SAND098-0768C
SAND--98-0768C

Simulation of the Environmental Fate and Transport of Chemical Signatures from Buried Landmines

CONF-980412--

James M. Phelan[a] and Stephen W. Webb[b]

Sandia National Laboratories, [a]Environmental Restoration Technologies Department and [b]Mission Analysis and Simulation Department, Albuquerque, NM 87185

ABSTRACT

The fate and transport of chemical signature molecules that emanate from buried landmines is strongly influenced by physical chemical properties and by environmental conditions of the specific chemical compounds. Published data have been evaluated as the input parameters that are used in the simulation of the fate and transport processes. A one-dimensional model developed for screening agricultural pesticides was modified and used to simulate the appearance of a surface flux above a buried landmine and estimate the subsurface total concentration. The physical chemical properties of TNT cause a majority of the mass released to the soil system to be bound to the solid phase soil particles. The majority of the transport occurs in the liquid phase with diffusion and evaporation driven advection of soil water as the primary mechanisms for the flux to the ground surface. The simulations provided herein should only be used for initial conceptual designs of chemical pre-concentration subsystems or complete detection systems. The physical processes modeled required necessary simplifying assumptions to allow for analytical solutions. Emerging numerical simulation tools will soon be available that should provide more realistic estimates that can be used to predict the success of landmine chemical detection surveys based on knowledge of the chemical and soil properties, and environmental conditions where the mines are buried. Additional measurements of the chemical properties in soils are also needed before a fully predictive approach can be confidently applied.

Keywords: Mine detection, chemical sensing, soil transport, computational simulation

1. INTRODUCTION

The goal of locating buried landmines is a significant challenge to science and technology (Dugan, 1996). The chemical signature of landmines is affected by multiple environmental phenomena that can enhance or reduce its presence and transport, and can affect the distribution of the chemical signature in the environment. For example, the chemical can be present in the vapor, aqueous, and solid phases. The distribution of the chemical among these phases, including the spatial distribution, is key in designing appropriate detectors, e.g. gas, aqueous or solid phase sampling instruments, and their optimum use. A fundamental understanding of the environmental conditions that affect the chemical signature is needed to describe the favorable and unfavorable conditions of a chemical detector based survey to minimize the consequences of a false negative. The fate and transport of the chemical signature emanating from the buried landmine is a fundamental property that is poorly understood. As an initial step in the evaluation of the landmine chemical signature, a screening model based on pesticide and Volatile Organic Compound (VOC) movement in soils has been adapted to evaluate landmine chemical behavior. This report addresses an initial evaluation of the fate and transport of this chemical signature including the dominant effects environmental conditions may have on the success of a chemical detector survey. Future efforts to develop more mechanistic and sophisticated chemical transport models and the low concentration physical chemical properties are needed to bridge the gap to more realistic fate and transport conditions.

Figure 1 shows a conceptual model of the environmental fate and transport processes that impact the movement of landmine chemical constituents to the surface for chemical detection. Chemical vapors emanate from a buried landmine by permeation through plastic case materials or through seals and seams, and from the initial surface contamination of the case. Vapor phase diffusion transports molecules away from the landmine. The vapors may partition into the aqueous phase of the soil water which may then be transported to the surface through advection, driven by evapotranspiration or to depth by precipitation infiltration, and through diffusion driven by concentration gradients. Under extremely dry soil conditions near the ground surface, vapor phases may be directly sorbed to soil particles. When in the liquid phase, chemicals may also sorb

DISCLAIMER

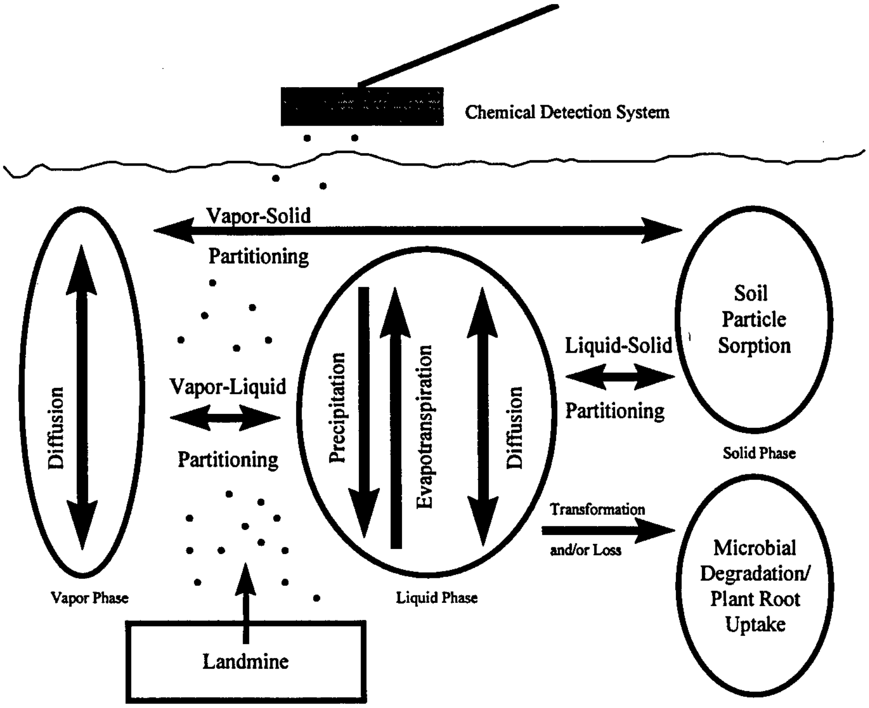

Figure 1. Environmental Fate and Transport Model for Chemical Detection of Buried Landmines

to the soil particles. Soil particle sorption can be considered a temporary storage reservoir for the explosive constituents, where they may be released under reversible partitioning reactions, but some proportion may also permanently bound through chemisorption reactions. Transformation and loss of explosive constituents also occurs during microbial degradation and uptake by the roots of certain plant species.

2. CHEMICAL TRANSPORT IN SOILS

Soils are porous media with a number of physico-chemical properties that affect the transport of explosive chemicals. Soil bulk density is a measure of the compaction of the soil and is defined as

$$\rho_b = \frac{M_s}{V_s} \qquad [1]$$

where ρ_b is the soil bulk density (g/cm^3), M_s is the mass of soil particles (g), and V_s is the volume of soil (cm^3). Soils under natural conditions have bulk densities ranging from 1.0 to 1.8 g/cm^3. However, soils that have been excavated and replaced, such as during the emplacement of a landmine, may have bulk densities much less than 1. The soil bulk density is inversely proportional to the soil porosity as follows

$$\phi = 1 - \rho_b / \rho_s \qquad [2]$$

where ρ_s is the soil particle density (ranges from 2.6 to 2.8 g/cm^3 for most soils). The soil porosity, or void volume, is defined as

$$\phi = \frac{V_w + V_a}{V_s} \qquad [3]$$

where ϕ is the soil porosity (cm^3/cm^3), V_w is the volume of soil water (cm^3) and V_a is the volume of soil air (cm^3). Soil porosity values range from 0.3 for sands to 0.6 for clay rich soils. The volumetric moisture content describes how much water is present in the soil and changes greatly during precipitation/drainage events and evaporation conditions. Volumetric water content is defined as

$$\theta = \frac{V_w}{V_s} \qquad [4]$$

where θ is the volumetric water content (cm^3/cm^3). Soil moisture contents have values from near zero up to the soil porosity value. When the soils are not fully saturated, the balance of the soil pore space not filled with water is termed the air filled porosity, and is defined as

$$a = \frac{V_a}{V_s} \qquad [5]$$

where V_a is the volumetric air content (cm^3/cm^3). It is often more convenient to use soil saturation (S_l) because it is a measure of the relative saturation of a particular soil pore space with water.

$$S_l = \frac{\theta}{\phi} \qquad [6]$$

Since the explosive chemicals can exist as solutes in the soil water and the movement of soil water can be a significant transport mechanism, water solubility is an important parameter. Water solubility is defined as

$$C_L = \frac{M_{chem}}{V_w} \qquad [7]$$

where C_L is the concentration in aqueous phase (g/cm^3 soil water) and M_{chem} is the mass of chemical (e.g. TNT) (g). Water solubility, however, is not constant and is typically an increasing function with temperature.

Henry's Law constant is a relative measure of the amount of the chemical that exists in the gas phase to that in the aqueous phase at equilibrium, and is defined as

$$K_H = \frac{C_G}{C_L} \qquad [8]$$

where K_H is the Henry's Law constant (unitless) and C_G is the concentration in gas phase (g/cm3 soil gas). Henry's Law constant is also a function of temperature because both C_G and C_L are functions of temperature. The soil partition coefficient is a relative measure of how much of the chemical is temporarily bound to the soil to that in the soil aqueous phase

$$K_d = \frac{C_S}{C_L} \qquad [9]$$

where K_d is the linear soil-water partition coefficient (cm^3/g) for water saturated soils and C_S is the concentration sorbed on the soil solid phase (g/g of soil). The soil water partition coefficient is often correlated with the fraction of organic carbon found in the soils. In this way, the variability between soils can be reduced. The organic carbon distribution coefficient is defined as

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad [10]$$

where K_{oc} is the organic carbon distribution coefficient and f_{oc} is the fraction of organic carbon.

3. SCREENING MODELS

The environmental fate and transport of organic chemicals including volatilization and leaching losses has been used to explore the distribution of agricultural pesticides in soils (Mayer et al. 1974, Farmer et al. 1980, and Jury et al. 1980). These models were primarily intended to simulate specific circumstances. However, Jury et al. (1983, 1984a, 1984b, 1984c) developed and validated a general screening model (Behavior Assessment Model, BAM) that included volatilization, leaching, and degradation to explore the major loss pathways of agricultural pesticides as a function of specific environmental conditions. The model simulations can be used to assess the behavior of different chemicals under particular environmental conditions, but is not intended to predict a definitive concentration distribution in the field. As such, the predictions from the screening model are only an indication of expected conditions.

This model is valuable in that it can express the total concentration of a chemical in the gas, aqueous and sorbed phases. The total concentration is expressed as

$$C_T = \rho_b C_S + \theta C_L + a C_G \qquad [11]$$

where C_S is the concentration sorbed to the soil, C_L is the solute concentration in the aqueous phase, and C_G is the gas phase concentration. In addition, Jury (1983) shows how equation [11] can be rewritten in terms of one of the variables alone

$$C_T = R_S C_S = R_L C_L = R_G C_G \qquad [12]$$

where

$$R_S = \rho_b + \frac{\theta}{K_d} + a\frac{K_H}{K_d} \qquad [13]$$

$$R_L = \rho_b K_d + \theta + a K_H \text{, and} \qquad [14]$$

$$R_G = \rho_b \frac{K_d}{K_H} + \frac{\theta}{K_H} + a \qquad [15]$$

are the solid, liquid and gas phase partition coefficients, respectively.

An adaptation of the BAM was developed to be applicable to the conditions of contaminated soil buried under a known depth of clean soil - Buried Chemical Model, BCM (Jury et al., 1990). Simulations based on a modification of Jury's BCM are used in this report to simulate the behavior of the chemical signature from buried landmines. The Buried Chemical Model of Jury et al. (1990) is based on the following assumptions. A detailed discussion of these assumptions is given in Jury et al. (1990).

1. The chemical may adsorb on the solid phase, be dissolved in the aqueous phase, or exist in the vapor phase.
2. The chemical flux is the sum of the vapor flux and the dissolved solute flux.
3. The porous medium factors for gas and liquid phase diffusion are given by the Millington and Quirk (1961) model as extended for liquid diffusion by Jury et al. (1983).
4. The chemical will undergo first-order degradation due to biological and chemical effects.
5. Chemical movement is one dimensional.
6. The adsorbed and dissolved phases undergo reversible, linear adsorption.
7. The dissolved and gaseous phase concentrations are related through Henry's law.
8. The soil properties are constant in space and time.
9. Water flux is constant in space and time (relaxed in the present application).
10. Volatilization of the chemical to the atmosphere is by vapor diffusion through an air boundary layer of constant thickness.

In the present implementation of Jury's model, a constant source term has been added to reflect the chemical source from the landmine at a specific location.

Under these assumptions (including the source term) the model formulation becomes

$$\frac{\partial C_T}{\partial t} + \mu C_T = D_E \frac{\partial^2 C_T}{\partial z^2} - V_E \frac{\partial C_T}{\partial z} + \sigma \qquad [16]$$

where C_T is the total chemical concentration, μ is the biochemical decay constant, and σ is the source term. The effective velocity (V_E) is defined as

$$V_E = \frac{J_w}{\rho_b K_d + \theta + aK_H} \qquad [17]$$

where J_w is the precipitation/evaporation flux. The effective diffusion coefficient (D_E) of the chemical is defined as

$$D_E = \frac{a^{10/3} K_H D_g^a + \theta^{10/3} D_l^w}{\phi^2 \left(\rho_b K_d + \theta + aK_H \right)} \qquad [18]$$

where D_g^a is the diffusivity of the gas phase of the chemical in air and D_l^w is the diffusivity of the chemical in aqueous phase . The boundary conditions for the problem are diffusion through a boundary layer at the upper surface, and a zero chemical concentration at infinity at the lower boundary. These boundary conditions can be expressed as

$$-D_E \frac{\partial C_T}{\partial z} + V_E C_T = -H_E C_T \qquad [19]$$

where

$$H_E = \frac{hK_H}{\rho_b K_d + \theta + aK_H} \qquad [20]$$

and

$$h = \frac{D_g^a}{d} \qquad [21]$$

and

$$C_T(\infty, t) = 0$$

The initial conditions are an initial concentration, C_0, over an interval from L to W, or

$$C_T(z,0) = 0 \qquad L \rangle z \rangle W$$

$$C_T(z,0) = C_0 \qquad L \leq z \leq W$$

The above model without the source term results in a closed form solution as a function of space and time; the results are rather lengthy and will not be presented here but are given by Jury et al. (1983, 1990). In the present simulations, the assumption of constant water flux in time is relaxed. Therefore, sequences of water fluxes representing desired conditions (rainfall followed by evaporation) can be simulated to determine the effect of water flux variations on the location of TNT in the soil and the surface TNT vapor flux. A numerical solution was developed and verified by comparison to the results given by Spencer et al. (1988) and Jury et al. (1990) (Phelan and Webb, 1997).

4. LANDMINE SOURCE TERM

The total mass of the initial deposit of chemicals after first emplacement of the landmine in soils is critical in the estimation of soil concentrations and surface vapor fluxes (Phelan and Webb, 1988). For the model used in this analysis, it has been assumed that the entire surface contamination was completely and uniformly transferred to the soil just prior to the beginning of the simulation runs. Surface contamination data (Hogan et al., 1992) showed a median surface contamination of 15 ng/cm^2 from 42 domestic and foreign landmines. However, the surface contamination values ranged from below instrument detection limits to 300-500 ng/cm2 and some outliers as high as 1000-5000 ng/cm2. Using the median surface contamination and the dimensions of an anti-tank (AT) mine of 30 cm diameter by 10 cm high, the surface contamination would provide 3.5×10^{-5} g of TNT for initial distribution in the soil. Using the volume of the AT mine that this mass of TNT is distributed into, the initial concentration (C_o) would be 5×10^{-3} μg/cm^3.

The continuous release of chemicals by permeation or leaks through seals and seams is also important if the rate is significantly large enough. However, few data exist. One effort established constant source term emanation rates derived from vapor collection chamber experiments on two mines (Spangler, 1975). Values ranged from 10^{-16} to 10^{-18} g/cm^2-s. The higher rate of 10^{-16} g/cm^2-s (8.6×10^{-6} μg/cm^2-day) was used in these simulations.

5. PHYSICAL CHEMICAL PROPERTIES OF EXPLOSIVES

The principal explosive chemicals found in landmines are TNT and RDX (NGIC, 1995). DNT, as a production by-product of TNT, is also considered to be a significant signature chemical for buried landmines. As a group, these chemicals have very low vapor densities and moderately low water solubility's. Table 1 shows these properties and the Henry's Law constant at 20°C (Phelan and Webb, 1997).

Table 1. Vapor Density, Water Solubility and Henry's Law Constant of Explosive Compounds at 20°C

	TNT	DNT	RDX
Vapor Density (μg/m³)	43.5	122	0.024
Water Solubility (mg/l)	130	270	50
Henry's Law Constant	3.35E-7	4.51E-7	4.73E-10

Pennington and Patrick (1990) measured the soil water partition coefficient (K_d) of TNT in fourteen soils from locations across North America. The mean value was 3.8 cm³/g with a standard deviation of 1.34. The highest value was 6.8 cm³/g and the lowest value was 2.3 cm³/g. Xue et al. (1995) evaluated two soils and showed mean values for TNT of 2.66 cm³/g and 3.64 cm³/g. DNT and RDX have very little data. Xue et al. (1995) showed values for RDX of 1.59 cm³/g and 1.57 cm³/g. McGrath (1995) showed a K_{oc} value of 251 for DNT. For the fourteen soils evaluated by Pennington and Patrick (1990), the mean value for the fraction of organic carbon was 0.0173 with a standard deviation of 0.011. Using these values, the K_d for DNT has a mean value of 4.4±2.7 cm³/g (one std. dev.). In summary, the soil water partitioning coefficients for TNT, DNT and RDX all fall into an approximate range between 1.5 and 7.0 cm³/g. This is a rather narrow range as common chemicals can have values one to two orders of magnitude lesser and greater than these.

The biochemical half-life of explosives in near surface soils has not been studied well outside of the biotreatment technology area for contaminated soils. However, long-term surface soil degradation tests at Los Alamos National Laboratory (LANL) followed the degradation of soils doped with 1000 mg/kg of various explosives over 20 years (Dubois and Baytos, 1991). Table 2 shows the half-lives estimated from these long-term experiments.

Table 2. Estimates of Half-Lives of Explosives from LANL Long-Term Surface Soil Tests

Explosive	Half-Life (years)
TNT	1
RDX	36
HMX	39
PETN	92

6. SIMULATION PARAMETERS

Using the modified Buried Chemical Model (BCM), simulations were performed using a landmine that has contributed an initial soil concentration (C_o) based on the median surface contamination of the landmine (Hogan et al., 1992) and the constant flux (J_c) from Spangler, 1975. The diffusivity of gas in air (D_g^a) and diffusivity of liquid in water (D_l^w) were selected from Jury et al. (1983). The biochemical half-life value of 365 days was selected from a long term field experiment (Dubois and Bayton, 1991). The physico-chemical properties of TNT were used at 25°C.

The precipitation/evaporation rates and periods followed in several of the simulations here were the low desert scenario from Phelan and Webb (1997). This scenario was derived from data found in HELP (Hydrological Evaluation of Landfill Performance) model (Schroeder et al., 1994a and 1994b). The HELP model showed that the low desert had 1 day of precipitation followed by 7 days of evaporation. For simplicity, total precipitation and total evaporation for each cycle are assumed to be equal and for these simulations the cycles were continued for approximately four years. Table 3 shows the input parameters used in the simulations.

Table 3. Simulation Parameters

parameter	units	base case	variant cases
θ	cm^3/cm^3	0.20	Figure 2: 0.243, 0.287
ϕ	cm^3/cm^3	0.434	*
ρ_b	g/cm^3	1.5	Figure 2: 1.25, 1.0
K_d	cm^3/g	3.8	*
K_H	--	5.9E-7	*
air boundary layer	cm	0.5	*
$t_{1/2}$	days	365	*
C_o	$\mu g/cm^3$	5E-3	*
J_c	$\mu g/cm^2$-day	8.6E-6	*
D_l^w	cm^2/day	0.432	*
D_g^a	cm^2/day	4320	*
burial depth, top	cm	10	Figure 3: 5, 1, 0 Figure 6, 7, 8 & 9: 5
burial depth, bottom	cm	20	Figure 3: 15, 11, 10 Figure 6, 7, 8 & 9: 15
precipitation	days	1	varies
evaporation	days	7	varies
precipitation rate	cm/day	0.44	Figure 4, 5: 0
evaporation rate	cm/day	- 0.063	Figure 4, 5: 0

* - same as the base case

7. DISCUSSION

Initial application of the screening model (Phelan and Webb, 1997) showed that explosive compounds such as TNT, DNT and RDX will have over 90% of the mass fraction sorbed to the soil solid phase, up to 10% present in the soil aqueous phase and less than 1E-6% in the soil vapor phase. The implications for this are that transport of these chemicals in soils will be dominated by movement as a solute in the aqueous phase. In addition, at soil water contents above about 0.1 cm^3/cm^3, the effective diffusivity (D_E) is dominated by liquid diffusion by one to five orders of magnitude. Next, the screening model was applied to three different environmental scenarios and results showed that maximum surface vapor fluxes were very low, requiring a sampling and concentration factor of 10^3 using currently available laboratory instrument detection limits. Surface soil concentrations showed that sampling modest amounts of soil would require a preconcentration factor of about 2.

Next, the impact of variations in several of the various input parameters was explored (Phelan and Webb, 1998). It was found that the variations in the Henry's Law constant are directly proportional to the changes seen in the steady-state surface vapor flux. Small changes in the soil water partitioning coefficient made large changes in the lag period and steady-state surface vapor flux. The initial source term and continuous source flux of chemicals from the landmines is poorly understood and expected to be highly variable. These simulations found that with the baseline case, if the continuous source flux was absent, there was no significant difference in the surface vapor flux or subsurface distribution at the end of the simulation period. This implies that the continuous source flux may be much less important than the initial surface contamination. It appears that the magnitude of the surface vapor flux is directly proportional to the amount of the initial surface contamination. The biochemical half-life is another parameter that is likely to have very different values depending on the location and climatic conditions. Simulations over ten years showed that the steady state surface vapor flux declines steadily when the biochemical half-life becomes smaller than one year. Finally, the importance of heavy precipitation (such as a monsoon season) followed by a dry season was explored. The impact of the heavy precipitation was to lower the surface flux seven orders of magnitude; however, the evaporation period that followed returned the surface flux to approximately the pre-monsoon surface flux.

This current effort has evaluated the impact of changes to the soil bulk density, burial depth, concentration in the soil layer, water flux, and the conditions that promote an enhanced surface layer. When a landmine is placed, the soil surrounding the mine is not compacted to the original bulk density. Over time the soil bulk density will increase. Figure 2 shows that soils with smaller soil bulk densities will have a shorter lag period and a steady state surface flux about two orders of magnitude greater than the base case.

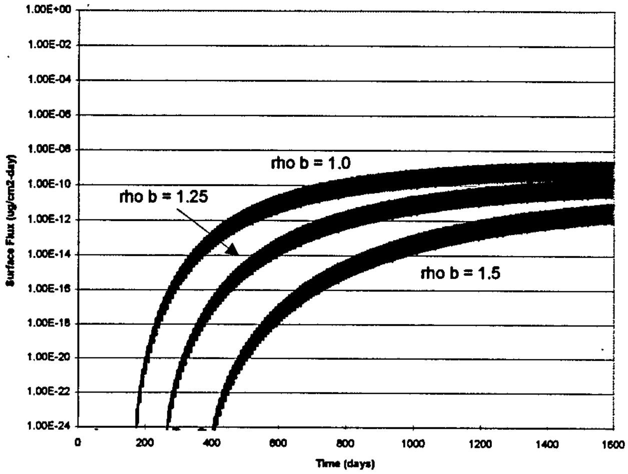

Figure 2. Effect of Soil Bulk Density Changes on Surface Flux

The effect of burial depth appears to be a very critical parameter, even over small distances of a few centimeters. Figure 3 shows how the lag time for the surface vapor flux becomes dramatically shorter by moving the top of the initial source zone up from 10 cm to 5 cm to 1 cm and 0 cm.

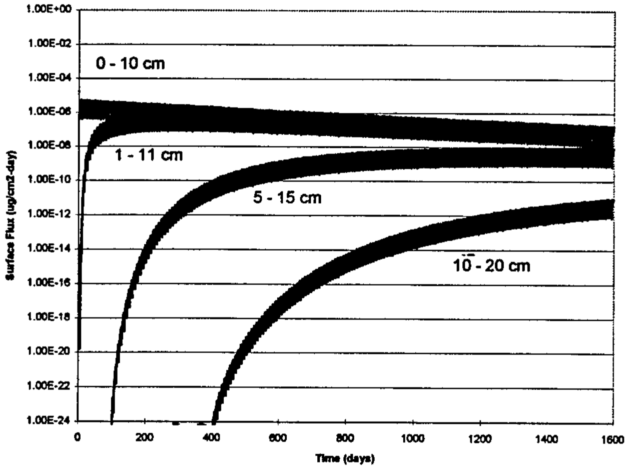

Figure 3. Effect of Burial Depth on Surface Flux

An important assumption made in the current numerical application to the landmine problem is the assumption of a uniform explosive concentration between the top and bottom of the mine. In reality, the explosive is concentrated on the top and the bottom surfaces, the mine is an impediment to transport, and the mine is not porous media. In order to assess the implication of smearing the concentration over the entire depth, Jury's original BCM without a source term and with zero water flux has been applied to the case of two buried chemical sources. The top source started at the top of the landmine location, while the bottom source ended at the bottom of the landmine, with a zero concentration region in the center of the landmine location.

A constant mass was used, and the concentration changed with the source width, which varied from 5.0 cm, the base case, down to 0.0005 cm. The 5.0 cm base case results in a uniform initial concentration between the top and bottom of the mine, while the 0.0005 cm case approximates two sources at the top and bottom surfaces. Fig 4 shows the vapor flux at the ground surface as a function of time for the various source widths. The parameters in this case are the same as for the base case in Table 3 without a source term and with no precipitation/evaporation. The results are similar, though not identical, to results given in Figure 2 (rho b = 1.5).

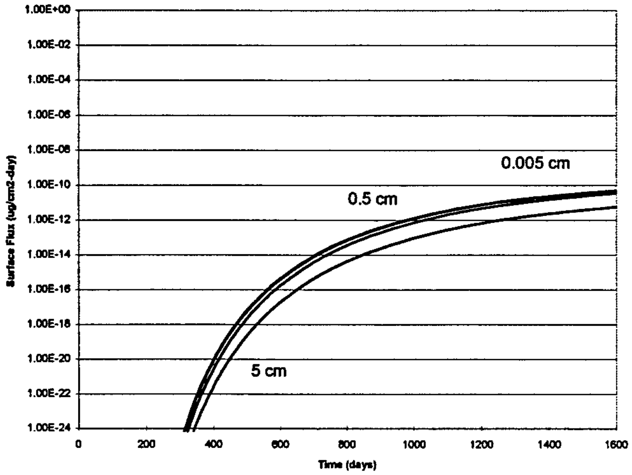

Figure 4. Effect of Layer Concentration on Surface Vapor Flux

Even if the parameters were the same, some differences would exist, particularly at earlier times and at lower concentrations, due to numerical issues such as roundoff and numerical diffusion. From Figure 4, the vapor flux increases as the width decreases, which is expected because a reduction in the width essentially moves the top source closer to the ground surface. Figure 5 shows the ratio of the vapor flux from the 0.0005 cm width case to the 5 cm case. The ratio decreases with time from about 50 to a value of 10 at late times.

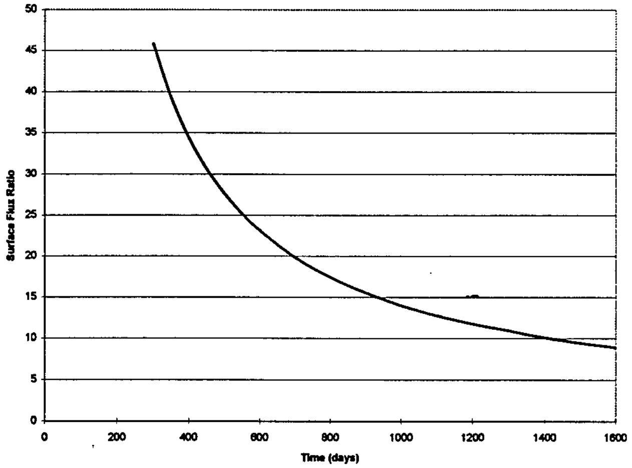

Figure 5. Ratio of Surface Flux from a 0.0005 cm Layer to 5 cm Layer

In addition to the effect of soil moisture content, the effect of precipitation (positive water flux, J_w) and evaporation (negative water flux, J_w) is probably one of the most important environmental factors in the transport of explosive chemicals in soils. Figure 6 shows that with only precipitation occurring, the surface flux is about 3 orders of magnitude less than the case of zero precipitation or evaporation. The case of constant evaporation is about 2 orders of magnitude greater than the zero water flux case. If one examines the model formulation, the mass transport upwards is controlled by the effective diffusion (D_E) and the effective chemical velocity (V_E). In the constant precipitation case, upward mass transport is a function of D_E

minus V_E. In the zero precipitation/evaporation, upward mass transport is a function of only D_E. In the constant evaporation case, upward mass transport is a function of D_E plus V_E.

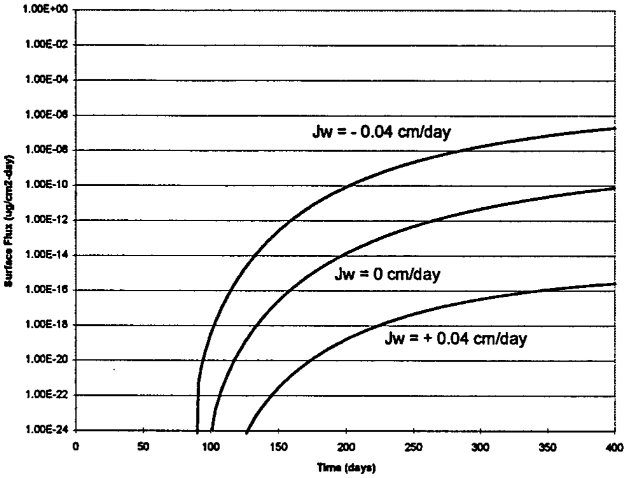

Figure 6. Effect of Water Flux (Precipitation/Evaporation) on Surface Flux

The occurrence of a surface soil layer that is greater in concentration than the subsurface soil layers, or a surface "crust", has been observed and modeled with agricultural pesticides (Spencer et al., 1988). This type of behavior is also thought to occur with explosive compounds due to similarities in the physical/chemical properties and some evidence from field surveys and lab experiments. Simulation runs were completed to evaluate what influences the creation of the enhanced concentrations in the surface soil layers. Initial simulation runs (Phelan and Webb, 1997) used cyclic precipitation/evaporation that was equal in magnitude. This condition did not create an enhanced surface layer. In order to create an enhanced surface layer, enough of the mass must be transported from deeper regions to the ground surface. This condition only occurs during evaporation conditions and in Figure 7 the buried chemical layer is shown to move upward until it intersects with the ground surface. Figure 8 shows more detail on the depth and magnitude of the enhanced layer. It is believed that the air boundary layer and the low Henry's Law Constant (K_H) contribute to the formation of the enhanced surface layer (Spencer et al., 1988). It appears that the upward transport through the soil exceeds the loss through the air boundary layer. Transport though the air boundary layer is controlled by vapor diffusion and limited by the transfer of chemical from the aqueous phase to the gas phase by the very low K_H.

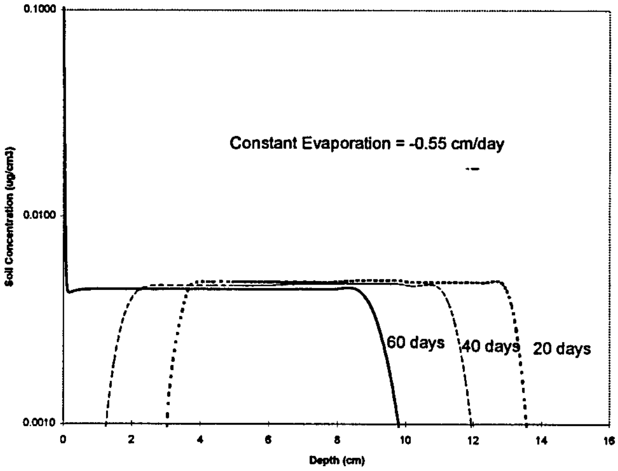

Figure 7. Upward Transport and Development of a Surface Layer

Figure 9 shows the effect of developing the enhanced surface layer with 60 days of evaporation (-0.5 cm/day), followed by precipitation for 5 days (0.5 cm/day). The enhanced surface layer found in the top 0.1 cm of soil is transported down leaving just a small enhancement at a depth of about 0.5 cm. Another simulation was run that included the same evaporation and precipitation, but was followed by another 5 day evaporation period (-0.5 cm/day) and the surface enhancement returned at about the same concentration.

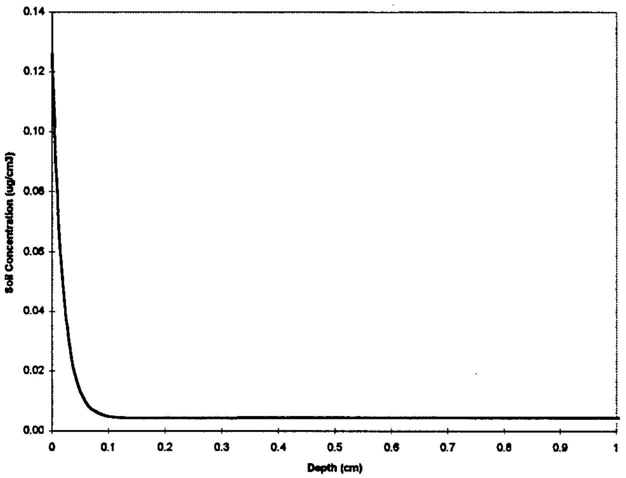

Figure 8. Detail of the Surface Layer Formed by Evaporation

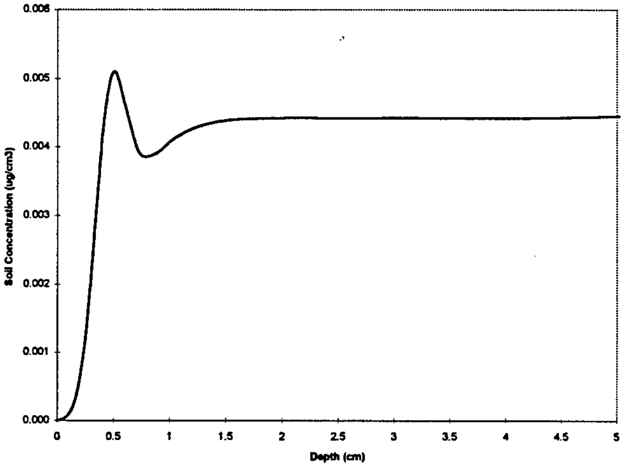

Figure 9. Effect of Precipitation on the Enhanced Surface Layer

8. SUMMARY AND CONCLUSIONS

Two previous efforts have evaluated the environmental fate and transport of chemical signature molecules from buried landmines (Phelan and Webb, 1997 and 1998). This effort evaluated the effect of changes in soil bulk density, burial depth, source term thickness, precipitation or evaporation, and the elements that produce an enhanced surface layer. Smaller soil bulk densities change the soil porosity and moisture content at constant soil saturations. Lower soil bulk densities increase the rate of transport as indicated by a shorter lag time and reach a higher steady state surface vapor flux. Burial depth has a dramatic effect on the lag time. With just a one centimeter soil cover, there appears to be almost no lag time and the surface vapor flux is five orders of magnitude greater than a soil cover of ten centimeters. The assumption of a uniform concentration over the depth of the landmine leads to under prediction of the vapor flux at the land surface by about an order of magnitude or more. The appearance of an enhanced surface layer is the result of evaporation driven mass transport that is constrained by vapor diffusion through the air boundary at the ground surface and the low aqueous to vapor transfer as a function of the low Henry's Law Constant. However, there are probably many other uncertainties in the present model which affect the quantitative results as well. The one-dimensional assumption demands that the mine itself is permeable, and the assumption of constant liquid content, both spatially and temporally, is obviously a great simplification. In order to address these and other issues, a multidimensional mechanistic code is being developed for application to the landmine problem. This code, which is based on the TOUGH code from Lawrence Berkeley Laboratory (Pruess, 1987,1991), will consider air, water vapor, and explosive vapor mass and heat flow in a porous media and will be able to address many of these questions.

9. ACKNOWLEDGEMENTS

This work was performed with internal laboratory-directed research and development funds at Sandia National Laboratories to explore applications for miniaturized chemical sensors. Follow-on work to develop a numerical model is just beginning with funds from the Strategic Environmental Research and Development Program (SERDP) for application to unexploded ordnance chemical sensing and from the Defense Advanced Research Projects Agency (DARPA) for application to buried landmines. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

10. REFERENCES

[1] Dugan, R.E., 1996. Detection of Land Mines and Unexploded Ordanance by Exploitation of the Chemical Signature. Defense Advanced Research Projects Agency, Conference presentation. April 1996.

[2] DuBois, F.W. and J. F. Baytos. 1991. Weathering of Explosives for Twenty Years. Los Alamos National Laboratory, Report LA-11931.

[3] Farmer, W.J., M.S. Yang, J. Letey, and W.F. Spencer. 1980. Hexachlorobenzene: its vapor pressure and vapor phase diffusion in soil. Soil Sci. Soc. Am. Proc. 44:676-680.

[4] Hogan, A., D. Leggett, T. Jenkins, P. Miyares. 1992. Results of Preliminary Analysis, Surface Contamination of Depot-Stored Land mines, Prepared as a briefing guide for planning DARPA mine detector trials. USACRREL. June 23, 1992. Includes: Test Plan Summary: Sampling of Mine Surfaces to Determine the Extent of Explosive Contamination.

[5] Jury, W.A., R. Grover, W.F. Spencer, and W. J. Farmer. 1980. Modeling Vapor Losses of Soil-Incorporated with Triallate. Soil Sci. Soc. of Am. J., 44, 445-50 (May-June 1980).

[6] Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior Assessment Model for Trace Organics in Soil: I. Model Description. J. Environ. Qual., Vol 12, no. 4, 558-564.

[7] Jury, W.A., W.J. Farmer, and W.F. Spencer. 1984a. Behavior Assessment Model for Trace Organics in Soil: II. Chemical Classification and Parameter Sensitivity. J. Environ. Qual., Vol. 13, no. 4, 567-572.

[8] Jury, W.A., W.F. Spencer, and W.J. Farmer. 1984b. Behavior Assessment Model for Trace Organics in Soil: III. Application of Screening Model. J. Environ. Qual., Vol 13, no. 4, 573-579.

[9] Jury, W.A., W.F. Spencer, and W.J. Farmer. 1984c. Behavior Assessment Model for Trace Organics in Soil: IV. Review of Experimental Evidence. J. Environ. Qual., Vol 13, no. 4, 580-586.

[10] Jury, W.A., D. Russo, G. Streile, and H. Abd. 1990. Evaluation of Volatilization by Organic Chemicals Residing Below the Surface. Water Resources Research vol 26, no 1, p 13-20, January 1990.

[11] Mayer, R., J. Letey, and W.J. Farmer. 1974. Models for predicting volatilization of soil-incorporated pesticides. Soil Sci. Soc. Am. Proc. 38:563-568.

[12] McGrath, C. 1995. Review of Formulations for Processes Affecting the Subsurface Transport of Explosives. US Army Corps of Engineers, Waterways Experiment Station, Technical Report IRRP-95-2, August 1995.

[13] Millington, R.J., and J.M. Quirk. 1961. Permeability of porous solids. Trans. Faraday Soc., 57:1200-1207.

[14] NGIC. 1995. Landmines and Demining: A Global Problem CD-ROM. National Ground Intelligence Center, Charlottesville, VA.

[15] Pennington, J.C. and W.H. Patrick. 1990. Adsorption and desorption of 2,4,6-trinitrotoluene by soils. J. Environ. Qual. 19:559-567.

[16] Phelan, J.M. and S. W. Webb. 1997. Environmental Fate and Transport of Chemical Signatures from Buried Landmines - Screening Model Formulation and Initial Simulations. Sandia National Laboratories, SAND97-1426. June 1997.

[17] Phelan, J.M. and S.W. Webb, 1998. Chemical Detection of Buried Landmines. Proceedings of the 3rd International Symposium on Technology and the Mine Problem, April 6-9, 1998. Mine Warfare Association.

[18] Pruess, K. 1987. TOUGH User's Guide, NUREG/CR-4645, SAND86-7104, LBL-20700, US Nuclear Regulatory Commission.

[19] Pruess, K. 1991. TOUGH2 - A General-Purpose Numerical Simulator for Multiphase Fluid and Heat Flow. LBL-29400, Lawrence Berkeley Laboratory.

[20] Schroeder, P.R., C.M. Lloyd, and P.A. Zappi. 1994a. The Hydrological Evaluation of Landfill Performance (HELP) Model User's Guide for Version 3. EPA/600/R-94/168a. U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

[21] Schroeder, P.R., T.S. Dozier, P.A. Zappi, B.M. McEnroe, J.W. Sjostrom, and R.L. Peyton. 1994b. The Hydrological Evaluation of Landfill Performance (HELP) Model: Engineering Documentation for Version 3. EPA/600-R-94/168b. U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

[22] Spangler, G.E.. 1975. Measurements on the Availability of TNT Vapor from Antitank Mines. Report No: MERADCOM-R-2159

[23] Spencer, W.F., M.M. Cliath, W.A. Jury, and L.-Z. Zhang. 1988. Volatilization of Organic Chemicals from Soil as Related to Their Henry's Law Constants. J. Environ. Qual. 17:504-509.

[24] Xue, S.K., I.K. Iskandar, and H.M. Selim. 1995. Adsorption-Desorption of 2,4,6-Trinitrotoluene and Hexahydro-1,3,5-Trinitro-1,3,5-Triazine in Soils. Soil Science, Vol. 160, No. 5. November 1995.

M98004465

Report Number (14) SAND--98-0768C
CONF-980412--

Publ. Date (11) 199803
Sponsor Code (18) DOE/CR , XF
UC Category (19) UC-900 , DOE/ER

DOE