An Investigation of Plume Response to Soil Vapor Extraction and Hypothetical Drum Failure


Soil vapor extraction (SVE) has been used at sites across the Department of Energy complex, including sites where legacy subsurface wastes represent a potential source of groundwater contamination. At Los Alamos National Laboratory (LANL), leakage from waste drums buried at an inactive chemical waste site has created a subsurface vapor plume of volatile organic compounds (VOCs). Soil vapor extraction operation in 2015 and rebound testing through 2017 were successful in reducing the plume's mass and mitigating VOC migration toward the water table. However, the possibility that waste drums could fail and release VOCs could pose a challenge in the future. To explore the impacts of drum failure, as well as the capabilities of SVE remediation, we simulated hypothetical contaminant release scenarios and subsequent SVE remediation. Three-dimensional subsurface VOC behavior, including advection, diffusion, and plume interactions with topography, were simulated using the porous flow simulator Finite Element Heat and Mass Transfer. Simulations of future site conditions have allowed identification of “sentry” boreholes that can be monitored for early detection in case of drum failure. Sentry boreholes can also be used to set concentration thresholds above which SVE should be initiated. For the LANL site, simulations show that SVE can be started 3 yr following drum failure and remain a viable remediation tool. More broadly, the principles outlined in this work can be used to support remediation planning at other subsurface waste sites. Predictive models of future releases can be analyzed to set concentration threshold values, guide selection of sentry boreholes, and increase operational efficiency.

Abbreviations: 3-D, three-dimensional; bgs, below ground surface; DCA, dichloroethane; FEHM, Finite Element Heat and Mass Transfer; IM, interim measure; LANL, Los Alamos National Laboratory; MDA, Material Disposal Area; PCE, tetrachloroethylene; SL, screening limit; SVE, soil vapor extraction; TCA, trichloroethane; TCE, trichloroethylene; VOC, volatile organic compound.

Subsurface volatile organic compound (VOC) remediation is a significant issue at USDOE sites (Riley and Zachara, 1992; Hirsch, 2005). Volatile organic compounds from legacy waste may accumulate in the unsaturated zone and, if untreated, serve as a potential source of groundwater contamination (Malek-Mohammadi and Tachiev, 2013; Oostrom et al., 2016). Soil vapor extraction (SVE), an in situ remediation method, is routinely used at USDOE sites to remove VOCs from the vadose zone (Switzer et al., 2004; White et al., 2008). This method is capable of removing large quantities of VOCs, although efficiency is known to decline during the period of operation, as indicated by decreasing VOC concentrations in the effluent (Rathfelder et al., 1995; Brusseau et al., 2010). Rebound testing, which entails alternating periods of active SVE with periods of inactivity, is often used to investigate contaminant flux processes and evaluate SVE performance (Switzer et al., 2004). Certain rebound characteristics, such as converging maximum and asymptotic concentration values, signal a decline in SVE effectiveness over the course of multiple cycles (Brusseau et al., 2010).
To assess plume behavior and optimize remediation efforts, SVE may be conducted in combination with hydrogeologic site characterization, numerical flow and transport modeling, and borehole monitoring (Fischer et al., 1996; Vrugt et al., 2008; Stauffer et al., 2011; Brusseau et al., 2013). These tools are particularly important for systematically addressing complex or long-term site remediation (Truex et al., 2013). For instance, at sites where the plume area is unstable or uncertain, borehole placement may be planned to particularly monitor vulnerable regions, locations that allow for early detection, or locations that capture the extent of the plume (Cullen et al., 1995; Hudak and Loaiciga, 1999). Sites that have a persistent VOC source or ongoing and/or potential leakage from waste containers further require robust modeling and simulations (Walton et al., 1990; Oostrom et al., 2010; Carroll et al., 2013). Models capable of simulating subsurface flow in three dimensions, such as Finite Element Heat and Mass Transfer (FEHM), Transport of Unsaturated Groundwater and Heat (TOUGH), and Subsurface Transport over Multiple Phases (STOMP), have been applied to a number of complex VOC-contaminated sites (Stauffer et al., 2007; Oostrom et al., 2010; Dafny, 2017).

We analyzed an interim measure (IM) designed to investigate the efficacy of SVE within a deep unsaturated zone. In 2015, Los Alamos National Laboratory (LANL) began SVE operations on a subsurface VOC vapor plume on lab property (Stauffer et al., 2005; Los Alamos National Laboratory, 2006, 2011). The results of this SVE IM, along with data collected from monitoring boreholes through 2017, were used to calibrate and validate a three-dimensional (3-D) numerical site model in FEHM and simulate future site conditions. Simulations of hypothetical waste drum failure provide insight into SVE system capabilities, i.e., the timing and extent of large-scale VOC removal. Additionally, the simulations were useful in assisting in selection of siren wells, suggesting threshold values of concentration indicative of drum failure, and increasing operational efficiency. Further, these simulations support remediation planning at analogous waste sites, particularly those where future contaminant releases are a concern.

Site Description

Material Disposal Area L (MDA L) is a former non-radioactive liquid chemical waste disposal site at the LANL in New Mexico (Fig. 1). From the 1960s to 1986, containerized and un-containerized wastes were buried at the site in one pit, three impoundments, and 34 shafts (Stauffer et al., 2005; Los Alamos National Laboratory, 2006, 2011). Little information was recorded about the specific chemicals, timing, and quantities of waste disposed at MDA L. In the years since disposal, VOCs gradually leaked from waste drums and now form a vapor plume in the unsaturated zone beneath the site (Stauffer et al., 2005).

Since 1985, a network of monitoring boreholes has been sampled to characterize the vapor plume, which extends laterally beyond the boundaries of the disposal area and to a depth of approximately 90 m below ground surface (bgs) (Fig. 1) (Los Alamos National Laboratory, 2018). Plume growth is controlled primarily by vapor diffusion, with VOCs exiting the subsurface by diffusive flux at the ground surface (Los Alamos National Laboratory, 2011). Downward expansion of the plume VOCs is slow, but a sudden release from drums in the source shafts could cause an increase in VOC concentration as well as mass diffusion deeper into the vadose zone (Stauffer et al., 2011). Lobes of the vapor plume have developed around two disposal shaft fields located on the east and west sides of the site (Los Alamos National Laboratory, 2006, 2016). Although the lobes are distinct in their chemical composition, each consists primarily of five VOCs: 1,1,1-trichloroethane (1,1,1-TCA), trichloroethylene (TCE), tetrachloroethylene (PCE), 1,2-dichloroethene (1,2-DCA), and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113). Of these constituents, 1,1,1-TCA is most prevalent and was therefore used as a representative VOC throughout our study (Hopkins, 2002).

Due to concerns that VOCs could migrate to the underlying fractured basalt and reach the water table (285 m bgs)—potentially resulting in VOC mobilization by groundwater flow—LANL has explored methods for remediation in the vadose zone at MDA L (Los Alamos National Laboratory, 2006, 2011, 2016). Soil vapor extraction wells were installed in 2006, and since then the wells have been periodically operated. Soil vapor extraction was used as an IM between January 2015 and November 2015, as well as for rebound testing between April 2016 and June 2017 (Los Alamos National Laboratory, 2006, 2011, 2018). These periods of SVE operation were intended to reduce VOC concentrations, collect data for remediation design and model calibration, and gain understanding of plume behavior (Los Alamos National Laboratory, 2006).

Geologic Setting

Material Disposal Area L is located on Mesita del Buey, a narrow finger mesa of the Pajarito Plateau (Fig. 2). It is surrounded by canyons on either side: Pajarito Canyon to the south and a tributary of Cañada del Buey to the north (Neeper, 2002). The water table is at a depth of about 285 m bgs at MDA L and has an approximate 1:100 gradient toward the Rio Grande (located 8 km away) in an east–southeast direction (Los Alamos National Laboratory, 2011; Purtymyn, 1995). The deepest geologic unit in the unsaturated zone, the Cerros del Rio basalt (TB4), was formed between 2.3 and 2.8 Ma from eruptions of the Cerros del Rio volcanic field (Broxton and Vaniman, 2005; WoldeGabriel et al., 1996). The basalts vary substantially in density from high-porosity rubbly breccias to fractured massive basalt (Turin, 1995; Broxton and Vaniman, 2005). Above the basalt are the rhyolitic flows of the Bandelier tuff and related clastic depositional layers formed by eruptions of the Jemez volcanic field and subsequent erosion. The plume is located primarily within the tuff units (Stauffer et al., 2005). The Otowi Member (Qbo) of the Bandelier Tuff, formed 1.61 Ma, consists of non-welded to poorly welded tuff with a basal...
Fig. 1. Material Disposal Area (MDA) L, showing pore gas monitoring and soil vapor extraction (SVE) boreholes, located at Los Alamos National Laboratory (Los Alamos National Laboratory, 2014, 2018).
layer of Guaje Pumice (Broxton and Vaniman, 2005; Stauffer et al., 2005). The Cerro Toledo interval (Qct) overlies the Otowi member and consists of interbedded volcano-clastic sediments that vary in size from silt to cobbles (Stauffer et al., 2005; Neeper 2002). Above the Cerro Toledo is the Tshirege Member (Qbt) of the Bandelier Tuff, formed 1.2 Ma (Broxton and Vaniman, 2005). The Tshirege Member of the Bandelier Tuff (layers Qbt2 through Qbtt) has vertical joints throughout and a basal layer of Tsankawi pumice (Qbtt) (Stauffer et al., 2005).

Waste Disposal at Material Disposal Area L

Disposal shafts at MDA L were assigned numerical designations based on their order of construction and are grouped in two clusters: 1 to 28 on the east (operated 1975–1985) and 29 to 34 on the west (operated 1983–1985) (Fig. 3) (Stauffer et al., 2005). During the early years of operation, 200-L (55-gallon) steel drums were emplaced in the shafts along with small containers and free liquid. By 1982, operations had evolved so that drums were emplaced in the shafts without the addition of un-containerized waste (Hopkins, 2002). Shafts were bored to a depth of approximately 18 m, the bottom meter of which was filled with crushed tuff (Hopkins, 2002; Los Alamos National Laboratory, 2011). The shafts were then packed with layers of one to six drums, depending on shaft diameter, which ranged from 0.9 to 2.4 m (3–8 ft) (Table 1). Each layer was covered with 15 cm (6 inches) of crushed tuff, and the top 1 m of the shaft was plugged with concrete (Hopkins, 2002; Los Alamos National Laboratory, 2011). Based on shaft depth and the approximate number of drums per row, it is estimated that the volume of the shafts could allow for 1284 drums, with 880 on the east side and 404 on the west side (Hopkins, 2002) (Table 1). However, due to limited documentation, the exact number of drums per shaft and their contents are unknown (Stauffer et al., 2005).

As the waste drums age, corrosion may result in general drum wall thinning across a large surface area as well as localized pitting perforation (Lyon et al., 1996). Previous studies have suggested that slow leaks from waste drums (i.e., through pinhole leaks or unsealed lids), which are simulated with 200 μL/L fixed sources on the east and west sides of the site, contribute a continuous VOC mass to the plume (Snyder et al., 2017). In the coming decades, VOC leakage may increase as drum walls lose thickness and structural integrity.

In 1996, estimates of corrosion rates were made using data collected from containers of transuranic waste under an earthen cover on the LANL property (Lyon et al., 1996). The Poisson probability distribution described in this study, coupled with an understanding of site conditions and drum properties, was the basis for predicting corrosion and drum failure rates at MDA L. Drum failure—defined as a discrete event in which breaching of the drum wall releases enough mass to reach saturated vapor pressure—has a low probability of occurring at MDA L at present. However, the increasing likelihood of drum failure in the next 10 yr and the consequences of such events are important to consider. In this study, we used a calibrated, site-scale, 3-D numerical model to simulate drum failure and resultant VOC leakage on the east side of MDA L. These simulations demonstrate the
Potential impact of drum failure events on plume mass, extent, and concentration. Potential SVE operation following hypothetical drum failure was also simulated to evaluate the efficacy of SVE for large-scale contaminant remediation. Further, model results were used to identify early-detection “sentry” boreholes and support the selection of concentration thresholds above which SVE operation should be initiated.

**Conceptual and Numerical Model**

A multiphase numerical model of MDA L that honors measured concentrations in the subsurface prior to the 2015 SVE IM was previously developed (Stauffer et al., 2005, 2007; Los Alamos National Laboratory, 2011; Snyder et al., 2017). The 3-D model was first calibrated with 1,1,1-TCA concentration data collected over several years at monitoring boreholes and then following a short SVE pilot test performed in 2006 (Stauffer et al., 2005, 2007). Numerical simulations of gas flow and transport were performed using the LANL developed FEHM transfer code, a multiphase porous flow simulator based on Darcy’s Law (Zyvoloski et al., 1997). The FEHM governing equations account for diffusion and advection, as well as Henry’s Law partitioning of VOC constituents between liquid and vapor phases. Governing equations include conservation of water mass,

\[
\frac{\partial A_m}{\partial t} + \nabla \cdot \mathbf{f}_m + q_m = 0
\]

and conservation of air mass,

\[
\frac{\partial A_\eta}{\partial t} + \nabla \cdot \mathbf{f}_\eta + q_\eta = 0
\]

where \(A_m\) and \(A_\eta\) are the mass per unit volume of water and air, respectively; \(\mathbf{f}_m\) and \(\mathbf{f}_\eta\) are water and air mass fluxes, respectively, with units of mass per area time; \(q\) is the source–sink term; and \(t\) is time. Water mass per unit volume, \(A_m\), is given by

\[
A_m = n \left[ S \left( r_v \right) \left( 1 - \eta_v \right) + S \left( r_l \right) \left( 1 - \eta_l \right) \right]
\]

and air mass is similarly

\[
A_\eta = n \left[ S \left( r_v \right) \left( 1 - \eta_v \right) + S \left( r_l \right) \left( 1 - \eta_l \right) \right]
\]

where \(S\) is the saturation and \(r\) is the density of the vapor phase and liquid phase (subscripts \(v\) and \(l\), respectively); \(n\) is porosity; and \(\eta\) is the mass fraction of air contained in the vapor phase. Air mass per unit volume is similarly

\[
A_\eta = n \left[ S \left( r_v \right) \left( 1 - \eta_v \right) + S \left( r_l \right) \left( 1 - \eta_l \right) \right]
\]

Mass fluxes for water and air are

\[
\mathbf{f}_m = \left( 1 - \eta_v \right) \rho_v \mathbf{u}_v + \left( 1 - \eta_l \right) \rho_l \mathbf{u}_l
\]

and

\[
\mathbf{f}_\eta = n \left( \eta_v \rho_v \mathbf{u}_v + \eta_l \rho_l \mathbf{u}_l \right)
\]

where \(\mathbf{u}\) is the volumetric flux. Darcy’s Law applies to the movement of the vapor and liquid:

\[
\mathbf{u}_v = -\frac{k_v}{\mu_v} \left( \nabla P_v - \rho_v \mathbf{g} \right)
\]

and

\[
\mathbf{u}_l = -\frac{k_l}{\mu_l} \left( \nabla P_l - \rho_l \mathbf{g} \right)
\]

where \(k\) is the relative permeability of the respective phases, \(P\) is pressure, and \(\mathbf{g}\) is the gravitational vector. Linear functions for relative permeability are given by

Fig. 3. Site map of Material Disposal Area L with disposal shaft, pit, and impoundment locations (Stauffer et al., 2005). The size of each shaft circle is proportional to its diameter.
where $S_{lr}$ is residual liquid saturation, $S_{vr}$ is residual vapor saturation, $S_{lmax}$ is maximum liquid saturation, and $S_{vmax}$ is maximum vapor saturation. The Corey relative permeability functions are given by

$$R_l = \frac{0, \quad S_l \leq S_{lr}}{S_{lmax} - S_{lr}}, \quad S_{lr} < S_l < S_{lmax}$$  \[9\]

$$R_v = \frac{0, \quad S_v \leq S_{vr}}{S_{vmax} - S_{vr}}, \quad S_{vr} < S_v < S_{vmax}$$  \[10\]  

$$\left(1 - S'_l\right)^2 \left(1 - S'_v\right)^2$$  \[12\]  

where $S'_l = (S_l - S_{lr})/(1 - S_{lr} - S_{vr})$ and $S'_v$ are the residual and liquid vapor saturations, respectively. In this study,
isothermal conditions, constant temperature, and no flow of the liquid phase due to low saturation are assumed. Conceptually, our model simulates (under non-pumping conditions) a vapor plume that is primarily controlled by diffusion away from two shaft fields with spreading in the vertical and horizontal direction. The model allows for diffusion across the ground surface and has pore water that provides VOC storage through equilibrium partitioning. However, due to the low moisture content and poor adsorption properties of the tuff matrix, as well as low VOC solubility, VOCs released from drums remain predominantly in the vapor phase (Los Alamos National Laboratory, 2002). Extraction data from prior studies indicate that there is no free liquid source of VOCs in the subsurface (Los Alamos National Laboratory, 2006). The model is calibrated to recent VOC concentration data and can be applied to simulate the plume behavior at MDA L.

The MDA L site model uses a 3-D computational mesh that is 411 m in the east–west direction by 290 m in the north–south direction. The mesh extends vertically from the ground surface, defined by a digital elevation model, to the water table (285 m bgs) (Stauffer et al., 2005). The grid resolution of 10 m horizontally and 1 to 25 m vertically, with higher resolution closer to the ground surface, results in a 142,707 node mesh. Two high-resolution SVE wells are embedded in the mesh to capture the impact of SVE during periods of active pumping (Stauffer et al., 2007). The MDA L mesh is based on a comprehensive, LANL-wide geologic model in which borehole data were interpolated to create stratigraphic unit boundaries (Cole et al., 2010).

**Model Calibration**

A previous MDA L site model was developed in three stages (Stauffer et al., 2011). First, a simulation of diffusive plume growth following waste placement between 1985 and 2006 was used to assess the conceptual model and evaluate the continuous VOC sources responsible for plume growth. A 2006 SVE pilot test was then used to calibrate the model while taking into account vapor migration (advection) during extraction. The third stage was a blind validation of the model that involved calculating the 2006 to 2010 plume rebound following the pilot test. Characteristics from different rock layers (e.g., permeability, porosity, and moisture content) were added to these simulations using site field data. Calibration targets included vapor concentration data collected in the monitoring boreholes for several years before the pilot test and data gathered during the pilot test (applied vacuum, extraction rate, and 1,1,1-TCA extraction concentration as functions of time) to estimate source concentrations and to generate permeability distributions that fit the data (Stauffer et al., 2011). The permeability calibration was revisited using data from the early part of the 2015 SVE IM, and it was determined that the existing AMALGAM (A Multi-Algorithm Genetically Adaptive Method) calibration on the west side of the site worked well (Vrugt et al., 2008). The previous calibration on the east side did not yield acceptable results (we believe the original drawdown pressure transducer was mis-calibrated). Thus, a manual recalibration was performed to simultaneously match pressure drawdown and flow rate on the east side. From early 2015 onward the re-calibrated permeability structure was used to both predict plume behavior and to verify the calibration using posterior data from early 2015 through June 2017 (Snyder et al., 2017). In the updated model, the initial fixed concentration in the source regions was adjusted from 300 to 200 μL/L based on data collected during the SVE IM in early 2015. Although 300 and 200 μL/L fixed source concentrations yield similar regressions to the measured plume in 2015, the 200 μL/L case results in a better match to concentrations in the SVE wells (Fig. 4) (Los Alamos National Laboratory, 2018). This updated model forms the basis for the drum failure scenarios presented below.

**Methods: Plume Analysis**

**Soil Vapor Extraction Remediation**

Soil vapor extraction is a well-established method for VOC remediation in the vadose zone (Truex et al., 2013; Fischer et al., 1996; Oostrom et al., 2014). Soil vapor extraction is conducted...
using wells that pull vapor from the subsurface and filter it for rough particulates. The effluent gas may be captured for treatment, or as in the case of the MDA L IM, permission was granted from the State of New Mexico for low masses of effluent to be vented to the atmosphere. In recent years, SVE has been tested as a possible remediation method for the plume at MDA L to keep vapor from migrating toward the groundwater (Los Alamos National Laboratory, 2006, 2016). Two SVE wells were installed at MDA L in 2006, one each on the east and west sides of the site (Fig. 1) (Los Alamos National Laboratory, 2006, 2016). From 0 to 20 m bgs both wells have steel casings, so contaminants are extracted from the deeper, uncased section of each well: between 20 and 35 m bgs for SVE-West and between 20 and 65 m bgs for SVE-East (Los Alamos National Laboratory, 2018). The VOCs are drawn upward by suction pumps at the tops of the SVE wells, where the main blower unit’s vacuum is set to achieve a flow rate of 0.055 kg/s (100 standard ft³/min). Condensed liquid is removed in the knock-out tank as the effluent gas is filtered for rough particulates and discharged (Los Alamos National Laboratory, 2016).

### Borehole and Soil Vapor Extraction Sampling

At MDA L, gas samples were collected from SVE wells and monitoring boreholes to provide concentration data to evaluate SVE effectiveness in reducing the plume’s mass and spatial extent (Fig. 1). The samples were collected in canisters and sent to an analytical laboratory (Eurofins Air Toxics, Inc.) for analysis using USEPA (1999) to determine VOC concentrations (Los Alamos National Laboratory, 2018).

In September 2014, prior to activation of the SVE units, all 25 monitoring boreholes at MDA L were sampled to provide a pre-remediation baseline for the plume concentration and extent. Sampling of these 25 boreholes was repeated annually in 2016 and 2017 to provide a full measure of the extent of the vapor plume. From 2015 onward, quarterly sampling was additionally conducted for a subset of 14 boreholes located within 45 m of the SVE wells (Fig. 1) (Los Alamos National Laboratory, 2014, 2018).

The SVE IM began in January 2015 and ran continuously (except for brief interruptions due to power failures and technical issues) using extraction wells SVE-East and SVE-West for 10 mo (Fig. 5). During 2016, continuous SVE was halted and the system switched to a rebound pattern that occurred quarterly (Los Alamos National Laboratory, 2016). The SVE units were run for 2 to 5 d, followed by multiple months of inactivity. During June 2017, the SVE-East unit was run for a final 25-d period. Suction, flow rate, and effluent concentration were measured during each period of active SVE operation.

### Tracking Plume Size and Concentration

Sampling data were spatially interpolated to determine the 1,1,1-TCA concentration and extent before, during, and after the SVE IM (Weston Solutions, Inc., 2015, 2016). The geology of MDA L, as well as the locations of SVE wells and monitoring boreholes, are included in our analysis. Plume contours are depicted relative to a 42,300 µg/m³ 1,1,1-TCA screening limit (SL) with 5×, 10×, 20×, and 30× the SL used to define each of the plume’s inner contours (Los Alamos National Laboratory, 2011). The 1,1,1-TCA SL is calculated as the threshold above which 1,1,1-TCA in water, based on Henry’s Law partitioning of a given 1,1,1-TCA pore gas concentration,

\[
H' = \frac{C_{\text{air}}}{C_{\text{water}}} \tag{13}
\]

exceeds the New Mexico Water Quality Control Commission regulatory standards for 1,1,1-TCA in groundwater:

\[
\text{SL} = \frac{C_{\text{air}}}{1000 H' G S} \tag{14}
\]

where \(C_{\text{air}}\) is the concentration of 1,1,1-TCA in a pore gas sample (µg/m³), \(H'\) is the dimensionless Henry’s Law constant (0.705), GS is the 1,1,1-TCA groundwater regulatory standard (60 µg/L), and 1000 is the conversion factor from liters to cubic meters (L to m³).

### Major Volatile Organic Compounds

Five major VOCs (1,1,1-TCA, TCE, PCE, 1,2-DCA, and Freon-113) make up the majority of the mass of the vapor plume at MDA L. To understand how these VOCs respond to SVE, gas samples were collected from both SVE wells and from a variety of borehole locations and depths. Samples collected at the SVE wells were analyzed to understand how the concentrations of major VOCs change with time in response to SVE operation. Soil vapor extraction samples were additionally analyzed to examine the mole fraction of each major VOC, which was calculated by dividing the concentration of each major VOC by the summation of all VOCs.

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**Fig. 5.** Timeline of soil vapor extraction (SVE) operations from January 2015 through June 2017. A black line following a blue box represents a 5-min period when atmospheric air entered the subsurface after the pump was shut off and before the SVE unit was sealed.
detected for a given sample. The concentrations of major VOCs at different monitoring borehole depths were examined to understand the role of stratigraphy and proximity to SVE wells on VOC concentrations. Samples collected before, during, and after SVE operation allow the determination of how VOC concentrations respond to SVE operation with time.

**Methods: Drum Failure Simulation**

**Corrosion and Drum Failure**

Because of uncertainty in the number of drums and remaining VOC source at MDA L, as well as corrosion processes in an unsaturated porous medium, it is difficult to predict how drum corrosion will impact future release scenarios. In the following analysis, drum failure for the east side of MDA L is estimated using a Poisson distribution of general corrosion rate data (Lyon et al., 1996). The drum walls are assumed to be 1.27 to 1.52 mm thick and to corrode at a rate of 0.0254 mm/yr due to the site’s relatively dry climate and the use of tuff as an absorbent material. The loss of each 0.0254-mm unit is considered an event. Thinning of the drum wall, also known as general corrosion, can be calculated as a probability distribution for the time (in years) when the corrosion depth (a function of corrosion rate and time) exceeds a certain drum wall thickness:

\[
P(T, L) = 1 - \sum_{j=0}^{L-1} \frac{\exp(-RT)(RT)^j}{j!}
\]

where \( T \) is time, \( R \) is the corrosion rate of the drum exterior, and \( L \) is the corrosion depth.

If corrosion depth \( L \) exceeds 1.52 mm, the structural integrity of the drum is seriously compromised. An incident of this scale, defined as drum failure, produces a sudden release of enough liquid VOC mass to reach the saturated vapor pressure. The cumulative probability of drum failure (\( L > 1.52 \) mm) remains close to 0% in the interval between 0 and 43 yr, while general corrosion (\( L > 1.27 \) mm) reaches 13% by 43 yr (Fig. 6).

As of 2018, the drums buried on the east side of MDA L (1975–1985) are between 33 and 43 yr old (Hopkins, 2002). Borehole monitoring data collected from 1985 onward show only small increases in 1,1,1-TCA concentrations, supporting the conceptual model of slow leaks but no prior drum failure events. However, the probability of drum failure is predicted to increase sharply in the coming decade as drums enter the 43- to 53-yr age range (Fig. 6). By 53 yr after disposal, there is a 15% chance of corrosion to the point of drum failure on the east side of MDA L. It is noted that drums may be only partially filled, either because they were not completely full when disposed of or because of slow leakage that has occurred over many years from pinhole failure. These scenarios would reduce the amount of free liquid available during a drum failure event, such that the hypothetical drum failure cases presented are end-member, worst case scenarios. In anticipation of these potential events, scenarios in which one, five, or 10 drums fail and release large amounts of 1,1,1-TCA are simulated. Simulating drum failure provides a numerical representation of what may happen in the future at MDA L, and these scenarios form a basis for remediation planning.

**Ten-Year Simulations**

In the scenarios presented below, plume development for cases with and without drum failure are simulated for a 10-yr period. For drum failure scenarios, simulated plume growth in un-remediated cases are compared with simulations that include SVE. To create a baseline case with no drum failure for comparison, 10 yr of plume growth with 200 µL/L leak sources on the east and west sides of the site is simulated. This initial condition is based on the calibrated model that best matches site conditions following the 2015 SVE IM and the subsequent 2-yr rebound period (Fig. 5). At the start of the baseline run in June 2017, the plume had a total mass of 413 kg 1,1,1-TCA, with concentrations reaching up to five times the 1,1,1-TCA SL (211,500 µg/m³) in the Qbt1g and Qct. During the subsequent 10-yr period, the volume of the plume expands, particularly in the upper strata, while maximum concentrations fall below \( 2 \times \) the 1,1,1-TCA SL (85,600 µg/m³) in most regions. During this time, there is also a net mass decrease to 397 kg 1,1,1-TCA, primarily by diffusion into the atmosphere.

![Fig. 6. Drum failure probability vs. time for 1.27, 1.40, and 1.52 mm of corrosion depth at Material Disposal Area (MDA) L. The purple region represents the 33- to 43-yr range and the blue region represents the 43- to 53-yr range.](image)
across the ground surface boundary because of the high concentration gradient between the plume and ground surface.

**Drum Failure Location and Setup**

After establishing baseline plume behavior, scenarios including drum failure are presented. Although the precise location of a future, hypothetical drum failure is unknowable, we establish a hypothetical drum failure source region that is within the shaft field on the east side of MDA L (Fig. 7). The source of the drum failure is further defined as 12 to 24 m bgs.

Each 200-L (55-gallon) drum at MDA L could contain a maximum estimated 264 kg mass (1979 mol) of pure liquid 1,1,1-TCA (Table 2). Scenarios are considered in which one, five, and 10 drums fail suddenly, releasing 1,1,1-TCA in a pulse of 1979, 9895, or 19,790 mol, respectively. However, due to the 1,1,1-TCA maximum vapor pressure of 160,000 L/L at 20°C, the available liquid is not all vaporized immediately (Rubin et al., 1944). Rather, 1,1,1-TCA stays in the liquid phase until the proximate vapor mass spreads enough to yield concentrations below the 160,000 L/L threshold. To simulate a one-drum failure event, the hypothetical drum source is fixed at 160,000 L/L to produce a pulse of 1,1,1-TCA for 1 d, the length of time required to produce 1979 mol. The five-drum failure simulation requires 159 d to produce 9895 mol with the source concentration fixed at 160,000 μL/L, and the 10-drum failure simulation requires 482 d to produce 19,790 mol (Table 2). Although vertical liquid transport was not computed, the source region between 12 and 24 m conceptually represents approximately 6 m of liquid flow below the deepest drums (18-m depth) before volatilization. Simulations started on 30 June 2017 following the conclusion of an SVE rebound study and continued for 10 yr.

**Monitoring and Remediating Drum Failure**

If drum failure were to occur at MDA L, it would be initially recognized through elevated sample concentrations at nearby monitoring boreholes. Accordingly, simulated changes in concentration are observed at a range of port depths and at relevant stratigraphic units for selected monitoring boreholes. These observations provide insight into 1,1,1-TCA migration, reveal which strata would be most affected by drum failure, and demonstrate how sentry boreholes can be monitored to provide early detection.

Although there are several existing boreholes on the east side of MDA L, three were selected for close monitoring due to their location and range of sampling port depths (Fig. 7). Boreholes 54-24238, 54-27642, and 54-24241 are 7.7, 14.2, and 36.3 m, respectively, from the simulated drum failure region (Table 3), encompassing a wide range of possible distances at which hypothetical drum failure could be detected. Each of these boreholes also has ports at multiple depths that could be observed to provide data on the timing, concentration, and migration of VOCs. Further, data provided by the three monitoring boreholes could be used to characterize the location, timing, and magnitude of a hypothetical drum failure event.

![Site Map of MDA L](image)

**Table 2. Quantity of 1,1,1-trichloroethane (TCA) injected in one-, five-, and 10-drum failure scenarios.**

<table>
<thead>
<tr>
<th>Drum failures</th>
<th>Quantity</th>
<th>Concentration</th>
<th>Simulated time until gas-phase saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>no.</td>
<td>L</td>
<td>mol</td>
<td>d</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>1,979</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>9,895</td>
<td>159</td>
</tr>
<tr>
<td>10</td>
<td>2000</td>
<td>19,790</td>
<td>482</td>
</tr>
</tbody>
</table>

*Fig. 7. Locations of monitoring boreholes 54-24241, 54-24238, and 54-27642, as well as the source region for drum failure and the soil vapor extraction (SVE) well on the east side of Material Disposal Area (MDA) L.*
The impact of hypothetical SVE remediation was explored by simulating advective flow from the SVE-East region. Hypothetical SVE remediation was initiated 3 yr after the beginning of hypothetical drum failure (June 2020) to provide a realistic time frame for detection, remediation planning, and any operational delays that could occur. A 3-yr window also allows for more extensive plume development and therefore serves as a greater test of hypothetical SVE capabilities.

Results and Discussion

Plume Response to Soil Vapor Extraction

Interpolated borehole measurements of 1,1,1-TCA suggest a significant decrease in total plume mass between the September 2014 baseline and the February 2016 post-SVE IM sampling round (Fig. 8 and 9). The 1,1,1-TCA mass was reduced by approximately 60% during this time period, from 740 to 305 kg (Weston Solutions, Inc., 2016). The 1,1,1-TCA concentration also decreased, with the portion of the plume mass above 10× the 1,1,1-TCA SL decreasing from 333 kg in September 2014 to 6 kg in February 2016 (Weston Solutions, Inc., 2016). The VOC concentrations measured at SVE-East and SVE-West decreased quickly in the initial months of the SVE IM, then more gradually. Although concentrations during the SVE IM reached a minimum of 0.43 μL/L at SVE-West and 14 μL/L at SVE-East, it was determined that neither of these values represents an asymptote (Fig. 4).

Borehole sampling on the west side of MDA L showed consistent concentration reductions in response to SVE operation (Fig. 10). Boreholes 54-27641 and 54-24240 are within 45 m of SVE-West, and during the SVE IM each of these wells showed significant decreases in 1,1,1-TCA concentration at 20 to 35 m bgs, a depth that coincides with the extraction interval of SVE-West. The VOC concentrations also decreased above the SVE extraction interval, as air from the surface swept the shallow part of the vapor plume toward the extraction interval. On the east side of MDA L, most boreholes within 45 m of SVE-East also showed reduced concentrations during the SVE IM (Fig. 10). However, at monitoring Boreholes 54-02089 and 54-24238, 1,1,1-TCA

Fig. 8. Interpolation of the 1,1,1-trichloroethane (TCA) vapor plume concentrations at Material Disposal Area L for sampling performed before the soil vapor extraction interim measure (September 2014) (Weston Solutions, Inc., 2016).

Table 3. Distance from drum failure source region to monitoring boreholes and soil vapor extraction (SVE) location.

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Distance from SVE-East</th>
<th>Distance from drum failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>54–27642</td>
<td>41.9</td>
<td>14.2</td>
</tr>
<tr>
<td>54–24238</td>
<td>29.7</td>
<td>7.7</td>
</tr>
<tr>
<td>54–24241</td>
<td>24.5</td>
<td>36.6</td>
</tr>
</tbody>
</table>
Fig. 9. Interpolation of the 1,1,1-trichloroethane (TCA) vapor plume at Material Disposal Area L for sampling performed (A) before the 2015 soil vapor extraction (SVE) measure (September 2014), (B) during SVE (April 2015), and (C) following SVE (February 2016) for cross-section A–A' (Weston Solutions, Inc., 2016).
Fig. 10. Measured 1,1,1-trichloroethane (TCA) concentrations as a function of depth in pore gas monitoring boreholes for September 2014 (before the soil vapor extraction interim measure [SVE IM] baseline), May 2015 (during SVE IM), May 2016, May 2017, and August 2017.
concentrations remained elevated; 1,1,1-TCA was consistently measured at 20× the SL at Borehole 54-24238. This persistently high concentration suggests that there may be leaking waste drums near Borehole 54-24238 contributing additional contamination during SVE operation.

During periods of SVE inactivity, i.e., subsequent to the SVE IM and each rebound test, contaminants diffuse back toward the SVE wells due to concentration gradients that develop during extraction. This concept is well documented in the literature and supported in the current study by high effluent concentrations at the beginning of each rebound test (Switzer et al., 2004). The plume may be further recharged by ongoing sources, such as pinhole leaks or unsealed drum lids. Although the MDA L plume exists predominantly in the vapor phase, an unknown quantity of VOCs stored in pore water and other immobile zones also re-volatilize under rebound conditions. The magnitude of the concentration reductions observed during active SVE, coupled with relatively high rebound rates, suggests that periodic SVE remediation is still a viable remediation strategy at MDA L.

Concentration of Major Volatile Organic Compounds

Based on effluent gas samples collected from SVE-East and SVE-West, all of the major VOCs decreased in concentration during the SVE IM and rebound testing (Fig. 11, top). The VOC concentrations on both sides of the site decreased rapidly at the beginning of the SVE IM and then declined more gradually with time. The west side had greater measured VOC concentrations

Fig. 11. Effluent concentration (top) and molar ratio (bottom) for five major volatile organic compounds (1,1,1-trichloroethane [TCA], trichloroethylene [TCE], tetrachloroethylene [PCE], 1,2-dichloroethane [DCA], and 1,1,2-trichloro-1,2,2-trifluoroethane [Freon-113]) at the soil vapor extraction wells SVE-West (left) and SVE-East (right).
when the SVE IM began in 2015 but showed larger reductions than the east side (Fig. 11, top). During the SVE IM, some variation was observed in the molar ratio of major VOCs extracted. Most noticeably, the mole fraction of PCE on the west side increased as the mole fraction of TCE decreased. Strong liquid partitioning of PCE is a possible factor in this increasing mole fraction of PCE (Los Alamos National Laboratory, 2018). The major VOCs 1,1,1-TCA, 1,2-DCA, and Freon-113 also decreased slightly in mole fraction during SVE operation (Fig. 11, bottom). These changes can be attributed, in part, to uneven VOC distributions throughout the plume.

**Drum Failure Simulation**

In simulations of hypothetical drum failure, total plume 1,1,1-TCA mass increases sharply from the 413 kg baseline observed in June 2017. For one-, five-, and 10-drum failure scenarios, the 1,1,1-TCA mass of the plume peaks at 665, 1719, and 2959 kg, respectively. Without simulated SVE remediation, the 1,1,1-TCA mass then gradually decreases to 539, 1161, and 1953 kg by Year 10 due to diffusion across the ground surface boundary. These masses are highly elevated relative to the scenario without drum failure, which simulated a 397-kg plume mass by June 2027.

For scenarios in which SVE is simulated starting 3 yr after drum failure, the plume’s 1,1,1-TCA mass decreases to the 413 kg baseline within 8, 13, and 16 mo for one-, five-, and 10-drum failures. With continuous SVE operation from Year 3 onward, the 1,1,1-TCA mass decreases to 159 kg, less than half the initial mass, by Year 10 (Table 4).

The increase in the 1,1,1-TCA plume mass following drum failure is accompanied by an increase in concentration, particularly near the source region. Following a one-drum failure event, 1,1,1-TCA concentrations in the Qbt1vu exceed 20× the SL at 3 yr and up to 10× the SL after 10 yr (Fig. 12). Following five- and 10-drum failure events, 1,1,1-TCA concentrations in the Qbt1vu exceed 20× the SL at both 3 and 10 yr (Fig. 13 and 14). However, with SVE beginning at 3 yr, the plume concentration decreases below the 1,1,1-TCA SL at all measured points for one-, five-, and 10-drum failures by Year 10 (Fig. 12, 13, and 14).

Table 4. The 1,1,1-trichloroethane (TCA) plume mass at 0, 3, and 10 yr with and without soil vapor extraction (SVE).

<table>
<thead>
<tr>
<th>Drum failures no.</th>
<th>Initial mass</th>
<th>3 yr</th>
<th>10 yr With no SVE</th>
<th>With SVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>413</td>
<td>623</td>
<td>539</td>
<td>159</td>
</tr>
<tr>
<td>5</td>
<td>413</td>
<td>1522</td>
<td>1161</td>
<td>159</td>
</tr>
<tr>
<td>10</td>
<td>413</td>
<td>2541</td>
<td>1953</td>
<td>159</td>
</tr>
</tbody>
</table>

Fig. 12. Simulation results for 1,1,1-trichloroethane (TCA) concentration following a one-drum failure event at 0, 3, 10 yr with soil vapor extraction (SVE) turned on at 3 yr, and 10 yr without SVE.
Fig. 13. Simulation results for 1,1,1-trichloroethane (TCA) concentration following a five-drum failure event at 0, 3, 10 yr with soil vapor extraction (SVE) turned on at 3 yr, and 10 yr without SVE. (SVE) turned on at 3 yr, and 10 yr without SVE.

Fig. 14. Simulation results for 1,1,1-trichloroethane (TCA) concentration following a 10-drum failure event at 0, 3, 10 yr with soil vapor extraction (SVE) turned on at 3 yr, and 10 yr without SVE.
Simulated concentrations by stratigraphic unit show that the Qbt1vu has the highest predicted peak concentrations of 1,1,1-TCA resulting from one-, five-, and 10-drum failures (Fig. 15). The most rapid increase in concentration also occurs in this unit, probably due to its proximity to the drum failure source region. For one-drum failure, 1,1,1-TCA concentrations measured in the Qbt1vu peak at 4700 µL/L at Borehole 54-24238, 1600 µL/L at Borehole 54-27642, and 330 µL/L at Borehole 54-24241 (Fig. 15). In the upper layers of the stratigraphy, as seen at the top of the Qbt1vu, Qbt1vc, and Qbt1g, peaks are followed by a decline in concentration as 1,1,1-TCA diffuses outward from the source region. At greater depths, such as at the top of the Cerro Toledo interval, concentrations are stable for several years before slowly increasing as the drum failure mass diffuses outward from high-to low-concentration areas. The 1,1,1-TCA concentration in the Cerros del Rio basalt remains relatively stable, rising only slightly during the 10-yr period from 12 to 16 µL/L. Nonetheless, plume behavior in the basalt is important to observe because it represents the pathway to the water table where future groundwater contamination could become a potential concern.

Fig. 15. Simulation results for 1,1,1-trichloroethane (TCA) concentration following one-drum failure at various depths below the ground surface (bgs) at Boreholes 54-24238, 54-27642, and 54-24241: concentrations in each stratigraphic unit (left), and concentrations at sampling ports (right).
Soil Vapor Extraction following Drum Failure

Soil vapor extraction remediation should be planned in accordance with site goals for VOC reduction. While complete remediation is difficult to achieve given the diminishing returns of SVE, goals may include keeping VOCs beneath a particular concentration threshold or preventing plume expansion beyond a certain region (Brusseau et al., 2013; Truex et al., 2013). Our simulations with SVE operation starting 3 yr after drum failure are based on the goal of returning the plume’s 1,1,1-TCA concentrations to pre-drum-failure levels (Fig. 16). From the beginning of SVE operation in June 2020, it takes 13, 18, and 20 mo, respectively, to reduce concentrations to this level in the Qbtvu region of Borehole 54-24238 for one-, five-, and 10-drum failures (Table 5). At the same borehole, 18, 24, and 27 mo, respectively, are...
needed to reduce concentrations to pre-drum-failure levels in the Qbt1vc for one-, five-, and 10-drum failures (Table 5). The Qbt1vc region of 54-24238 takes the longest time of all measured boreholes and strata and can therefore be used to create a conservative estimate of the time needed for SVE remediation to pre-drum-failure levels. A more basic site goal of preventing VOCs from reaching the basalt at high concentrations (i.e., above the SL) is also accomplished through post-drum-failure SVE operation.

### Monitoring Borehole Efficacy

A well-designed borehole network is important for optimizing remediation operations. At MDA L, monitoring for early detection of potential drum failure is a priority, as is ensuring that high concentrations of VOCs do not reach the fractured basalt units. Therefore, boreholes located in the potential source region with sample ports at appropriate depths have been selected as sentry boreholes for future sampling and monitoring. On the east side of MDA L, Boreholes 54-24238, 54-27642, and 54-24241 are most well sited to meet these criteria (Fig. 17). In particular, Borehole 54-24238 has three ports located in the Qbt1vu and can thus be expected to show a strong concentration increase if drum failure occurs. In simulations of one-drum failure, 1,1,1-TCA concentrations at Borehole 54-24238 increased by a factor of $95 \times 10^{1.60}$ the baseline (June 2017) concentration within 6 mo. Borehole 54-27642, which has seven ports at a range of depths extending from 8 to 103 m bgs, also has potential as a sentry borehole for early drum failure detection. Simulations show that while concentrations at the lower ports of Borehole 54-27642 remain relatively stable for 6 mo following one-drum failure, the 1,1,1-TCA concentration in the Qbt1vu increases by a factor of 100 during this time frame (Fig. 17). On the west side of MDA L, periodic monitoring in Boreholes 54-24240 and 54-27641 could be used similarly for early drum failure detection. These two boreholes are in close proximity to the west-side shaft region and have monitoring ports located at 10 to 47 and 10 to 102 m bgs, respectively.

Based on the simulated values, project planners will be able to guide the development of specific concentration thresholds for MDA L. Large concentration increases—above $100 \times$ the baseline concentration, for instance—may be used in the future to determine that a drum has failed, necessitating active SVE remediation. These same principles can be applied to other waste sites, where predictive models of future releases could guide site planning, selection of sentry borehole locations, and setting threshold concentration values to trigger SVE operation.

### Conclusions

We present results from a calibrated flow and transport model for the Los Alamos National Laboratory liquid waste disposal facility, MDA L. The site model has improved with a recalibration of flow and transport parameters for the east side of

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**Table 5. Soil vapor extraction remediation time to achieve pre-drum failure 1,1,1-trichloroethane concentration.**

<table>
<thead>
<tr>
<th>Unit</th>
<th>Drum failures</th>
<th>Remediation time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Borehole 54-24238</td>
<td>Borehole 54-27642</td>
</tr>
<tr>
<td></td>
<td>no.</td>
<td>mo</td>
</tr>
<tr>
<td>Qbt1vu</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Qbt1vc</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>27</td>
</tr>
<tr>
<td>Qbt1g</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

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**Fig. 17.** Measured 1,1,1-trichloroethane (TCA) concentration (June 2017) and simulated 1,1,1-TCA concentration (December 2017–December 2018) for Boreholes 54-24238 and 54-27642 following one-drum failure. Concentration is displayed as a function of depth.
MDA L. Confidence in the model calibration comes from using only pressure and flow data from prior to early 2015 in the calibration (anterior data) and using data from after early 2015 through June 2017 to verify the model behavior (posterior verification). Posterior verification includes periods of both active SVE and plume rebound, where the model and data show excellent agreement.

Following the SVE IM, substantial decreases in total VOC mass were observed at MDA L. Decreases in VOC concentration occurred at a wide range of monitoring boreholes and port depths, although small amounts of leakage near Borehole 54-24238 seem to contribute additional contamination to the plume. We note that concentration increases due to leaking drums are much lower than the increases assumed with drum failure of pure product.

The calibrated model was used to simulate 1,1,1-TCA concentrations following hypothetical one-, five-, and 10-drum failures on the east side, as well as SVE remediation in the case of drum failure. Our results indicate that SVE is a feasible remediation strategy for reducing VOC mass and mitigating the possibility of the plume reaching the water table and contaminating the groundwater, even when considering potential drum failure. After no more than 2.25 yr of simulated continuous operation, SVE reduces 1,1,1-TCA to pre-drum-failure concentrations at selected boreholes following one-, five-, and 10-drum failure events.

At MDA L, sampling boreholes adjacent to existing buried drums can act as an early warning system for leaks that could occur due to increased corrosion or drum failure. In particular, Boreholes 54-24238 and 54-27642 are able to quickly detect elevated VOC concentrations on the east side of the site. Based on simulation and rebound results, sampling sentry Boreholes 54-24238 and 54-27642 every 1 to 2 yr should be sufficient for early warning. After detection, SVE operation could be further delayed up to 3 yr from the date of initial drum failure and still effectively remediate the site to concentrations below the SL.

At contaminated sites across the USDOE complex, simulations bounding potential leakage scenarios could likewise be used to determine the usefulness of SVE related to future releases. Factors such as matrix characteristics, water table depth, fractures, and contaminant mass vary greatly across sites. However, 3-D flow and transport models incorporating these variables could be used to support site-specific remediation goals, locate sentry wells, and suggest threshold concentrations to trigger active SVE.

Acknowledgments

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