59.

Not shown on Figure 4.2_2 are the no-asphalt, leaky asphalt, fixed basalt, and fixed north and west boundary examples. The leaky and no asphalt cases have intercepts which plot well to the right of the 1:1 line and both have $R = 0.84$. The fixed basalt example has $R = 0.88$ and an intercept of 0.3. The fixed north and west boundary case (NW) has $R = 0.84$.

4.3 RESULTS FROM THE BEST-FIT SIMULATION

4.3.1 Basic results

 The best-fit simulation maintains the north and west boundaries and the basalt at a concentration of zero for all times. The justification for fixing the basalt to zero comes from observations that the air pressure in the basalt is in phase with and of the same magnitude as the

Figure 4.2_2 Regression plot of simulations presented, based on removing potentially spurious data.

atmospheric pressure. The north and west boundaries are set to zero concentration to minimize boundary effects caused by the size of the model domain. Figure 4.3.1_1 shows the effect of fixing the boundaries and basalt to $C=0$. on concentrations in the deep domain. The base simulation results in a plume that reaches much further into the basalts. The concentrations seen in the bestfit scenario are much closer to the data and support the idea that the basalt is readily exchanging air with the atmosphere.

For the best-fit simulation, we next show a more detailed look at the distribution of the plume, both along the axis of the mesa and perpendicular to the axis of the mesa. Figure 4.3.1_2 shows the relationship of the plume to the geologic units on a cross-section B-B' running through

Vertical slice through the model domain A-A'

Figure 4.3.1¹ The effect of fixing the basalt, and the north and west boundaries to zero concentration on the concentrations deep in the model domain.

MDA L perpendicular to the mesa top. Figure 4.3.1_3 shows the relationship of the plume to the geologic units on a cross-section C-C' running through MDA L along the axis of the mesa top. Boundary effects are seen in both cross-sections, at B' and at C. Boundary effects do not appear to be effecting the plume to the southeast, as shown by the smoothly varying plume in the directions of B and C'.

Another useful way to compare the base simulation with the best-fit simulation is to examine the amount of TCA in the system, the amount of TCA removed from the system, and the total amount of TCA added to the system as functions of time. This will provide quantitative

Figure 4.3.1 2 Vertical slice through the best-fit simulation (fixed N. and W. boundaries, and basalt C=0.) at cross-section B-B'. Contours are marked as TCA concentration in ppmv.

estimates of absolute plume growth that are difficult to see in cross-section or horizontal slices. Figure 4.3.1_4 shows the total number of gallons of TCA that are in the subsurface of the model as a function of time for the base simulation and the best-fit simulation. Clearly, the best-fit simulation reaches a steady-state plume mass equal to about three 55 gallon drums full of liquid TCA. The base simulation continues to add mass to the subsurface beyond the year 2050 and leads to a plume mass equal to about five 55 gallon drums of liquid TCA. The differences in the two simulations are due to the zero concentration north and west boundary conditions, and especially the fixed zero concentration in the basalts. These two cases represent end-members, with the bestfit simulation probably underestimating the true growth of the plume, while the base simulation

Figure 4.3.1 3 Vertical slice through the best-fit simulation (fixed N. and W. boundaries, and basalt C=0.) at cross-section C-C'. Contours are marked in TCA concentration in ppmv.

definitely overestimates plume growth because of the no-flow boundary effects. We next compare the total amount of TCA introduced from the source to the subsurface, as well as the amount of TCA that has escaped the system. Figure 4.3.1_5 shows that the amount of TCA added to the base simulation is nearly the same amount added to the best-fit simulation. The best-fit simulation, however, loses more TCA to the atmosphere (and the zero concentration basalts) and thus is able to reach a steady-state plume, as shown in Figure 4.3.1_4.

A conservative estimate for the total available source can be calculated by assuming that the shafts were filled with drums containing pure liquid TCA. There are 23 shafts having diameters

Figure 4.3.1_4 Amount of TCA in the subsurface as a function of time. Vapor-phase mass has been converted to equivalent mass in liquid gallons for comparison to waste emplacement.

Figure 4.3.1_5 Amount of TCA injected and produced as a function of time. Vapor-phase mass has been converted to equivalent mass in liquid gallons for comparison to waste emplacement.

of 3 and 4 feet, in which one barrel per layer was emplaced, seven shafts having diameters of 6 feet in which a maximum of five barrels per layer were emplaced, and four shafts having diameters of 8 feet in which six barrels per layer were emplaced. Assuming that each layer takes 4 feet and that there are 3 feet at the top used for capping the waste suggests a maximum of 14 layers of barrels

per shaft. The maximum TCA source is then found by summing the total number of barrels as: $14x(7x5 + 23x1 + 4x6) = 1148$ barrels (63,140 gallons) of TCA. As shown in Figure 4.3.1 5, the total amount injected into the subsurface during the simulations is less than 1/10 of the maximum possible source. A more realistic estimate of the available TCA source is probably on the order of 1/10 or less of the maximum computed value, suggesting that the contaminant source may only last until the year 2060 (or less). Once the contaminant source is completely volatilized, the plume will begin to dissipate significantly on a time scale of decades, as suggested by the relaxation time of catastrophic drum failure presented in a later section.

4.3.2 Current plume growth

Predicted pore-gas concentrations as a function of time are examined at several locations to determine the current rate of plume growth for the best-fit simulation. Figure 4.3.2_1 shows simulated concentration values at a depth of 49 m (160 ft.) for five locations to the southeast of shaft cluster #1. These locations are chosen to show the variation in concentration for regions with

Figure 4.3.2_1 Best-fit simulation, change in concentration with time at five locations. Distance in legend shows distance to the southeast of shaft cluster #1, depth is 49 m (160 ft.) bgs.

high, medium and low values. The figure shows that the simulated concentrations change quite slowly in the year 2000. In fact, the plume is at near steady conditions, in agreement with Figure 4.3.1_4. Yearly monitoring would adequately capture the current plume growth.

4.3.3 Future plume growth: Year 2000 to 2050

The best-fit simulation was next run from the present (year 2000) to the year 2050 to demonstrate expected plume growth during the next 50 years. Figure 4.3.3_1 shows the simulation results at year 2000 (black line), year 2020 (red line), and 2050 (white line), sliced on a horizontal plane 48.8 m (160 ft.) below the mesa top. Of particular significance is the fact that the 50 ppmv

Figure 4.3.3¹ Best-fit simulation, future plume growth. 50 ppmv contours shown for the years 2000, 2020, and 2050.

contour does not move outward from the source at an appreciable rate. This is because the plume is reaching a steady-state equilibrium with the atmospheric boundary condition, where the amount of TCA released from the source over a given time is equal to the amount lost to the atmosphere. Our estimate of plume growth is conservative with respect to the size of the future plume, because the source is maintained at current levels. A less conservative estimate might include a source that decreases in strength with time. Increases in source strength are possible if individual drums of
concentrated solvent burst suddenly (Section 4.3.4), however drum corrosion data suggest slow leaking to be a more plausible scenario [Lyon et al., 1996].

4.3.4 Simulating catastrophic drum failure with the best-fit simulation

We next present the results of a simulation designed to explore catastrophic drum failure. We assume, for a worst case scenario, that approximately 55 gallons of pure TCA liquid are introduced to the system suddenly by the failure of a drum at the bottom of a shaft. The liquid flows downward, smearing homogeneously to a depth of 30 m below the shaft bottom, or 50 m below the top of the mesa. We next assume that the TCA volatilizes rapidly to create a subsurface cloud having a concentration of 20,000 ppmv. This drum failure simulation begins in the year 2000, and uses the best-fit scenario at the year 2000 as the initial condition. Figure 4.3.4_1 shows side-byside comparisons of the best-fit simulation and the drum failure simulation in the years 2001, 2010, and 2020.

Initially, the size of the plume increases under shaft cluster #1 for the drum failure case. The 302 kg of TCA (60 gallons) that were added to the system lead to a locally elevated region of TCA concentration that extents for tens of meters laterally from the location of the failure. The extra 60 gallons injected in this simulation increases the mass of TCA in the simulation by approximately 40%, as seen in Figure 4.3.1_4. Therefore, the simulation truly represents a catastrophic event. The rate of removal of the spill from the subsurface is shown in Figure 4.3.4_2. After one year, 22% of the initial pulse from the drum failure has been vented to the atmosphere. After two years, 31% has been removed, and after five years 50% has been removed. During this time period, monitoring should be able to detect such a catastrophic occurrence, especially during the first two years following drum failure.

By the year 2010 however, monitoring will probably not be able to detect the effect from the drum failure because 70% of the original catastrophic spill is gone from the system, and the remaining 30% is beginning to spread from the source region. As seen in Figure 4.3.4_1, the plume is slightly larger directly below the source region, where the 100 ppmv contour is pulled into the Cerro Toledo. By 2020, 88% of the spill has left the system, and the plume is nearly identical to the scenario with no drum failure (Figure 4.3.4_1).

As shown in Figure 4.3.4_2, the time rate of removal of TCA from the system can be fit nicely with an exponential curve. This final result is particularly satisfying because analytical solutions to the diffusive transport equations generally follow solutions of an exponential form.

Best-fit simulation with no drum failure. Best-fit simulation with drum failure.

Contours lines are TCA **concentration labeled in ppmv.**

Figure 4.3.4_1 Comparison of no drum failure simulation with drum failure simulation. 302 kg of TCA are added as a pulse in the year 2000. Cross-section C-C' is shown in Figure 4.3.1_3.

Figure 4.3.4_2 Time dependence of TCA removal from the mesa after catastrophic drum failure.

4.4 Simulations in support of Revision #1

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We now present results from new simulations performed to address the concerns of a group of independent reviewers, organized through the ITRD Program. Although the initial goal of the site model was to determine if the first-order process of pure vapor-phase diffusion could explain the bulk of the data, the reviewers ideas for improving the fit between model and data are quite useful in showing that the conceptual model for TCA transport is valid, and that the numerical model should prove quite robust in exploring the fate of the VOC plume for various remediation options at this site.

Our ability to do extensive sensitivity analyses was limited by time/funding allotted for this revision, therefore we present only a select set of simulations that demonstrate improved model/ data correlation. The most important assumption inherent in the limited sensitivities performed for this section is that we fix the saturations in the subsurface to values within the measured range that would tend to accentuate the effects of Henry's Law and vapor-phase diffusion as a function of saturation. For example, measured saturations in Unit 2 range from 2% to 10%, however for this study we chose to use the lowest value of 2%. Unit 1v was set to 5% saturation and Unit 1g was

fixed at 10%. The Cerro Toledo and Otowi units were both fixed at the high end of measured values (40% and 35%) based on the observed data. Deeper units play little role in transport at this site and units below the Otowi were set to 2% saturation. Four additional processes were incorporated into the numerical model that considerably improved the correlation between the observed data and the model output.

The first modification to the base simulation described in section 4.1 was to add Henry's Law fractionation between TCA in the vapor phase and TCA in the porewater within the mesa. The dimensionless Henry's coefficient for 1,1,1-TCA at standard pressure and temperature is 1.46 [Jury et al., 1990], defined as the concentration in the vapor phase divided by the concentration in the liquid phase, both expressed in moles of TCA per liter of fluid. The second modification was to reduce the effective diffusion coefficient in the more saturated Otowi and Cerro Toledo units from 4.e-6 m^2/s to 4.e-7 m^2/s based on the work of Fuentes et al. (1991). Next, we explored the possibility that the source at shaft cluster #1 was higher in the past. A limited sensitivity to source strength in shaft cluster #1 found that by fixing concentration in this region to 11,000 ppmv for the first 8 years (1975-1983), we are able to more accurately capture the magnitude of the plume seen in the boreholes to the east of the site. Justification for higher source concentration during this time frame comes from site records that indicate waste was better packed after the early 1980's due to guidance from regulatory agencies [LANL, 2000]. The final adaptation was to examine the model sensitivity to reduction in the flux across the land/air interface. Justification for reducing the diffusion coefficient in the very near surface comes from boundary layer arguments found in Jury et al. (1990). Furthermore, measured surface flux is well below that predicted by the modeling. Sensitivity to this parameter showed that a reduction from 4e-6 m^2/s to 1e-6 m^2/s in the near surface gave the best fit to the data with only 8 points failing the cut-off, however a value of 2e-7 m^2 /s yielded a very good fit with 14. points failing the cut-off. The highest modeled surface flux using 1e-6 m^2 /s on the surface predicted in revision #1 is still more than one hundered times greater than the values reported in Trujillo et al. (1998). As the land-surface diffusion coefficient is decreased below 2e-7 m^2 /s, the model begins to diverge considerably from the data.

These modifications improved the overall model/data correlation without the need to fix zero concentration on the north or west boundaries nor in the basalt. The total number of points failing the 3x cut-off was reduced to 8, of which six are located beneath the canyon hinge in the angled boreholes (1015 and 1016) above the Otowi and Cerro Toledo units. This implies that we are still missing a second-order effect that tends to reduce concentrations in the area beneath the

canyon bottom. These same six points fail the cut-off criterion for all simulations that have reasonable overall fits.

To compare the previous 'best fit' result from Section 4.3.1 to the current results from revision #1, we employ a least squares regression in log_{10} space (Figure 4.4_1). The only points not included in the calculation of the correlation coefficient (r^2) are those having both model and data values below 10 ppmv, however all data points passing the cut-off are included in Figure 4.4_1, so that there are 124 points plotted for the revised simulations and 121 points plotted for the original 'best fit' simulation. The old 'best-fit' simulation yields an r^2 of 0.926, while the revision #1 best-fit simulation yields an r^2 of 0.973. Figure 4.4 1 shows that the revision #1 best fit is more clustered around the data=model line. Finally, the results of the second order analyses are

Old 'Best fit' simulation Revision #1 best fit simulation with Henrys Law, diffusion as a function of water content, higher source in cluster #1 until 1983, and surface diffusion of 1e-6 m2/s.

Figure 4.4_1 Comparison of Revision #1 best fit to the best fit of Section 4.3

presented below in Table 3. The last four rows in this table give results that are quite similar, leading us to conclude that the most important second order effects are diffusion as a function of saturation $(D[*](sat))$, Henrys Law partitioning between soil moisture and pore-gas, and increased historical source strength. $D^*(sat)$ appears to have a more positive effect on the Base Case,

however all of the best fit cases from Revision #1 include Henrys partitioning. The final case in the table is the best fit from Revision #1 and is shown in Figure 4.4_1.

Simulation	points failing the cut-off	r^2 (log) %
Base Case (BC)	25	91.3
BC with fixed zero concentration boundaries (Best Fit of the initial simulations)	11	92.6
Simulations in support of Revision #1		
$BC + Henrys$	31	93.0
$BC + higher$ early source	29	93.0
$BC + D^*(sat)$	20	91.6
$BC + D^*(sat) + higher early source$	29	91.8
$BC + Henrys + surface flux reduction$	21	92.4
$BC + Henrys + higher early source$	11	96.6
$BC + Henrys + D*(sat)$	9	97.0
$BC + Henrys + higher early sources + D*(sat)$	11	97.0
$BC + Henrys + higher early sources + D*(sat) +$ surface flux reduction	8	97.3

Table 3: Goodness of fit statistics: Examining second order effects

4.5 Future work

As LANL acquires increased understanding of the subsurface, we will continue to update the conceptual and numerical models of VOC transport at MDA L. One major task waiting to be accomplished is the creation of an average data set for use in comparison with model results. Currently we are comparing to only one quarter of data and have not had funding to incorporate all relevant quarters of data. Additionally, the model currently does not explain low measured concentrations in the upper ports of wells 1015 and 1016. Fitting this data will require a more sophisticated conceptual model that may include higher local infiltration based on topographic gradients [Stauffer et al., 2000]. We have also created a high resolution grid of the site with six embedded well bores. We plan to use the high resolution grid to explore remediation and closure options once the Technical Advisory Group has recommended an appropriate technology.

Modeling of potential remediation will require examination of the effects of fractures on local flow paths and thier potential to short circut a passive venting system.

5.0 - CONCLUSIONS

The site numerical model is calibrated using the pore-gas data gathered at MDA L. The model demonstrates that diffusive behavior captures the general characteristics of the vapor plume. The base-case diffusion coefficient of $4x10^{-6}$ m²/s fits the data better than either $1x10^{-6}$ or $8x10^{-6}$ $\rm m^2/s$. A goodness-of-fit analysis is used to determine the model that best fits the data. The best-fit simulation maintains a zero concentration boundary in the subsurface basalt unit and along the northern and western boundary of the model. Also, no liquid source is used, in agreement with field observations.

The observed site data and simulated results indicate that the vapor plume is currently at a near steady condition, both in size and in concentration. The constant flushing of the plume at the mesa sides and in the deep basalt should maintain the plume at its current size until the liquid source, which remains in buried drums, has been exhausted. Therefore, we do not expect that the vapor plume will spread any closer to White Rock or to the deep aquifer than its current location. Also, because no migration of liquid is thought to occur, we do not expect that VOCs can travel as liquids to the deep aquifer either. Estimates based on a conservative TCA source predict that the plume will start to shrink when the source is depleted, before the year 2060.

The site numerical model also shows that the asphalt cover at MDA L acts as a nondiffusive barrier that forces VOCs to migrate downward and laterally to reach pathways to the atmosphere. Little or no flux emanates from the asphalt itself, but enhanced flux from the mesa top to the atmosphere occurs around the edges of the asphalt. This predicted behavior agrees qualitatively with the surface flux measurements also gathered at the site. In the future, the site model will provide a useful tool for exploring the effects of potential corrective measures, such as venting and/or removing the asphalt cover at MDA L.

The agreement of the numerical model with the pore-gas and surface flux data indicates that the monitoring program has successfully defined both the nature and extent of the vapor plume at MDA L. The simulations show that both current and future plume growth (over the next 50 years) are quite small. These results, combined with the recent observations of slowly changing pore-gas concentrations, indicate that pore-gas monitoring could be performed less frequently than the current three-month interval. Yearly monitoring should be sufficient to capture any changes in the plume. In fact, the simulation of catastrophic drum failure predicts that the results of such an event would be apparent in the monitoring data for several years. Therefore, yearly monitoring is

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not only capable of capturing the current rate of plume growth, it should also be capable of detecting a large perturbation, such as a drum burst.

Revision #1 shows that second order effects can help to improve the match between the data and the model. Furthermore, the second order processes remove the need to fix zero concentration boundaries to achieve data/model correlation. The r^2 correlation coefficient (in log space) was improved from a value of 0.926 to 0.973 by including second order processes. The most important second order processes were diffusion as a function of saturation, inclusion of Henrys Law, and changes in source strength through time. These three processes interact in a complex manner making it difficult to determine which is the dominant driver. Surface flux reduction due to boundary layer effects had less of an impact on the data/model correlation. This revision helps to show that our conceptual model is appropriate for this site, and also suggests that the conclusions drawn from the initial report are still valid.

6.0 - ACKNOWLEDGEMENTS

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7.0 - REFERENCES

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Appendix J

Summary Report: Conceptual Model Review and Remediation Options for Los Alamos National Laboratory Technical Area 54, Material Disposal Area L

Innovative Treatment & Remediation Demonstration Program

Summary Report: Conceptual Model Review and Remediation Options for Los Alamos National Laboratory Technical Area 54, Material Disposal Area L

October 2002

Editors: Marilyn Gruebel Nirmala Khandan Bruce Thomson

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Innovative Treatment & Remediation Demonstration Program Summary Report:

Conceptual Model Review and Remediation Options for Los Alamos National Laboratory Technical Area 54, Material Disposal Area L

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Abstract

 From June 2001 through September 2002, the Innovative Technology and Remediation Demonstration (ITRD) Program conducted an evaluation of possible remediation technologies at the DOE Los Alamos National Laboratory (LANL) in New Mexico. For ten years (1975 to 1985), LANL disposed of liquid chemical wastes at Material Disposal Area L. Large amounts of the liquid waste have volatilized to create a plume of organic vapor in the subsurface. A Technical Advisory Group (TAG) was formed from the ITRD Program to assess two issues—the conceptual modeling previously performed by LANL Environmental Restoration (ER) and remediation options for the site. The goal of the project was to evaluate a corrective measure strategy proposed by LANL ER, passive venting, with respect to other corrective measures. Although the TAG did not recommend a particular technology, it concluded that, based on LANL's vapor transport modeling, soil vapor extraction is a reasonable remediation method that is likely to be successful. The TAG also provided a more general recommendation: LANL ER and the New Mexico Environment Department should continue to work together to identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at MDA L.

Acknowledgments

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October 2002

ITRD LANL TA54 MDA L Technical Advisory Group

One of the purposes of the ITRD program is to provide an independent evaluation of remediation approaches and applicable technologies on a site-specific basis. The "target audience" for ITRD reports includes both the specific site's Technical Advisory Group, which includes DOE site project managers, M&I/O scientists and engineers, regulators, public stakeholders, and technology experts, and also interested parties with similar challenges at other sites throughout the DOE complex. The intent of the program is to provide technical assistance by developing treatment and deployment information on potentially useful innovative technologies, and to make recommendations in conjunction with all of the parties to a remedial action decision. It has been demonstrated that this inclusive process can help build consensus on a site's eventual technology selection and treatment approach.

Because the ITRD process is inclusive and seeks to present information to all interested parties in a fair manner, the *Conceptual Model Review and Remediation Options for Los Alamos National Laboratory Technical Area 54, Material Disposal Area L* Summary Report includes a series of comments and responses in Appendix C between members of the Technical Advisory Group and LANL Environmental Restoration personnel involved with the project.

Several exchanges of comments and responses resulted in no substantial changes to the original Technical Advisory Group findings and recommendations from the draft May 2002 reports, but some text was modified to provide clarification in the context of continued discussion and more recent work. Inclusion of the comments and responses in Appendix C seeks to indicate that there was a diversity of opinion over some issues that was not resolved within the Technical Advisory Group report.

Marilyn Gruebel ITRD LANL Projects Technical Lead

Innovative Treatment and Remediation Demonstration (ITRD) Summary Report: Conceptual Model Review and Remediation Options for Los Alamos National Laboratory Technical Area 54, Material Disposal Area L

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FIGURES

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EXECUTIVE SUMMARY

From June 2001 through September 2002, the Innovative Technology and Remediation Demonstration (ITRD) Program conducted an evaluation of possible remediation technologies at the DOE Los Alamos National Laboratory (LANL) in New Mexico. For ten years (1975 to 1985), LANL disposed of liquid chemical wastes, including uncontained liquid waste and liquid waste contained in drums at Material Disposal Area L (MDA L). Large amounts of the liquid waste, which were disposed of in pits, impoundments, and shafts, have volatilized to create a plume of organic vapor in the subsurface. Testing indicates volatile organic compounds (VOCs) disposed of at this site include 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), trichlorotriflouroethane (FREON), and lesser amounts of chloroform, toluene, benzene, cyclohexane, methyl chloride, and other similar solvents.

A Technical Advisory Group (TAG) was formed from the ITRD Program to assess two issues—the conceptual modeling previously performed by LANL Environmental Restoration (ER) and remediation options for the site. The goal of the project was to evaluate a corrective measure strategy proposed by LANL ER, passive venting, with respect to other corrective measures. The specific objectives of the TAG were: (1) review the site characterization data and conceptual modeling for the contaminant plume at MDA L, (2) screen remediation technologies to determine those with direct applicability, and (3) identify the most appropriate technology or technologies for remediation of the contaminant plume at MDA L. The criteria used in this evaluation included technical, regulatory, and public acceptability.

Although the TAG did not recommend a particular technology, it concluded that, based on LANL's vapor transport modeling, the proposed soil vapor extraction strategy is a reasonable remediation method that is likely to be successful. However, additional data would significantly improve the understanding of the extent and movement of the subsurface vapor plume. The TAG recommended collection of additional information on vapor flux to the water table and on surface vapor flux. Because a site-specific design has not yet been selected for MDA L, the TAG was unable to evaluate cost-effectiveness, environmental safety and health risk reduction for workers, and safety and risk reduction for the public and the environment.

The TAG also provided a more general recommendation: LANL ER and the New Mexico Environment Department should continue to work together to identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at MDA L. In particular, the following regulatory requirements need to be identified to allow comparison of specific vapor extraction technologies: off-gas emission requirements, process monitoring requirements for soil vapor extraction, contaminant plume monitoring requirements, required soil vapor cleanup levels, final monitoring requirements, acceptable public and worker risk levels, and public participation requirements.

ACRONYMS

1. INTRODUCTION

Based on a request from Los Alamos National Laboratory (LANL), the Innovative Technology and Remediation Demonstration (ITRD) program established a Technical Advisory Group (TAG) to conduct a peer review for a project dealing with remediation options for Material Disposal Area L (MDA L) in Tech Area 54 at LANL. During the second half of 2001, the TAG received background materials provided by the Site Project Manager and briefings from LANL Environmental Restoration (ER) project members. The TAG held its meeting on December 12, 2001, in Pojoaque, New Mexico. At the beginning of the meeting, the TAG was introduced to the ITRD process and the desires of LANL ER and the U.S. Department of Energy (DOE) for an independent peer review. Two subteams of experts were formed to review specific issues: one to review the conceptual modeling previously performed by LANL ER and another to evaluate remediation options for the site. Based on subsequent conference calls and analysis, the TAG prepared this report.

The goal of this project is to assess a corrective measure proposed by LANL ER, passive venting, with respect to other possible corrective measures. The specific objectives are as follows:

- 1. Review the site characterization data and conceptual modeling for the contaminant plume at MDA L.
- 2. Screen remediation technologies to determine those with direct applicability to MDA L.
- 3. Recommend the most viable technology or technologies for remediation of the contaminant plume at MDA L.

The Conceptual Modeling subteam addressed Objective 1. The Remediation Options subteam addressed Objectives 2 and 3. This report combines the work of the two subteams.

Section 2 of this report provides background information on MDA L. Section 3 identifies the criteria that were used to review the conceptual modeling and the remediation options. Sections 4 and 5 summarize the findings and recommendations of the two subteams. Section 6 provides biographical information about the subteam members.

Appendices A and B contain the analyses conducted by the Conceptual Modeling and Remediation Options subteams, respectively, and the results of their evaluations. Appendix C contains comments and responses about issues that were not fully resolved in the TAG report.

2. BACKGROUND INFORMATION ON MDA L

Los Alamos National Laboratory is located in Los Alamos County in north-central New Mexico, approximately 97 km (60 mi) north-northeast of Albuquerque and 40 km (25 mi) northwest of Santa Fe (Figure 1). LANL occupies an area of about 112 km^2 (43 mi²) located directly south of the town of Los Alamos. LANL is situated on the Pajarito Plateau, which lies between the Jemez Mountains and White Rock Canyon of the Rio Grande River. The Bandelier Tuff, a thick sequence of ash-flow and air-fall pyroclastics, caps the Pajarito Plateau. Erosion of the relatively soft tuff created numerous deep canyons that separate narrow, finger-like mesas. MDA L is a 2.58-acre site on top of Mesita del Buey, within TA-54, that was historically used as a disposal site for laboratory-generated hazardous (nonradioactive) wastes. Land disposal stopped in 1985. It is presently used for RCRA-permitted hazardous waste storage and treatment and for mixed waste storage under interim status authority.

 Figure 1. Location of Los Alamos National Laboratory

2.1 LANL MDA L PLUME

From 1975 to 1985, LANL disposed of liquid chemical wastes, including uncontained liquid waste and liquid waste contained in drums, in pits, impoundments, and shafts at MDA L. Large amounts of the liquid waste have volatilized to create a plume of organic vapor in the subsurface. Testing indicates volatile organic compounds (VOCs) disposed of at this site include 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), trichlorotriflouroethane

(FREON), and lesser amounts of chloroform, toluene, benzene, cyclohexane, methyl chloride, and other similar solvents.

2.2 MDA L SITE BACKGROUND

Violent eruptions of volcanic ash from the Valles Caldera between 1.2 and 1.6 million years ago deposited tuff layers in the LANL area. Since then, the tuff has eroded to leave a system of alternating finger-shaped mesas and canyons. MDA L is located atop one such mesa, Mesita del Buey, with the waste disposed in shallow pits (4 m or 13 ft deep) and shafts (approximately 20 m or 66 ft deep). The surrounding canyons, Canada del Buey and Pajarito Canyon, lie 30 m (98 ft) below the steep-sided mesa, and the regional aquifer is located approximately 300 m (984 ft) below the disposal pits. The strata immediately below MDA L are composed of nonwelded to moderately welded rhyolitic ash-flow and ash-fall tuffs interbedded with thin pumice beds. The rhyolitic units overlie a thick basalt unit, which in turn overlies a conglomerate formation (Figure 2).

Figure 2. Generalized Cross-Section at Los Alamos National Laboratory

LANL has conducted quarterly sampling at MDA L since 1990, monitoring the pore gas in the VOC plume resulting from the disposal of liquid waste. The pore gas monitoring provided sufficient data for the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) to estimate the nature and extent of the VOC vapor plume at MDA L. Rock samples from boreholes as deep as 92 m (300 feet) indicated no condensed liquid VOC or sorption of organic compounds on the matrix. This observation was consistent with expectations based on the absence of organic carbon, low moisture content, and low specific surface area of the matrix.

As part of the RFI, LANL ER conducted a Pilot Extraction Study Project (PESP) to examine both active and passive vapor extraction with the goal of reducing the size of the VOC vapor plume. LANL gained extensive experience with vapor venting in Bandelier Tuff during the PESP and the RFI investigation at MDA L. During active vapor extraction, the vapor moved at the same velocity as the pore gas, showing no retardation. The absence of retardation was expected due to the absence of condensed liquid VOC. In the PESP, LANL measured both the *in situ* horizontal permeability as a function of depth at several boreholes and the penetration of barometric pressure variations within the Bandelier tuff and the underlying Cerros del Rio basalt. Data analysis shows that, in one stratigraphic unit, vertical gas motion is dominated by fracture flow. LANL also measured the flow in open boreholes that is induced by barometric pressure variations. Close agreement of the data with theory indicates that the flow into and out of a borehole is governed by the horizontal permeability as measured *in situ*, and is reduced by the vertical penetration of barometric pressure variations into the earth from ground surface. Sites with extensive pavement (such as in MDA L) may be slower to respond to atmospheric pressure variations, thereby enhancing the vapor flow in a borehole that is open to the atmosphere.

3. PEER REVIEW CRITERIA

The two subteams developed criteria for reviewing the LANL MDA L conceptual model and the remediation options. Section 3.1 lists the criteria for the conceptual model review; Section 3.2 provides the criteria for the remediation options evaluation.

3.1 CRITERIA FOR CONCEPTUAL MODELING REVIEW

The TAG assessed LANL ER's conceptual modeling based on the following review criteria:

- 1. Has the Site Project Team adequately reviewed the pertinent, current technical literature in this area?
- 2. Are the conclusions cited in their reports supported by the work performed?
- 3. Have the practical limits of detection been determined in terms of minimum and maximum depth, plume size, and type of contaminant being detected?
- 4. Do site conditions offer any unique opportunities or constraints in terms of characterization or modeling?
- 5. Has the Site Project Team collected sufficient data to respond to regulatory, stakeholder, and risk evaluations?
- 6. Have the technical uncertainties associated with the model been adequately identified and addressed?
- 7. Does the model adequately represent the field data?

3.2 CRITERIA FOR REMEDIATION OPTIONS ANALYSIS

The TAG assessed the options for remediation at the site based on the following review criteria:

- 1. Has the Site Project Team adequately reviewed the pertinent, current technical literature in this area?
- 2. Is the Site Project Team's proposal for remediation a logical extension of existing technology?
- 3. Do site conditions offer any unique opportunities or constraints in terms of characterization or remediation?
- 4. Have the technical uncertainties associated with the application of this technology been adequately identified and addressed?
- 5. Is there a clear path shown towards measuring the success of the technology?
- 6. Does this technology show a clear benefit in terms of (a) cost effectiveness, (b) environmental safety and health risk reduction for workers, and (c) safety and risk reduction for the public and the environment?
- 7. Has the Site Project Team collected sufficient data to respond to regulatory, stakeholder, and risk evaluations?

8. Based on the overall assessment of the site proposal, should it be initiated? If not, what remediation technology should be used and why?

4. FINDINGS OF THE PEER REVIEW SUBTEAMS

Sections 4.1 (Conceptual Modeling) and 4.2 (Remediation Options) contain findings of the Peer Review Subteams. Background information for the findings is described in more detail in Appendix A (Overview of the Conceptual Model) and Appendix B (Summary of Remediation Technologies). Some of the findings in Section 4.1 generated considerable discussion between LANL ER and the Conceptual Modeling Subteam. Several exchanges of comments and responses have resulted in no substantial changes to the original TAG findings from the draft May 2002 reports, but some text has been modified to provide clarification of the findings in the context of the continued discussion and more recent work. The comments and responses are included in this report as Appendix C to indicate that there was a diversity of opinion that was not resolved within the TAG report.

4.1 CONCEPTUAL MODELING

The conceptual model of the site is by nature a historically inclusive snapshot in time that must evolve as additional accurate information is added to the current site data set. The information that improves the conceptual model is often additional measurements but can also include application of more accurate theoretical behavior of the modeled system or inclusion of results from numerical simulations using the mathematical description of the system dynamics in the numerical model. The conceptual model is the most important construct for characterizing and remediating a contaminated waste site and should be as accurate as possible; however, the development of the conceptual model cannot supercede the primary goal of remediating of the site.

The TAG recognizes that, ultimately, the conceptual model must provide the framework for making correct decisions for the next step on the path to site remediation. If the correct decisions can be made from a scientific basis at a particular time, the conceptual model has served its purpose even though the model may include elements that are not precisely descriptive of the physical behavior of the system. It is important to maintain the perspective of improving the accuracy of the model in the context of cleaning up the site.

The TAG has reviewed the work of the LANL ER project team and agreed with their general conclusions on choices for site remediation and the general conceptual model used to select those choices. The TAG has also identified some areas and made some recommendations for potentially improving the conceptual model of the site.

- 1. In most areas, the Site Project Team has adequately reviewed the pertinent, current technical literature. The areas lacking are:
	- a. Surface flux including modeling of the boundary layer. The model for the boundary layer is very simplistic and will influence the surface flux of TCA and the plume size. This topic is discussed in more detail as Recommendation 2 in Section 5.1.
	- b. Vapor-solid sorption. Vapor-solid sorption can be important for TCE as experimentally investigated by Ong and Lion (1991) for Bandelier tuff. However, their data indicate that it will only be significant when the moisture content is less than about 1-2%. The minimum *in situ* moisture content is about 2%, with the majority of the units having moisture contents of 10% or greater (Stauffer et al,

2000). Therefore, the TAG does not believe it will play a significant role in this case. However, we recommend that the phenomenon at least be acknowledged and discussed rather than ignored.

- c. *In situ* degradation. The TAG does not recall any discussion of *in situ* degradation of the plume. Of course, neglecting degradation would be conservative.
- d. Gas diffusion model. The gas diffusion model is based on Fick's law. For low permeability media, it is well known that Fick's law is inadequate due to the influence of gas-solid interactions and coupling between diffusive and advective effects (Webb, 1998). It is recommended that the permeability of the various units be listed. If the values are greater than 10^{-13} m² (1.1 x 10^{-12} ft²), Fick's law is adequate. If the permeabilities are lower than 10^{-13} m² (1.1 x 10^{-12} ft²), an alternative model such as the Dusty Gas Model should be employed (Webb and Pruess, 2002). The site project team subsequently reviewed the permeability of the sediments and found that the majority of the sediments were greater than 10^{-13} m² (1.1 x 10^{-12} ft²).
- e. Diffusion coefficient. The diffusion coefficient used in the conceptual model is for gas only; liquid diffusion is neglected. As discussed in Jury et al., 1984a, the effective diffusion coefficient may be influenced by the liquid diffusion value even at low values of moisture content, depending on the value of Henry's constant. The effective diffusion coefficient should be evaluated.
- 2. The conclusions cited in Site Project Team reports are adequately supported by the work performed.
- 3. In some instances, determinations of the practical limits of detection are insufficient. While the best-fit simulation shows that the vapor plume is unlikely to reach the water table, the vertical extent of the plume as illustrated by field data is not presented in the report. Two issues are of concern:
	- The New Mexico Environment Department (NMED), the U.S. Environmental Protection Agency (EPA) Region 6, and the public may require site-specific data before they accept that the vapor plume has not and will not reach the water table; and
	- While the imposition of a zero concentration condition appears justified, its exact location as determined by field data or a comparison of modeling results to field data is not known.

Installation of deeper wells capable of providing concentration data at the bottom of the plume is recommended. Data from such wells will directly address the first concern and can also be used to refine the modeling of transport processes at the bottom of the plume.

At the time the report was written, no core sample measurements were available for the Cerros del Rio Basalts (Figure 2). Therefore, the numerical model was formulated using a surrogate porosity and a modeled saturation value. Further refinements to the numerical simulations can be realized if property measurements can be made on the basalts via the deep wells.

4. Site conditions offer some unique features in terms of characterization and modeling. Some of the units are known to have fractures, yet the conceptual model developed by Stauffer et al., 2000, is a porous media approach without fractures. Because many of the

fractures are vertical, they would enhance the vertical migration of the plume and could conceivably increase the calculated migration of the plume.

- 5. LANL ER has collected a considerable amount of site characterization data, much of it directly related to constructing the site conceptual model, responding to anticipated regulatory and stakeholder concerns, and understanding risks associated with site remediation. However, LANL ER should be aware that, in at least a couple of situations, the data may be considered insufficient by regulators and stakeholders. For example, the depth of the plume is not adequately defined, and the predicted surface flux of the contaminants seems inconsistent with the data.
- 6. Many of the technical uncertainties associated with the model have been adequately identified and addressed. The diffusion model was selected for this site after analysis of the available site characterization data and in consideration of the magnitude of the plume, the objectives of the model (determine a remediation strategy and predict gross behavior of the plume), and the complexity of the geology. In general the model seems to predict the current characterization data set. There are, however, some technical uncertainties that need to be addressed, such as the boundary layer modeling and the effect of fractures on plume growth or dissipation, and contaminant transport.

The conceptual model described in (Stauffer et al., 2000) does not provide sufficient background information regarding

a. Surface flux predictions. The surface flux predictions by the model are based on two assumptions that need to be further justified.

The first one is the thickness of the boundary layer. The model assumes this to be 1 m (39 in) thick: What is the basis for this assumption?

The second one is the overall mass transfer coefficient or diffusion coefficient used in this calculation.

- b. Treatment of fractures. It has been reported that some of the geological units at the MDA L are vertically fractured, which can enhance the release of the vapors. The manner in which fractures are included in the conceptual model needs to be described in more detail or evaluated further.
- 7. The model seems to give reasonable answers compared to the field data. However, some of the details are insufficiently explained, and some additional data or modeling studies are needed. Appendices to the Stauffer report (Stauffer et al., 2000) of the available concentration data would be useful. The current model can be used to select and implement some remediation field tests and develop general strategies for contaminant control and remediation. The current model can also be used to focus the next set of characterization data needs and identify areas for more refined numerical modeling.

4.2 REMEDIATION OPTIONS

1. The subteam believes the Site Project Team has adequately reviewed the pertinent, current technical literature in the area. Given the conceptual model based on the characterization data to date, they have reviewed the available remedial alternatives and have focused on strategies that are likely to be successful. These are generally technologies based on either active or passive soil vapor extraction (SVE).

- 2. The Site Project Team's proposal for remediation is a logical extension of existing technology. However, specific aspects of the technology and the configuration of the cleanup have not been determined. There are techniques within SVE that could be used, but these are yet to be determined.
- 3. Site conditions at MDA L offer unique opportunities in terms of characterization and remediation. Site characterization data indicate that air is found in the formation below the mesa and flows upward. This effect produces a zero-boundary condition for contaminant concentrations. LANL has already used these characteristics in their modeling, but they may also be able to capitalize on this condition for cleanup opportunities.
- 4. LANL ER has addressed some of the technical uncertainties associated with the application of this technology. Soil vapor extraction is commercially available and appropriate for this application, and it is the presumptive cleanup remedy of the EPA. However, the Site Project Team has not yet provided a formal proposal for the technology design. Soil vapor extraction has been tried in various modes and it will work, but the exact configuration for MDA L has not been determined. Some of the specific aspects of SVE that must be considered are
	- Passive/active venting
	- Off-gas treatment
	- Surface flux
	- Type of mass removal to be achieved
	- Location (impact on site operations)
	- Risk assessment
	- Specific design parameters
- 5. The subteam believes that LANL ER will be unable to measure the success of the technology until the regulator and the site reach consensus on clear performance metrics. LANL ER undertook this project even though quarterly monitoring and sampling indicate the vapor plume at MDA L poses no current threat to either human health or the environment. LANL ER and the NMED need to work together to identify the regulatory requirements that will guide the process. One possibility is a risk-based corrective action (RBCA) study showing the remaining contaminant sources are below some threshold after the bulk of the contaminants have been removed.
- 6. The technology was examined to evaluate benefits in terms of (a) cost effectiveness and (b) environmental safety and health risk reduction for workers and safety and risk reduction for the public and the environment:
	- The technology screening performed by this subteam (see Appendix A) indicates that SVE is generally a cost-effective cleanup remedy. However, for application to MDA L, the overall cost will depend on the technology design, which has not yet been determined for MDA L.
- Soil vapor extraction has been used safely and successfully in many different applications. However, for application to MDA L, the overall safety and risk will depend on the technology design. Some general comparisons to alternatives may provide insight into general risks, such as comparisons to excavating the source and comparisons between active and passive systems with respect to disruptions in site operations. Risk and safety may also depend on choices of system components, such as the strategy for off-gas treatment.
- 7. The Site Project Team has collected sufficient data to adequately support most of its conceptual modeling assumptions and its proposal for remediation. However, additional data collection for a few parameters could strengthen the site's case for using SVE. For example, additional data could be collected for
	- Flux to the water table (also an NMED concern)
	- Surface flux to the atmosphere
- 8. Based on site characterization data and modeling for the site, the subteam believes the Site Project Team proposal to use SVE at MDA L should be initiated. However, the subteam can give only a qualified endorsement until it has an opportunity to examine the site-specific design for MDA L.

5. RECOMMENDATIONS

Sections 5.1 (Conceptual Modeling) and 5.2 (Remediation Options) contain the recommendations of the Peer Review Subteams. Some of the recommendations in Section 5.1 generated considerable discussion between LANL ER and the Conceptual Modeling Subteam. Several exchanges of comments and responses have resulted in no substantial changes to the original TAG recommendations from the draft May 2002 reports, but some text has been modified to provide clarification of the recommendations in the context of the continued discussion and more recent work. The comments and responses are included in this report as Appendix C to indicate that there was a diversity of opinion that was not resolved within the TAG report.

5.1 CONCEPTUAL MODELING

Based on a careful assessment of the information presented to the TAG and the findings developed in response to the review criteria, the Peer Review Subteam provides the following recommendations:

1. Surface emission measurements. The TAG has agreed that the quarterly monitoring at TA 54 MDA L can be relaxed. However, the TAG recommends that additional surface flux measurements be made, preferably by perforating the impermeable cap at some locations. The rationale for this recommendation is as follows:

It is being proposed by the Remediation Sub-committee of TAG to use the conceptual model in evaluating and designing remediation alternatives. Before the model can be used for this purpose, it needs to be further validated. Previous validations have compared measured subsurface vapor phase concentrations and surface emissions against model predictions.

While the agreement between measured and predicted subsurface concentrations were reasonable, there were notable differences between the corresponding surface fluxes. By perforating the cap, two "data points" can be obtained to further calibrate and/or validate the conceptual model: sampling of the gas phase concentration as well as measurement of the flux.

In response to the original TAG report on the conceptual model (Appendix A to this report), Don Neeper of LANL suggested that $CO₂$ measurements could be correlated to VOC emissions due to barometric pumping. This is a reasonable approach; however, the correlation between $CO₂$ emissions and VOC emissions has to be first demonstrated.

A further benefit of surface flux measurements will be in risk evaluation that is being recommended by the two subteams of the TAG.

The parameters used in the model to predict the surface emissions (viz. the boundary layer thickness and the diffusion coefficient) need to be re-evaluated (see Recommendation 2 below).

2. Surface flux. The size of the contaminant plume, including whether or not the plume continues to grow or shrink, is based on a balance between the estimated source of the
contaminants and the loss to the atmosphere, or the surface flux. Therefore, the surface flux is a significant factor in the long-term behavior of the plume.

The modeled surface flux is based on a porous media diffusion coefficient and a 1-m (39 in) transition to a zero concentration in the atmosphere, or boundary layer. This approach is extremely simplified. A more accurate representation of the boundary layer thickness is suggested by Jury et al. (1984b) to be typically 0.5 cm (0.2 in), although values can range up to 1 m (39 in) for very low wind speeds and stable conditions (Webb et al., 1999). The diffusion coefficient should also be that for open conditions, not for a porous media, which would tend to increase flux to the atmosphere.

Surface flux measurements that were made at x discrete points showed much lower flux (up to 300 times less) than indicated by the model. The discrepancy raises concern with the accuracy of the model. However, these measurements were not made according to standard methods for quantitative flux measurement and were made at a limited number of locations. Given the natural and anthropogenic heterogeneities of the surface and shallow subsurface, it is likely that these small numbers of flux measurements are not representative of an average flux over the waste site area. They are therefore of limited value in model validation. Further model runs were completed using reduced surface flux values (similar to those measured), which provided dramatically different plume shape and extent results that conflicted with subsurface gas concentration measurements. Given the larger data set and higher accuracy of the subsurface concentration measurements, it is important that the model faithfully simulate these data. Nevertheless, since the growth of the plume is significantly affected by the value of surface flux, efforts should be made to devise a strategy for quantifying this parameter.

To more closely represent the dynamics of the surface/subsurface processes, it is recommended that the model be modified in the future to correct boundary behavior and that additional quantitative flux measurements eventually be made to reconcile and verify the model. These recommendations would be appropriately implemented to support work on the selection of remedial alternatives.

3. Presence of Fractures. Some of the units are known to have fractures, yet the conceptual model developed by Stauffer et al., 2000, is a porous media approach without fractures. This approach may be justified if the fractures are filled with porous media. However, if the fractures are of a higher permeability than the bulk formation and because many of the fractures are vertical, they could enhance downward vertical migration of the plume or increase flux of the contaminant out through the surface.

Apparently vertical fractures are mainly found in the welded section of TSH Unit 2 and much less commonly below; therefore these fractures may not impose a significant additional plume migration risk. However, it is recommended that the effect of fractures on plume migration and potential remedial strategies be investigated when evaluating the selection of remedial alternatives.

4. Alternative Methods for Gas Sampling and Analysis at MDA L Site. The TAG recommends continuing to acquire more concentration data at the site using inexpensive but accurate field screening or simple laboratory techniques to support the selection of remedial alternatives as well as to evaluate the effectiveness of the performance of the remediation technique.

To obtain a more accurate conceptual model of the subsurface contamination at the MDA L site, more soil gas measurements are required. Current protocol calls for analysis using Summa Canister collection and contract lab analysis by EPA protocol. This procedure is expensive and not well suited for obtaining a better conceptual understanding of the gas plume at the site. To understand the dynamic behavior that is characteristic of subsurface contaminant gas phase plumes, many inexpensive measurements would be most useful. There are a variety of field and local laboratory (i.e., on site or mobile lab) gas sampling and analysis methods available for deployment. These methods range from standard laboratory methods brought to the field (e.g., gas chromatography/mass spectrometry) to simple detectors sensitive primarily, but not exclusively, to the species of interest (e.g., photoionization detectors, portable acoustic wave sensors, chemiresistors, etc.). Any of these methods may be appropriate depending on the analytes in the gas stream, the detection levels required, the frequency of measurement, etc.

LANL site personnel have been using a method that falls between these types of sensors (Innova Model 1312 infrared photoacoustic spectrometer). This instrument is species selective based on the infrared absorption spectrum of the target analyte(s). The instrument is capable of simultaneously and accurately measuring concentrations of 5 different species so long as their infrared spectra have no significant overlaps. The instrument is capable of detecting gas concentrations of the species of interest (volatile chlorinated organic compounds) to approximately 1 ppmv and can cover a dynamic range that approaches the vapor pressure limits of many of the compounds. It is also capable of semi-continuous monitoring (every 1 to 4 minutes) and unattended field deployment. Comparisons of the instrument with the baseline gas chromatography (GC) methods show that the Model 1312 is at least as stable, repeatable, and accurate as GC. One significant issue that may affect the selection of this technology for gas sampling and analysis at a site is the error introduced by analytes with interfering infrared (IR) spectra. Even low concentrations of some compounds with rich IR absorption spectra may affect accurate analyses of species with nearby IR peaks. Some of the freon compounds (Freon 11, 12, and 113) have particularly rich IR spectra and can interfere with measurements of PCE, TCE, and TCA. Freons have been detected at MDA L, and the site has performed measurements comparing results from the B&K Model 1312 and baseline Summa canister gas chromatography. The comparisons show a strong correlation between the two analytical methods for the contaminants of concern (TCA and TCE). The B&K model 1312 is therefore a satisfactory technique for tracking plume behavior.

Other gas analysis technologies may also be suitable for the characterization and monitoring needs of the site and should be evaluated on the basis of the data objectives of the owners, regulators, and other stakeholders of the site.

Some percentage of split samples should be sent for analysis by the baseline method to ensure the analysis performed using an alternative technique to the baseline protocol is an adequate representation. Often, the ratio of alternative method to baseline analyses is 90:10. For the MDA L, the ratio of alternative method samples to baseline may be more or less depending on the performance of the method, the characteristics of the gas sample, the number of samples needed and other issues decided by a consensus of the site and regulators.

5.2 REMEDIATION OPTIONS

Based on a careful assessment of the information presented to the TAG and the findings developed in response to the review criteria, the Peer Review Subteam provides the following eight recommendations. The supporting details for the recommendations are included in Appendix B.

Site Hydrogeologic Conditions and Contaminant Distribution

- 1. Identify a small number of extraction well configurations, perhaps three alternatives each for an active system and three for an atmospheric pumping system, and use the model to evaluate contaminant removal from the subsurface environment for each of these alternatives.
- 2. Due to the large body of knowledge that has already been collected (as discussed in Appendix B), additional pump testing of vapor extraction wells is not needed at this site.

Characterization of the Source Term

- 3. Perform a corrective measures study to determine the feasibility of removing the waste materials from the disposal shafts or stabilize them in place.
- 4. The remedial system design should include consideration of future drum burst events and provide assurance that contaminant release does not pose an excessive risk to human health and the environment.

Nature of Site Operational Activities

- 5. Technical Area (TA)-54 site managers should be contacted and asked to identify facility operations that might be impacted by an SVE system. A map of the site should be prepared which delineates structures or areas that cannot have wells, piping or SVE equipment located near them. Areas where site personnel spend large amounts time should also be identified so that the system design can minimize work place hazards.
- 6. Once a preferred SVE option has been determined, TA-54 site managers should review the plan and the construction phasing to be sure that its impact on site operations will be acceptable. As construction progresses, this coordination should be maintained.

Regulatory Constraints

7. LANL and NMED should continue to work together and identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at TA-54. In particular, the following information must be identified: off-gas emission requirements, SVE process monitoring requirements, contaminant plume monitoring requirements, required soil vapor cleanup levels, final monitoring requirements, acceptable public and work risk levels, and public participation requirements.

Cost

8. LANL should conduct a design study that includes variations of the SVE remediation process—specifically, the use of active, passive, and combinations of the two vapor

extraction methods along with active or passive soil gas flushing (clean air or other). Each design should incorporate all of the components needed to comply with regulatory requirements including off-gas emission treatment as needed. The length of time needed to achieve site remediation or achieve the consensus environmental goals (e.g., limit flux to the receptors) should be determined for each. The annualized and total costs of each alternative and the benefit with respect to the goals should be determined and used in selection of a final remediation process.

6. BIOGRAPHICAL SUMMARIES OF THE MEMBERS OF THE PEER REVIEW SUBTEAMS

N. Nirmala Khandan (Subteam Chair) [NMSU] - N. Nirmala Khandan, Ph.D., P.E., is a Professor of Environmental Engineering at the New Mexico State University in Las Cruces, NM. He received his undergraduate degree in mechanical engineering from the University of Ceylon, Sri Lanka and his graduate degrees (M.S. & Ph.D.) in environmental engineering from Drexel University, Philadelphia, PA. Dr. Khandan has had over ten years of turnkey engineering experience in system designs, project implementation, R&D services in water supply and treatment and has had consulting appointments with over twenty-five U.S. industrial, chemical municipal, biotechnical, environmental, and consulting companies. He has also served internationally – training, presenting papers, giving workshop/short-course presentations, and demonstrating pilot research projects throughout the world. Dr. Khandan has co-written over fifty journal articles and twenty-six-conference proceedings. Amongst the many awards and recognitions that he has received are the following: Founders Award for the Outstanding Research Paper published in Water Research (1991), Instructor, General Motors Distance Education Program (1998) and El Paso Natural Gas Foundation Faculty Achievement Award (1996); and Bromilow Award for Outstanding Research (2001) at New Mexico State University.

John Kupar [TechCon] - John M. Kupar (B.S., Geology and Economics, Syracuse University, June 1979) has over 17 years of experience in international and domestic environmental project implementation with emphasis on technical management and project development. Several of the technologies he has successfully deployed include; *in situ* and *ex situ* chemical fixation, thermal desorption, groundwater treatment, wetlands treatment, and dredging. His current interests include the characterization and remediation of contaminated sediments. Since 2000, he has served as a staff member of Argonne National Laboratory's Environmental Assessment Division where he supports the Department of Energy's TechCon program. In this role, he provides technical assistance to DOE environmental restoration project teams in the identification and selection of environmental technologies. Mr. Kupar is a registered Professional Geologist in the Commonwealth of Pennsylvania.

Joe Rossabi [SRTC] - Joe Rossabi is a fellow engineer in the Environmental Sciences and Technology Division of the Savannah River Technology Center where he performs applied research and development of environmental characterization and remediation technologies and strategies. His research involves field-testing and implementation of cone penetrometerbased characterization and remediation methods, multiphase flow processes including dense non-aqueous phase liquid (DNAPL) fate and transport, and passive methods for characterization and remediation of subsurface contaminants. Dr. Rossabi was part of a team that deployed a cone penetrometer-based spectral gamma probe to characterize the Cesium plume at the R Reactor Seepage Basin site at SRS. He was also the principal investigator of Department of Energy projects that successfully developed innovative DNAPL characterization methods and implemented barometric pumping for subsurface characterization and remediation of volatile contaminants. Rossabi has numerous publications on subsurface characterization and remediation and has served on national

committees (DOE and EPA) to review characterization and sensing technologies. Before coming to the Savannah River Technology Center eleven years ago, Rossabi performed research and development in the areas of laser communications and atmospheric transmission and spectroscopy for Bell Laboratories in Holmdel, NJ, and a defense contractor in McLean, VA. He has a Ph.D. in Environmental Engineering from Clemson University, an MS in Environmental Engineering from the University of North Carolina at Chapel Hill, and MS and BA degrees in Physics from the State University of New York at Binghamton.

Malcolm Siegel [SNL] - Dr. Malcolm D. Siegel (BA, Chemistry, Columbia University; MA, Ph.D., Geological Sciences, Harvard University) is the Technical Coordinator of the Innovative Treatment Remediation Demonstration program and a Principal Member of the Technical Staff at Sandia National Laboratories. He has had over 21 years of research and project management experience involving geochemical laboratory studies, reactive transport simulations, and performance assessment calculations in support of the Waste Isolation Pilot Plant program, the proposed Yucca Mountain high level nuclear waste repository, design of reactive treatment zones and studies of natural attenuation. He is the author of over 45 scientific articles, chapters and peer-reviewed reports.

Mike Smith [TechLaw, Inc.] - As an environmental engineer and researcher, Mr. Smith possesses 21 years of experience in the analysis and modeling of transport processes, the assessment of human health and environmental risks, and the collection and analysis of worker health and safety information. For the past eleven years, Mr. Smith has performed analyses related to human health and ecological risk assessments ranging from the dispersion and deposition of constituents emitted from open burn/open detonation processes to the impact of hazardous constituents on indoor air quality. He has reviewed a variety of multimedia/multi-pathway risk analyses submitted to EPA under RCRA and CERCLA. He has conducted permit reviews and analyses and presented training information in support of EPA's RCRA program. Current areas of concentration include dispersion modeling of air emissions and the assessment of human health and environmental risks for hazardous waste combustion units.

Bruce Thomson (Subteam Chair) [UNM] - Bruce Thomson is a Professor in the Department of Civil Engineering at the University of New Mexico. He has a B.S. degree in Civil Engineering from the University of California at Davis, and M.S. and Ph.D. degrees in Environmental Science and Engineering from Rice University, Houston, TX. He is a registered Professional Engineer in the State of New Mexico. His research interests focus on the chemical behavior and treatment of radioactive and inorganic water contaminants in both surface and ground water systems. He has worked onremediation of contamination from uranium mining and milling activities, biological transformation of arsenic and other metals, development of treatment technologies for arsenic removal, evaluation of point-of-use treatment systems, and estimation of the costs of treatment. He was a member of the National Research Council's Committee on Mixed Waste and is currently a member of the NM Mining Commission, the City of Albuquerque Technical Standards Comm

Steve Webb [SNL] - Stephen W. Webb is from Sandia National Laboratories in Albuquerque, New Mexico. He is a Principal Member of the Technical Staff in the Environmental Technology Department and received his Ph.D. in Mechanical Engineering from Lehigh University where he specialized in heat transfer and fluid flow modeling and analysis. He has performed fluid flow and heat transfer research in such varied fields as

nuclear reactor accident analysis, gas flow in porous media, the effect of weather boundary conditions on transport in soil, explosive chemical movement in soil, natural convection in underground caverns and repositories, and plume dispersion in the atmosphere. He has over 75 publications including journal articles and conference proceedings.

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APPENDIX A: OVERVIEW OF THE CONCEPTUAL MODEL

OF SUBSURFACE VAPOR-PHASE PLUMES AT TA54- MDA L AT LANL

ITRD Conceptual Modeling Subteam Dr. Nirmala Khandan, Chair

Executive Summary

Evaluation of the alternatives for restoration of the Material Disposal Area L, (MDA- L) in Technical Area 54 (TA54) is an Innovative Treatment and Remediation Demonstration (ITRD) project at Los Alamos National laboratory (LANL). The major concern at this site has been identified to be organic solvent vapors in the subsurface resulting from disposal of mixed liquid wastes during 1975 -1985. Under LANL's Environmental Restoration Project, extensive sampling and pilot extraction studies have been undertaken at this site to-date; a conceptual model to characterize the subsurface plume has also been developed.

In mid-2001, a Technical Advisory Group (TAG) was formed by ITRD to provide technical assistance in the selection of remedial actions for MDA L. The specific goals of the TAG are to evaluate the site and assess passive and active venting versus other applicable technologies to remediate the site. The first meeting of TAG was held in Dec 2001. The objectives of this meeting were to provide background information on the project to TAG members; to review the conceptual model; and to identify innovative technologies that could be adapted at MDA L.

This report is a follow-up to the TAG's first meeting, documenting the discussions relating to the conceptual model developed by LANL's Environmental Restoration Project Group. Included in this report are: the background to the contamination at MDA- L TA 54 as it relates to the conceptual model; the reasons for developing the model; the simplifying assumptions behind the model; the modeling approach; model simulation results; and conclusions and suggestions.

Background

The MDA L facility has been receiving hazardous and radioactive liquid wastes from the late 1950s until its closure in 1986. Up to 1975, the materials were disposed of in bulk liquid form in open pits, allowing high vapor pressure constituents to evaporate into the atmosphere. From 1975 onwards, organic liquids were disposed of in a series of 20-m (65-ft) deep shafts, ranging in diameters from 1 m to 2 m (3 ft to 6 ft). The bottom of these shafts were ~300 m (~980 ft) above the regional aquifer. These shafts received organic liquids in free liquid form as well as in containerized form. Upon closure, most of the 2.5 acres of the site were covered with asphalt.

Based on the analysis of core samples and pore gases at the site, the following conclusions have been made:

− 34 disposal shafts are the Potential Release Sites (PRS) at MDA L;

- − free organic liquid is not found below the shafts;
- sorbed organics are not found below the shafts;
- − pore gases are contaminated with volatile organic compounds (VOCs);
- the VOC vapor plume has migrated over 100 m (330 ft) laterally from the shafts;
- − the total mass of VOCs in the plume is approximately 1000 kg (2200 lbs);
- − the primary constituents of the plume are 1,1,1-trichloroethane (75%); trichloroethene (12.5%); and Freon (11%).

The conceptual model was built upon the above conclusions; hence the validity of the conceptual model is highly dependent upon these conclusions.

Reasons for Modeling

A mathematical model of MDA L at TA 54 may be a valuable tool for one or more of the following functions:

- to analyze the current state of the plume
- to evaluate sensitivity of characteristics of the medium and/or contaminants
- to predict the state of the plume in the future
- to predict surface fluxes and emissions
- to optimize sampling and monitoring
- to evaluate impacts of catastrophic releases
- to evaluate the effectiveness of alternate remediation technologies

Mathematical models are approximations of the real world. They are constructed based on (1) simplifying assumptions; (2) understanding of the processes involved; and (3) the characteristics of the medium and the contaminants. It is, therefore, prudent to make appropriate and valid assumptions in developing the model. It is also necessary to calibrate and validate the model using past data from the site to justify the assumptions, so that the model can be used confidently for predictive purposes.

Assumptions in Modeling

Based on historic data as well as pore gas and core sampling data obtained at site, the following simplifying assumptions have been made in developing the conceptual model for MDA L at TA 54:

- Infiltration is negligible and the subsurface is therefore unsaturated.
- − Since 75% of the plume averaged over 140 sampling locations is 1,1,1-trichloroethane (TCA), it is chosen as the target contaminant.
- − Since the maximum observed concentration of TCA (~ 3,400 ppmv) is almost two orders of magnitude less than its vapor pressure $(\sim 150,000$ ppmv), and 170 core samples from

18 boreholes did not reveal any liquid form, no free liquid form of VOCs is present anywhere within the model boundaries.

- − Barometric pumping is included in the model as enhanced diffusion, with no air flow through the bulk soil medium.
- − Since no air flows through the bulk soil medium, transport of the VOC vapors within the model boundaries is by diffusion only and not by advection.
- − The contaminants are nonreactive (as demonstrated in a study at UNM).

Modeling Approach

The conceptual model for MDA L at TA 54 is a 3-D finite element formulation based on conservation of mass. Following the assumptions listed above, the general advectivediffusive transport equations reduce to a diffusion equation in this case. The model requires inputs for soil and contaminant characteristics; contaminant sources; and numerical discretization and appropriate boundary conditions.

Soil and contaminant characteristics:

The subsurface at the site has been simplified into seven stratigraphic units. The primary hydrogeologic properties relevant to the conceptual model are the porosity and the saturation; the transport property is the diffusion coefficient. The values used in the model are tabulated below.

The shafts, asphalt cover, and the uncovered surfaces are modeled with the following base characteristics:

The porosity and saturation values for the Puye Formation are estimated. Corresponding values for the basalt are from similar soils studied elsewhere. All other hydrogeologic data had been measured at site from core samples. Diffusion coefficient for TCA vapor measured on core samples of Bandelier Tuff at TA 54 is used for all the units. A value for the diffusion coefficient in asphalt was assumed.

To evaluate the reliability of the above data, sensitivity analyses were conducted by running the model at various values around the above base values. The model results were relatively insensitive to the properties of the Puye Formation and the basalt.

Contaminant sources:

Based on historic data, one pit, three surface impoundments, and 34 disposal shafts had been in use at MDA L for varying purposes over varying periods of time. Out of these, the surface pit and impoundments had not received any organic liquids; the 34 shafts are known to have received organic liquids, in pure liquid form as well as in containerized form. Hence, only the shafts are included in the model as contaminant sources. Shafts 1 through 28 were in operation from 1975 through 1985; shafts 29 to 34 were in operation from 1983 through 1985.

In the model, organic liquids are assumed to leak slowly from the containers (55-gal drums) and volatilize immediately. The migration of the vapors through the subsurface is modeled as a time-release phenomenon. Because of the coarse node spacing in the model, each shaft is not identified as an individual source; rather, they are grouped into two clusters: cluster #1 with shafts 1 through 28, and cluster # 2 with shafts 29 through 34.

Typical model simulations begin in 1975 with a constant TCA concentration of 3,000 ppmv in cluster # 1; the simulation is then paused in 1983, and cluster # 2 is added, with a constant TCA concentration of 3,000 ppmv; simulations are then continued till 1985, at which point the asphalt cover is added to the model by changing the diffusion coefficient at the surface.

Numerical discretization and boundary conditions:

The model domain is rectangular in plan view, 411 m (1350 ft) in the east-west direction and 290 m (950 ft) in the north-south direction. Vertically, the model domain extends from the land surface to below the water table. The top surface is modeled after the topography of the site while the bottom surface is horizontal. The volume of model domain is $\frac{43 \times 10^6 \text{ m}^3}{2}$ (1.5) x 10⁹ ft³). The node spacing is set at 15.24 m (50 ft) in both horizontal directions; in the vertical direction, it varies from 1 m to 15.24 m (3 ft to 50 ft). These spacings were chosen to achieve a reasonable computation time, with a total of 25,456 nodes and 147,438 tetrahedral elements.

At the top boundary, the atmosphere is fixed at a constant temperature of $10^{\circ}C$ (50 $^{\circ}F$) and a pressure of 0.078 Mpa (1630 lb/ft²). The TCA concentration at the nodes above the surface is fixed at zero. The bottom boundary is set as a no flow boundary, at a constant temperature of 25ºC (77ºF). The vertical side boundaries are set as no flow boundaries.

Model Simulation Results

The conceptual model has been run under various conditions for calibration, validation, and sensitivity analyses. Model results have been compared against observed data in terms of TCA concentrations and surface fluxes.

TCA concentrations:

Following accepted practice, a modified percentage error and an outlier deletion algorithm have been proposed to demonstrate the goodness of fit between the predicted and observed TCA concentrations. Measured data from the second quarter of FY 99 were used to compare against the model predictions. After deleting 29 data points from a total of 142, a reasonable agreement $(R = 0.84)$ was found between measured data and the model predictions with baseline input data.

The best fit between simulation results and measured data was found for the following conditions: zero TCA concentration along the north and west boundaries, and the basalt unit at all times. When compared on the basis of amount of TCA in the subsurface as a function of time, the results predicted with base line data indicate that the system will taker longer than the best fit simulation to reach steady state. Also, it will result in a larger mass of TCA in the subsurface. This result is as expected because of the zero-concentration boundary conditions imposed for the best fit simulations.

Surface flux:

Surface concentrations predicted by the base line model were used to estimate surface flux assuming a D value of $\frac{4 \times 10^{-6} \text{ m}^2\text{/s}}{4.3 \times 10^{-5} \text{ ft}^2\text{/s}}$ and a transition zone of 1 m (39 in) thick. The predicted flux was about 300 times greater than the measured flux $(0.1 \text{ kg/m}^2 \text{ yr})$ vs. 0.00034 kg/m² yr [0.02 lb/ft² yr vs. 0.00007 lb/ft² yr]). A simple estimate of the flux assuming a TCA concentration of 1000 ppmv, however, results in a flux of 0.144 kg/m² yr $(0.03 \text{ lb/ft}^2 \text{ yr})$ with the same D value. This anomaly has been ascribed to rain fall during the sampling period.

Conclusions and Suggestions

The TCA concentrations predicted by the model are in reasonable agreement with the measured data. Thus, the basic assumptions upon which the model has been constructed, as well as the boundary conditions and the model inputs seem to be appropriate for MDA L at TA 54. Consequently, the model can be used with confidence for predicting future state of the TCA plume as well as the effectiveness of any remedial actions.

The best fit model indicates that the plume is currently reaching near steady state conditions, implying that the mass of TCA released by the sources is balanced by the atmospheric emissions. This condition is expected to last until 2060, when all the liquid TCA will be depleted; thereafter, the plume will begin to shrink. Based on this prediction, subsurface sampling frequency may be reduced.

The development of a statistical technique to demonstrate that the plume is not growing is recommended. Ways to estimate mass of TCA in the plume using the measured data are also recommended. In addition, monitoring of emissions, instead of subsurface sampling, may be beneficial in further validating the model.

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APPENDIX B: SUMMARY OF REMEDIATION TECHNOLOGIES

DEVELOPED FOR HALOGENATED VOLATILE ORGANIC COMPOUNDS AT LANL TECHNICAL AREA 54

ITRD Remediation Subteam Dr. Bruce Thomson, Chair

Introduction

Los Alamos National Laboratory (LANL) has developed a proposed process for remediating volatile organic compound (VOC) contamination from unsaturated formations at Technical Area (TA) 54, Material Disposal Area (MDA) L. The contaminants of concern principally consist of chlorinated solvents including tetrachloroethene (PCE), trichloroethene (TCE),1,1,1-trichloroethane (TCA) and vinyl chloride (VC). Lesser amounts of other solvents, freons and other contaminants were also disposed at this site (LANL, 2001a). The contaminated formations are primarily unsaturated soils and volcanic tuff in which the contaminants are believed to be present in the vapor phase and adsorbed to soil materials; no phase separated liquid is believed to be present. Four sites within TA 54 are contaminated. Details of the site geology, hydrology, and extent of contamination were presented at a meeting on 12/12/01 of the Innovative Treatment and Remediation Demonstration (ITRD) project team. Additional information has been summarized on a CD-ROM prepared by LANL (2001b).

The remediation strategies proposed by LANL focus on passive and active extraction of subsurface soil gas. Much work has been conducted to model vapor phase transport at this site to support this strategy (Stauffer, et al. 2000). In addition, some field scale pilot testing has been performed to develop preliminary estimates of the performance of potential vapor extraction alternatives (Neeper, 2001).

One of the objectives of the ITRD process is to evaluate innovative technologies in the context of existing and more established remediation methods. Significant experience has been gained over the past 15 years in remediation of soil and ground water contamination from chlorinated aliphatic hydrocarbons (CAH or halogenated VOCs) such as those present at TA-54 MDA-L. The objective of this paper is to identify other options that have been used for remediating unsaturated soils contaminated with halogenated VOCs and briefly to consider their applicability at LANL.

Methods

It is beyond the scope of the ITRD program or this evaluation to provide a review of all candidate technologies that might have application at LANL. Instead, the Technical Advisory Group (TAG) used a remediation technologies screening matrix that was originally developed by the U.S. Environmental Protection Agency (EPA) and U.S. Air Force in 1993 (US EPA, 1993) and has subsequently been updated and revised twice. The most recent version (Van Deuren et al, 1997) was revised by the Federal Remediation Technologies Roundtable consisting of representatives from the EPA, Department of the Energy, Department of the Interior, Department of Defense, Department of the Air Force, Department of the Army, and the Department of the Navy. An on-line version of this report is available at http://www.frtr.gov/matrix2/top_page.html. The remediation technologies screening matrix identifies processes that have been used to clean up contaminated soil and ground water with some degree of success. The technologies are briefly described, and information is presented to assist in evaluating them for potential application at a site. This review considers only technologies that are applicable to remediation of unsaturated formations contaminated with halogenated VOCs, which is the situation at TA-54.

The evaluation described in this document is based on application of the remediation technologies screening matrix by Van Deuren et al. (1997). Information on the geology and hydrology of the TA-54 MDA L site, on the nature of contaminants and on the extent of the plume was provided to the ITRD and is in the references cited.

Review of the Remediation Technologies Screening Matrix

Van Deuren et al. (1997) identified 14 categories of treatment technologies for soil and ground water remediation. They are:

(For soil, sediment, and sludge:)

- *In situ* biological treatment
- *In situ* physical/chemical treatment
- *In situ* thermal treatment
- *Ex situ* biological treatment (assuming excavation)
- *Ex situ* physical/chemical treatment (assuming excavation)
- *Ex situ* thermal treatment (assuming excavation)
- Containment
- Other treatment processes

(For ground water, surface water, and leachate:)

- *In situ* biological treatment
- *In situ* physical/chemical treatment
- *Ex situ* biological treatment (assuming pumping)
- *Ex situ* physical/chemical treatment (assuming pumping)
- Containment
- Air emissions/off-gas treatment

64 technologies were considered in the remediation technologies screening matrix. A brief description of each treatment technology is presented at the beginning of each process description. The information provided for each technology includes the following:

 Technology Profile number (refers to Section 4) Scale status (full scale vs. pilot scale)

A brief description of each treatment technology is presented at the beginning of each process description. The technologies applicable to remediation of halogenated VOCs are listed in Table 1. Explanations of the terms in the table are presented in Table 2 and Table 3.

Table 1. Treatment Technologies Screening Matrix: Treatment of halogenated volatile organic compounds (numbers refer to technologies described by Van Deuern et al., 1997)**.**

Technology	Devel. Status	Use Rating	Applicability	Reliability	Cleanup Time	Function	
SOIL, SEDIMENT AND SLUDGE							
3.1 IN SITU BIOLOGICAL TREATMENT							
4.1 Bioventing	Full	Limited	Refer to profile	Refer to profile	Refer to profile	Destruct	
4.2 Enhanced Biodegradation	Full	Limited	Better	Refer to profile	Refer to profile	Destruct	
4.3 Land Treatment	Full	Limited	Better	Refer to profile	Refer to profile	Destruct	
4.4 Natural Attenuation	Full	Limited	Refer to profile	Refer to profile	Worse	Destruct	
4.5 Phytoremediation	Pilot	Limited	Average	Average	Worse	Destruct	
3.2 IN SITU PHYSICAL/CHEMICAL TREATMENT							
4.6 Electrokinetic	Full	Limited	Average	Average	Average	Destruct	
4.8 Soil Flushing	Pilot	Limited	Better	Average	Long	Extract	
4.9 Soil Vapor Extraction	Full	Wide	Better	Better	Average	Extract	
4.10 Solidication/ Stabilization	Pilot	Limited	Better	Below Average	Average	Extract/ Destruct	
3.3 IN SITU THERMAL TREATMENT							
4.11 Thermally Enhanced SVE	Full	Limited	Average	Better	Worse	Extract	
3.4 EX SITU BIOLOGICAL TREATMENT (ASSUMING EXCAVATION)							
4.12 Biopiles	Full	Limited	Better	Better	Average	Destruct	
4.13 Composting	Full	Limited	Better	Better	Average	Destruct	
4.15 Landfarming	Full	Limited	Better	Better	Worse	Destruct	
4.16 Slurry Phase Bio. Treatment	Full	Limited	Better	Average	Average	Destruct	

^b Presumptive remedy - A presumptive remedy is a technology EPA believes, based on its past experience, generally will be the most appropriate remedy for a specified type of site. EPA established presumptive remedies to accelerate site-specific analysis of remedies by focusing the feasibility study efforts. EPA expects a presumptive remedy, when available, will be used for all Comprehensive Environmental Response Compensation Act (CERCLA) sites except under unusual circumstances.

 $NA = Not Available.$

NOTE: Specific site and contaminant characteristics may limit the applicability and effectiveness of any of the technologies and treatments listed below. This matrix is optimistic in nature and should always be used in conjunction with the referenced text sections, which contain additional information that can be useful in identifying potentially applicable technologies.

Application of the Screening Matrix to TA-54

There are several considerations at the TA-54 MDA L disposal area that are particularly relevant in evaluating technologies that may be applicable for remediation. These include:

- Absence of phase separated liquid (free product)
- Large depth to bottom of VOC plume (~100 m or 330 ft)
- Very low organic carbon in tuff resulting in easy desorption of adsorbed VOCs
- Large distance between bottom of VOC plume and underlying aquifer $(\sim 200 \text{ m or } 660 \text{ ft})$
- The presence of 34 waste disposal shafts, each about 20 m (65 ft) deep, which likely represent a continuing source of contaminants
- The presence of asphalt pavement on much of the site that serves as a cover and LANL would prefer to not move
- High permeability of tuff and corresponding presence of fractures

These conditions are used to evaluate the technologies in the screening matrix.

Technologies Eliminated from Consideration

The fact that contamination is limited to unsaturated formations 200 m (660 ft) above the aquifer eliminates any technology involving ground water (technologies 3.9 through 3.13 in Table 1). The very large depth to the bottom of the plume eliminates any remediation strategy that would require excavation from further consideration. Eliminating excavation is due in part to the costs associated with removing large volume of material, the difficulty and hazards associated with excavating tuff, and the environmental impact that would be incurred by an excavation of this magnitude. These considerations eliminate all *ex situ* remediation options from further consideration (technologies 3.4 through 3.6 in Table 1).

In Situ Biological Treatment Technologies

Van Deuren et al. (1997) identify five *in situ* biological treatment technologies that are applicable to remediation of halogenated VOCs: bioventing, enhanced biodegradation, land treatment, natural attenuation, and phytoremediation. All are based on biological destruction of the contaminants. Their appropriateness for application at TA-54 MDA L is considered below.

4.1 Bioventing: Bioventing involves use of injection and extraction wells to deliver oxygen to contaminated unsaturated soils by forced air movement that increases biodegradation of the contaminants by aerobic soil microorganisms. This process is widely used at leaking underground storage tank (LUST) sites to achieve degradation of petroleum hydrocarbons. Because air is used, bioventing is appropriate only for contaminants that degrade under aerobic conditions. It is well established that the more halogenated VOCs such as TCA, TCE and PCE will degrade only under strongly reducing conditions (Rittmann and McCarty, 2001). Therefore, bioventing is not an appropriate technology for remediation of chlorinated VOCs.

4.2 Enhanced Bioremediation: In this process, the activity of naturally occurring microbes is stimulated by circulating water-based solutions through contaminated soils to enhance *in situ* biological degradation of organic contaminants or immobilization of inorganic contaminants. Nutrients, oxygen, or other amendments may be used to enhance bioremediation and contaminant desorption from subsurface materials. Enhanced bioremediation may be used to achieve degradation under either aerobic or anaerobic conditions.

The principal constraint to enhanced bioremediation is that it is based on the ability to circulate water through the contaminated formation; therefore, it is not applicable to contaminants present in the vadose zone. Since the contaminant plume at TA-54 is located in unsaturated tuff, it is therefore not an appropriate remediation technology at this site.

4.3 Land Treatment: Land treatment is used to treat contaminated surface soil in place by tilling to achieve aeration, and if necessary, by addition of amendments. Periodically tilling, to aerate the waste, enhances the biological activity. The contaminants at TA-54 are very deep, hence this technology is not appropriate for application.

4.4 Natural Attenuation in Soils: Natural attenuation relies upon natural processes in soil to reduce contaminant concentrations to acceptable levels. These processes may include dilution, dispersion, volatilization, biodegradation, adsorption, and chemical reactions with soil materials. Natural attenuation may be considered for remediation of contaminants in soils if site-specific factors support its use. The factors include (van Deuren et al, 1997):

- Protection of potential receptors during attenuation
- Favorable geological and geochemical conditions
- Documented reduction of degradable contaminant mass in a reasonable time frame in the surface and subsurface soils
- Confirmation in microcosm studies of contaminant cleanup
- For the persistent or conserved contaminants, ensured containment during and after natural attenuation

Natural attenuation was developed for application at LUST sites in which soil and/or ground water hydrocarbon pollution was noted to persist for many years, yet due to hydrogeologic conditions and the absence of an exposure pathway, there was minimal risk of human exposure to these contaminants. Furthermore, it was observed that in many cases, the size of the contaminant plume actually decreased with time as a result of natural degradation and dilution processes. At sites with very low risk, regulatory agencies have allowed application of this management approach as a way to provide a high degree of protection of health and the environment through relatively modest expenditure of remediation funds.

Natural attenuation is not itself a technology, but rather a management strategy in which the nature and extent of the contaminant plume is determined, potential pathways by which the contaminants might be transported to human receptors or the environment are identified, and then a combination of modeling and monitoring is developed to assure that the risk of exposure is below some acceptable level. Incorporation of modeling in the natural attenuation strategy is important to its success because site managers must convince the regulatory agencies and the public that pollutants will remain below appropriate standards forever and for a variety of future developments. Because the model results are used to

quantify risk assessment, a much higher degree of confidence is needed in the modeling than with other remediation strategies. In some states including New Mexico, ground water regulatory agencies will allow compliance with relaxed alternate ground water standards for selected pollutants at LUST sites at which the risk of exposure is especially low. These alternate standards are established based on the results of a formal risk assessment calculation.

Another factor that is very important in evaluating natural attenuation as a management strategy is incorporation of a monitoring program in the remediation system design. The purpose of the monitoring program is two-fold. First, it will provide data used to validate the models used in the risk assessment. Second, the monitoring program will provide data to confirm that the contaminant plume is behaving as expected and to determine whether contaminants are moving towards a receptor (usually a water supply well).

Use of the natural attenuation management strategy is frequently controversial as it has been characterized as a "do nothing" strategy. In contrast to active remediation methods, it is frequently difficult to convince stakeholders that it is in fact a viable strategy with adequate protection of human health and the environment. Though it has been widely used at LUST sites for hydrocarbon contaminants, the use of natural attenuation for halogenated VOCs has been limited. A DOE site such as LANL will have to include an extensive public participation program to identify its remediation strategy; hence site managers must be able to quantify the risks associated with this option and clearly explain them to the public.

Factors that may limit application of natural attenuation include (Van Deuren et al. 1997):

- 1. Toxicity of degradation and transformation products may exceed that of the original contaminants.
- 2. High risks occur at sites where geological characteristics such as fracture bed rock or karst landscapes may prevent assessment of stable plume control for contaminants leached from soil.
- 3. Contaminants may migrate (erosion, leaching, volatilization) before they are degraded or transformed.
- 4. Ground water at the site contaminated by the soil source will not be available for an extended period of time.
- 5. Extensive free product, as nonaqueous phase liquids, may have to be removed before natural attenuation can restore soil in a reasonable time frame.
- 6. Conservative metals may be only temporarily immobilized with remobilization when natural attenuation reestablishes oxygenated soil conditions.

Only the fifth criterion, the presence of a continuing source of contaminants, appears to be present at TA-54. LANL staff have indicated that a Corrective Measures Study (CMS) for the TA-54 MDA L will eventually be performed, and that this study will evaluate the technical feasibility and risks associated with removing the potential source terms remaining in the waste disposal shafts. However, this study is not expected to be initiated for one to two years. Thus, the magnitude of the source term and the contaminant release characteristics are at present unknown.

Based on the large depth to ground water, the large distance to the nearest water supply well, and the apparent lack of other credible exposure pathways, natural attenuation may be a viable alternative at TA-54. A further consideration is that the extensive modeling done to date can be used to support a risk assessment.

4.5 Phytoremediation: Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soil and sediment. Contaminants may be either organic or inorganic. The mechanisms of phytoremediation include enhanced rhizosphere biodegradation, phyto-extraction (also called phyto-accumulation), phyto-degradation, and phyto-stabilization. Much of the TA-54 MDA L site is covered with asphalt; hence there is no plant growth. More importantly, most of the contaminants at TA-54 are well below the root zone; hence phytoremediation is not expected to be a viable remediation process at this site.

4.6 Electrokinetic Separation: The Electrokinetic Remediation (ER) process removes metals and organic contaminants from low permeability soil, mud, sludge, and marine dredging. ER uses electrochemical and electrokinetic processes to desorb, and then remove, metals and polar organics. This *in situ* soil processing technology is primarily a separation and removal technique for extracting contaminants from soils. Targeted contaminants include metals, anions, and polar organics. The contaminants at TA-54 are mostly volatile organics of low polarity.

Contaminants in the soil are mobilized through eletromigration and/or electroosmosis. Electromigration is movement of ionic constituents as a result of electrostatic attraction to an oppositely charged electrode placed in the soil. Electroosmosis is movement of water due to ionic concentration gradients resulting from electromigration and generally, is a much less important contaminant transport mechanism than electromigration.

Electrokinetic separation is almost certainly not feasible at TA-54 for two primary reasons. First, the contaminants are not electrostatically charged, hence their mobility in an electrostatic field would be due only to electroosmosis, which is very small and requires a large amount of energy. Second, this process requires high water contents in the soil. Van Deuren (1997) report that performance drops off dramatically at moisture contents below 10%. Physical parameters used in LANL's modeling effort consist of gravimetric moisture contents of less than 2% in the Tshirege member (top 41 m or 135 ft) and about 20% in underlying formations.

Electrokinetic separation is in an early stage of development and has seen very limited application at field scale. The contaminants are not those that are readily amenable to mobilization by electrokinetic methods. The site conditions at TA-54 are not well suited for this process. Therefore, it does not appear that electrokinetic separation is an appropriate remediation technology for application at TA-54.

4.8 Soil Flushing: *In situ* soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soils using an injection or infiltration process. Extraction fluids must be recovered from the underlying aquifer, and when possible, they are recycled. Because the contaminant plume at TA-54 is in unsaturated tuff at a distance of ~ 200 m (660) ft) above the water table, soil flushing is not an appropriate technology for application at this site.

4.9 Soil Vapor Extraction: Soil vapor extraction (SVE) is an *in situ* unsaturated zone soil remediation technology in which a vacuum is applied to the formation to induce the controlled flow of air and remove volatile and some semivolatile contaminants from the soil. The gas leaving the soil may be treated to recover or destroy the contaminants, depending on local and state air discharge regulations. Vertical extraction vents are typically used at depths of 1.5 meters (5 feet) or greater and have been successfully applied as deep as 91 m (300 ft). Horizontal extraction vents (installed in trenches or horizontal borings) can be used as warranted by contaminant zone geometry, drill rig access, or other site-specific factors. Soil vapor extraction is widely used to remove volatile petroleum hydrocarbons at LUST sites.

Factors that may limit the effectiveness of SVE include (Van Deuren et al., 1997):

- Soil that has a high percentage of fines and a high degree of saturation will require higher vacuums (increasing costs) and/or hindering the operation of the *in situ* SVE system.
- Large screened intervals are required in extraction wells for soil with highly variable permeabilities or stratification, which otherwise may result in uneven delivery of gas flow from the contaminated regions.
- Soil that has high organic content or is extremely dry has a high sorption capacity of VOCs, which results in reduced removal rates.
- Exhaust air from *in situ* SVE system may require treatment to eliminate possible harm to the public and the environment.
- As a result of off-gas treatment, residual liquids may require treatment/disposal. Spent activated carbon will definitely require regeneration or disposal.
- SVE is not effective in the saturated zone; however, lowering the water table can expose more media to SVE (this may address concerns regarding light non-aqueous-phase liquids [LNAPLs]).

Because of the low organic carbon content of the tuff, halogenated VOCs are not strongly adsorbed to the soil. Furthermore, the low solubility of the contaminants at TA-54 suggests that the bulk of their mass is in the vapor phase. These two factors lead to the expectation that the VOC concentration in the off-gas from an SVE system would be high, and in fact this was confirmed for an abbreviated pilot scale vapor extraction test reported by Neeper (2001). Accordingly, it should be expected that application of SVE at TA-54 will require an off-gas treatment system. While this will add to the cost of remediation, it will also increase public acceptability by ensuring that all contaminants are captured and managed properly.

Based on current knowledge of the site, it would appear that conditions at TA-54 are well suited for application of SVE to achieve remediation. The high volatility and low sorption of the halogenated VOCs at TA-54 suggest that contaminant removal rates by some form of vapor extraction would be very high and that the site could rapidly be remediated by this process.

4.10 Solidification/Stabilization: *In situ* solidification/stabilization (S/S) involves addition of a stabilizing compound such as a cement grout or wax to a contaminated subsurface zone to achieve immobilization of the pollutants. Immobilization may be achieved through both physical and chemical mechanisms. This technology is at a very early stage of development and has been demonstrated at the pilot scale at a limited number of field sites. Its target

contaminant group is inorganics including radionuclides. Conditions at TA-54 that limit application of *in situ* S/S include:

- *In situ* S/S requires drilling wells and injecting the stabilization media to the bottom of the contaminant plume, which is not feasible at MDA L.
- The most common media used for *in situ* S/S are based on cement grouts. This material has limited effectiveness for immobilizing halogenated VOCs.
- Maximum effectiveness of *in situ* S/S requires a high degree of mixing of the stabilization media and the soil. Mixing can be achieved with an auger or through use of high pressure jets to penetrate the surrounding soil. The principal subsurface materials at TA-54 consist of welded tuff that will limit mixing.

A variation of the *in situ* S/S process described by Van Deuren et al. (1997) is the *in situ* vitrification process. In this process electrodes are placed in the ground and sufficiently high current is passed between them that resistive heating melts the soil. Volatile contaminants are either combusted, pyrolyzed, or volatilized and captured by an off-gas collection and treatment system. There are many challenges associated with this process including:

- It is limited to a maximum depth of about 10 m for practical reasons.
- Containment of escaping volatile contaminants is difficult and expensive.
- There are many operational problems that complicate the technology and present appreciable risk to workers.

Based on the large depth of the contaminant plume and the difficulty of stabilizing halogenated VOCs in place, it is apparent that *in situ* S/S is not an appropriate process for application at TA-54.

4.11 Thermally Enhanced Soil Vapor Extraction: Thermally enhanced SVE is similar to conventional SVE but includes the addition of a heat source to increase the volatility of organic contaminants and thus accelerate their removal by vapor extraction. Methods of heating subsurface soils that have been used include electrical resistance heating, application of radio frequency electromagnetic fields and injection of hot air or steam. Except when steam is applied, the heating provides the additional benefit of drying the soil, thereby increasing its permeability, which in turn facilitates passage of air through the formation.

Thermally enhanced SVE is primarily intended to remediate semi-volatile organic compounds such as heavy oils, pesticides, and PCBs. It may also have application to increase the extraction rate of VOCs in soils containing high concentration of natural organic material that, because of its high adsorption capacity, limits their volatility.

Because the contaminants at TA-54 are highly volatile and because there is very little adsorption of these contaminants onto the subsurface soil materials, thermally enhanced SVE does not offer any significant benefit over conventional SVE at this site. Furthermore, because of the large depth and extent of the contaminant plume, it would be difficult and expensive to heat the subsurface soils.

Summary of the Results of the Screening Analysis

The results of the screening analysis are summarized in Table 4. Only two of the technologies identified by Van Deuren et al.(1997) appear to have application for remediation at TA-54 MDA L: natural attenuation and soil vapor extraction. There are two obvious limitations to natural attenuation. First, the presence of wastes in the 34 waste disposal shafts constitutes a source term for the contaminants that is likely to continue to release pollutants into the formation for many years or decades. Thus, although the extent of the contaminant plume appears to be static based on both modeling efforts (Stauffer et al., 2000) and monitoring results (LANL, 2001a), it is likely that a natural attenuation management strategy would require extensive and costly site monitoring for many decades to assure that the plume did not pose a threat to human health or the environment. The second concern with natural attenuation is that associated with public acceptability. This management strategy is commonly perceived by the public as a "do nothing" alternative and will certainly draw extraordinary scrutiny from citizen activist groups.

Soil vapor extraction is the other process that appears to be feasible for remediation of TA-54. This document constitutes a screening analysis, so details of the process, costs, and duration of remediation activities have not been considered. The preliminary field testing and analyses performed by Neeper (2001) show that large masses of contaminants can readily be removed from deep formations at this site and that air flow through these formations can be easily achieved. Use of atmospheric pumping to achieve air flow through the formation may be feasible at this site. However, an engineering design and economic analysis should be conducted to determine whether the cost savings of no pumping offset the additional costs associated with closer well spacing and longer remediation schedule. A further consideration that needs to be addressed is the design and cost of the off-gas treatment system.

Technology Suitability for Application at TA-54 MDA L Comments 3.1 *In situ* **Biological Treatment** 4.1 Bioventing Low Low Halogenated VOCs are not aerobically degradable 4.2 Enhanced Biodegradation Low **• Halogenated VOCs are not aerobically degradable** 4.3 Land Treatment Low Low Plume is deeper than can be treated by land application 4.4 Natural Attenuation High High Possible because of large depth to ground water & limited exposure pathways • Will require modeling & monitoring for long duration • Questionable public acceptability 4.5 Phytoremediation Low Low **•** Contaminants deeper than root zone **3.2** *In situ* **Physical/Chemical Treatment** 4.6 Electrokinetic mobilization Low \bullet VOCs not mobilized by electrokinetic effects 4.8 Soil Flushing Low Low Feasibility limited by large distance between bottom of plume & aquifer 4.9 Soil Vapor Extraction | High **• High mobility of VOCs** due to volatility & low sorption • High permeability of tuff • Success of limited pilot testing • Off-gas treatment needed 4.10 *In situ* Solid./Stab. Low **Limited by depth of plume** • Formation not conducive to grouting **3.3** *In situ* **Thermal Treatment** 4.11 Thermally Enhanced SVE Moderate • Enhancement not needed due to volatility & mobility of VOCs **Technologies Which Are Not Applicable at TA-54 3.5** *Ex situ* **Biological Treatment** Excavation is not feasible at TA-54 **3.6** *Ex situ* **Thermal Treatment** Excavation is not feasible at TA-54 **3.9** *In situ* **Biological Treatment** Ground water not contaminated at TA-54 **3.10** *In situ* **Physical/Chemical Treatment** Ground water not contaminated at TA-54 **3.11** *Ex situ* **Biological Treatment 1 Ground water not contaminated at TA-54 3.12** *Ex situ* Physical/Chemical Treatment **Ground water not contaminated at TA-54 3.13 Containment Ground water not contaminated at TA-54**

Table 4. Summary of screening analysis of technologies for remediation of contaminants at TA-54 MDA L (numbers refer to technologies described by Van Deuern et al., 1997)

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Van Deuren, Julie, Wang, Zhao, Ledbetter, John, (1997). "Remediation Technologies Screening Matrix and Reference Guide," 3rd Ed., U.S. Army Environmental Center, Federal Remediation Technologies Roundtable, Aberdeen Proving Ground, MD. (see also http://www.frtr.gov/matrix2/top_page.html)

Attachment to Appendix B

LANL TA-54 MDA L INFORMATION NEEDED FOR DESIGN OF SOIL VAPOR EXTRACTION SYSTEM

Introduction

Based on the current understanding of site hydrogeology, including the nature and distribution of contaminants and the hydrologic characteristics of the contaminated formations, the ITRD group conducted an evaluation of remediation technologies that might be appropriate for application at TA-54. This evaluation was done using information and procedures developed by the Federal Remediation Technologies Roundtable consisting of representatives from the EPA, Department of the Energy, Department of the Interior, Department of Defense, Department of the Air Force, Department of the Army, and the Department of the Navy (Van Deuren, 1997). The Roundtable developed a screening matrix that contains 64 remediation technologies that have been developed for cleanup of subsurface contaminated soils, vapors, and ground water. The ITRD group used this screen matrix to determine whether any other technologies, in addition to those considered by LANL, might be appropriate for remediation of the TA-54 MDA L.

The analysis by the ITRD group suggested that two technologies might be appropriate for application at TA-54: monitored natural attenuation and soil vapor extraction. The comparative merits of each process are summarized in Table 1. The uncertainties associated with monitored natural attenuation appear to be much more significant than for SVE, especially the public acceptability of the process. Accordingly, the ITRD group has recommended that LANL conduct a more formal analysis of the SVE process to determine the system design, whether off-gas treatment is needed and how it might be configured, and identify the risks to workers and the public that would be associated with this process.

Process	Positive Attributes	Concerns		
Monitored Natural Attenuation	Reduced remediation costs ٠ Limited impact on TA-54 site activities ٠	Public acceptance: It is perceived as "do ٠ nothing" approach. May require very long term monitoring Will require risk assessment Poorly quantified source term may ٠ complicate process.		
Soil Vapor Extraction	Contaminants & site hydrogeology are \bullet conducive to efficient SVE remediation. Use of atmospheric pumping may reduce ٠ costs. Should achieve rapid remediation ٠	Off-gas treatment may be required. Disruption of TA-54 site activities may ٠ occur. May increase risk to workers ٠ Poorly quantified source term may ٠ complicate process.		

Table 1. Summary comparison of monitored natural attenuation and soil vapor extraction for remediation of TA-54 MDA L

This section identifies the major aspects that would be needed to complete the design of an SVE system that would contain sufficient detail to enable determination of the costs; to compare atmospheric pumping to use of mechanical blowers; to determine potential disruption of TA-54 site operations; and to provide information necessary to conduct an analysis of the risks associated with the remediation activities including both contaminant exposure to workers and the public, and occupational risks to the workers. The recommendations in this section are based on common practice for SVE systems; however, it must be recognized that design of these systems is very site specific. Hence, it is likely that there are other factors that will influence the implementation of this process at LANL.

Information Needed for System Design

There are five major factors that are likely to determine the design of an SVE system at TA-54: 1) site hydrogeologic conditions, including the nature and distribution of the contaminants, and the hydrologic properties of the contaminated formation; 2) the magnitude and characteristics of the source term; 3) the nature of site operational activities which may be affected by the remediation process; 4) regulatory constraints that may be imposed on the site and 5) costs. The discussion in the following sections are presented in the context of two possible variations of the SVE process: an active system based on use of mechanical blowers, and a passive system which removes soil vapors through atmospheric pumping.

It should be recognized that design of any type of soil remediation system is an iterative process that consists of proposing a design, analyzing its effectiveness and costs, and then refining the design. All four factors will influence the design, and it is to be expected that development of an optimal system will require two or more iterations.

Site Hydrogeologic Conditions and Contaminant Distribution

Much of the information needed for the design of an SVE system has already been collected and analyzed by LANL staff through their monitoring programs and in the process of developing a contaminant transport model. The accuracy and completeness of this information has been reviewed by the ITRD team. The well-developed contaminant transport model is of special value in designing an SVE system because it will facilitate evaluation of a variety of extraction alternatives.

Neeper (2001) presented the results of a brief SVE experiment. Data from this test can be used in conjunction with the transport model to estimate the effectiveness of different pumping strategies for contaminant removal. At this point, LANL staff should be able to identify and evaluate the effectiveness of various contaminant extraction alternatives. The effectiveness of each alternative would be considered primarily in terms of contaminant removal rate and the time needed to complete remediation. However, other important factors to be considered include the number, size and depth of wells needed; the air flow rates and pressure drops; the location of the wells relative to surface activities; and the contaminant concentrations in the off-gas and their evolution with time.

Recommendation 1: Identify a small number of extraction well configurations, perhaps three alternatives each for an active system and three for an atmospheric pumping system, and use the model to evaluate contaminant removal from the subsurface environment for each of these alternatives.

Recommendation 2: Due to the large body of knowledge that has already been collected, additional pump testing of vapor extraction wells is not needed at this site.

Characterization of the Source Term

The wastes that are present in the 34 disposal shafts represent a significant uncertainty for any remediation process because it is not possible to predict what the magnitude of future contaminant release rates might be. While it is possible to do bounding calculations that will predict the effects of a drum burst scenario on soil vapor contaminant concentrations, the number of intact drums, bottles or other containers is not known, nor is it possible to know when or if they will burst.

There are at least four ways in which this uncertainty may be addressed. First, it may be possible to remove the source term. LANL staff have indicated that a future corrective measures study will consider the practicality, the costs, and the risks associated with source term removal. A second possibility may be to stabilize the contaminants in place. This might be done through physical methods such as *in situ* grouting or by using thermal methods such as thermally enhanced vapor extraction. Third, it may be possible to design the SVE system so that in can operate for the foreseeable future if contaminants continue to be detected. For instance, an active system would be designed and operated to remove all of the halogenated VOCs presently in the subsurface environment. Once this is completed, an atmospheric pumping system might be left in place to remove residual contaminants from future drum bursts. Fourth, it may be possible to show that once the existing vapor plume has been removed, natural attenuation becomes a credible method of remediating contaminant releases from future drum burst events. Such an analysis would show that contaminant concentrations and surface release rates would be so low that they did not pose an excessive risk to human health or the environment.

Recommendation 3: Perform a corrective measures study to determine the feasibility of removing the waste materials from the disposal shafts or stabilize them in place.

Recommendation 4: The remedial system design should include consideration of future drum burst events and provide assurance that contaminant release does not pose an excessive risk to human health and the environment.

Nature of Site Operational Activities

The intention has been conveyed to the ITRD team that TA-54 will continue to remain an operational facility that is integral to waste management activities at LANL for the foreseeable future. These activities have already affected the ability to characterize the site by preventing installation of monitoring wells at some desirable locations. Examples of remediation components that may be constrained by site operational activities include: siting of SVE and monitoring wells, location of SVE pumping and off-gas treatment equipment, and routing of surface piping leading to the vapor extraction (or injection) wells. In addition to the actual components of an SVE system, the installation of monitoring and extraction wells involves use of large equipment such as drill rigs, water trucks, flat bed trucks, and boom trucks. Thus, installation of the wells will result in a large surface disruption for times ranging from many weeks to many months, depending on the number of wells. In addition, the risk to site operations personnel must be considered. This risk may include exposure to

contaminants from the extraction wells as well as usual work place hazards associated with any industrial process.

The impact on site operational activities can be minimized by clearly identifying the nature of these activities and conveying this information to system designers. During the preliminary design phase of an SVE system, the designers will develop a good estimate of the number and location of wells needed for the process, along with the approximate sizes and characteristics of the piping, pumping, and off-gas treatment system. It will then be necessary for managers and remediation system designers to compare the site's operational activities with the SVE system design and collaboratively develop an SVE system design that will achieve remediation having an acceptable impact on TA-54 operations.

Recommendation 5: TA-54 site managers should be contacted and asked to identify facility operations that might be impacted by an SVE system. A map of the site should be prepared which delineates structures or areas that cannot have wells, piping or SVE equipment located near them. Areas where site personnel spend large amounts time should also be identified so that the system design can minimize work place hazards.

Recommendation 6: Once a preferred SVE option has been determined, TA-54 site managers should review the plan and the construction phasing to be sure that its impact on site operations will be acceptable. As construction progresses, this coordination should be maintained.

Regulatory Constraints

The regulatory constraints that must be met by the remediation system are likely to be important factors in process selection and final design. They must be clearly identified early in the design process, and regulators must continue to be included in discussions involving the remediation system.

Some of the information that system designers need to obtain from regulators include:

- Emission limitations
- Process monitoring requirements
- Site monitoring requirements
- Required cleanup levels
- Long term site monitoring requirements
- Acceptable risk criteria for workers and the public
- Public participation requirements

One of the most important regulatory issues that must be resolved early on is determination of the limitations that may be applied to process emissions, as this will determine whether an off-gas treatment process is required. This limit will likely affect both the concentration of VOCs in the exhaust gas as well as the total mass that may be discharged each day. If the emission limits are not too strict, it may allow use of a slower remediation process such as atmospheric that doesn't require an off-gas treatment process. Slower remediation would involve a trade-off in which a less expensive process is operated for a longer period of time,

in contrast to operation of a more expensive, aggressive SVE system that includes off-gas treatment.

From a regulatory perspective, it is likely that the only process monitoring requirements will be off-gas monitoring. However, it will be necessary to determine what types and frequency of monitoring will be required.

During remediation periodic monitoring of the subsurface contaminant distribution will be required to assess the remediation process and to provide assurance that the contaminant plume is not expanding. The type and frequency of this monitoring must be determined.

The required cleanup level is the residual soil vapor chlorinated VOC concentration that must be met to achieve remediation of the site. The target cleanup levels must be determined. The NMED should clearly identify the cleanup levels and monitoring requirements that LANL must meet in order achieve cleanup of this site. If soil vapor monitoring is to be continued after remediation is complete, the nature, extent and frequency of this monitoring should be identified.

If a risk-based corrective action strategy such as monitored natural attenuation is chosen for application at TA-54, LANL must be informed of the level of risk that is acceptable to the public and to site workers.

A public participation process will be required prior to selection of a final remediation process for this site. NMED and LANL should agree to the nature and scope of this process soon to facilitate development of an effective process and to allow LANL managers to develop an accurate estimate of its cost.

Recommendation No. 7: LANL and NMED should continue to work together and identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at TA-54. In particular, the following information must be identified: off-gas emission requirements, SVE process monitoring requirements, contaminant plume monitoring requirements, required soil vapor cleanup levels, final monitoring requirements, acceptable public and work risk levels, and public participation requirements.

Cost

The major costs associated with any remediation process can be categorized as either capital costs or operations and maintenance costs. For a soil vapor remediation system, the major capital costs include:

- Drilling and construction of monitoring and extraction wells
- Piping costs associated with connecting extraction wells to the pump system
- Pumping system
- Off-gas treatment system
- Monitoring and control systems
- Civil costs associated with access, utilities, security, etc.

Operations and maintenance (O&M) costs include:

- Personnel costs
- Power costs (electricity, natural gas, water)
- Equipment maintenance
- Process monitoring
- Contaminant plume monitoring

Typical cost estimation practice is to combine the capital costs and the O&M costs to generate an annualized cost. This is done by amortizing the capital costs over the life of the project using an appropriate interest rate that is available to the owner of the process. The annual O&M costs are adjusted for inflation. The two costs are then added to get the annual cost per year. The total cost can be determined by summing the annualized costs over the life of the project. This approach allows direct comparison of systems that have different capital costs, O&M costs, and require different times to achieve remediation.

It is apparent that two general approaches to SVE may be appropriate for this site: an active SVE system that relies upon use of mechanical blowers to circulate air through the formation, and a passive SVE system that relies upon atmospheric pumping for air circulation. Based on the limited pilot work by Neeper (2001), the active system would be expected to move large volumes of air through the formation and have a large radius of influence. Thus, fewer wells would be required and remediation would be accomplished more quickly. However, an active system would require one or more blower systems, an offgas treatment system, and more extensive piping to connect all of the wells. A passive system relying upon atmospheric pumping would require more wells, less piping, and less or possibly no off-gas treatment, if chlorinated VOC emissions were sufficiently low. The downside of this option is that it would require much longer to achieve cleanup due to the lower contaminant removal rates.

Recommendation No. 8: LANL should conduct a design study that includes two variations of the SVE remediation process: one that uses blowers to circulate air through the formation and another that uses atmospheric pumping to circulate air through the formation. Each design should incorporate all of the components needed to comply with regulatory requirements including off-gas emission treatment. The length of time needed to achieve site remediation should be determined for each. The annualized and total costs of each alternative should be determined and used in selection of a final remediation process.

References

Neeper, D. (2001). RFI Investigation, presentation to ITRD, Pojoaque, NM, 50 p.

Van Deuren, Julie, Wang, Zhao, Ledbetter, John, (1997). "Remediation Technologies Screening Matrix and Reference Guide," 3rd Ed., U.S. Army Environmental Center, Federal Remediation Technologies Roundtable, Aberdeen Proving Ground, MD. (see also [http://www.frtr.gov/matrix2/top_page.html\)](http://www.frtr.gov/matrix2/top_page.html)

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APPENDIX C: COMMENTS AND RESPONSES ABOUT THIS REPORT

One of the purposes of the ITRD program is to provide an independent evaluation of remediation approaches and applicable technologies on a site-specific basis. The "target audience" for ITRD reports includes both the specific site's Technical Advisory Group, which includes DOE site project managers, M&I/O scientists and engineers, regulators, public stakeholders, and technology experts, and also interested parties with similar challenges at other sites throughout the DOE complex. The intent of the program is to provide technical assistance by developing treatment and deployment information on potentially useful innovative technologies, and to make recommendations in conjunction with all of the parties to a remedial action decision. It has been demonstrated that this inclusive process can help build consensus on a site's eventual technology selection and treatment approach.

Because the ITRD process is inclusive, it seeks to present information to all interested parties in a fair manner. Some of the material and recommendations in this Summary Report for LANL MDA L generated controversy. To capture the discussion about these issues, this appendix contains a series of comments and responses between members of the Technical Advisory Group and LANL Environmental Restoration personnel involved with the project.

Although there were several exchanges of comments and responses, the text of this report includes no changes to the original Technical Advisory Group findings and recommendations from the draft May 2002 reports. However, inclusion of the comments and responses seeks to indicate that there were some areas of dissension that were not resolved within the Technical Advisory Group report.

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Steve Webb proposed adding the following text at the end of Section 4.1 (Findings) of the TAG report:

Subsequent to these findings, the original model report (Stauffer et al., 2000) was revised (Stauffer, et al., 2002). This revised report addressed many of the concerns in items 1, 4, and 6. Specifically, the revised model considers the following processes not included in the original report. The adequacy of the model revision in resolving the concern is summarized below.

- 1. Henry's law for dissolved gas (Finding 1e above) finding resolved.
- 2. Boundary layer effects (Finding 1a and 6a) finding not resolved as discussed in the Recommendation section.
- 3. Gas-Liquid Diffusion Coefficient (Finding 1a and 6a) finding resolved.
- 4. Higher source concentrations pre-1985.
- 5. Fractures (Findings 4 and 6b) finding not resolved.
- 6. Gas diffusion model (Finding 1d) discussion added no model modifications made - finding not important in present application.
- 7. Gas-Solid sorption (Finding 1b) discussion added no model modifications made - finding not important in present application.

He also proposed adding the following text at the end of Section 5.1 (Recommendations) of the TAG report:

Subsequent to the above original recommendations, the original model report (Stauffer et al., 2000) was revised (Stauffer, et al., 2002) as mentioned earlier. We do not believe that the revised model adequately addresses any of the above recommendations. There has been limited progress on the surface flux issue (Recommendation 2), but much more work remains before the issue is adequately addressed. Therefore, the original recommendations remain unchanged by the revised model report.

Dennis Newell and Phil Stauffer (LANL ER) provided the following information: Below are mine and Phil's responses to the TAG conceptual model recommendations and Steve Webb's suggested additions to the report. The report reads as if a great deal of work is recommended, which is contrary to what we have been getting from the conference calls.

Section 5.1

[Recommendations] 1 and 2. Surface Emission measurements and Surface Flux (we are evaluating these together due to their similarity): Further validation of the model is recommended. Comparison of the model the subsurface concentrations shows that the model is adequate; however surface flux measurement vary significantly from predicted values.

We believe the subteam is assuming that the measure flux values are "correct". In reality, the surface flux will vary with the permeability of the surface. The surface footprint of the plume in very heterogeneous; it is covered with soil, asphalt, base coarse, and has areas of bare, weathered tuff. Additionally, the effective porosity of most of these materials varies due to fluctuating near surface moisture conditions. A "point-in-time"

flux measurement is unlikely to correspond with the predictions. The near surface in the model is greatly simplified.

The team recommends further measurements including penetrating the asphalt cap and taking measurements. We do not understand what that will provide as far as further validation. We have sub-asphalt measurements in the pore gas wells at depths of \sim 20 ft that agree well with the model. Additional surface flux measurements could be made, but the same surface heterogeneity will impact the agreement with the model. The previous measurements were taken after rain, which will not provide a maximum flux. Measurements would have to be made during dry surface conditions; measurements of the asphalt cap would have to be made.

However, how important are surface flux measurements? We primarily use surface flux to provide a surface expression of the subsurface plume to aid in extent determination. The model fits the subsurface extent. As far as risk assessment of vapors, the surface flux method we used is not accepted; expensive EPA flux chambers would have to be used followed by modeling of the emissions to human receptors. However, for the RFI, SUMMA canister samples of atmosphere at the site were collected to evaluate present day risk, and no such risk was found.

Additionally, surface flux was reduced in the model with the result showing that the goodness of fit becomes poor when surface flux is reduced by even one order of magnitude. Given that the measured surface flux is more than 2 orders of mag. lower than the model predicts, the modeling suggests that surface flux measurements should be used only qualitatively.

[Recommendation] 3. Presence of Fractures. The uppermost unit (Unit 2) at MDA L is moderately welded and hosts near vertical fractures. This unit contains the upper ~50 ft of the vapor plume and is in contact with the atmosphere at the surface and mesa sides. One consideration is that the fractures are likely filled to partially filled in the near surface by translocated soils/fill, clay, and carbonates. This would limit vertical movement of vapors through fractures. The geologic unit beneath the uppermost unit is poorly welded and does not host many fractures, and thus any influence of fractures on vapor transport would be insignificant. If the fractures in Unit 2 are included in the model as increased vertical diffusion, much greater loss to the atmosphere would result (which limits the lateral extent of the plume), preventing matching of the model to the data.

Given that the plume is larger than if the upper unit fractures were increasing vapor movement, we do not think additional studies on fractures are warranted. Fracture spacing may need to be included in detailed passive venting studies where fractures could have a profound 'short circuit' effect on vent wells that are open in the Unit 2 interval. The current analysis being reviewed, however, is the model of the site-wide plume.

[Recommendation] 4. Alternative Methods for Gas Sampling and Analysis at MDA L site. I have previously provided comments on this topic. The early pore gas monitoring program explored different methods of pore gas detection, including tedlar bags and GCs. The present day methodology has proved to be the most reliable and cost effective method, providing consistent, quality results.

Yes, the B&K results for TCA, TCE, etc can be impacted by the presence of freons. However, we include freon screens in our B&K set-up to compensate for this potential problem. We have not seen a significant problem with interference, except with water vapor at certain times of the year. Over the last few years the correlation between the B&K and associated SUMMA analytical results has been very good, measuring within the expected error in the B&K. The B&K screening has been used primarily to get a very large data set for extent definition. SUMMAs are the ground truth and are used to define nature. Our proposed future monitoring phases out the B&K and moves towards limited SUMMA samples at key locations.

We do not agree with this recommendation and do not think experimentation with additional pore gas methodologies will improve our data set. More likely, it would be costly and take several years of data before an evaluation could be made.

In response to Steve Webb's additional comments:

We state again that the main purposes of the modeling are to show that we have a reasonable understanding of the mechanisms that have created the VOC plume, and that our numerical model of the plume can be used to predict its behavior into the future.

In light of purpose of the model, we disagree with Steve Webb's additional comments. We do not believe that the surface flux issues and the fracture subject are significant enough to warrant additional efforts.

The model has incorporated second order effects, which improve the data/model correlation significantly. We feel that the work performed in support of the ITRD review has shown that the basic modeling was sound, and that the revised model can be used as a starting point for analysis of future plume behavior and remediation options.

We need to consider the scale of the problem. Given the magnitude of the plume (relatively small) and the risk it poses (minimal), we need to ask the question, does the existing model adequately describe the plume for the purposes of proposing and implementing remediation options. We do not need to explore details unless they significantly alter the outcome, with respect to risk to the environment and public. The characterization phase of this project has passed, and we need to move towards a conclusion.

Steve Webb responded to the above comments as follows:

1. Surface Flux

If a mechanistic model of the surface flux had been included, such as Jury's model, I might agree with their assessment. However, the current model is not mechanistic and is ad hoc. Because the decrease in the plume size is predominantly due to losses to the atmosphere, I feel this process should be modeled mechanistically and in more detail. It shouldn't be a large effort to include this effect.

2. Fractures

Isn't the Cerros del Rio Basalts formation fractured in places? Inclusion of these fractures could significantly increase vertical migration towards the water table. I seem to recall that there a very few measurements under the plume in this formation - please correct me if I'm wrong.

Dennis Newell responded to Steve Webb's comments:

RE: #2. Fractures. Yes, the Cerros del Rio basalts are highly fractured, with other features such as breccia zones and rubble zones, as well as massive, unfractured zones. However, the monitoring near and within the basalts has shown that the plume decreases to detection limit concentrations before the basalt contact. Any vapors entering the basalt are at extremely low, at or below detection limit concentrations. With the extremely high air permeability of the basalt, these are flushed away essentially instantly. The basalt appears to act much like the atmosphere.

As far as the amount of data within the basalt. We have two angle boreholes that penetrate the basalt; they are located directly beneath the two major source areas at MDA L. We have ~5 sample ports in each borehole within the basalt. We have a good data set from these ports, but only sporadic, near detection limit hits, and that is why the data looks sparse.

Joe Rossabi had the following comments about the discussion among Dennis Newell and Phil Stauffer (LANL ER) and Steve Webb:

I think we are getting away from the general agreement (from the NM meeting) that the numerical model and conceptual understanding of the site was adequate to move on to the next phase but that there were some things that could be done to improve both the numerical and conceptual models. We're not using the right words that express our agreements, areas for improvement, and perhaps the priority or value of the suggestions for improvement.

Specifically to Dennis and Phil's responses:

I believe the subteam recognizes that the surface flux measurements to date are probably not representative. They are, however, field measured data and are assumed to be reasonably accurate. The issue of disparity between the measurements and the model predictions was not raised as an indictment of the model, it merely indicated an opportunity for better understanding of the system. The suggested additional measurements by quick cutting through the asphalt were an attempt to help resolve the disparity at minimal cost. I believe everyone recognizes that we will be subject to the same heterogeneity issues as were encountered in the previous flux measurements; however, the measurements would add to the data set and may be able to provide a better understanding of the surface flux disparity. The fact that the previous surface flux measurements were made under conditions that may have biased the flux rate low strengthens the argument for additional flux measurements. Although the model may indeed be more representative of how the system is behaving than the point measurements indicate, I think we need to be careful with statements that have the flavor of "the data don't match the model".

The inclusion of fractures might also be a nice addition to the model if the cost for incorporating them is not too great.

Frankly, I like the B&K method and would prefer to use it precisely for the reasons that you all have been using it, i.e., large, very accurate data set. I am familiar with the crosscompensation methods that the $B\&K$ folks use to deconvolute overlapping spectra (as

occur with some freons and other VOCs) and have had mixed results in accuracy depending on the amount and type of freon in the soil gas mix when compared with standard GC results. The final arbiter of the use of B&K are the comparisons that you all have made using analytical equipment that is not subject to interference from overlapping spectra (e.g., GC). If the B&K is doing the job, that's good enough for me. With respect to onsite GC (Tedlar bags or whatever) versus Summa and offsite, if the Summas are accurate and more cost effective (or more defensible, would not require costly training or change in protocol, etc.) in comparison to on site GCs or other methods – go for it.

Despite these somewhat long winded responses to responses, I agree that we need to bear in mind the purpose and scope of the model, i.e., to have a reasonable first order understanding of the plume and its behavior to determine the next step in treating or monitoring the plume. Given this, the suggestions for additional work on improving the numerical and conceptual model should be balanced with the activities planned for the next phase of the project. If the value of the additional work is of low priority with respect to other planned activities, then it should be placed in its proper position on the list.

Michael Smith provided comments on two sections of text in the report. *Dennis Newell* provided responses to these comments:

[M. Smith]: I'd also like to suggest two small changes to the text.

1. Section 2 (Background Information on MDA L) of the final ITRD report on MDA L contains the following sentence:

The pore gas monitoring provided sufficient data for the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) to estimate the nature and extent of the VOC vapor plume at MDA L.

I don't think NMED has "accepted" or "approved" the estimate. As I recall, NMED wants some more data taken. I'm proposing the following revision to the sentence:

The pore gas monitoring provided data for LANL to estimate the nature and extent of the VOC vapor plume at MDA L as part of the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI).

[D. Newell]: I agree; however if the TAG also feels that N&E can be estimated with some confidence, then it would be useful if the report reflected that.

[M. Smith]:

2. I'm also recommending adding some wording to our Findings under point 7 of Section

4.1. I've typed in the paragraph below with my changes in bold italics.

The model seems to give reasonable answers *when compared to a single field data set*. However, some of the details are open to question, and some additional data or modeling studies are needed. Appendices of the available concentration data would be useful. Confidence in the model would increase through successful comparisons to additional field data sets. The current model can be used to select and implement some remediation field tests and develop general strategies for contaminant control and remediation. The

current model can also be used to focus the next characterization data needs and areas for more refined numerical modeling.

[D. Newell]: It is true that the model is compared to one, representative quarter of data. However, the plume is relatively static, which implies that the model compares well to other quarters. The RFI report for MDA L that is being modified goes into depth on the behavior of the plume over time with respect to both nature and extent. I think this report would be too lengthy to provide that discussion also. Again, the RFI report will provide all the data used to assess the plume.

Also, providing concentration in an appendix does not seem appropriate in this case. The analytical data is provided to NMED in quarterly reports from LANL, and the RFI report will provide the entire data set.

Appendix K

Stratigraphy and Surface Water Assessment

APPENDIX K STRATIGRAPHY AND SURFACE WATER ASSESSMENT

K-1.0 STRATIGRAPHY

Bandelier Tuff

Figure K-1 shows the generalized stratigraphy of the Bandelier Tuff beneath TA-54. In the discussions below, the term *welding* is used to differentiate between tuffs that are uncompacted and porous (nonwelded) and those that are more compacted and dense (welded). In the field, the degree of welding in tuff is quantified by the degree of flattening of pumice fragments (a higher degree of flattening and elongation equals a higher degree of welding). Petrographically, welded tuffs show adhesion (welding) of grains, while nonwelded tuffs do not. The term *devitrified* is applied to tuff whose volcanic glass has crystallized.

Tshirege Member

The Tshirege Member of the Bandelier Tuff is a compound-cooling unit that resulted from several successive ash-flow deposits separated by periods of inactivity, which allowed for partial cooling of each unit. Properties related to water flow and contaminant migration (e.g., density, porosity, degree of welding, fracture content, and mineralogy) vary both vertically and laterally as a result of localized emplacement temperature, thickness, gas content, and composition.

Tshirege Member Unit 2

Unit 2 of the Tshirege Member of the Bandelier Tuff is competent, resistant caprock that forms the surface of Mesita del Buey. Its thickness varies from 35 ft (10.7 m) to 40 ft (12.2 m) at MDA L (Appendix H). Where it is exposed, unit 2 forms nearly vertical cliffs on the sides of the mesa. The rock is described as a moderately welded ash-flow tuff composed of crystal-rich, devitrified pumice fragments in a matrix of ash, shards, and phenocrysts (primarily potassium feldspar [sanidine] and quartz [Broxton and Reneau 1995, 49726]).

Unit 2 is extensively fractured as a consequence of contraction during postdepositional cooling. The cooling-joint fractures are visible on mesa edges and on the walls of pits. In general, the fractures dissipate at the bottom of unit 2. On average, fractures in unit 2 are nearly vertical. Mean spacing between fractures ranges between 1.9 ft and 2.6 ft (0.6 m and 8.8 m), and fracture width ranges between less than 0.03 in. and 0.51 in (1 mm and 13 mm) with a median of 0.12 in. (3 mm). Fractures are typically filled with clays to a depth of about 9.9 ft (3 m); smectites are the dominant clay minerals present. Smectites are known for their tendency to swell when water is present and for their ability to strongly bind certain elements, both of which have implications for transport of radionuclides in fractures. Opal and calcite can occur throughout the fractured length, usually in the presence of tree and plant roots (live and decomposed); the presence of both the minerals and the roots indicates some water at depth in fractures.

At the base of unit 2 is a series of thin, less than 3.9-in.-thick (10-cm-thick), discontinuous, crystal-rich, fine- to coarse-grained surge deposits. Bedding structures are often observed in these deposits. The surge beds mark the base of unit 2.

Tshirege Member Unit 1v

Tshirege Member unit 1v is a vapor-phase-altered cooling unit underlying unit 2. This unit forms sloping outcrops, which contrast with the near-vertical cliffs of unit 2. Unit 1v is further subdivided into units 1vu and 1vc (Broxton and Reneau 1995, 49726).

Unit 1vu. The uppermost portion of unit 1v is devitrified and vapor-phase-altered ash-fall and ash-flow tuff and has been designated unit 1vu, where u signifies upper. Its thickness varies from 60 ft (18.3 m) to 75 ft (22.9 m) at MDA L. Unit 1vu is unconsolidated at its base and becomes moderately welded nearer the overlying unit 2. Only the more prominent cooling fractures originating in unit 2 continue into the more welded upper section of unit 1vu but die out in the less consolidated lower section. More typically, fractures in unit 2 do not extend into unit 1vu.

Unit 1vc. Beneath unit 1vu is unit 1vc, where c stands for colonnade, named for the columnar jointing visible in cliffs formed from this unit. Unit 1vc is a poorly welded, devitrified ash-flow tuff at its base and top, and becomes more welded in its interior. Unit 1vc is approximately 25 ft (7.6 m) thick at MDA L.

Tshirege Member Unit 1g

The basal contact of unit 1vc is marked by a rapid change (within 0.7 ft [0.2 m] vertical) from devitrified (crystallized) matrix in unit 1vc to vitric (glassy) matrix in the underlying unit 1g. Vitric pumices in unit 1g stand out in relief on weathered outcrops, while devitrified pumices above this interval are weathered out. In outcrop, this devitrification interval forms a prominent erosional recess termed the *vapor-phase notch*. There is no depositional break associated with the vapor-phase notch; the abrupt transition suggests that this feature is the base of the devitrification that occurred in the hot interior of the cooling ash-flow sheet after emplacement.

Unit 1g is a vitric, pumiceous, nonwelded ash-flow tuff underlying the devitrified unit 1vc. It is about 140 ft (42.7 m) thick at MDA L. Few fractures are observed in the visible outcrops of this unit, and weathered cliff faces have a distinctive Swiss-cheese appearance because of the softness of the tuff. The uppermost 5 ft to 20 ft (1.5 m to 6.1 m) of unit 1g are iron-stained and slightly welded. This portion of unit 1g is resistant to erosion, helping to preserve the vapor-phase notch in outcrop. A distinctive pumice-poor surge deposit forms the base of unit 1g.

Tsankawi Pumice Bed

The Tsankawi Pumice Bed is the basal air-fall deposit of the Tshirege Member of the Bandelier Tuff. It is a thin bed of gravel-sized vitric pumice. It is about 3 ft (1 m) thick at MDA L.

Cerro Toledo Interval

The Cerro Toledo interval consists of thin beds of tuffaceous sandstones, paleosols, siltstones, ash, and pumice falls; the Cerro Toledo interval separates the Tshirege and Otowi Members of the Bandelier Tuff. The Cerro Toledo interval also includes localized gravel- and cobble-rich fluvial deposits predominantly derived from intermediate composition lavas eroded from the Jemez Mountains west of the Pajarito Plateau. This interval varies between 15 ft (4.6 m) and 30 ft (9.1 m) thick at MDA L.

Otowi Member

The Otowi Member tuffs are about 80 ft (24.4 m) thick at MDA L. The tuffs are a massive, nonwelded, pumice-rich, and mostly vitric ash flow. The pumices are fully inflated, supporting tubular structures that have not collapsed as a result of welding. The matrix is an unsorted mix of glass shards, phenocrysts, perlite clasts, and minute, broken pumice fragments.

The Guaje Pumice Bed is the basal air-fall deposit of the Otowi Member of the Bandelier Tuff. The thickness of the unit has been measured at 10 ft (3.1 m) beneath MDA L. The pumice bed is nonwelded but brittle. Pumice tubes are partially filled with silica cement.

Cerros del Rio Basalts (Tb4)

In the vicinity of TA-54, the Cerros del Rio basalts lie directly beneath the Otowi Member of the Bandelier Tuff (Figure K-1). In R-32, the basalts are 636 ft (193.9 m) thick; in R-22 the basalts are 983 ft (299.6 m) thick. In both wells, the regional water table occurs within these basalts. Local borehole cores at MDA L show that the basalts consist of both angular rubble and dense, fractured masses, with zones of moderately to very porous lavas. Deeper drilling at R-22 demonstrated wide variety of lithologies within the basalts, including massive flows, interflow rubble or scoria zones, sediments and paleosols.

Puye Formation (Tpf, Tpp) and Older Fanglomerate

The Puye Formation is a conglomerate deposit derived primarily from volcanic rocks to the west, with varying lithologies including stream channel and overbank deposits, ash and pumice beds, debris flows and lahar deposits. Well tests on the plateau confirm that the unit is very heterogeneous with both high and low permeability zones present (Nylander et al 2002). The formation is poorly lithified, and as such is unlikely to sustain open fractures.

As shown in Figure K-1, the Puye Formation thins from west to east beneath TA-54. At PM-2, the Puye (including fanglomerate, pumiceous units and ancestral Rio Grande deposits) is approximately 800 ft (243.8 m) thick; at R-23 the Puye is completely absent. Recent drilling across the plateau has suggested that the Puye is frequently underlain by alluvial fan deposits, similar in lithology to the Puye, yet considerably older. These deposits are of considerable thickness at PM-2, were penetrated at R-22 (approximately 80 ft [24.4 m] thick) and were absent at R-23. The Puye Formation was also encountered at R-16 (351 ft [106.9 m] thick); the water table occurs within the Puye Formation at this location.

Totavi Lentil Deposits (Tpt)

The Totavi Lentil is an ancestral Rio Grande deposit composed of coarse gravels and sands with abundant quartzite. The deposit has been alternatively conceptualized as a series of distinct north-south trending ribbons (Reneau 1995, 50143) and a continuous thin sheet at the base of the Puye Formation. Like the overlying Puye Formation it has both high permeability and low permeability zones (Nylander et al 2003, 76059).

Santa Fe Group (Tsf, Tf, and Ts) and Santa Fe-Age Basalts (Tb1 and Tb2)

The Santa Fe Group is an alluvial-fan deposit comprised of medium to fine sands and clays. Numerous north-south trending faults are present in the Santa Fe Group (Kelly 1978, 11659). Santa Fe Group rocks are deep below MDA G (1500 ft [457.2 m] below ground surface at PM-2) and were not penetrated by R-20, R-32, or R-22. Most water supply wells on the eastern edge of the Pajarito Plateau and elsewhere in the basin are completed in these rocks. The Santa Fe Group units are characterized with the lowest permeability compared to the other units in the regional aquifer.

Basaltic lava flows occurred during the time that the Santa Fe Group was deposited; these basalts occur both within the Santa Fe Group and within the Pre-Puye sands, gravels, and conglomerates that were penetrated by R-20 and R-22. These old basalts appear to have fewer open fractures than the younger Cerros Del Rio basalts.

Geochemistry

Certain minerals present in Bandelier Tuff are important in terms of sorption of chemical species from water. Among them are alkali feldspar and a combination of three silica polymorphs (i.e., quartz, cristobalite, and tridymite). These minerals are found throughout the thickness of the Bandelier Tuff, and their absolute abundance throughout the tuff can have a significant effect on the retardation of several constituents in the TA-54 MDA inventories. Less important in terms of transport are organic materials, which can react with certain constituents to form relatively mobile compounds. The organic content of geologic materials on the Pajarito Plateau mesas is typically less than 1 wt %. However, the fractures can contain higher organic concentrations than the tuff matrix.

In addition to the minerals found in the tuff matrix, clay minerals are found in abundance in fractures and interbeds in the Bandelier Tuff. The primary clay minerals are smectites, with lesser amounts of kaolinite. The clay minerals have high sorptive capacity for many TA-54 inventory constituents. Hematite (i.e., iron oxide) coatings are also found but with less frequency than clay coatings. Hematite has a very large surface area for binding certain metals and is therefore also important when considering transport in fractures.

Clay, iron oxide, carbonate minerals, and solid organic matter are known to be present in ancient, buried soils (paleosols) found elsewhere across the Laboratory. In particular, the Cerro Toledo interval, Guaje Pumice Bed, and Puye Formation are known to have buried soils. The occurrence of clay-rich horizons in the subsurface is not known beneath TA-54; however, they may be important (e.g., the Cerro Toledo interval commonly contains paleosol horizons). Vertical water flow may be inhibited and lateral flow enhanced by clay layers; clay has a low permeability. Furthermore, certain inventory constituents would be sorbed onto or complexed with the soil minerals and organic matter present in such zones. Because of these potentially important effects, field and laboratory investigations are underway to identify and characterize clay-rich soil horizons beneath Mesita del Buey.

K-2.0 SURFACE WATER ASSESSMENT

The surface water assessment for MDA L, dated July 25, 2001, is attached at the end of this appendix.

K-3.0 REFERENCES

The following list includes all references cited in this document. Parenthetical information following each reference provides the author, publication date, and a record identification (ER ID) number, when available. These numbers can be used to locate copies of actual documents at the RRES-RS Records Processing Facility.

Broxton, D. E., and S. L. Reneau, August 1995. "Stratigraphic Nomenclature of the Bandelier Tuff for the Environmental Restoration Project at Los Alamos National Laboratory," Los Alamos National Laboratory report LA-13010-MS, Los Alamos, New Mexico. (Broxton and Reneau 1995, 49726)

Kelley, V. C., 1978. "Geology of Espanola Basin, New Mexico," Geologic Map 48, New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico. (Kelley 1978, 11659)

Nylander, C. L., K. A. Bitner, G. Cole, E.H. Keating, S. Kinkead, P. Longmire, B. Robinson, D.B. Rogers, and D. Vaniman, March 2003. "Groundwater Annual Status Report for Fiscal Year 2002," Los Alamos National Laboratory document LA-UR-03-0244, Los Alamos, New Mexico. (Nylander et al. 2003, 76059) Reneau, S. L., June 1995. "Geomorphic Studies at DP Mesa and Vicinity," in *Earth Science Investigation for Environmental Restoration Los Alamos National Laboratory Technical Area 21*, Los Alamos National Laboratory report 12934-MS, Los Alamos, New Mexico. (Reneau 1995, 50143)

Figure K-1. Generalized stratigraphy of Bandelier Tuff at TA-54

Los Alamos National Laboratory

Environment, Safety & Health Division
ESH-18 Water Quality & Hydrology Group

Erosion Matrix for PRS 54-006 Surface Water Assessment

10.6

Total Score

100

MAX. POSSIBLE EROSION MATRIX SCORE:

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Appendix L

Source Term and Batch Waste Source Term Databases

OPERABLE UNIT 1148 DATA REPORT

Prepared for:

Los Alamos National Laboratory Los Alamos, New Mexico

Prepared by:

IT Corporation 557 Oppenheimer Rd., Suite 200 Los Alamos, New Mexico 87544

September 1992

Technical Area 54, Area L **3.0**

3.1 Source Term Data Base Information

3.1.1 Assumptions

The TA-54, Area L, source term data base was constructed from the original waste disposal records found in the TA-54, Area L, logbooks. The inconsistent and often incomplete nature of the original logbook entries required that assumptions be made in order to build the data base effectively. The assumptions used in this section are as follows:

- 1. Shafts were "active" (i.e., receiving waste) during the entire month they were being drilled.
- 2. Shafts were "inactive" during the entire month they were being capped.
- 3. Logbook entries indicating disposal of a material into an inappropriate shaft (e.g., oil into an inorganic shaft) were considered valid.
- 4. An entry of "0.0000" under "VOLCUFT" indicated a value of zero or a volume of <0.0001 ft³.
- 5. When two disposal dates were given, the date associated with the disposal site was used.
- 6. Disposal locations from logbook entries indicating disposal into a pit or shaft that was not "active" on the date of disposal were considered invalid.
- 7. When a logbook entry listed only one volume for disposal of multiple items and no disposal location was specified, only one record with a single volume amount was entered in the data base.
- 8. When a logbook entry listed only one volume for disposal of multiple items and a disposal location was specified for at least one of the multiple items, the volume amount was equally divided between all of the items and multiple records were entered in the data base.
- 9. When a logbook entry listed only one date with multiple items and provided a volume amount for each item, multiple records were entered in the data base.
- 10. When a logbook entry indicated disposal of acids or bases into Shaft No. 1, at a time when Shaft No. 1 was "inactive," Shaft No. 2 was entered into the data base.

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11. Only logbook entries that specified a unique disposal location were assigned a "Y" in the location field.

3.1.2 Definitions

The definitions of the fields and field variables used in the TA-54, Area L, source term data base are as follows:

3.1.3 Data Base

The TA-54, Area L, source term data base is provided at the end of this section.

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3.2 Batch Waste Source Term Data Base Information

3.2.1 Assumptions

All available waste disposal records were used to compile the information contained in the TA-54, Area L, batch waste source term data base. In most cases, information was entered into the data base as it appears in logbook records. In some cases an interpretation of original record information was necessary to derive the maximum amount of information from existing records. Where interpretations were necessary (e.g., some chemical compound names required examination to discern the intended meaning of the technician), notes were inserted in the original records. The assumptions used for this section are as follows:

- 1. When only one volume was written in an entry line and that entry line was followed by others that did not indicate a volume, volume was entered for the first entry only.
- 2. An entry "0.0000" in the volume field indicates that no volume was given for that record or that the procedure outlined in Item 1 above had been followed. The same procedure applies to MO, DY, and YR fields, as indicated by "00".
- 3. The date entered in the data base is the date of disposal unless the date of disposal was not listed. In the event that date of disposal was not listed in the records, the date received was used if it was available.
- 4. If a pit or shaft number was indicated, a "Y" was entered in the LOCATION field indicating that the disposal location is known. If no pit or shaft number was given in the record, an "N" was entered in the LOCATION field indicating that the disposal location is not known.
- 5. Discrepancies exist between column headings used for information entry in the original records. There are two different forms used to record waste disposal information. The following assumptions were made to correlate information from one recording format to the other.
	- A column heading "SOURCE" is equivalent to "ORIGIN".
	- A column heading "CONTENT" is equivalent to "ANALYSIS".
	- A column heading "REMARKS" is equivalent to "AMOUNT".

3.2.2 Definitions of the Fields and Field Variables

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3.2.3 Data Base

The TA-54, Area L, batch waste source term data base follows the source term data base at the end of this section.

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MDA L Investigation Work Plan

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BATCH WASTE SOURCE TERM DATA BASE

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