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# Conceptual Model for Vapor Movement at MDAs: Organic Vapor Plume Movement at MDA L

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Vapor phase contaminants are of potential concern at several Material Disposal Areas (MDAs) at Los Alamos National Laboratory (LANL). One such contaminant is tritium, which is present at MDA G, Technical Area (TA) -54 and at MDAs at TA-21. Contaminants at MDA L, TA-54 include vapors of volatile organic compounds (VOCs) such as the organic solvents 1,1,1,-trichloroethane (TCA) and trichloroethylene (TCE). Because their density is greater than water and they do not readily dissolve in water, these compounds are dense non-aqueous phase liquids or DNAPLS. This document is a step towards developing a conceptual model (or modeling approach) for modeling vapor flow beneath MDAs at LANL. The focus here is a conceptual model for the organic vapor plume within the mesa beneath MDA L.

**Model Purpose**

The goal of modeling the organic vapor plume at MDA L is to demonstrate an understanding of the processes controlling movement of the plume, leading to a prediction of future movement. This understanding indicate whether vapor fluxes at the mesa surface present a future health threat. Other risks can be evaluated, such as the possibility of organic vapors reaching the regional aquifer and causing contamination that exceeds drinking water standards.

The purpose of this conceptual model is to identify the physical processes or aspects of the system (such as boundary conditions or source term) that have a major impact on vapor movement and on movement of organic contaminants at MDA L. To carry out an efficient model investigation, the problem must be simplified by only considering the system's most important physical processes and characteristics. Many processes (for example, subsurface seasonal temperature variations) affect vapor movement.

Part of the conceptualization of the flow system includes recognizing the geometric and hydraulic properties of the system (such as permeability structure and boundary conditions) and environmental properties (such as barometric pressure forcing) that may affect vapor and contaminant movement. Conceptualization of contaminant movement

requires recognition of chemical and physical properties of the contaminant (contaminant quantity and disposal history, residual saturation, vapor pressure, vapor density, partitioning into soil moisture) that affect contaminant storage and movement.

It may not be necessary or possible to include every process or feature of the system in a numerical model. Particular processes may not have a large influence on vapor movement, or insufficient information may exist to evaluate its significance other than by sensitivity analysis. Once a set of important processes is selected, if model results cannot account for observations, additional evaluation of the conceptual model may be necessary.

**MDA L Background**

The following background discussion for MDA L is liberally abstracted from the RFI Work Plan for OU 1148 (LANL 1992). MDA L is a 2.58 acre site that was historically used as a disposal site for hazardous chemicals. Much of the MDA surface is covered with asphalt. Land disposal occurred from the late 1950s to 1985. Solvents were disposed in one pit (Pit A), and 34 disposal shafts. Three impoundments were also used for waste disposal at the MDA, but there is no information on what solvents were disposed in the impoundments.

MDA L is located on the flat mesa top of Mesita del Buey, a finger mesa. The mesa extends in an east-southeast direction and is approximately 400 ft wide at MDA L. Mesita del Buey rises about 120 feet above the canyons on its north and south sides. The mesa is formed from ashflows of the Bandelier Tuff, which extend to a depth of 400 ft below the mesa top. Underlying the tuff is a thin layer of alluvial fan deposits making up the Puye Formation (about 10 ft thick). Basalts of the Cerros del Rio underlie the Puye. The regional aquifer lies at a depth of about 850 ft beneath MDA L.

Portions of the Bandelier Tuff and the Basalts are fractured (that is, contain cooling joints). The uppermost unit of the tuff at MDA L, known as Unit 2, has the most prevalent cooling joints (Neeper 1997b). This unit makes up the first 40 ft of rock below

the ground surface. The Bandelier Tuff also contains higher permeability surge beds, flow unit boundaries, and pumice falls. Air permeability of the Bandelier Tuff lies in the range of $10^{-9}$ to $10^{-7}$ $cm^2$ (or 0.1 to 10 darcies) (LANL 1992). The underlying basalt is also jointed, with air permeability perhaps as high as $2x10^{-6}$ to $10^{-4}$ $cm^2$ (240-1200 darcies) (Neeper 1997a). Studies of airflow in the basalt suggest that air in the basalt is connected with and vented to the atmosphere. Air pressure fluctuations within the Bandelier Tuff are decreased in amplitude compared to atmospheric variations, indicating that the air in the tuff is not well connected with the atmosphere (Neeper 1997a).

Records of what solvents were disposed and in what amounts at MDA L are incomplete. The RFI Work Plan for OU 1148 (LANL 1992) identifies five disposal units as the organic vapor plume source. The five units are Pit A, surface impoundment B, and shafts 17, 24, and 33. Available records indicate that shafts 17, 24, and 33 received 11.77 $ft^3$, 44.10 $ft^3$, and 58.81 $ft^3$ of TCA.

As a result of disposal, a subsurface organic vapor plume extends within the mesa both east and west of MDA L. Subsurface monitoring of the vapor plume has occurred since 1988. The observed concentrations of TCA and TCE are quite variable in time and space but the plume has evidently not changed significantly during the last decade (Neeper 1999). Variation of measured values over time appears to result from use of different sampling techniques and sampling protocols. Sampling problems include sampling ports that have been open to the atmosphere when not in use, leading to dilution of subsurface pore gas (Neeper 1999).

In terms of total contaminant mass and extent, TCA is the main organic contaminant, with a plume dimension of about 1200 ft along the mesa axis. The plume evidently intersects both the north and south mesa edges. The maximum TCA vapor concentration in 1990 was 6000 ppm; in 1992 it was above 4000 ppm (LANL 1992). Southeast of MDA L, the TCA concentration peaks at about 50 ppm at 120 ft depth (D. Neeper presentation 4/26/99) and dies away at about 300 ft. Within MDA L the peak is shallower. TCA may have been found near the detection limit in the basalt 600 ft below the mesa top at about 5 ppm in well 54-1016 (Neeper 1997a). The validity of the organic

vapor measurements in the basalt needs to be reevaluated (D. Neeper, personal communication, 1999).

Based on differences in chemical content, the plume north and west of MDA L differs from that east and south of the MDA (Neeper 1999). This could mean that the different disposal areas contribute to different portions of the plume, and that the plume is not well-mixed in the subsurface.

Estimates of the total contaminant mass contained in the plume in 1990 showed that the plume south and west of MDA L contained 850 lbs (vapor phase) of volatile organic compounds. TCA comprised the majority of this contaminant mass at 659 lbs, followed by TCE (134 lbs), carbon tetrachloride (28.9 lbs), chloroform (14.2 lbs), and several other compounds (LANL 1992).

Shallow drilling beneath MDA L has not discovered any residual solvent saturation, although vapor concentrations do not preclude the presence of residual saturation. The maximum vapor concentrations occur beneath the base of the disposal units, suggesting that liquid phase movement may have occurred (LANL 1992).

In summary, past organic liquid disposal on the mesa surface and in pits and shafts from the late 1950s to 1985 created an organic vapor plume within the mesa. There is no evidence of liquid saturation of organic solvents within the mesa at present. The amount of organic liquids that was disposed of is poorly known.

**Factors Controlling VOC Movement**

VOCs may occur in the subsurface in both the liquid and vapor phases. Some of these modes of occurrence must be included in a model of the MDA L organic vapor plume. The liquid phase might be present at or near the source, such as solvent contained in or leaking from barrels. Upon being discharged into the ground, the liquid percolates through the underlying pore space. In its wake, the infiltrating NAPL leaves a zone of residual NAPL saturation. Schwille (1988) found that the retention capacity for TCA in one sand sample was about 25 $L/m^3$.

Within the vadose zone, water fills the small pores between grains. As a NAPL moves through the pores, it moves over the surface of the water, displacing the soil air (Fetter 1993). Because the NAPL is the nonwetting phase (water wets the mineral surfaces) and occupies larger portions of the pore space, it will move with a higher permeability and at a faster rate. Thus, even though water movement in unsaturated rock may be slow, liquid NAPL movement can occur at a much greater rate and to greater depths.

The depth of penetration of NAPL into the vadose zone reflects a balance determined by the supply of NAPL, the rate of NAPL release, the amount of water present in the pores, and the rate at which the NAPL is evaporated into the soil air.

Upon coming in contact with air that occupies pores of soil or rock, VOCs begin to evaporate into the air. The vapor phase VOCs move away from the source by diffusion or advection. Diffusion occurs due to concentration gradients, while advection might occur due to vapor density differences or to forcing such as by atmospheric pressure variations. The vapor phase VOC can then further dissolve into capillary water or be adsorbed onto mineral surfaces or soil organic matter. These latter processes slow movement of the vapor phase in soil air. The dissolution of VOCs from soil air into capillary water creates a secondary source of contamination, as the soil water infiltrates to the water table.

A NAPL with a low water/air partition coefficient remains in the vapor phase, while one with a high water/air partition coefficient (benzene, TCA, TCE) will have a significant concentration in soil water.

Evidence from extraction tests at MDA L indicates that there is no underground source of vapor phase VOCs (that is, no liquid phase is present and there is not significant adsorbed phase present), or that the supply rate is slower than the extraction rate. This conclusion is supported by the observation that the VOC and $CO_2$ ratios are similar before and after the test (D. Neeper presentation 4/26/99). The role of vapor retardation due to partitioning into soil moisture needs to be quantified, if only to demonstrate that it is small.

**Effect of Vapor Density on Flow**

Mendoza and Frind (1990) evaluated the possibility that organic vapor density affects vapor movement in the subsurface. Density driven flow increases the migration rate of an organic vapor plume, and alters the distribution of the plume. Mendoza and Frind (1990) concluded that advection due to vapor density plays is important at permeability greater than $10^{-11}$ $cm^2$ (10 darcies). This is the upper limit for air permeability stated earlier for the Bandelier Tuff, so vapor density probably does not play an important role at MDA L.

Other important controls on the likelihood of density driven advection are organic vapor pressure and the molecular weight of the compound (Mendoza and Frind, 1990). Based on relatively low air permeability, vapor movement beneath MDA L will be dominated by diffusion. It may be worth considering how good the permeability measurements are for the tuff, and whether density driven flow could be significant within fractures or high permeability units that are part of the tuff. Although the basalt has high air permeability, organic vapor concentrations are too low for vapor density to play a role.

**Boundary Conditions Affecting Plume Migration**

Mendoza and Frind (1990) also evaluated the effect of the upper boundary condition (that is, whether the ground surface was open to the atmosphere) on movement of the plume. A cover on the surface increases the rate of movement of a diffusion-driven plume, because less mass is lost to the atmosphere. The asphalt cap at MDA L thus could play an important role in plume movement.

The lower hydraulic boundary underlying MDA L is an important part of the physical setting that affects plume migration. Air exchange with the basalt that underlies the Bandelier Tuff may provide a removal mechanism for organic vapor. Neeper (1997a) concluded that the air in the basalt was readily connected to the atmosphere, unlike the air in the Bandelier Tuff. Based on evaluation of tracer gas concentrations, he estimated that the exchange of air in the basalt with the atmosphere was at most 1% per day.

**Conclusion: Strategy for Modeling VOC Movement**

Depending on the air permeability of the medium, movement of organic vapor plumes can often be represented as a diffusive process (Conant et al. 1996). Auer et al. (1996) showed that in a homogeneous medium subject to atmospheric pressure variations plume migration is diffusion-like. In this case the diffusion process has a higher effective diffusion coefficient than in the isobaric case.

We propose to initially investigate vapor movement at MDA L as a purely diffusive process. If the results are unsatisfactory, other processes can be considered. Given the lack of knowledge regarding the organic vapor source and its timing, as well as the relatively low air permeability and organic vapor concentrations, consideration of diffusive transport is a reasonable first step.

The source term (amounts, timing, and location of VOC disposal) are poorly known at MDA L. Due to variations in monitoring methodology, we do not have a detailed picture of plume concentration through time (Neeper, 1999). This means that the problem of predicting plume movement is poorly constrained. The best way to approach the problem is to try some plausible source term scenarios (or an initial plume distribution) and see how the modeled plume behaves.

Given the narrow mesa shape and likely important effects of upper (land surface) and lower (basalt) boundaries, a three-dimensional model will be necessary to account for the geometry of the MDA L setting.

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