SAND98-1394C
SAND--98-1394C
CONF-980559--

Prediction of the TNT Signature from Buried UXO/Landmines

RECEIVED
JUN 30 1998
OSTI

Stephen W. Webb[1], Stefan A. Finsterle[2], Karsten Pruess[2], and James M. Phelan[1]
[1]Sandia National Laboratories, Albuquerque, NM 87185
[2]Lawrence Berkeley National Laboratory, Berkeley, CA 94720

ABSTRACT

The detection and removal of buried unexploded ordnance (UXO) and landmines is one of the most important problems facing the world today. Numerous detection strategies are being developed, including infrared, electrical conductivity, ground-penetrating radar, and chemical sensors. Chemical sensors rely on the detection of TNT molecules, which are transported from buried UXO/landmines by advection and diffusion in the soil. As part of this effort, numerical models are being developed to predict TNT transport in soils including the effect of precipitation and evaporation. Modifications will be made to TOUGH2 for application to the TNT chemical sensing problem. Understanding the fate and transport of TNT in the soil will affect the design, performance and operation of chemical sensors by indicating preferred sensing strategies.

INTRODUCTION

The goal of locating buried UXO and landmines is a significant challenge to science and technology. The chemical signature is affected by multiple environmental phenomena that can enhance or reduce its presence and transport behavior, 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. 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 UXO/landmine is poorly understood. As an initial step in the evaluation of the chemical signature, a screening model based on pesticide and Volatile Organic Compound (VOC) movement in soils has been adapted to evaluate UXO/landmine chemical behavior. Future efforts to develop more mechanistic and sophisticated chemical transport models 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 UXO/landmine chemical constituents, such as TNT and DNT, to the land surface for chemical detection. Chemical vapors emanate from a buried UXO/landmine by permeation through plastic case materials or "leakage" through seals and seams, and from surface contamination of the case.

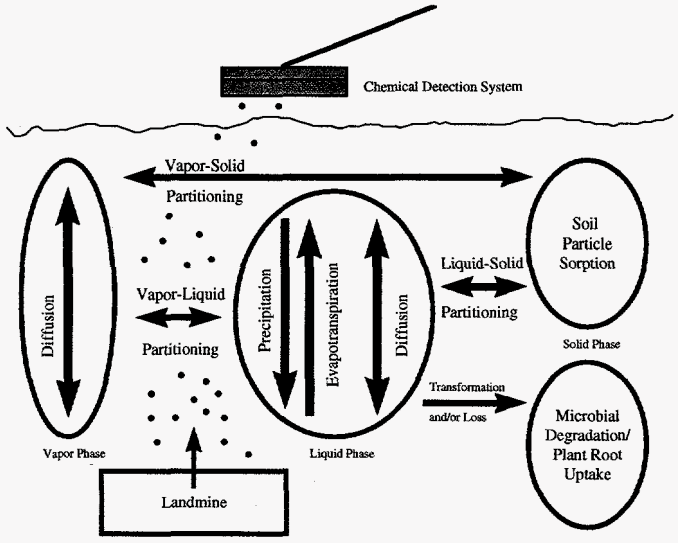

Figure 1. Environmental Fate and Transport Model for Chemical Detection of Buried UXO/Landmines.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

Table 1. TNT and DNT Properties at 20°C

	TNT	DNT
Vapor Density ($\mu g/m^3$)	43.5	122
Water Solubility (mg/l)	130	270
Henry's Law Constant	3.35E-7	4.51E-7
Sorption Coefficient (cm^3/g)	3.8	4.4

CHEMICAL PROPERTIES

The chemical properties of TNT and DNT are important in determining the transport rate of these vapors through the soil. These chemical vapors exist in the gas, liquid, and solid phases of the soil. Typical properties for TNT and DNT are shown in Table 1. Because of the low value of Henry's constant and the value of the soil water partition coefficient, about 90% of the explosive mass fraction is sorbed to the soil solid phase, about 10% is in the water; and less than 10^{-6}% is in the gas phase as shown in Figure 2.

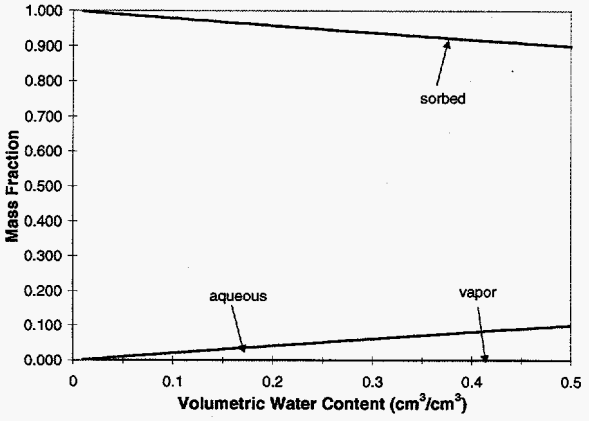

Figure 2. Phase Mass Fraction of TNT

The transport rate of TNT in soil can be estimated by evaluating pure diffusion conditions. An effective diffusivity can be defined for the total chemical concentration by considering the distribution among the phases (Jury et al., 1983). By applying the Millington and Quirk (1961) tortuosity relationship to the liquid phase, the effective diffusivity for the total chemical concentration can be expressed as

$$D_E = \frac{a^{10/3} K_H D_g^a + \theta^{10/3} D_l^w}{\phi^2 (\rho_b K_d + \theta + a K_H)} \qquad (1)$$

Figure 3 shows the variation in this effective diffusivity with water content. Note that the diffusivity value is low due to the value of Henry's constant and sorption onto the solid phase that acts as a sink for the explosive chemical. The effective diffusivity is generally much higher at higher moisture contents.

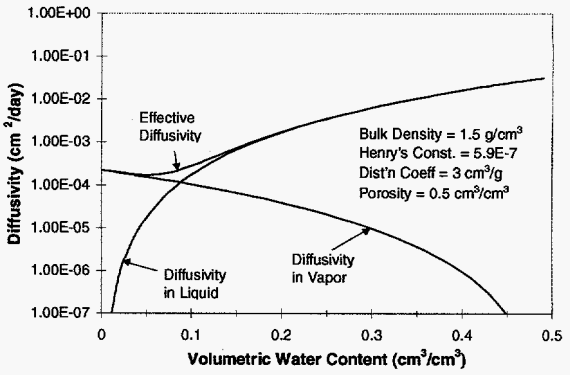

Figure 3. TNT Effective Diffusivity

INITIAL TRANSPORT STUDIES

Jury and his colleagues (Jury et al., 1983, 19841,b,c) developed a one-dimensional screening model to study the behavior of various pesticides under different environmental conditions. Mechanisms modeled include gas and liquid diffusion, sorption onto the soil, degradation, and infiltration/precipitation. Subsequently, this model was extended to buried chemicals, such as VOCs, by Jury et al. (1990). TNT properties (Henry's constant and sorption coefficient) are very similar to some pesticides, especially Prometron. Therefore, Jury's model has been used for some initial studies of the TNT transport in soils from buried UXO/landmines.

In addition, Prometron exhibits some interesting behavior that may be particularly important for the sensing of TNT for UXO/landmine detection. Under evaporation conditions, a surface "crust", or a soil layer greater in concentration than the subsurface soil, has been observed in laboratory tests; this surface "crust" is also predicted by Jury's screening model (Spencer et al., 1988). Some evidence of this type of behavior for TNT has been noted in field surveys and lab experiments, although the data are not definitive. The occurrence of a surface "crust" would greatly enhance the concentration available to chemical sensors and the efficiency of the technique.

Initial studies of the transport rate of TNT in soils from UXO/landmines have been conducted by Phelan and Webb (1997, 1998a,b) using Jury's model. The results of Phelan and Webb for UXO/landmine detection indicated a significant influence of the soil type and environmental conditions, including precipitation and evaporation, on the TNT flux at the soil surface which is available to chemical detectors.

Table 2. Phase Specific Concentration of TNT at the Ground Surface After One Year				
		Volumetric Water Content/Saturation		
Concentration	Units	0.20/0.46	0.25/0.58	0.30/0.69
Solid Phase	µg TNT/g soil	1.8E-8	3.1E-6	2.8E-5
Liquid Phase	µg TNT/ml soil water	4.8E-9	8.4E-7	7.6E-6
Gas Phase	µg TNT/cm^3 soil air	2.8E-15	5.0E-13	4.5E-12

Results from this screening model are shown below for a UXO/landmine buried 5 to 15 cm beneath the surface; details are given by Phelan and Webb (1997, 1998a,b). Note that the screening model was developed to assess the behavior of different chemicals under specific environmental conditions; it is not intended as a purely predictive model due to a number of simplifying assumptions, such as constant soil moisture content. Therefore, these results are only an indication of expected conditions, and more detailed numerical models, such as TOUGH2, are necessary for a fully predictive simulation.

Figure 4 shows the TNT surface flux at the land surface for a Gulf coastal lowlands soil type as a function of soil saturation. The oscillations in the surface flux are a result of precipitation/evaporation cycles, which were constant over the simulation. As the soil saturation increases, the surface flux increases dramatically.

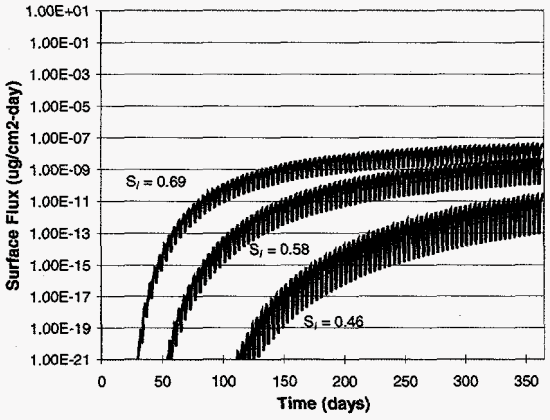

Figure 4. Surface Flux of TNT

Figure 5 shows the surface distribution of TNT after 1 year for the three soil saturations. The UXO/landmine was buried from 5 to 15 cm below the ground with an initial concentration based on contamination on the casing. In addition, UXO/landmines "leak" TNT through the casing, which was represented by a source at 10 cm. The movement of the TNT away from its initial location is slow and is a function of the liquid saturation.

Note the low total concentrations in Figure 5. The total concentration can be further broken down into solid, liquid, and gas phase values as summarized in Table 2, which indicate extremely small concentrations in the gas phase. This information will be valuable in the design and operation of chemical sensors for UXO/landmine detection.

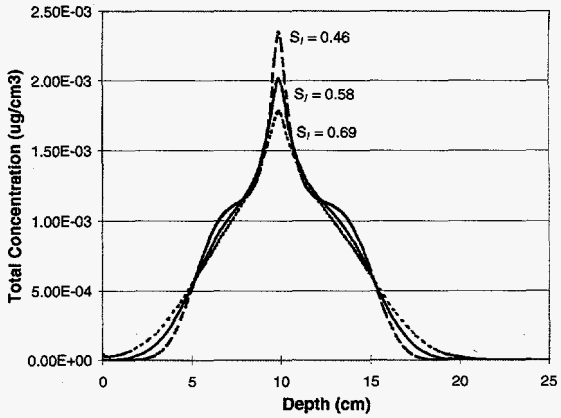

Figure 5. Subsurface Distribution of TNT After One Year

The effect of burial depth is a critical parameter. Figure 6 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.

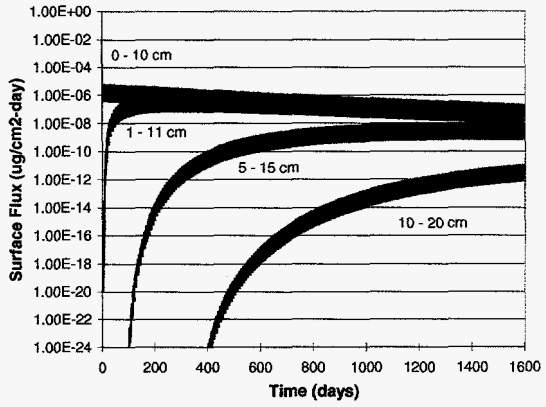

Figure 6. Effect of Burial Depth on Surface Flux

The effect of precipitation (positive water flux, J_w) and evaporation (negative water flux, J_w) is one of the most important environmental factors in the transport of explosive chemicals in soils. Figure 7 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. For the case of 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.

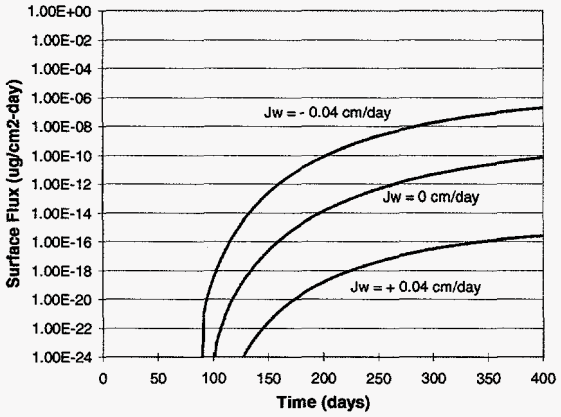

Figure 7. Effect of Water Flux (Precipitation/Evaporation) on Surface Flux

The occurrence of a surface soil layer that is greater in concentration than the subsurface soil layers, or a surface "crust", was discussed earlier. Simulations were performed to evaluate what influences the creation of the enhanced concentrations in the surface soil layers. Initial simulation runs (Phelan and Webb, 1997, 1998a) 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. In Figure 8 the buried chemical layer is shown to move upward until it intersects with the ground surface. Figure 9 shows 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 diffusion and limited by the transfer of chemical from the aqueous phase to the gas phase by the very low K_H.

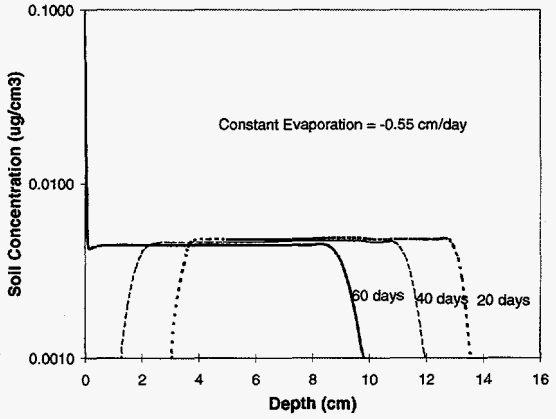

Figure 8. Upward Transport and Development of a Surface Layer

Figure 10 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.

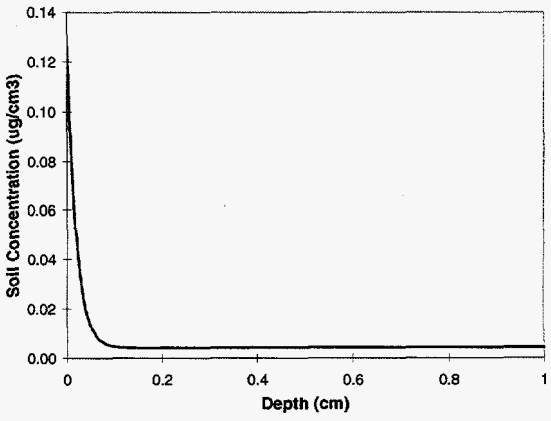

Figure 9. Detail of the Surface Layer Formed by Evaporation

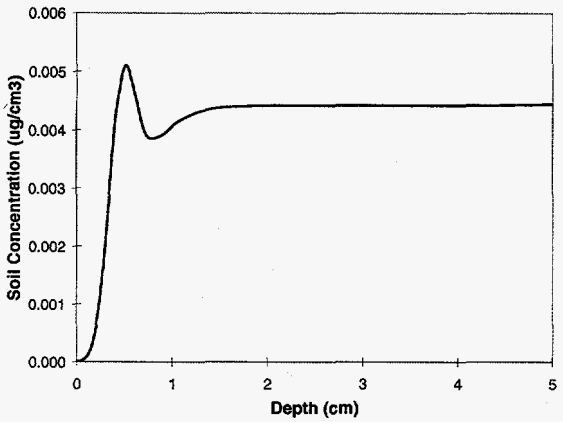

Figure 10. Effect of Precipitation on the Enhanced Surface Layer

DISCUSSION

As a result of these initial results, a more detailed mechanistic numerical model is being developed. This model is being based on TOUGH2 (Pruess, 1991) with modifications pertinent to the UXO/landmine application and will be called T2TNT. Modifications being made or planned to be made include:

1. Addition of TNT and DNT vapor components. – UXO/landmines typically emit TNT and DNT vapors. The vapor pressure of DNT is higher than TNT and, if present, will probably reach any chemical sensor before TNT.
2. Dusty Gas Model for gas diffusion. – Gas diffusion is a dominant transport mode for TNT and DNT vapors in the subsurface. Therefore, the Dusty Gas Model (Webb, 1998) will be implemented.
3. Liquid diffusion of dissolved TNT and DNT. – Liquid diffusion is not present in the standard version, although some special EOS modules include it. Liquid diffusion analogous to gas diffusion will be included because of the significant chemical concentration in the liquid phase.
4. Partition coefficient as a function of saturation. – The solid partition coefficient may be a strong function of saturation, especially at low moisture content where the partition coefficient may increase dramatically (Petersen, et al. 1995).
5. Boundary layer specifications for transport at soil surface. – For transport from the soil to the atmosphere, a boundary layer for heat and mass transfer will be implemented. The exact modifications are still being developed.
6. Precipitation and evaporation boundary conditions. – Precipitation boundary conditions will be added. The evaporation boundary condition may simply involve specification of a boundary layer and a boundary relative humidity, which will be time dependent.
7. Diurnal and seasonal variations in atmospheric conditions – In order to simulate daily and seasonal fluctuations, time-dependent boundary conditions for the pressure, temperature, and relative humidity will be implemented.

The resulting code will be used to develop an effective operational strategy for the design and deployment of UXO/landmine chemical sensors. The code will also be used within the ITOUGH framework to assist in the design of column experiments to be conducted at New Mexico Tech during the next few years. T2TNT will play an important part in the effective use of chemical sensors for UXO/landmine detection and removal.

CONCLUSIONS

The environmental fate and transport of chemical signatures from UXO/landmines is important for the design and operation of chemical sensors. The explosive vapors are predominantly found sorbed to soil particles or in the liquid phase; only a small fraction is present in the gas phase. As a result, diffusion and advection of the liquid water dominates the transport of the chemicals from the buried UXO/landmine to the land surface. Precipitation and evaporation also strongly influence the movement of the chemical signature. The results of initial screening studies have confirmed the influence of environmental conditions and soil parameters. The burial depth of the UXO/landmine is a significant factor. For shallow UXO/landmines, the chemical appears much sooner and at a much higher concentration than for deeper UXO/landmines. Precipitation and evaporation have a significant effect on the transport of TNT in the subsurface. The chemical concentration at the surface varies by many orders of magnitudes depending upon whether precipitation or evaporation is occurring. Under evaporation conditions, a surface "crust" can form where the surface concentration is higher than in the subsurface. These conditions would greatly enhance the detection capability of chemical sensors. As a result, a mechanistic numerical model based on TOUGH2 (Pruess, 1991), called T2TNT, is currently being developed. T2TNT will include a number of modifications and enhancements that should be of general interest to many TOUGH2 users. The use of T2TNT in understanding the environmental fate and transport of TNT in the soil will contribute to the improved design, performance and operation of chemical sensors in the detection of buried UXO/landmines.

NOMENCLATURE

a air volume fraction = $\phi - \theta$
D diffusion coefficient
K_d distribution coefficient for sorption
K_H Henry's Law constant
θ volumetric moisture content
ϕ porosity
ρ density

Subscripts
E effective
g gas
l liquid

Superscripts
a air
w water

ACKNOWLEDGMENTS

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 (UXO) 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.

REFERENCES

Jury, W.A., Spencer, W.F., and Farmer, W.J., 1983, "Behavior Assessment Model for Trace Organics in Soil: I. Model Description," *J. Environ. Qual.*, 12:558-564.

Jury, W.A., Farmer, W.J., and Spencer, W.F., 1984a, "Behavior Assessment Model for Trace Organics in Soil: II. Chemical Classification and Parameter Sensitivity," *J. Environ. Qual.*, 13:567-572.

Jury, W.A., Spencer, W.F., and Farmer, W.J., 1984b, "Behavior Assessment Model for Trace Organics in Soil: III. Application of Screening Model," *J. Environ. Qual.*, 13:573-579.

Jury, W.A., Spencer, W.F., and Farmer, W.J., 1984c, "Behavior Assessment Model for Trace Organics in Soil: IV. Review of Experimental Evidence," *J. Environ. Qual.*, 13:580-586.

Jury, W.A., Russo, D., Streile, G., and Abd, H., 1990, "Evaluation of Volatilization by Organic Chemicals Residing Below the Surface," *Water Resour. Res.*, 26:13-20.

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

Petersen, L.W., Rolston, D.E., Moldrop, P., and Yamaguchi, T., 1994, "Volatile Organic Vapor Diffusion and Adsorption in Soils," *J. Environ. Qual.* 23:799-805.

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

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

Phelan, J.M. and Webb, S.W., 1998b, "Simulation of the Environmental Fate and Transport of Chemical Signatures from Buried Landmines," International Symposium on Aerospace/Defense Sensing, Simulation, and Controls, Orlando, FL, April 13-17, 1998, SPIE.

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

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

Webb, S.W., 1998, "*Gas Diffusion in Porous Media: Comparison of Models*," TOUGH '98 Workshop, Lawrence Berkeley National Laboratory, May 4-6, 1998.