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Environmental Fate and Transport of Chemical Signatures from Buried Landmines–Screening Model Formulation and Initial Simulations

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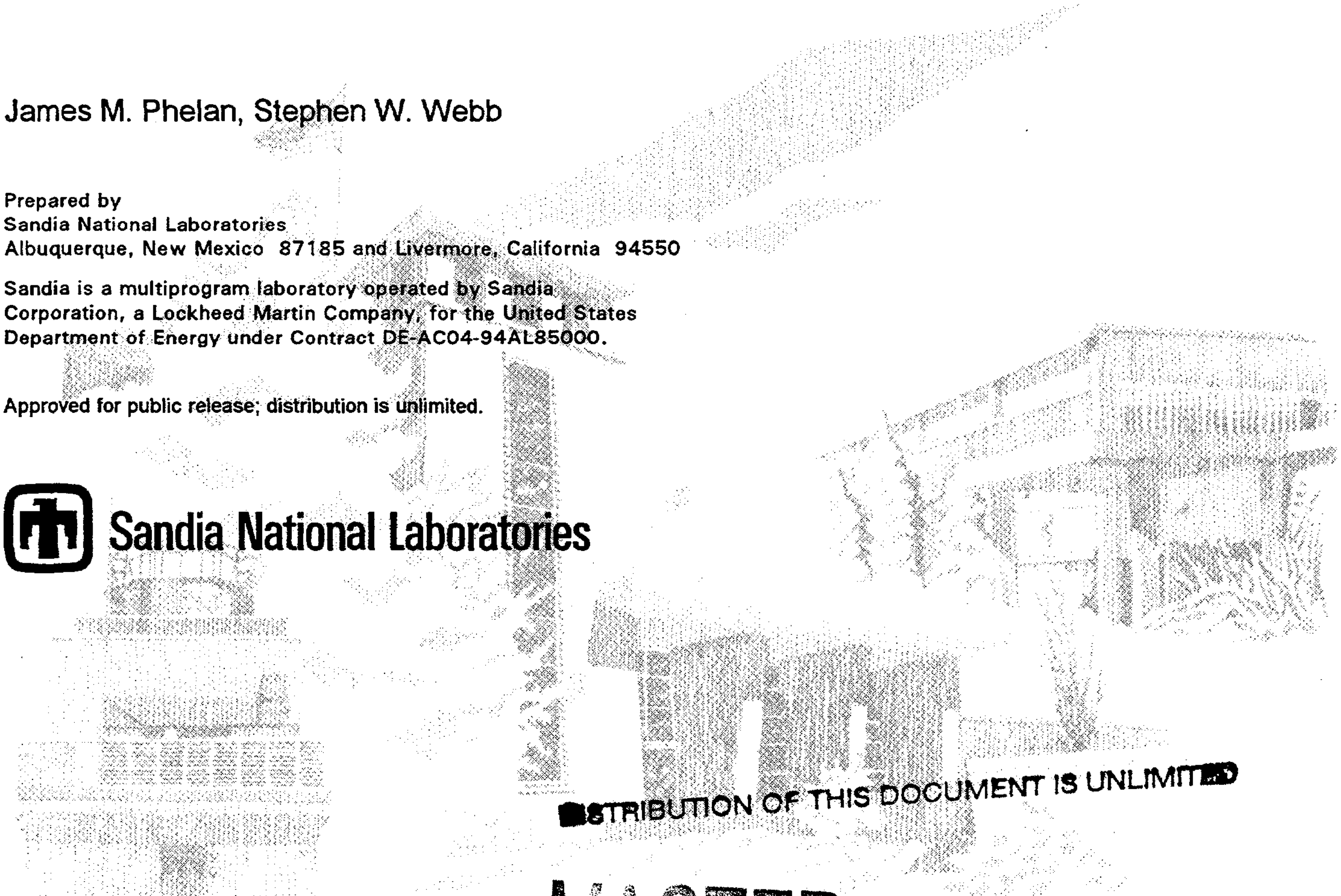

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Environmental Fate and Transport of Chemical Signatures from Buried Landmines - Screening Model Formulation and Initial Simulations

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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, estimate the subsurface total concentration. and show the phase specific concentrations at the ground surface. 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.

Acknowledgments

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1.0 Introduction

The goal of locating buried unexploded ordnance (UXO) is a significant challenge to science and technology (Dugan, 1996). UXO is a broad class of explosive-containing materials that includes landmines. Detection strategies may vary for unexploded ordnance that has penetrated deep into the soil versus near surface buried landmines. The work discussed here applies to both UXO and buried landmines, but will focus first on the near surface landmine problem. Application of the present model to other buried UXO is complicated by the deeper depths of some UXO.

The chemical signature of UXO such as 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 - an approach to develop a better transport model is outlined to achieve this objective.

A review of the literature shows that there have been many research efforts exploring individual fate and transport phenomena; but, there have been few modeling efforts that have incorporated multiple phenomena to assess the detection of buried landmines from the chemical signature. However, there is a strong correlation between the movement of explosive signature molecules in the near subsurface soil and that of applied agricultural pesticides as both can be low vapor density organic molecules. The well documented research on pesticide fate and transport in the subsurface can be leveraged in the evaluation of explosive signatures.

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 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.

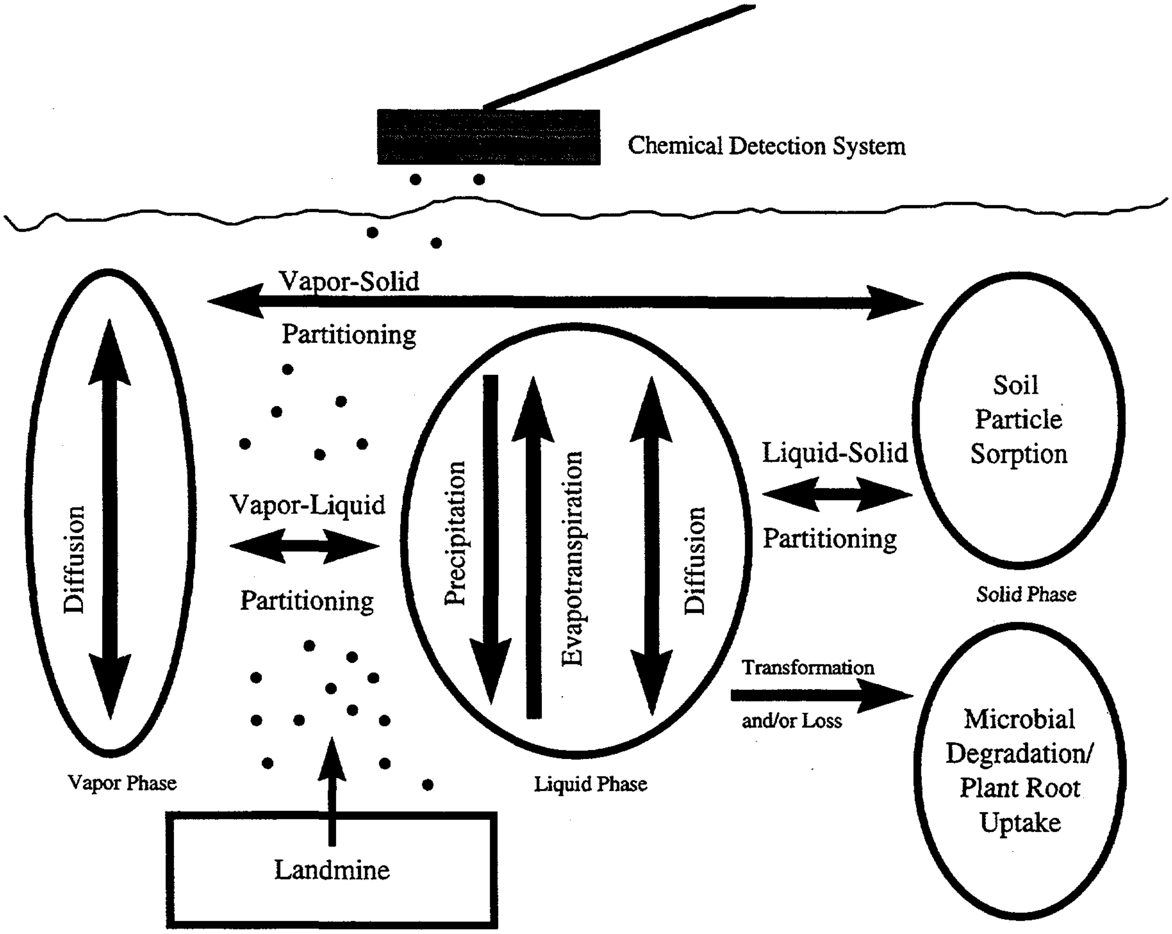

Figure 1. Environmental Fate and Transport Model for Chemical Detection of Buried Landmines.

2.0 Source Term

Selecting the optimal chemical for detection of buried landmines is dependent on the explosive formulation of the main charge and the physical/chemical properties of the chemical constituent. Spangler et al. (1974) tabulated the composition of the main charge and booster of about 132 foreign and domestic mines. Most of the mines contained TNT (90 listed, 68%) as the primary main charge with substantially fewer containing Composition-B (6 listed, 5%), Tetryl (5 listed, 4%), Amatol (4 listed, 3%), RDX (3 listed, 2%), PETN (3 listed, 2%) and others with two or less listed.

Murrmann and Nakamo (1971) used trace gas analytical techniques to identify the presence and concentration of solid and vapor phase isomers of TNT and DNT in military grade TNT. Table 1 shows the results where the vapor phase equilibrium tests at room temperature (28°C) were completed from undersaturation.

Table 1. Solid and Vapor Phase Composition of Military Grade TNT

Compound	Solid Phase Composition (%)	Vapor Phase Composition (%)
2,4,6 TNT	99.80	58
2,3,5 TNT	0.08	trace
2,3,4 TNT	0.02	3
2,4 DNT	0.08	35
2,5 DNT	<0.01	4
3,5 DNT	<0.01	trace
3,4 DNT	trace	trace
2,6 DNT	trace	trace
Other impurities	None detected	Not analyzed

from: Murrman and Nakano, 1971

This effort showed that the primary vapor phase impurity was 2,4 DNT which was at about the same concentration as 2,4,6 TNT. However, Leggett et al. (1977) completed laboratory analyses to determine the chemical composition of solid and headspace vapors from military grade TNT and found the 2,4 DNT to be at concentrations much greater than the 2,4,6 TNT. The headspace tests were performed at 2, 12, 20 and 32 °C The type of explosives used included cast, flaked and crystalline TNT mostly from batch, 3-stage nitration, and one sample from continuous nitration. Table 2 shows the solid phase concentrations of the primary isomers of DNT and TNT.

Table 2. Solid Phase Concentrations of the Primary Isomers of TNT and DNT

Impurity	Percent by Weight
2,4,5 TNT	0.068
2,3,4 TNT	0.203
2,4 DNT	0.077
2,3 and 3,5 DNT	0.018

from: Leggett et al., 1977

Headspace concentrations of 2,4 DNT were greater than any of the other DNT isomers and much greater than 2,4,6 TNT. Table 3 shows the partial pressures of 2,4 DNT and 2,4,6 TNT at various temperatures and the concentration factor of 2,4 DNT over that of 2,4,6 TNT.

Table 3. Headspace Concentrations of 2,4-DNT and 2,4,6-TNT from Military Grade TNT

Temperature °C	2,4 DNT mmHg	2,4,6 TNT mmHg	Concentration Factor 2,4 DNT/2,4,6 TNT
2	2.9E-06	0.1E-06	29
12	10.0E-06	0.3E-06	33
20	20.1E-06	1.2E-06	16
32	68.7E-06	9.4E-06	7

from: Leggett et al., 1977

When all domestic and foreign headspace analyses at 22°C were pooled, the average 2,4 DNT partial pressure was 19.1×10^{-6} mmHg and for 2,4,6 TNT was 1.7×10^{-6} mmHg. This indicates the 2,4 DNT is present at a concentration 11 times greater than that of 2,4,6 TNT. Leggett et al. (1977) found that a solid phase empirical Henry's Law constant could be described that was linear over the temperatures ranges studied (log K_H vs. 1/T).

Under typical soil temperatures, the predicted 2,4 DNT vapor pressure is about 10 to 30 times greater than 2,4,6 TNT even though it is a minor constituent (about 0.1 mole %) in the solid phase. While one may reason that depletion of 2,4 DNT could be of concern, no evidence was found that indicated the mole fraction of 2,4 DNT in the TNT samples evaluated was significantly different in samples differing in age of about 30 years.

Different TNT production and purification processes will produce variable levels of isomeric impurities. The current American purification process uses continuous countercurrent treatment of molten TNT (>80°C) with an aqueous solution of anhydrous sodium sulfite (Kaye, 1980). The meta isomers of TNT react with the sodium sulfite to produce water soluble sulfonates. Table 4 shows the impurities present before and after purification. These results show the 2,4 DNT to be at much higher concentrations than found by Leggett et al. (1977) and the purification process has no effect on the 2,4 DNT concentration.

Table 4. Impurities Present in TNT by Continuous Nitration and Purification

Compound	Approximate Maximum Nominal Concentration (%)	
	Crude	Finished
2,4,5 TNT	2.50	0.30
2,3,4 TNT	1.75	0.20
2,3,6 TNT	0.50	0.05
2,3,5 TNT	0.05	0.05
2,6 DNT	0.25	0.25
2,4 DNT	0.50	0.50
2,3 DNT	0.05	0.05
2,5 DNT	0.10	0.10
3,4 DNT	0.10	0.10
3,5 DNT	0.01	0.01
1,3 Dinitrobenzene	0.02	0.02
1,3,5 Trinitrobenzene	0.15	0.10
2,4,6 Trinitrobenzyl alcohol	0.25	0.25
2,4,6 Trinitrobenzaldehyde	0.25	0.25
2,4,6 Trinitrobenzoic acid	0.50	0.05
α-Nitrato-2,4,6 TNT	0.10	0.10
Tetranitromethane	0.10	none
2,2'-Dicarboxy-3,3',5,5'-tetranitroazoxybenzene	0.35	0.05
2,2',4,4',6,6'-Hexanitrobibenzyl	none	0.40
3-Methyl-2',4,4',6,6'-pentanitrodiphenylmethane	none	0.40
3,3',5,5'-Tetranitroazoxybenzene	none	0.01

from: Kaye, 1980

However, Kaye (1980) notes that the British and West German process uses solid TNT in this process and is said to produce a higher yield of more pure TNT and "removes nearly all of the DNT isomers." It is also noted that complete purification may not be warranted in some cases with modern bomb assembly and sealing techniques and additives to prevent the exudation of cast TNT mixtures.

The presence of 2,4 DNT in TNT is not desirable because it, along with other isomers of DNT and TNT, can cause exudation (Kaye, 1980). Exudation is a sweating out of liquid materials from an explosive composition through the pores, seals or joints of the casing. This phenomenon is usually associated with dynamites, but has also been described in gun shells loaded for WWII. Exudation is caused by a lower melting point of the final product (80.2°C vs. 80.75°C) and migration of much of the impurities to the center of a cast explosive due to differential cooling from the outside inward. When the shell was stored at elevated temperatures the center would liquefy, expand and exude through weak points in the casing.

Chemical detection of explosive vapors requires that landmines are inherently leaky to provide sufficient mass for the fate and transport processes to act upon. Spangler (1975) placed landmines in vapor collection chambers and measured the concentration increase over time. The methods included removing the main explosive charge, washing the casing to insure that the mines were free of explosive materials, then loading the inner well with a foil coated with acetone recrystallized TNT to insure no external contamination was present prior to initiating the experiments. The TNT flux rates averaged over the surface area of the mines were 10^{-16} to 10^{-18} g/cm^2-s.

Hogan et al. (1990) hypothesized that the outer surface of a mine could become contaminated during production and/or storage and releases from these surfaces could provide the source term needed for chemical detection. Small pieces of painted surfaces were placed in a large jar with granules of TNT for 15 to 30 days. The materials were moved to a clean chamber, and, after 24 hours, ambient air was passed over these surfaces with TNT mass measured as a function of time. Values for painted surfaces (comparable to a painted metal mine) were about 10^{-14} g/cm^2-s.

To explore the total amount of surface contamination on depot-stored landmines, Hogan et al. (1992) collected surface swipe samples from 42 foreign and domestic landmines. The median surface contamination of TNT was found to be about $1.5\text{x}10^{-8}$ g/cm^2 and RDX was $1\text{x}10^{-9}$ g/cm^2. Once a landmine is buried, if the landmine TNT source term was solely from the external deposits and was released to the soil environment through vaporization from the surface, the source would be depleted within about 17 days using the flux rate from Hogan et al. (1990) (10^{-14} g/cm^2-s). For chemical detection to be successful, continuous permeation through plastic mine case materials or leakage through ports or seals is required since the surface contamination from external sources will be depleted much too rapidly.

3.0 Physical Chemical Properties

The most prevalent data available is on TNT vapor pressure and water solubility at various temperatures. Dionne et al. (1986) performed vapor pressure experiments on five explosive materials and compiled previous data to generate linear LOG P vs. 1/T relationships. Lenchitz and Velicky (1970) performed vapor pressure experiments for TNT and DNT. Table 5, 6 and 7 presents original data and conversions to other popular units for TNT, DNT and RDX, respectively. Henry's Law Constants (K_H) were calculated from vapor pressure and water solubility values using:

$$K_H = \frac{C_g}{C_l}$$

Table 5. Vapor Pressure, Water Solubility and Henry's Law Constant for TNT

Temp	Vapor Pressure			Vapor Density	Water Solubility		Henry's Law Constant	
°C	ppb (1) (v/v)	mmHg	atm	µg/m^3 (3)	mg/l (2)	mol/m^3	cm^3,w/cm^3,a	atm-m^3/mol
0	0.20	1.49E-07	1.96E-10	2.0	100	0.44	1.99E-08	4.46E-10
5	0.45	3.43E-07	4.51E-10	4.5				
10	1.01	7.64E-07	1.01E-09	9.8	110	0.48	8.94E-08	2.08E-09
15	2.18	1.66E-06	2.18E-09	21.0	120	0.53	1.75E-07	4.13E-09
20	4.61	3.50E-06	4.61E-09	43.5	130	0.57	3.35E-07	8.05E-09
25	9.49	7.21E-06	9.49E-09	88.1	150	0.66	5.87E-07	1.44E-08
30	19.09	1.45E-05	1.91E-08	174.3	175	0.77	9.96E-07	2.48E-08
35	37.54	2.85E-05	3.75E-08	337.2	225	0.99	1.50E-06	3.79E-08
40	72.25	5.49E-05	7.22E-08	638.5	285	1.26	2.24E-06	5.75E-08
45	136.19	1.04E-04	1.36E-07	1184.8	360	1.59	3.29E-06	8.59E-08
50	251.74	1.91E-04	2.52E-07	2156.1	475	2.09	4.54E-06	1.20E-07
55	456.70	3.47E-04	4.57E-07	3851.9	570	2.51	6.76E-06	1.82E-07
60	813.84	6.19E-04	8.14E-07	6760.9	675	2.97	1.00E-05	2.74E-07

(1) from Dionne et al. 1986. Data taken from 10 to 140°C.
Tabulated data uses LOG P (ppb) = -5481/T(°K) + 19.37.
(2) from Stephen and Stephen, 1963
(3) at 1 atm

Table 6. Vapor Pressure, Water Solubility and Henry's Law Constant for DNT

Temp	Vapor Pressure			Vapor Density	Water Solubility		Henry's Law Constant	
°C	ppb (v/v)	mm Hg (1)	atm	$\mu g/m^3$ (3)	mg/l (2)	mol/m^3	cm^3,w/cm^3,a	atm-m^3/mol
0	0.84	6.36E-07	8.37E-10	6.8				
5	1.82	1.39E-06	1.82E-09	14.6				
10	3.87	2.94E-06	3.87E-09	30.3				
15	7.98	6.07E-06	7.98E-09	61.5				
20	16.08	1.22E-05	1.61E-08	121.8	270	1.48	4.51E-07	1.35E-08
25	31.65	2.41E-05	3.17E-08	235.6				
27	41.23	3.13E-05	4.12E-08	304.9				
30	60.91	4.63E-05	6.09E-08	445.9				
40	211.85	1.61E-04	2.12E-07	1501.2				
60	2047.52	1.56E-03	2.05E-06	13637.7				

(1) from Lenchitz and Velicky, 1970, data taken from 59 to 69°C, tabulated data extrapolated based on LOG P (mmHg) = -5139.058/T°K + 12.6177.

(2) from Verschueren, 1983

(3) at 1 atm

Figure 2 shows a chart of the differences in vapor pressure of TNT and DNT at normal environmental temperatures which displays about a two to four fold increase of DNT vapor pressure over TNT. However, the Henry's Law Constants are about equivalent which implies that the vapor-liquid partitioning will behave similarly.

Table 7 shows the vapor pressure, water solubility and Henry's Law Constants for RDX. Note that the vapor pressure and Henry's Law Constant is about 3 orders of magnitude less than that for TNT and DNT at a similar temperature. This means that RDX will be at even lower vapor phase concentrations than TNT and DNT in a soil water system.

Table 7. Vapor Pressure, Water Solubility and Henry's Law Constant for RDX

Temp	Vapor Pressure			Vapor Density	Water Solubility		Henry's Law Constant	
°C	ppb (1) (v/v)	mm Hg	atm	$\mu g/m^3$ (3)	mg/l (2)	mol/m^3	cm^3,w/cm^3,a	atm-m^3/mol
20	0.00256	1.95E-09	2.56E-12	0.0237	50	0.22	4.73E-10	1.16E-11
40	0.06599	5.02E-08	6.6E-11	0.5707	127	0.56	4.49E-09	1.18E-10
60	1.15	8.76E-07	1.15E-09	9.4	300	1.32	3.12E-08	8.72E-10

(1) from Dionne et al., 1986. Data taken from 40 to 140°C. Tabulated data uses LOG P (ppt) = -6473/T°K + 22.50.

(2) from Gibbs and Popolato, 1980

(3) at 1 atm

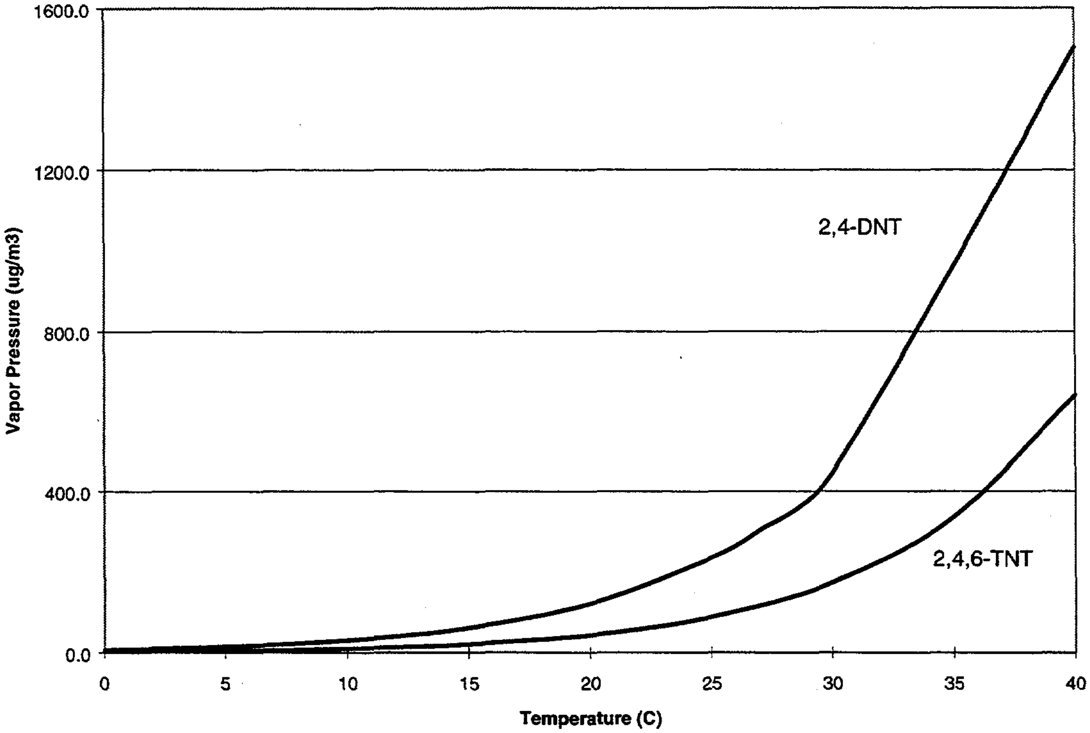

Figure 2. Vapor Pressure of 2,4,6-TNT and 2,4-DNT.

Along with vapor pressure and water solubility, vapor diffusivity is another major parameter that has profound influence on the transport of explosive vapors in soils. Diffusion constants have been determined for many chemical substances by several methods. Diffusion constants vary linearly with pressure and exponentially with temperature ($T^{1.75}$ to $T^{2.0}$) (Hamaker, 1972).

Over the last 30 years, researchers have explored the effect of soil physical properties on the magnitude of the diffusion coefficients of individual compounds. Hamaker (1972) shows data where the diffusivity of a vapor in air decreases by a factor of three or more when the same vapor diffuses in a soil. Diffusion constants in soil are expected to be lower due to the tortuosity of the flow path, reduce flow area, and due to interaction with the soil (adsorption) and soil water (solution). Early efforts developed an effective diffusion coefficient for soil as an aggregate parameter included vapor and liquid phase diffusion, vapor-liquid partitioning, and liquid-solid partitioning. Vapor pressure, water solubility and phase partitioning coefficients were integrated to provide an effective diffusion coefficient for soil in a given state. The most widely used function for soil diffusivity is an adjustment of the diffusivity of a gas in air based on the volumetric air content and porosity using the tortuosity model of Millington and Quirk (1961):

$$D_g^s = (a^{10/3} / \phi^2) D_g^a$$

Jury (1983) applied this same concept to the diffusivity of a solute in soil with the volumetric water content and porosity:

$$D_l^s = \left(\Theta^{10/3} / \phi^2\right) D_l^w$$

Combining the Millington and Quirk, 1961 tortuosity model with phase partitioning functions, Jury (1983a) established an effective diffusion coefficient that describes whether diffusion is predominantly in the vapor or liquid phase and the dependence on phase partitioning coefficients and soil moisture content:

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

There are several methods available to estimate the diffusivity of explosive signature compounds in air. The diffusivity of TNT and DNT in nitrogen was derived from mobility data on a plasma chromatograph (Spangler, 1974). At 27°C, the diffusivity for TNT was 0.0447 cm^2/s and for DNT was 0.0476 cm^2/s. Using the analytical method of FSG described in Lyman et al. (1990), the diffusivity of TNT in air at 25°C and 1 atm was calculated to be 0.0644 cm^2/s and for DNT was 0.0686 cm^2/s. This method allows calculation of the diffusivity at other temperatures and pressures; however, for temperatures of 0 to 60°C the diffusivity increases only 40% $((T°K)^{1.75})$ and from atmospheric pressures of 760 mmHg to 620 mmHg (atmospheric pressure at an elevation of 5,000 ft.) the diffusivity increases only by 22% (1/P).

Sorption of chemical constituents to soil particles can occur directly through vapor-solid partitioning or in solution through liquid-solid partitioning. Most environmental research has explored the liquid-solid partitioning due to concerns regarding aquifer contamination and the assumption that soil particles are almost always coated with an aqueous film (Kenaga and Goring, 1980). However, with agricultural soil fumigation, researchers have found that volatilization of applied organic chemical pesticides is prevented by dry surface soils. Ehlers et al. (1969a, 1969b) studied lindane (MW 290.8, VP @20°C is $3.2x10^{-5}$ mmHg, water solubility 10 mg/l) which has physicochemical properties close to that of TNT. In his work, the diffusion coefficient for lindane remains constant from near soil saturation down to 10 weight percent water content. Below 5 weight percent water, the diffusion coefficient doubles and then precipitously drops to zero near 3 weight percent. This is interpreted as strong adsorption of lindane to soil particles when there is insufficient water to compete for soil sorption sites. This has been reported for other soil applied herbicides (Hamaker, 1972). Petersen et al. (1994) reports for trichloroethylene that the vapor-solid partition coefficients were consistent with values predicted by Henry's Law Constants and the aqueous-solid partitioning coefficients at water contents higher than four molecular layers of water surface coverage. Less than this, the sorption increased by orders of magnitude. A one-parameter exponential model has been developed for trichloroethylene that describes well the vapor-solid partitioning coefficient as a function of soil water content in the non-linear range (Petersen et al., 1995). This phenomenon has had little research for explosive signature compounds, but has large implications for chemical detector systems for buried landmines. Whether this sorption is temporary or permanent and whether the soil can act as an in-situ concentration device needs to be explored. In addition, soil microbiological activity would be expected to be low in very dry soils limiting the permanent loss by biodegradation.

Liquid-solid partitioning has been studied much more. The parameter describing this phenomena is the distribution coefficient, K_d, defined as:

$$K_d = \frac{C_s}{C_l}$$

or

$$K_{oc} = \frac{C_s}{C_l f_{oc}}$$

where K_{oc} is the organic carbon partition coefficient.

Comfort et al. (1995) performed batch short-term and long-term sorption experiments due to concerns over transport and fate of TNT from past waste disposal practices at a military ordnance plant. They present evidence that the sorption isotherms are non-linear when looking at a wide range of solution concentrations (6.3 and 70 mg/l TNT). This work also shows that after 14 days, up to 50% of the sorbed TNT remains irreversibly sorbed. Others have found similar results during composting studies for soil restoration (Kaplan and Kaplan, 1982; Caton et al., 1994) - this would be expected with the high soil organic carbon content found in compost media. The TNT recovery was apparently concentration dependent with lower recoveries at lower concentrations. In addition, it was found that TNT amino degredates were formed and partially sorbed as well. They found 4-amino-2,6-dinitrotoluene (4ADNT) and 2-amino-4,6-dinitrotoluene (2ADNT) being formed through abiotic and biotic processes.

Pennington and Patrick (1990) report that biotic reduction exceeded abiotic reduction under both oxidizing and reducing conditions. They also found that TNT sorption has a higher correlation to cation exchange capacity than the fraction of organic carbon. Tucker et al. (1985) also previously reported this with the variation in K_d accounted by organic carbon (64%) and cation exchange capacity (78%). In contrast to the permanent retention of TNT found by Comfort et al. (1990), Pennington and Patrick (1990) found with three sequential desorption steps that 88 to 93% of adsorbed TNT was desorbed. The soils were equilibrated with TNT solutions from 1.0 to 16 mg/l. The magnitude of the linear adsorption coefficients (K_d) ranged from 2.3 to 6.8 cm^3/g (mean of 4.0) for 14 different soil types from Army Ammunition Plants across the nation.

Because of this conflicting data, Xue et al. (1995) performed equilibrium and kinetic sorption studies for TNT and RDX with solution concentrations of about 1 to 10 mg/l. With a bentonite/sand mix, no sorption hysteresis was found indicating a fully reversible sorption mechanism. However, when two soils were used, the fully reversible adsorption-desorption behavior was not found and little of the adsorbed TNT was released. Using actual aged contaminated soils from the Louisiana Army Ammunition Plan, about 50% of the TNT in the soil samples was unextractable. This effort quantified the linear adsorption coefficient (K_d) for TNT at 2.7 and 3.6 cm^3/g, and for RDX at 1.6 cm^3/g for two soil types.

Cataldo (1993) incorporated 60 ppm of TNT in three soil types (0.5%, 1.7% and 7.2% organic matter) and followed extractable, unextractable and parent compounds over 60 days. The parent TNT concentrations fell below 3% of the original concentrations within 10 days. Extractable parent compound and transformation products showed exponential decline reaching near steady state at 60 days. The unextractable fraction showed similar response, growing to about 40% at 60 days. In the high organic matter soil, permanent sorption reaches a greater level (~50%) and the extractable/unextractable fractions reaching near steady-state much faster (about 10 days). Work with RDX showed that there was very little transformation and most of the parent compound remained at 60 days. Chemical analysis of the extractable fraction found isomers of aminodinitrotoluene and a range of unidentified more polar compounds. The production of more polar compounds is typical of biotransformation processes to produce more water soluble compounds - which makes the transformation products less volatile and available for vapor phase collection, concentration and detection. These occur by either fortuitous reactions or, less frequently, through catabolic utilization (Spain, 1995).

Very little information has been found on the intrinsic biodegradation rates of explosives in soils. Much of the literature has shown data for active restoration methods such as composting or bioreactors where there is little correlation to in-situ ambient conditions.

The kinetics of these sorption and degradation reactions are fast enough to limit the long-term storage and future release of landmine released chemical constituents for buried landmine detection, except possibly under very dry surface soil conditions. Hamaker (1972) claims that in the majority of cases, semivolatile compounds will be lost more through soil decomposition processes than through volatility. The continuous release of these compounds under favorable transport conditions will be necessary for surface detection by chemical sensing systems - implying again, that timing of a survey with optimal environmental fate and transport conditions is very important to insure success.

There have been few experimental evaluations to validate the predicted flux of explosive signature molecules from buried landmines. In 1972-73, Jenkins et al. (1974) evaluated the appearance of cyclohexanone from buried antitank mines and surrogates doped with excess cyclohexanone. Cyclohexanone is a common trace constituent in military grade Composition-B and RDX - cyclohexanone is used in recrystallization (Murrmann and O'Reilly, 1973). In the first test series, the only positive identification occurred for sponges and mines spiked with excess cyclohexanone. Samples from the actual landmines did produce a gas chromatographic peak at the correct retention time for cyclohexanone, but insufficient mass was available for mass spectral determination. This effort occurred in December when the temperatures were below freezing at night and the ground was frozen at the beginning of the sampling periods. The second test series were run in June when the temperatures were warmer and there was no rainfall for one week prior to the field tests. Estimated flux rates of cyclohexanone under these conditions were around 10^{-12} to 10^{-13} g/cm^2-s. Cyclohexanone has a vapor pressure of 4.8 mmHg at 25°C, a water solubility of 23,000 mg/L at 25 °C and a Henry's Law Constant of $1.2x10^{-5}$ atm-m^3/mole (Howard, 1990).

4.0 Screening Model

For the development of a chemical detector based landmine survey system, the surface flux of the marker chemical is needed to engineer the vapor collection and concentration components. Spangler (1974) developed a mathematical model for the release and transport of TNT and DNT to the ground surface. A diffusion only case is developed where the soil water is stationary, the gas phase is static air, soil particle sorption is proportional to soil particle surface area which is proportional to the soil water content, liquid phase solubility is proportional to Henry's Law constant, and liquid-solid phase partitioning is insignificant. The TNT vapor concentration at the mine surface is assumed to be in equilibrium with the solid phase; no reduction in concentration due to the mine encasement is assumed. Values of the initial surface flux were about 10^{-19} g/cm^2-s. Spangler (1975) described the steady state case where the partitioning processes are at equilibrium which generated values about 10^{-13} g/cm^2-s. Again, no reduction in concentration due to the mine casing was considered. Webb (1996a) provides a discussion of the correction of the flux values presented in Spangler, 1974.

Spangler (1974) also reports on the liquid phase transport of TNT and DNT by evaporation of water at the ground surface. A relationship is developed that shows the rate of transport of TNT/DNT is related to the rate at which water arrives at the surface, the vapor-liquid partitioning coefficient of TNT/DNT and the liquid phase concentration of TNT/DNT in the soil water. For typical evaporation rates of water and TNT/DNT at saturation throughout the soil, the flux of TNT/DNT range from 10^{-9} g/cm^2-s to 10^{-13} g/cm^2-s. Again, in Spangler (1975), the mass transport of TNT/DNT by soil water movement values presented in Spangler (1974) were judged to be unreasonably high.

In his discussion of the calculated surface fluxes, Spangler (1975) comments that the flux is limited to what is available from the mine. He presents data that shows that the release of vapors from the mine is much lower than the flux rate given above - so, the flux is constrained to the mine vapor release rate, estimated to be 10^{-16} g/cm^2-s to 10^{-18} g/cm^2-s.

Spangler's model as discussed above was an interesting first step which considered the relevant fate and transport processes for chemical movement. However, his model was restricted to an analytical solution which necessitated numerous simplifying assumptions. A more general model developed by Jury et al. (1983) is described below.

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.

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 using Fick's law.
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

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

where

$$V_E = \frac{J_w}{\rho_b K_d + \theta + aK_H}$$

is the effective velocity of the chemical, and

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

is the effective diffusion coefficient of the chemical.

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

$$-D_E \frac{\partial C_T}{\partial z} + V_E C_T = -H_E C_T$$

where

$$H_E = \frac{hK_H}{\rho_b K_d + \theta + aK_H}$$

and

$$h = \frac{D_g^a}{d}$$

and

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

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

$$\begin{array}{ll} C_T(z,0) = 0. & L \rangle z \rangle W \\ C_T(z,0) = C_0 & L \leq z \leq W \end{array}$$

The above model 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 simulation, the assumption of constant water flux in time will be 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.

Based on initial applications of Jury's BAM screening model for TNT, concentrations may increase dramatically at the soil surface. In order to allow for the possible dramatic variation in concentration near the surface, and to minimize the numerical overhead, the Keller Box Method (Keller, 1970, Cebeci and Bradshaw, 1984) has been used. The method allows for variable mesh point spacing, such as required in fluid boundary layer analysis, and results in a tridiagonal matrix, which can be solved directly by the Thomas algorithm. Both of these factors contribute to a numerically efficient procedure which is especially beneficial for the present application. Details are given in Appendix A.

The computer program resulting from application of the Box method has been verified by comparison to results given by Spencer et al. (1988) for the BAM and Jury et al. (1990) for the BCM; Appendix B shows the comparisons. The results of Spencer et al. (1988) for the pesticide prometon are especially interesting and are also discussed here due to their relevance to possible TNT behavior. According to Jury's screening model (Jury et al., 1984b), prometon is a Category III chemical (K_H much less than 2.65 x 10^{-5}) such that under evaporating conditions, the concentration at the soil surface and the volatilization rate increase dramatically with time. Based on an estimated value of K_H of 5.9 x 10^{-7}, TNT is also a

Category III chemical. Spencer et al. (1988) compared model predictions with experimental data for volatilization flux and concentration profiles for prometon; TNT behavior may be similar.

In the experiments performed by Spencer et al. (1988), prometon is initially present at a uniform concentration in the soil from the surface to a depth of 10 cm. Experiments with zero water flux and evaporation water flux were conducted and compared to the model predictions of Jury et al. (1983). Water evaporation significantly increases the volatilization rate of prometon compared to no water flux. Prometon concentrations increase by orders of magnitude at the surface with evaporation. When water evaporates from the surface, prometon is left behind resulting in a greatly enhanced surface concentration and surface flux under evaporative conditions, which is also expected for TNT due to its similarity to prometon.

The results above indicated the importance of environmental factors, such as evaporation and precipitation, on the fate and transport of landmine chemical signature molecules in the soil subsurface, and its potential impact on operational strategy for landmine detection. Therefore, the surface volatilization flux and subsurface distribution were estimated using the Jury Buried Chemical Model, modified to include a source term and cyclic precipitation/evaporation described below.

Using this solution, simulations were performed of a landmine that has contributed an initial soil concentration (C_o) based on the surface contamination of the landmine. 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. Using the dimensions of an anti-tank (AT) mine of 30 cm diameter by 10 cm high, the surface contamination would provide $4.1\text{x}10^{-5}$ 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 $4.6\text{x}10^{-3}$ µg/cm^3.

The constant source term emanation rate was 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 ($8.6\text{x}10^{-6}$ µg/cm^2-day) was used in these simulations. If the top of the AT mine was buried at a depth of 5 cm, the burial zone of the initial contamination is from 5 to 15 cm, and the constant source term is placed at a depth of 10 cm.

Three climatic conditions were established from data found in the HELP (Hydrological Evaluation of Landfill Performance) model (Schroeder et al., 1994a and 1994b). These included a low desert environment typified by Phoenix, Arizona; a gulf coastal lowland typified by Brownsville, Texas; and, a mid-continental area typified by Cincinnati, Ohio. The average annual rainfall simulated was 20 cm for the low desert, 72 cm for the gulf coastal lowland, and 103 cm for the mid-continental area. The HELP model showed that the low desert had 1 day of precipitation followed by 7 days of evaporation; the gulf coastal lowland had 1 day of precipitation followed by 3 days of evaporation; and the mid-continental area had 2 days of precipitation followed by 3 days of evaporation. For simplicity, total precipitation and total evaporation for each cycle are assumed to be equal and for these initial screening simulations the cycles were continued for approximately one year.

The physical/chemical properties of TNT used in these simulations included a constant value for the Henry's coefficient (K_H) of 5.9E-7 (see Table 5, data for 25°C). The soil-water partition coefficients (K_d) were selected from the data collected at Army Ammunition Plants (Pennington and Patrick, 1990) as discussed earlier. The total porosity values were derived from the bulk density ($\rho_b = 1.5$) and particle density ($\rho_s = 2.65$) as follows:

$$\phi = 1 - \rho_b / \rho_s$$

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). Since there is no published data found for the biological half-life of TNT, a value of 180 days was selected based on a range of 15 to 868 days for tabulated pesticides (Jury, 1984b). Table 8 shows the input parameters used for three scenarios.

Table 8. Parameters for TNT Simulation

		Scenario 1: Mid-Continental Region	Scenario 2: Gulf Coastal Lowlands	Scenario 3: Low Desert
θ	cm^3/ cm^3	0.30/0.25/0.20	0.30/0.25/0.20	0.30/0.25/0.20
ϕ	cm^3/ cm^3	0.434	0.434	0.434
ρ_b	g/cm^3	1.5	1.5	1.5
K_d	cm^3/g	6.8	3.7	2.5
K_H	--	5.9E-7	5.9E-7	5.9E-7
air boundary layer	cm	0.5	0.5	0.5
$t_{1/2}$	days	180	180	180
C_o	$\mu g/cm^3$	4.6E-3	4.6E-3	4.6E-3
J_c	$\mu g/cm^2$-day	8.6E-6	8.6E-6	8.6E-6
D_l^w	cm^2/day	0.432	0.432	0.432
D_g^a	cm^2/day	4320	4320	4320
burial depth, top	cm	5	5	5
burial depth, bottom	cm	15	15	15
cycles/yr	--	73	91	45
precipitation	days	2	1	1
evaporation	days	3	3	7
precipitation rate	cm/day	0.71	0.79	0.44
evaporation rate	cm/day	- 0.47	- 0.26	- 0.063
total precipitation/ evaporation	cm/year	103	72	20

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5.0 Discussion

General Behavior

Using Jury's model, an example of the importance of the influence the soil water content has on the chemical distribution and the effective diffusivity of TNT are shown in Figure 3 and 4, respectively.

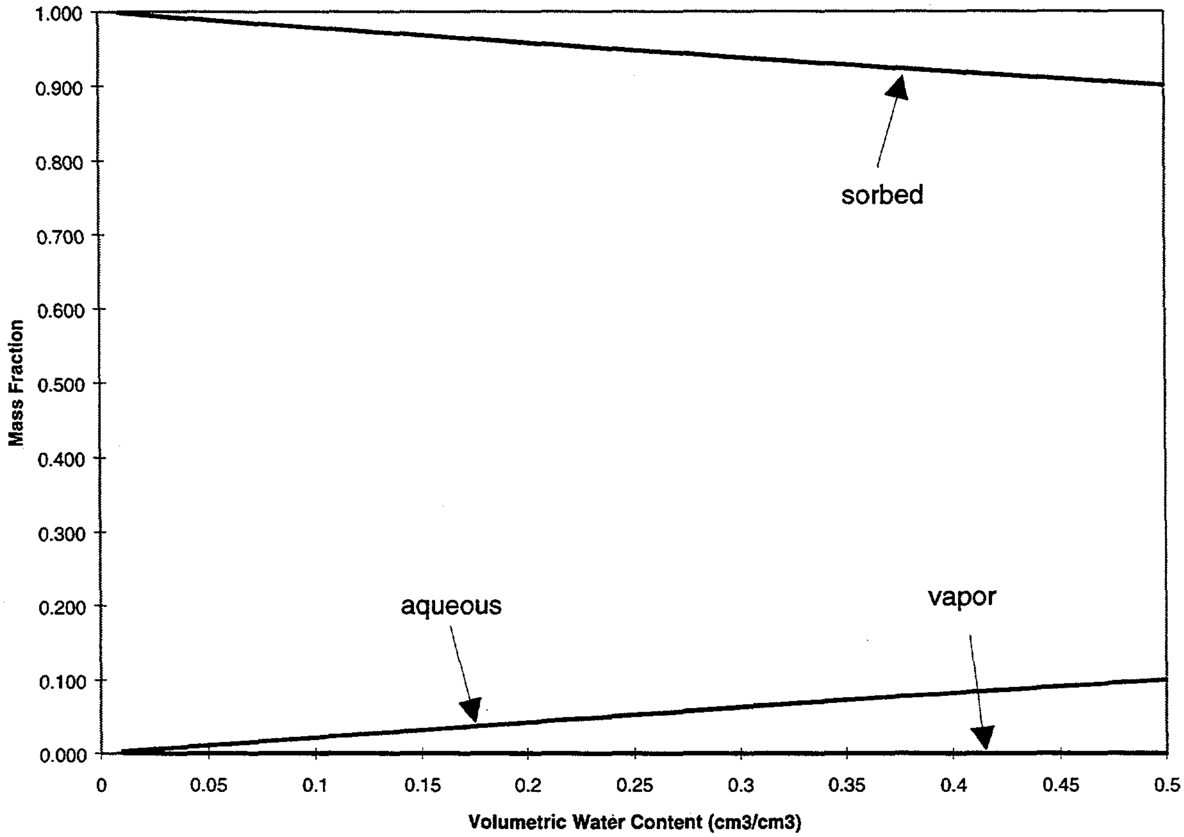

Figure 3. Phase Mass Fraction of TNT.

Figure 3 shows that over 90% of the TNT is sorbed to the solid phase, about 10% remains in the liquid phase and about 10^{-6} is in the vapor phase. This implies that the movement of a significant mass of TNT will only occur in the liquid phase and the majority of the mass is immobilized on the soil solid phase. Therefore, the surface flux is expected to be very low. This information also indicates that a soil particle sampling strategy may be more effective than strictly a vapor phase sampling effort for use of a chemical detector based landmine survey.

Figure 4 shows how the effective diffusivity switches from being mostly vapor driven to mostly liquid driven as the moisture content increases up to saturation; and, the effective diffusion coefficient changes by orders of magnitude with water content. This indicates that when the moisture content is below a critical point, the effective mass transfer of TNT to the soil surface is limited.

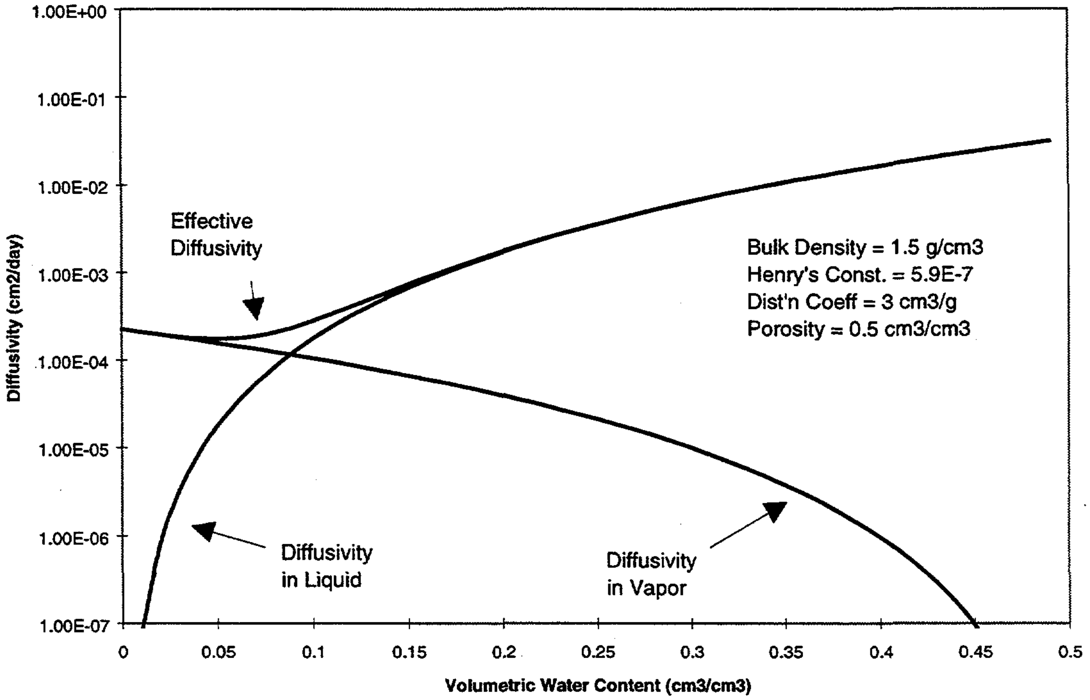

Figure 4. TNT Effective Diffusivity.

Simulations - Initial Surface Flux and Subsurface Concentrations
Simulation runs were performed using the parameters listed in Table 7 for about one year. Figure 5 shows the surface flux of TNT for Scenario 1 - Mid Continental Region, with constant liquid phase saturation (S_l) levels of 0.69, 0.58 and 0.46 ($S_l = \theta/\phi$).

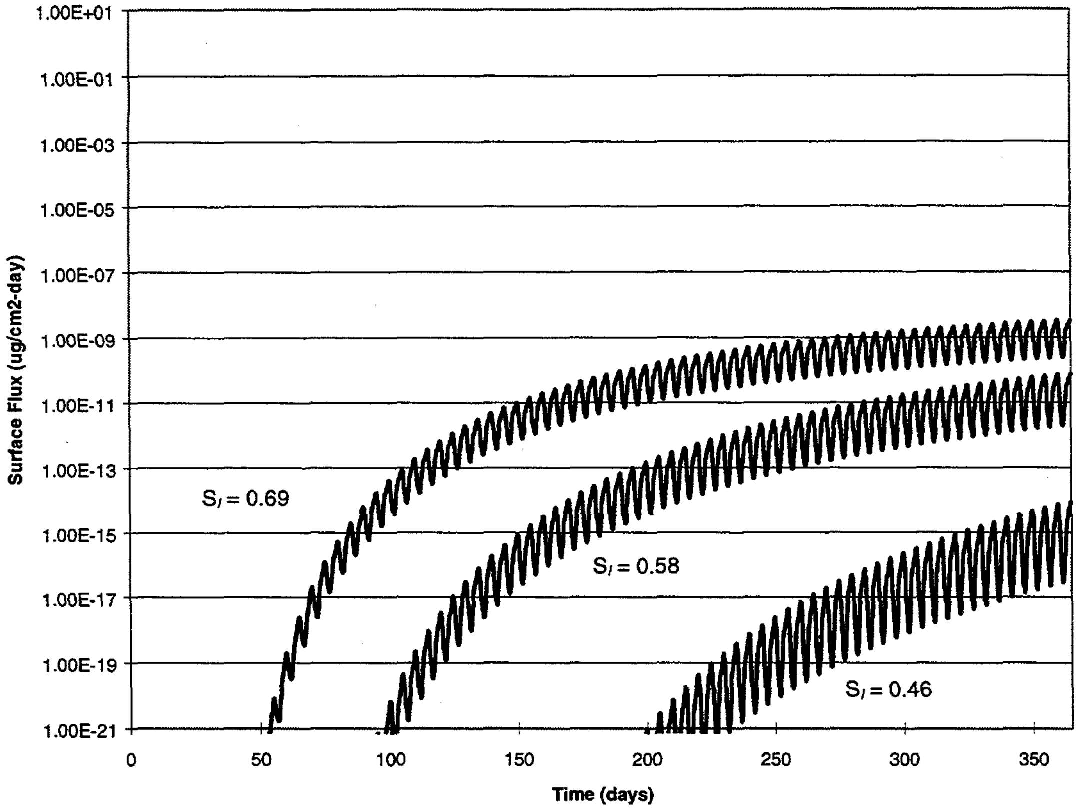

Figure 5. Surface Flux of TNT, Scenario 1: Mid-Continental Region.

The significant delay in appearance of the TNT signature at the surface is a result of the complex transport processes occurring in the 5 cm of overburden soil. The precipitation/evaporation cycles caused oscillations in the surface flux of a factor of about 10. The shape of the curves indicate a transient period reaching a near steady state flux after 200 to 250 days. A significant feature of this model is the impact of the constant soil water saturation over the duration of the simulation. As the saturation (and, moisture content) decreases, the delay in appearance of the surface flux increases significantly, the peak magnitude is reduced by orders of magnitude, and the precipitation/evaporation oscillations significantly increase.

Figure 6 shows the subsurface concentration of TNT for the three saturation levels at the end of the one year simulation.

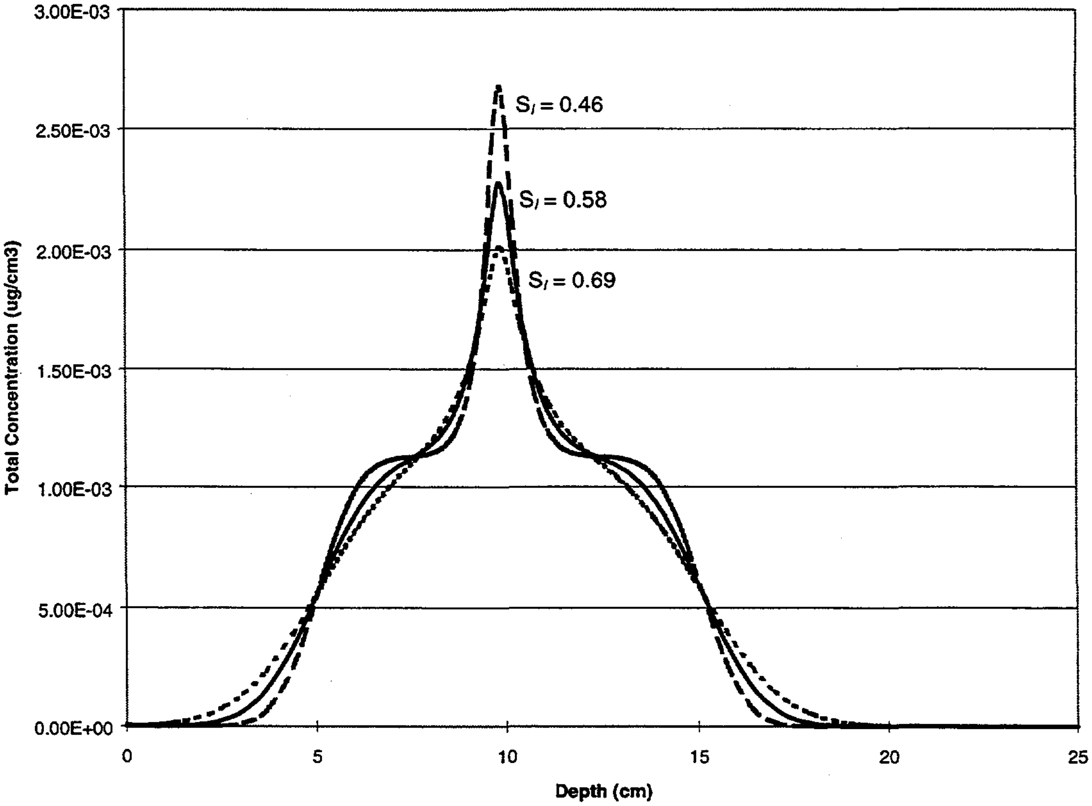

Figure 6. Subsurface Distribution of TNT After One Year, Scenario 1: Mid-Continental Region.

Recall that the initial concentration (C_o) was placed from 5 to 15 cm at a concentration of 4.6×10^{-3} $\mu g/cm^3$ and the constant source term was placed at 10 cm at a rate of 8.6×10^{-6} $\mu g/cm^2$-day. The shoulders of the curves at 5 and 15 cm are a result of the initial concentration and the peak due to the constant source term. The lower value compared to the initial concentration is due to biological decay. At the lowest saturation (0.46), the peak concentration is greatest but only by a small fraction compared to the highest saturation (0.69). However, for the lower saturation simulation, the concentration diminishes at a greater rate as the depth nears the ground surface. As shown earlier in Figure 4, the effective diffusivity of TNT generally decreases with decreasing saturation, or moisture content. Therefore, migration of TNT is slower for lower saturations.

At the end of the one year simulation, the total concentration of TNT at the ground surface can be distributed into the three soil fractions - solid phase, liquid phase and gas phase. Table 9 shows the concentrations in each phase for each of the three simulations performed.

Table 9. Phase Specific Concentration of TNT at the Ground Surface After One Year Simulation, Scenario 1: Mid-Continental Region

		Volumetric Water Content/Saturation		
Concentration	Units	0.20/0.46	0.25/0.58	0.30/0.69
Solid Phase	µg TNT/g soil	9.1E-12	9.4E-8	4.2E-6
Liquid Phase	µg TNT/ml soil water	1.3E-12	1.4E-8	6.2E-7
Vapor Phase	µg TNT/cm^3 soil air	7.9E-19	8.1E-15	3.6E-13
Total	µg TNT/cm^3	1.8E-11	1.6E-07	6.8E-06

Note that as the saturation increases, the concentration increases by several orders of magnitude and that the vapor phase concentration is significantly less than either the liquid or solid phase. This is consistent with the phase distribution as shown in Figure 3.

Figure 7 shows the surface flux of TNT for Scenario 2 - Gulf Coastal Lowlands, with constant liquid phase saturation (S_l) levels of 0.69, 0.58 and 0.46 ($S_l = \theta/\phi$).

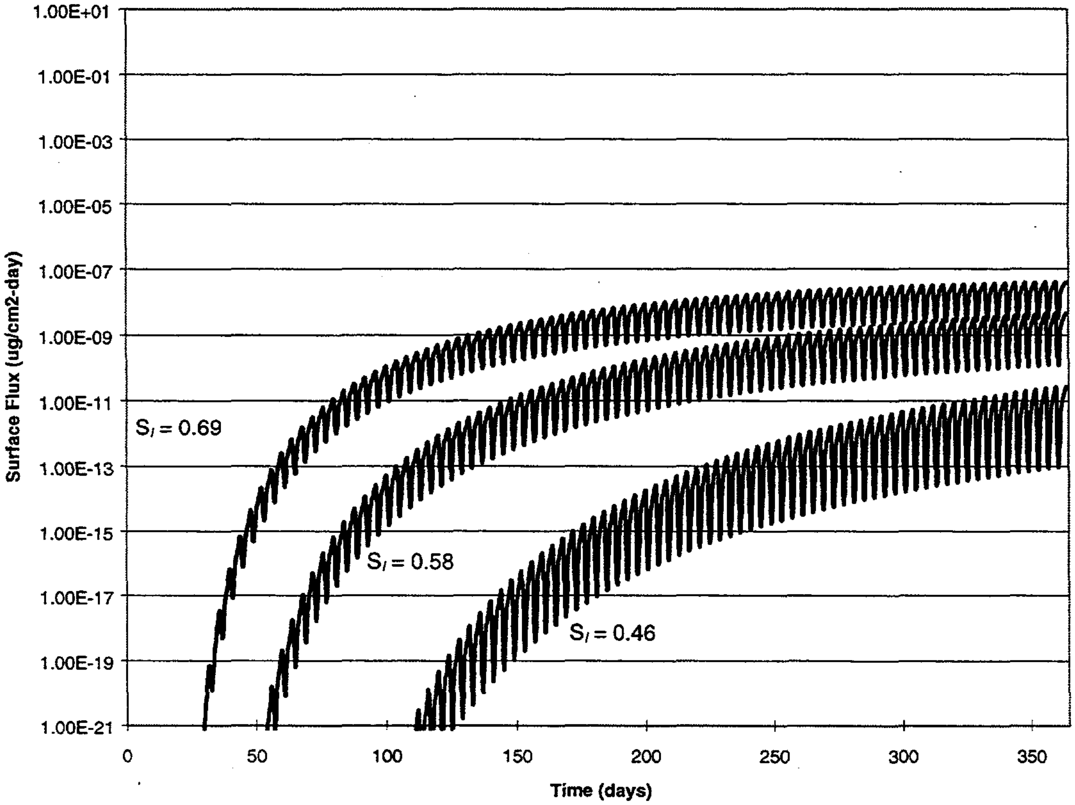

Figure 7. Surface Flux of TNT, Scenario 2: Gulf Coastal Lowlands.

This figure shows the same trends as that for the Mid-Continental Region simulations. The primary parameter changed in the Gulf Coastal Lowlands simulation was a solid-liquid phase partitioning coefficient (K_d) shift from 6.8 down to 3.7. This allowed more of the TNT mass to be in the liquid phase and be available for transport to the surface. Therefore, the emergence of TNT is sooner and reaches a greater surface flux. Figure 8 shows the subsurface distribution of TNT at the end of the Scenario 2, Gulf Coastal Lowlands simulation. This figure is nearly identical to Figure 6 for the Mid-Continental Region.

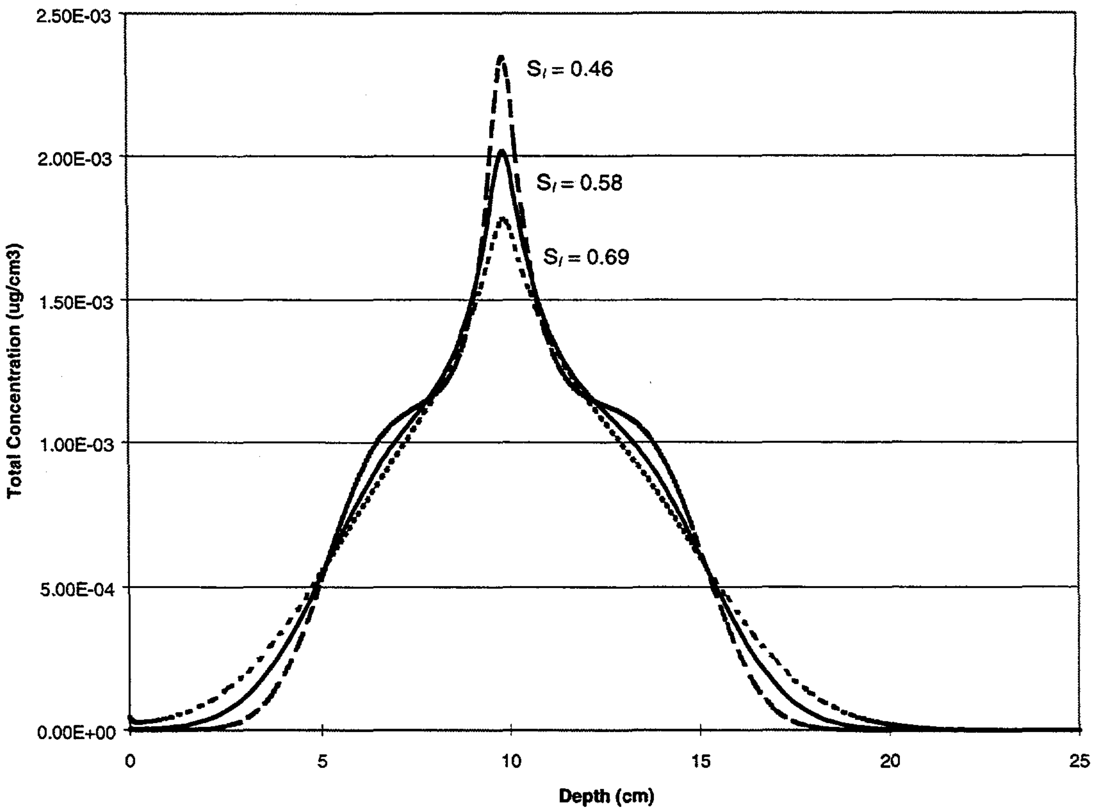

Figure 8. Subsurface Distribution of TNT After One Year, Scenario 2: Gulf Coastal Lowlands.

Table 10 shows the final concentration distributed into the three soil phases for Scenario 2 - Gulf Coastal Lowlands. When compared to Table 9 for the Mid-Continental Region, the results are significantly greater at the lowest saturation level and slightly greater for the two higher saturations.

Table 10. Phase Specific Concentration of TNT at the Ground Surface After One Year Simulation, Scenario 2: Gulf Coastal Lowlands

		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
Total	µg TNT/cm^3	3.0E-08	5.1E-06	4.5E-05

Figure 9 shows the surface flux of TNT for Scenario 3 - Low Desert, with constant liquid phase saturation (S_l) levels of 0.69, 0.58 and 0.46 ($S_l = \theta/\phi$).

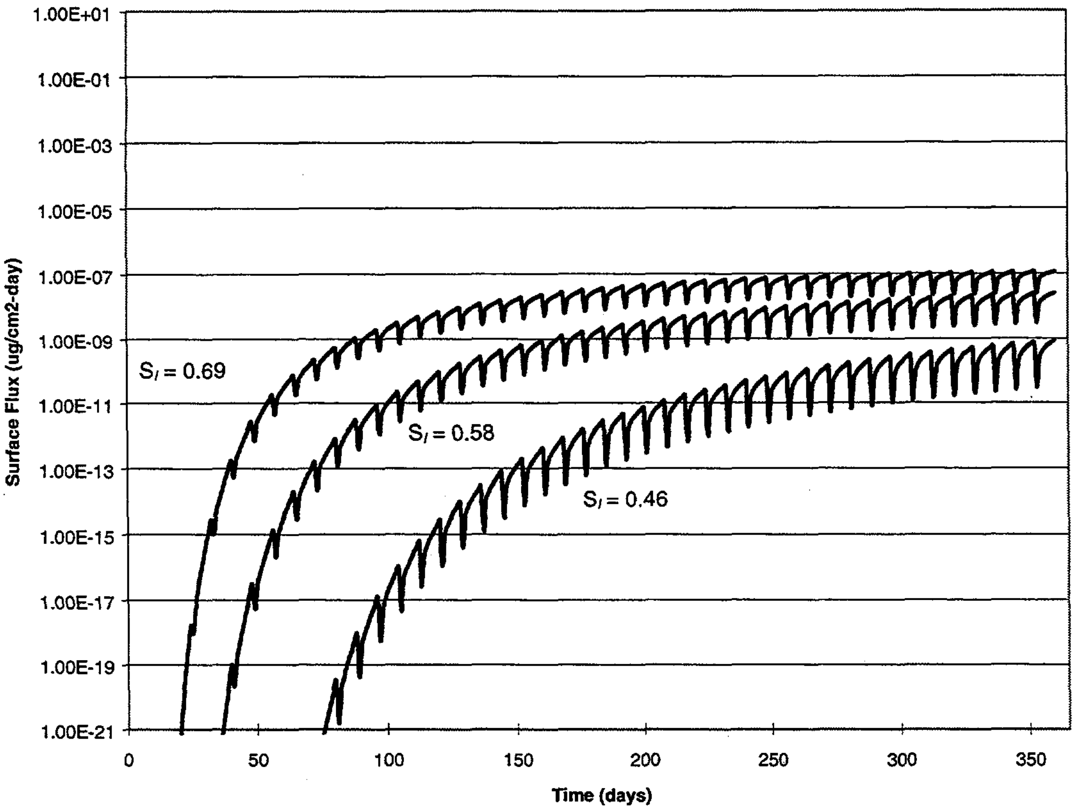

Figure 9. Surface Flux of TNT, Scenario 3: Low Desert.

This primary difference in this scenario is a decrease in the solid-liquid phase partitioning coefficient (K_d) from 6.8 (Mid-Continental Region) or 3.7 (Gulf Coastal Lowlands) to one of 2.5. Again, this decrease in K_d causes an earlier emergence of the TNT surface flux which rises to a slightly greater magnitude at steady state and the precipitation/evaporation oscillations are of smaller magnitude. Figure 10 shows the subsurface distribution of TNT for Scenario 3. Again, there is no significant difference in the majority of the mass distribution in the subsurface soils. Table 11 shows the soil phase specific concentrations at the end of the one year simulation for Scenario 3 - Low Desert. This simulation shows slightly higher concentrations than Scenarios 1 and 2.

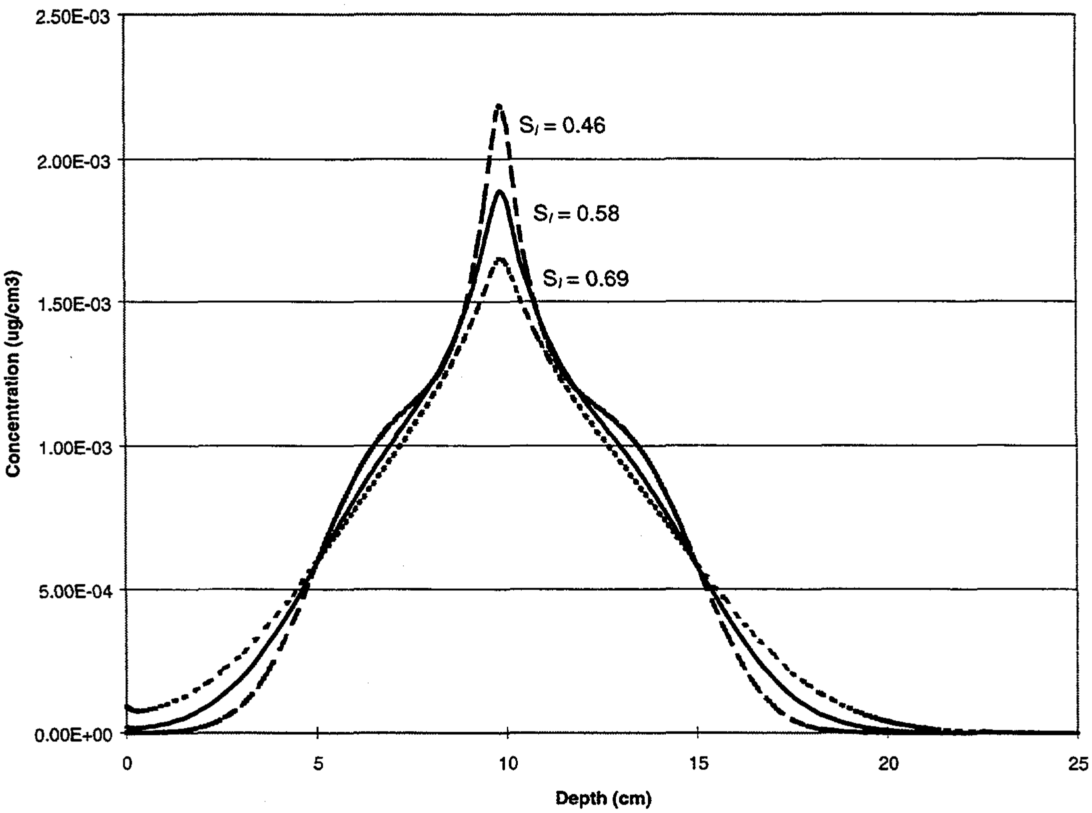

Figure 10. Subsurface Distribution of TNT After One Year, Scenario 3: Low Desert.

Table 11. Phase Specific Concentration of TNT at the Ground Surface After One Year Simulation, Scenario 3: Low Desert

		Volumetric Water Content/Saturation		
Concentration	Units	0.20/0.46	0.25/0.58	0.30/0.69
Solid Phase	μg TNT/g soil	4.2E-7	1.3E-5	5.6E-5
Liquid Phase	μg TNT/ml soil water	1.7E-7	5.0E-6	2.3E-5
Gas Phase	μg TNT/cm^3 soil air	9.9E-14	3.0E-12	1.3E-11
Total	μg TNT/cm^3	6.6E-07	2.0E-05	9.2E-05

Simulations - Sampling and Pre-Concentration Requirements

These simulations can be used to estimate the required concentration factors needed for a vapor sampling system directly collecting the surface flux above the soil. Some chemical signature detection systems currently under development are based on an ion-mobility spectrometer (IMS) detector. The IMS detectors currently available use a routine lower linear calibration range of 1 to 10 ng (10^{-9} g) of TNT, with extrapolation down to 0.1 ng possible. Using higher instrumentation gain, it is possible to detect TNT down a factor of 100 to about 1 pg (10^{-12}g). If one assumes a sampling area of 900 cm^2 (the area of an antitank mine) over a nominal sampling period of 60 seconds, the IMS (at a 0.1 ng detection limit) would be able to sense a surface flux of about 2×10^{-4} μg/cm^2-day. The greatest steady state surface flux simulated using the current model was about 10^{-7} μg/cm^2-day (Scenario 3, liquid phase saturation (S_l) levels of 0.69. This indicates a minimum concentration factor of 10^3 is required. It is likely that much greater concentration factors will be needed for effective use of chemical signature detection technology.

If one was to directly sample the soil and the soil water phases from the ground surface the expected mass of TNT would be greater. Using the Scenario 3: Low Desert simulation at a liquid phase saturation (S_l) levels of 0.69, the soil phase contains 5.6×10^{-5} µg TNT/g soil and 2.3×10^{-5} µg TNT/ml of soil water. If a one gram sample containing soil and soil water is collected, about 6.1×10^{-5} µg TNT would be present. If the TNT extraction efficiency is 100%, then a concentration factor of about 1.6 would be needed for an IMS detection limit of 0.1 ng.

Simulations - Synopsis

As previously mentioned, Jury (1983, 1990) developed this model for screening various agricultural pesticides to categorize the transport properties. As such, assumptions such as constant moisture content, porosity, saturation, soil bulk density, temperature and biological half-life were necessary to develop an analytical solution. Therefore, the quantitative values shown in this report should only be used for initial screening purposes. Figure 11 shows a generic surface flux chart that shows the main features of the simulations found in this effort.

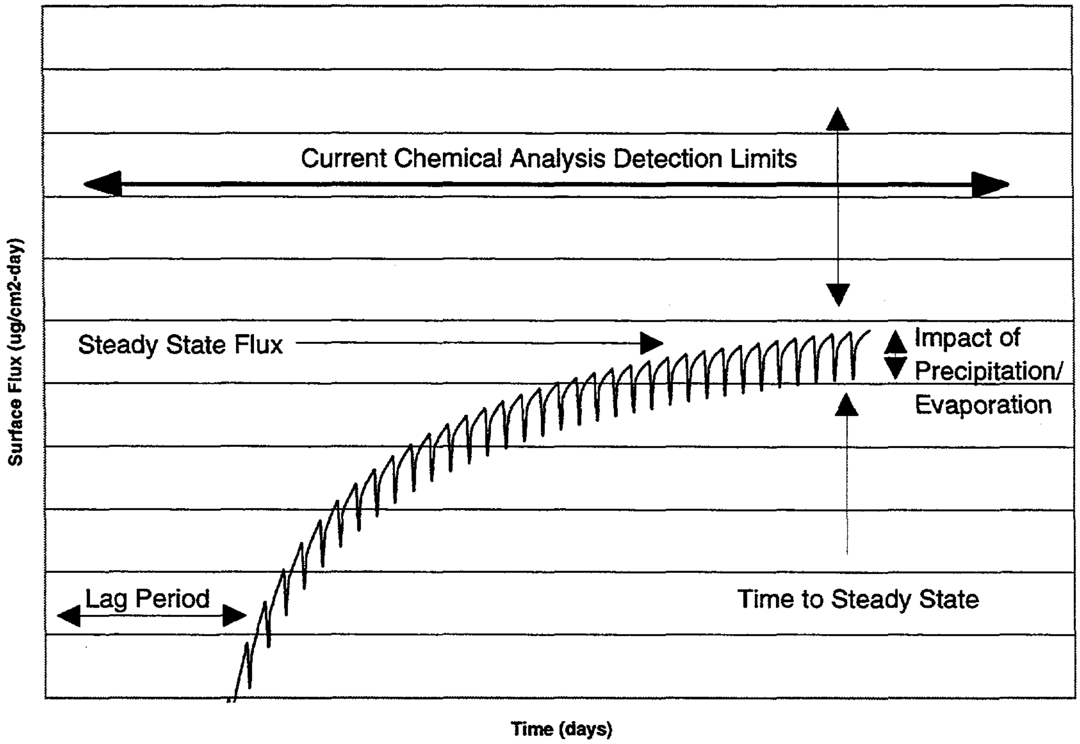

Figure 11. General Features of Surface Flux Simulation.

The surface flux steady-state magnitude, time to steady-state, lag time, effect of precipitation/evaporation cycles, and comparison to detector detection limits are the principal features of these initial simulation results. The sensitivity of individual chemical properties and environmental transport parameters are an important task that was not included in the scope of this initial effort; but, is important to identify the rank importance of individual parameters to the success of detecting chemical signatures from buried landmines.

Simulations - Future Needs

While Jury's models are excellent tools for screening of chemicals and initial evaluation of environmental scenarios, a more sophisticated tool is needed to more accurately represent the soil transport processes including changing soil water content, soil temperature and soil bulk density. A multidimensional tool including flow and transport of all the species (gas, liquid, chemical) is needed for more accurate chemical location predictions including the landmine chemical signature "footprint" on the soil surface.

In order to more rigorously evaluate the fate and transport of TNT, a more detailed numerical model is needed. There are many numerical models available to explore the fate and transport of organic chemicals in soils. However, the fundamental principles employed in the development of the code must be consistent with the problem being explored. T2VOC (Falta et al., 1995) is a numerical code for modeling the fate and transport of a single-component non-aqueous phase liquid-volatile organic compound, air and water (liquid and vapor) in porous media. T2VOC is an extension of the TOUGH2 code (Pruess, 1987, 1991), which has been widely used in environmental remediation, nuclear waste isolation, and geothermal applications (Pruess, 1995). This code includes many, but not all, of the fundamental principles needed to model the fate and transport of chemical signatures from buried landmines. The physical processes and assumptions in T2VOC include:

- Air, water (liquid and vapor), and a single-component water-soluble chemical are modeled in three phases (gas, aqueous, chemical)
- Gas phase may include air, water vapor and chemical vapor
- Aqueous phase may include water, dissolved air and soluble liquid chemical
- Chemical phase may include liquid chemical and dissolved air (no liquid water) - at the low concentrations expected with the buried landmine problem a liquid chemical phase is not expected
- Transport is due to advection in the gas and liquid phases (aqueous and chemical) and due to diffusion in the gas phase
- The chemical vapor may be adsorbed on the porous medium and may undergo biodegradation
- Interphase mass transfer assuming equilibrium phase partitioning
- Heat transfer

These physical processes and assumptions are mostly consistent with the modeling of explosive vapors from buried landmines which is dominated by diffusion in the gas and liquid phases, advection in the aqueous phase, and sorption onto the soil solid phase. The only physical processes not included in the standard version are diffusion in the liquid phase, precipitation, runoff and evapotranspiration. Plans are underway to add these environmental factors to the TOUGH2 series of codes. In addition, modification of the gas diffusion algorithm to better reflect the coupling between advection and diffusion, is being performed (Webb, 1996b).

6.0 Summary and Conclusions

This effort has completed an initial exploration of the complex phenomena of the fate and transport of chemical signature molecules from buried landmines. The results are produced as initial input parameters for the design of sampling and analysis sub-systems that will be incorporated into detection platforms for use in field surveys. The fundamental processes affecting the fate and transport have been identified in a comprehensive model that includes: source emission rates; partitioning reactions between liquid, solid and vapor phases; advective and diffusive transport; and, transformation/loss reactions with soil minerals and indigenous microbes.

The primary chemical signature molecule in most landmines is TNT. DNT is a manufacturing impurity found in TNT that may be a valuable chemical signature molecule; however, there is much less data on the solid-liquid phase partitioning parameter that is important in the modeling of the fate and transport processes. RDX is the next most prevalent chemical signature molecule; but, it has an even lower vapor pressure and water solubility than TNT. Thus, if a TNT signature can not be detected, it is unlikely that an RDX signature will be found.

A review of the sorption parameters shows that there is conflicting data on the reversibility of TNT sorption on soils. Some research has shown no desorption hysteresis and others have shown that up to 50% of the sorbed mass is unextractable. In addition, vapor-solid phase sorption can be extremely important when the soil system becomes very dry. When the water surface coverage of soil particles becomes less than about four layers, the sorption partitioning coefficients increase dramatically, limiting the transport and release of TNT at the soil surface. This may occur frequently when the surface soils dry between periods of precipitation. This area is a critical data gap because a majority of the TNT is sorbed by the soil particles either from the liquid phase or from the vapor phase.

Simulations using the Jury et al. (1983a, 1990) models developed to screen agricultural pesticides have provided an initial basis on the expected surface flux and subsurface distribution of TNT from a buried landmine. These simulations show that the current detection limits of the Ion Mobility Spectrometer detector are at least 10^3 times greater than the steady state vapor flux at the ground surface occurring many months after the simulation start time. Sampling surface soils are another potential chemical signature detection platform strategy that may have merit since more of the TNT mass is located there and that only a concentration factor of less than 10 may be needed.

The simulations produced in this effort, however, are based on some assumptions necessary to produce an analytical solution to the transport equation. These assumptions do not always make physical sense (e.g. constant soil moisture content during precipitation/evaporation cycles); therefore, the quantitative magnitudes should be used with caution. Numerical codes being developed under other programs will soon have the necessary physical processes that are more realistic for the simulation of the fate and transport of chemical signature molecules from buried landmines. It is recommended that a continued effort to develop a simulation tool take place in conjunction with the development of buried landmine chemical detection systems. In addition to developing a more realistic simulation tool, laboratory experiments are needed to measure individual parameters at the very low concentrations expected under landmine conditions and to validate the physical models.

Nomenclature

a	air volume fraction = $\phi - \theta$
C	concentration
d	boundary layer thickness
D	diffusion coefficient
f	fraction
J	flux
h	transport coefficient across boundary layer
H_E	effective gas transport coefficient
K_d	distribution coefficient for sorption
K_H	Henry's Law constant
K_{oc}	organic carbon partition coefficient
L	top of initial chemical location
p	dummy variable for Box method
S	saturation
t	time
$t_{1/2}$	half life
V	velocity
W	thickness of initial chemical layer
z	depth coordinate

Greek

μ	decay constant = $0.693/t_{1/2}$
θ	volumetric moisture content
ϕ	porosity
ρ	density
σ	source term

Subscripts

b	bulk soil
c	chemical (e.g. TNT)
E	effective
g	gas
l	liquid
oc	organic carbon
s	soil particle
T	total
w	water
0	initial value

Superscripts

a	air
w	water
s	soil

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Appendix A
Box Numerical Method

Based on initial applications of Jury's BAM screening model for TNT, concentrations may increase dramatically at the soil surface. In order to allow for the possible dramatic variation in concentration near the surface, and to minimize the numerical overhead, the Keller Box Method (Keller, 1970, Cebeci and Bradshaw, 1984) has been used. The method allows for variable mesh point spacing, such as required in fluid boundary layer analysis, and results in a tridiagonal matrix, which can be solved directly by the Thomas algorithm. Both of these factors contribute to a numerically efficient procedure which is especially beneficial for the present application.

The Box method is based on writing the equation of interest as a series of first-order equations. In this case, Jury's equation can be written as

$$p = \frac{\partial C_T}{\partial z}$$

$$\frac{\partial C_T}{\partial t} + \mu C_T = D_E \frac{\partial p}{\partial z} - V_E p$$

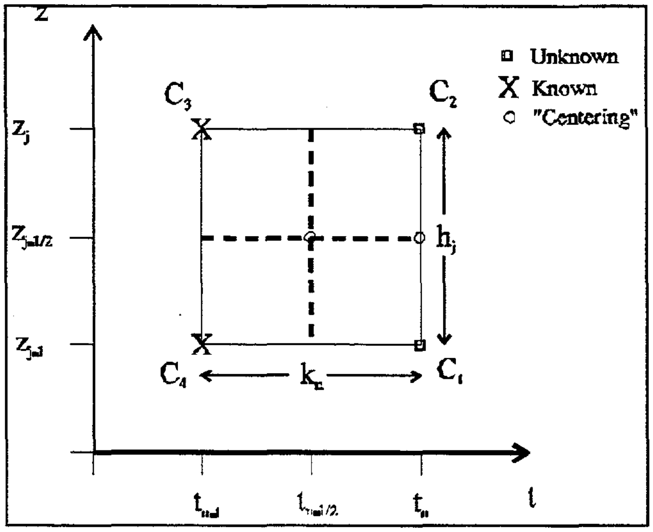

Figure A-1
Finite-Difference Grid for the Box Method
(after Cebeci and Bradshaw, 1984)

The above equations are written in terms of simple two-point derivatives. The derivatives are based on the values at the corners of the "box" as shown in Figure A1. The first equation is centered around $(t_n, z_{j-1/2})$, while the second equation is centered around $(t_{n-1/2}, z_{j-1/2})$. Similar equations can be written for the j to j+1 interval, and the p variable (see equation 9) can be eliminated. The resulting equation is in terms of $C_{t,j}$ at t_n in terms of the values at j-1 and j+1, as well as the old values at time t_{n-1}. Thus, the matrix is tridiagonal which is solved directly (no iteration is required) by the Thomas algorithm.

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Appendix B
Verification of Simulation Program

The computer program resulting from application of the Box method has been verified by comparison to results given by Spencer et al. (1988) for the BAM and Jury et al. (1990) for the BCM. The results of Spencer et al. (1988) for the pesticide prometon are especially interesting. According to Jury's screening model (Jury et al., 1984b), prometon is a Category III chemical (K_H much less than 2.65×10^{-5}) such that under evaporating conditions, the concentration at the soil surface and the volatilization rate increase with time. Based on an estimated value of K_H of 5.9×10^{-7}, TNT is also a Category III chemical. Spencer et al. (1988) compared model predictions with experimental data for volatilization flux and concentration profiles for prometon; TNT behavior may be similar.

Spencer et al. (1988) Results In this problem, prometon is initially present at a uniform concentration in the soil to a depth of 10 cm; the model parameters are summarized in Table B1.

Table B-1. Parameters for Prometon Simulation from Spencer et al. (1988)

Henry's Constant (K_H)	1.0×10^{-7}
Distribution Coefficient (K_d) - Sorption	2.20
Half Life	∞
Air Diffusion Coefficient	4320 cm^2/day
Water Diffusion Coefficient	0.432 cm^2/day
Soil Porosity	0.411
Bulk Density	1.56 g/cm^3
Water Content	0.31
Initial Pesticide Concentration	10.3 μg/g
Initial Pesticide Depth	10 cm
Boundary Layer Thickness	0.022 cm
Evaporation Rate	0.0; 0.55 cm/day

Experiments with zero water flux and evaporation water flux were conducted and compared to the model predictions of Jury et al. (1983). The volatilization rates for prometon with and without water evaporation are shown in Figure B1a including experimental data and model predictions. Water evaporation has a significant effect on the volatilization rate of prometon. The evaporation rate predicted by the present code is shown in Figure B1b; the agreement between the present implementation and the results given by Spencer et al. (1988) is excellent. Similarly, Figure B2a shows the distribution of prometon with depth after 14 days of evaporation; the data and model predictions show reasonable agreement. The distribution predicted by the present code is shown in Figure B2b. Similar to the volatilization rate, the agreement between the present results and the model predictions of Spencer et al. (1988) is excellent.

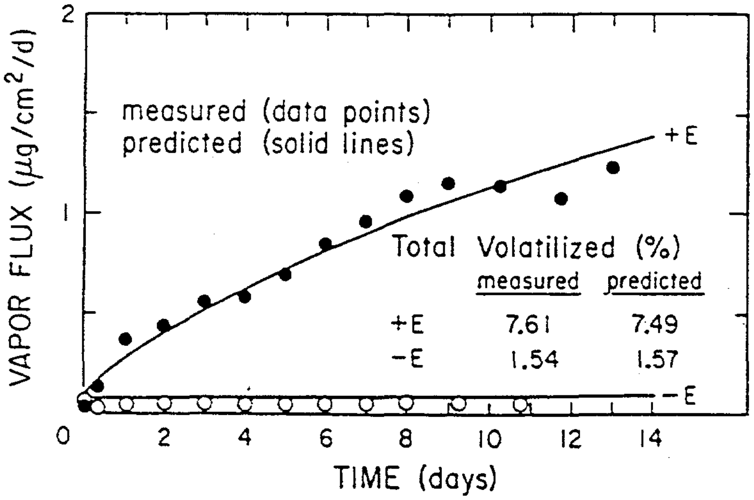
Jury et al. (1990) Results Benzene is initially present at a concentration of 25 μg/cm^3 at a depth of 100 to 130 cm in clayey soil; the model parameters are given in Table B2. There is zero water

Table B-2. Parameters for Benzene Simulation from Jury et al. (1990)

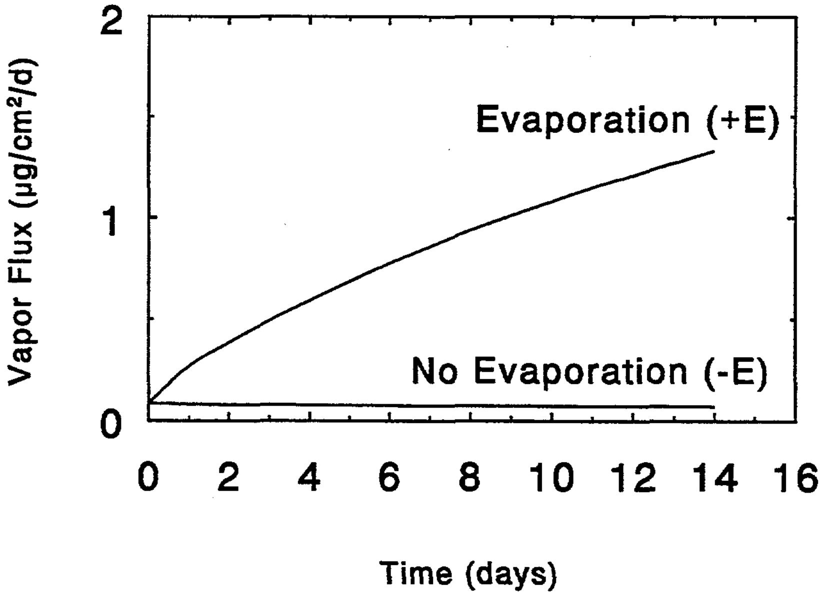
for Clayey Soil

Henry's Constant (K_H)	0.22
Distribution Coefficient (K_d) - Sorption	2.0
Half Life	365 days
Air Diffusion Coefficient	4320 cm^2/day
Water Diffusion Coefficient	0.432 cm^2/day
Soil Porosity	0.5
Bulk Density	1.32 g/cm^3
Water Content	0.375
Initial Benzene Concentration	25 $\mu g/cm^3$
Initial Benzene Depth	100 to 130 cm
Boundary Layer Thickness	0.5 cm
Evaporation Rate	0 cm/day

flux, and the volatilization flux and concentration distribution are predicted at 1 year. The results from Jury et al. (1990) and the present code are given in Figure B3 for the volatilization flux; Figure B4 compares the concentration distribution after 365 days. The agreement is excellent in both cases.

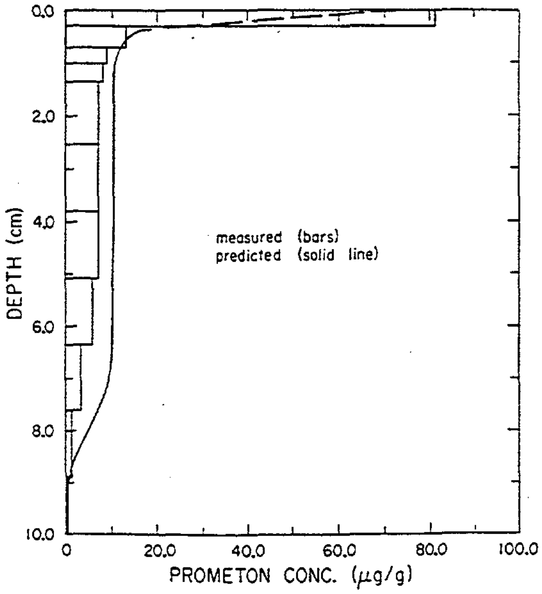


(a) Results from Spencer et al. (1988)

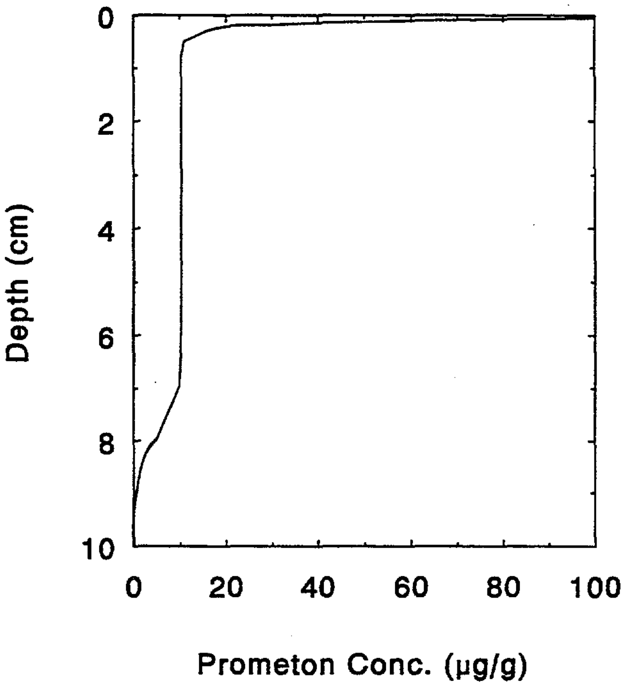


(b) Results from Current Program

Figure B-1
Volatilization Flux of Prometon



(a) Results from Spencer et al. (1988)



(b) Results from Current Program

Figure B-2
Distribution of Prometon After 14 Days

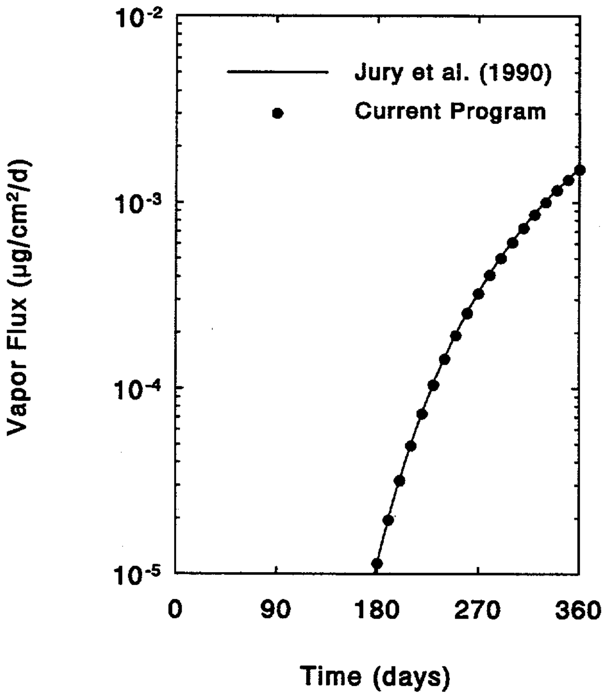


Figure B-3
Volatilization Flux of Benzene

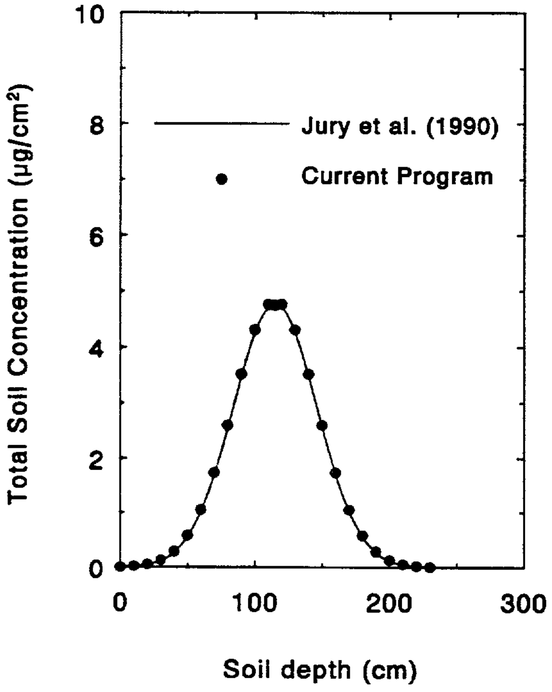


Figure B-4
Distribution of Benzene After 365 Days

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