NATURAL ATTENUATION ASSESSMENT OF MULTIPLE VOCS IN A DEEP VADOSE ZONE

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ABSTRACT:

The fate of six volatile organic compounds (VOC) in a 150-meter deep vadose zone was examined in support of a RCRA Corrective Measures Study of the Chemical Waste Landfill at Sandia National Laboratories, Albuquerque, New Mexico. The study focused on the modeling of potential future transport of the VOCs to exposure media upon the completion of two separate voluntary corrective measures - soil vapor extraction and landfill excavation - designed to significantly reduce contaminant levels in subsurface soils. Modeling was performed with R-UNSAT, a finite-difference simulator that was developed by the U.S. Geological Survey. R-UNSAT facilitated a relatively unique and comprehensive assessment of vapor transport because it (1) simulated the simultaneous movement of all six VOCs, taking into account each constituent’s diffusion coefficient as affected by its mole fraction within a mixture of chemicals, and (2) permitted simultaneous assessment of risk to human health via volatilization (air) and drinking water (groundwater) pathways. Modeling results suggested that monitored natural attenuation would represent a viable remedial alternative at the landfill after both voluntary corrective measures were completed.

INTRODUCTION

The Chemical Waste Landfill (CWL), shown in Figure 1, is a facility operated by Sandia National Laboratories (SNL) in Albuquerque, New Mexico. From 1962 to 1985, the landfill received a variety of wastes among which were volatile organic compounds (VOC). In 1990, one of the VOCs, trichloroethylene (TCE), was discovered at part-per-billion levels in local groundwater, which is currently approximately 150 meters (m) below ground surface. Subsequent investigations of the site, all performed under the auspices of the Resource Conservation and Recovery Act (RCRA), indicated that moisture contents in the vadose zone below the landfill are relatively low, and that downward migration of aqueous-phase contaminants has been and continues to be extremely slow. Alternatively, unsaturated zone vapor transport from liquid sources just a few tens of feet below the base of the landfill to the saturated zone hundreds of feet below was identified as the most likely cause of TCE presence in groundwater.

In recent years, the CWL has undergone two Voluntary Corrective Measures (VCM). The first comprises a soil vapor extraction (SVE) action, which was begun in 1997 and terminated in 1999. The second consists of landfill excavation (LE), a process that began in 1999 and will be completed in 2002.
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Though both VCMS appear to be very effective in reducing contaminant levels to non-threatening levels, it is possible that some VOC contamination from past CWL practices will ultimately remain at low levels in the subsurface. Such a possibility was the subject of a preliminary risk evaluation conducted under the early stages of a RCRA corrective measures study (CMS). The purpose of the risk evaluation was to assess the potential for remaining VOCs to influence human exposures through two separate pathways: (1) air inhalation via constituent volatilization, and (2) water ingestion via groundwater pumping. Because post-SVE assessments have shown that multiple volatile organic constituents may continue to exist deep within the subsurface after the LE is finished, the challenge for the preliminary risk study was to provide estimates of the simultaneous transfer of all VOCs to both exposure media. Such estimates were provided using a model of multi-species, vapor-phase transport in the vadose zone. An indirect product of the evaluation was a measure of each VOC’s capacity to attenuate naturally.

Natural migration of the VOCs was simulated using the finite-difference code R-UNSAT, recently developed by the U.S. Geological Survey (USGS) (Lahvis and Baehr, 1997). Application of R-UNSAT at the CWL accounted for multi-dimensional vapor diffusion and equilibrium partitioning constituent mass among three porous media phases. Several features of the model, such as an accounting of a finite-mass source of contaminants and chemical mixture effects on diffusion coefficients, were especially advantageous for evaluating natural attenuation.
Objective. This study was conducted to provide a preliminary assessment of future health risks stemming from contamination remaining in subsurface soils upon completion of recent and ongoing corrective actions. To make the study as realistic as possible, it was based on risk analysis approaches and techniques discussed in the Soil Screening Guidance (SSG) published by the U.S. Environmental Protection Agency (EPA, 1996a; 1996b). In particular, the modeling performed emulated to the best possible extent the following site-specific conditions: (1) human exposure to contamination at the levels currently observed in remaining subsurface pockets is unlikely (i.e., concentrations are attenuated by transport through unsaturated porous media); (2) remaining subsurface contamination comprises a finite mass; and (3) the apportionment of constituents between competing pathways (i.e., contaminants leaving the subsurface via volatilization are not available to the groundwater pathway).

CONTAMINANT TRANSPORT PROCESSES AT THE CWL

Subsurface transport at the CWL is quite unique because of the 150-m thick unsaturated zone underlying the site. Alluvial sediments in this zone strongly attenuate concentrations of contaminants as they gradually migrate to points of exposure. Of additional significance are the especially dry soil conditions observed in the unsaturated zone, where volumetric moisture contents of about 5 to 12 percent are routinely observed. Such dry conditions are reflective of the very small background infiltration rates of 0.06 to 0.61 cm/yr that have been measured during the SNL Sitewide Hydrogeologic Characterization Project (SNL, 1996). These low rates in turn indicate that, at a minimum, it will take more than 1,000 years for dissolved constituents at landfill level to migrate to the saturated zone. Such hydraulic considerations do not take into account the additional retardation of dissolved inorganic movement attributed to sorption on unsaturated sediments. The apparent slow movement of aqueous-phase constituents indicates that the most significant pathways for VOCs to exit the unsaturated zone consist of volatilization across the ground/atmosphere interface and downward vapor transport to the water table. At the latter interface, contamination transfers to groundwater via phase partitioning governed by each contaminant's Henry's Law constant. Once in groundwater, the constituent concentrations are diluted due to mixing of contaminated water with clean water.

Recent post-SVE monitoring identified a vapor plume centered at a depth of about 80 m below ground surface near the CWL’s southeast corner. The plume contained six VOCs: trichloroethylene (TCE), toluene, Freon 113, methylene chloride, trichloroethane (TCA), and 1,1 dichloroethene (1,1 DCE). Observed concentrations of the constituents indicated that no immiscible-phase liquids were present. Thus it could be assumed that there are no continuing VOC sources in the plume other than those stemming from associated aqueous-phase and sorbed contaminants. Accordingly, future unsaturated zone transport of these chemicals will lead to attenuation of contaminant mass and concentrations by losses to the atmosphere and the saturated zone.
**R-UNSAT MODEL**

The multi-species transport code R-UNSAT (Lahvis and Baehr, 1997) is based on algorithms that incorporate Fick's laws of multi-dimensional vapor flux and assume equilibrium partitioning of constituent mass among the vapor, aqueous, solid, and immiscible phases. Simultaneous, one-dimensional (1-D) downward transport of constituents in the aqueous phase is also simulated with the code. To account for transport of organic constituents below the southeast corner of the CWL, R-UNSAT was used to simulate two-dimensional, axisymmetric (r,z) vapor diffusion in a domain affected by sediment layering and depth-dependent sediment properties. A domain encompassing 200 m in the radial direction and 150 m in the vertical direction was used for the CWL model. The distance between adjacent nodes in the horizontal (r) direction was set at a uniform value of 2 m, and in the vertical direction, at 3 m. Input to the R-UNSAT model consisted of both physical and chemical descriptors.

Alternative means of representing contaminant sources were available in R-UNSAT to selectively characterize any existing contaminant sources. However, because the observed subsurface concentrations of organic constituents at the site indicate that none of them exists in the immiscible phase, R-UNSAT was operated in a manner that omitted continuing contaminant sources. This meant that the model would simulate the eventual, natural fate of the contaminants, whose initial distributions were defined by recently observed subsurface concentrations. Boundary conditions consisted of (1) a prescribed zero concentration along the top of the model (ground surface) where volatilization losses occur and (2) impermeable boundaries along the model domain base (water table) and the outermost radial boundary.

**Model Physical Properties.** Ten separate sediment layers were assigned to the model domain used to represent the plume beneath the CWL’s southeast corner. The layer thicknesses and their physical properties were selected to reflect conditions commonly observed in lithologic logs recorded for wells drilled in the east portion of the landfill. In general, these conditions reflect the tendency of sediments to become finer-grained and less permeable with depth. The most notable transitions from shallower materials, which are dominated by relatively coarse-grained sands, to clays and clayey sands, are typically observed at 70 to 82 m below ground surface. Table 1 lists the layer-specific physical properties that were adopted in R-UNSAT; the bottom of the first layer represents the top of the saturated zone, and the top of the tenth layer represents ground surface. An additional domain property affecting transport of VOCs was the downward seepage rate of soil moisture, which was assigned a uniform rate of 0.33 cm/yr.

**Chemical-Specific Parameters.** Chemical-specific parameters required by R-UNSAT included molecular weight and atomic diffusion volume, which were
used to calculate each chemical’s binary diffusivity (Lahvis and Baehr, 1997)

\[
d_{ki} = \frac{0.00143 \ T^{1.75}}{P \ M_{g}^{0.5} \ (\zeta_{i}^{-1/3} + \zeta_{k}^{-1/3})}
\]  

(1)

where \( d_{ki} \) = vapor-phase diffusivity of the kth constituent in a binary mixture of the ith and kth constituents (cm²/sec),

\( T \) = temperature (°K),

\( P \) = pressure (atmospheres),

\( \zeta_{i}, \zeta_{k} \) = atomic diffusion volumes of the ith and kth constituents (unitless),

\( M_{g} = 2(\omega_{i}^{-1} + \omega_{k}^{-1})^{-1} \), and

\( \omega_{i}, \omega_{k} \) = molecular weights of the ith and kth constituents (g).

<table>
<thead>
<tr>
<th>Layer</th>
<th>Top Elevation (m)</th>
<th>Thickness (m)</th>
<th>Porosity (unitless)</th>
<th>Moisture Content (unitless)</th>
<th>Bulk Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>3</td>
<td>0.4</td>
<td>0.2</td>
<td>1.65</td>
</tr>
<tr>
<td>2</td>
<td>27</td>
<td>24</td>
<td>0.4</td>
<td>0.15</td>
<td>1.65</td>
</tr>
<tr>
<td>3</td>
<td>51</td>
<td>24</td>
<td>0.4</td>
<td>0.12</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>9</td>
<td>0.35</td>
<td>0.07</td>
<td>1.65</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>15</td>
<td>0.4</td>
<td>0.2</td>
<td>1.65</td>
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<tr>
<td>6</td>
<td>96</td>
<td>21</td>
<td>0.35</td>
<td>0.07</td>
<td>1.65</td>
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<tr>
<td>7</td>
<td>114</td>
<td>18</td>
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<td>0.07</td>
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<tr>
<td>8</td>
<td>124</td>
<td>10</td>
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<td>0.07</td>
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</tr>
<tr>
<td>9</td>
<td>132</td>
<td>8</td>
<td>0.35</td>
<td>0.07</td>
<td>1.65</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
<td>18</td>
<td>0.35</td>
<td>0.07</td>
<td>1.65</td>
</tr>
</tbody>
</table>

The diffusion coefficient for a constituent in a mixture of N vapor-phase components was determined using the formula (Lahvis and Baehr, 1997)

\[
D_{a,i} = \frac{1 - \chi_{i}}{\sum_{i=1,\text{not}}^{N} \chi_{i} / d_{si}}
\]  

(2)

where \( \chi_{i} \) = mole fraction of the ith constituent in the vapor phase.

Accounting for each chemical’s relative concentration per equation 2 helped to avoid overprediction of volatilization fluxes (Benson et al., 1993) that sometimes occurs with simpler models of a single constituent.

To derive appropriate diffusion coefficients per equations 1 and 2, an ambient temperature of 20°C (293 K) and a total vapor-phase pressure of 0.82 atmospheres were assumed. Within the model, the bulk-vapor diffusion coefficient for each VOC was also modified by a tortuosity parameter reflective of the convoluted path that each passes through in porous media. This parameter was calculated in the R-UNSAT code using the porosity and moisture content data from Table 1 in a formula developed by Millington (1959).
Additional chemical-specific parameters used in the model included a Henry’s Law constant, \( H \) (unitless), and a soil-water partition coefficient, \( K_d \) (L/kg), for each chemical. The former expresses the equilibrium ratio of a constituent’s vapor concentration to its aqueous-phase concentrations, whereas the latter comprises the ratio of a chemical’s concentration in the sorbed phase (mg/kg) to its dissolved concentration in the aqueous phase (mg/L). \( K_d \)'s were computed as the product of a soil-water partition coefficient, \( K_{oc} \) (L/kg), and a soil organic carbon content, \( f_{oc} \), the latter of which was assigned a uniform value of 0.001 (0.1%). Values of \( H \) and \( K_{oc} \) were estimated using data provided in the Technical Background Document (TBD) of EPA’s SSG (EPA, 1996b). Aqueous-phase diffusion coefficients, \( D_w \), were also considered chemical-specific parameters; however, each constituent was assigned a constant \( D_w \) of \( 1 \times 10^{-5} \) cm\(^2\)/sec since this parameter is typically two orders of magnitude less than a comparable vapor diffusion coefficient and thus not expected to strongly affect simulation results.

The values assigned to all model-related chemical-specific descriptors for the six organic chemicals are listed in Table 2. An ancillary parameter, chemical solubility in water, is also listed to provide some measure of each constituent’s proclivity for partitioning into soil moisture versus the soil and vapor phases. Because each VOC had non-zero Henry’s Law constants and soil-water partition coefficients, its vapor transport was retarded by partitioning of contaminant mass into the aqueous (soil moisture) and solid (sediment) phases. An effective retardation factor for each chemical was calculated in R-UNSAT.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Molecular Weight (g)</th>
<th>Atomic Volume (unitless)</th>
<th>Henry’s Law Constant, ( H ) (unitless)</th>
<th>Organic Carbon Coefficient, ( K_{oc} ) (cm(^3)/g)</th>
<th>Solubility (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1 Dichloroethene</td>
<td>96.94</td>
<td>78.42</td>
<td>1.07</td>
<td>31.6</td>
<td>2250</td>
</tr>
<tr>
<td>Freon 113</td>
<td>187.4</td>
<td>138.9</td>
<td>13.08</td>
<td>389</td>
<td>170</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>84.93</td>
<td>62.52</td>
<td>0.0898</td>
<td>11.7</td>
<td>13000</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.14</td>
<td>111.5</td>
<td>0.272</td>
<td>182</td>
<td>526</td>
</tr>
<tr>
<td>1,1,1 Trichloroethane</td>
<td>133.4</td>
<td>101.7</td>
<td>0.705</td>
<td>110</td>
<td>1330</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>131.4</td>
<td>97.11</td>
<td>0.422</td>
<td>166</td>
<td>1100</td>
</tr>
</tbody>
</table>

**RESULTS AND CONCLUSIONS**

Using recently observed vapor concentrations centered at a depth of approximately 80 m as initial conditions, the model was used to simulate a period of 100 years. A sequence of cross-sectional snapshots of computed TCE concentrations from three years through 30 years is presented in Figures 2(a) through 2(d). Temporal plots for the next 40 years of (1) TCE concentration just below ground surface and at the water table; and (2) cumulative TCE mass within the unsaturated zone and exiting the model domain at ground surface (volatilization) are shown in Figures 3(a) and 3(b), respectively. The snapshots clearly demonstrate the capacity of the large unsaturated zone to decrease concentrations with time. As shown by the temporal plots, TCE is expected to
begin releasing to the atmosphere via volatilization approximately three years beyond zero time. However, concentrations of this constituent near ground surface are relatively small until 10 years, and begin decreasing after this time. In contrast to TCE levels near the ground surface, notable concentrations of this constituent do not appear at the water table until about eight years of simulation time, and are still increasing after 30 years. Simulation results for the remaining VOCs were similar to those for TCE. However, two of the constituents, Freon 113 and 1,1 DCE, with relatively high Henry’s Law constants of 13.08 and 1.07, respectively, were observed to volatilize and reach the saturated zone much earlier than TCE. Similarly, computed vapor concentrations of these more volatile constituents at the water table began decreasing after 14 years of simulation time.

![Figure 2. TCE concentrations at (a) 3, (b) 10, (c) 20, and (d) 30 years.](image)

**Preliminary Risk Evaluation.** The volatilization pathway was evaluated using model-computed average vapor fluxes of each constituent over the first 30 years of simulation. These fluxes were applied in a relatively simple model (EPA, 1996b) for assessing the impacts of dispersion on emission fluxes to the atmosphere. The resulting calculations indicated that emission fluxes would be
relatively insignificant and would thus not create unacceptable risks due to air inhalation. To analyze the effects of vapor diffusion on groundwater, the largest vapor concentrations occurring over time at the top of the saturated zone were translated into equivalent groundwater concentrations. This was accomplished by assuming that each chemical would partition into groundwater in accordance with its Henry’s Law constant, and would subsequently be diluted by a default factor of 20 due to mixing with uncontaminated groundwater (EPA, 1996a; 1996b). For each constituent, the resulting computed groundwater concentration was less than the chemical’s maximum contaminant level (MCL).

![FIGURE 3. (a) TCE concentrations near the ground surface and at the water table. (b) TCE mass in the vadose zone and the atmosphere.](image)

This investigation demonstrated that the simultaneous, eventual fate of multiple VOCs remaining in a deep vadose zone after site remediation could be examined with a numerical model for insight into the contaminants’ potential effects on two risk exposure pathways. The 150-m deep vadose zone in this study appeared to be large enough to both minimize risk measures at key exposure points and effectively attenuate VOC concentrations to non-threatening levels.

REFERENCES


U.S. Environmental Protection Agency (EPA), 1996b. *Soil screening guidance: technical background document.* Publication 9355.4-17A.