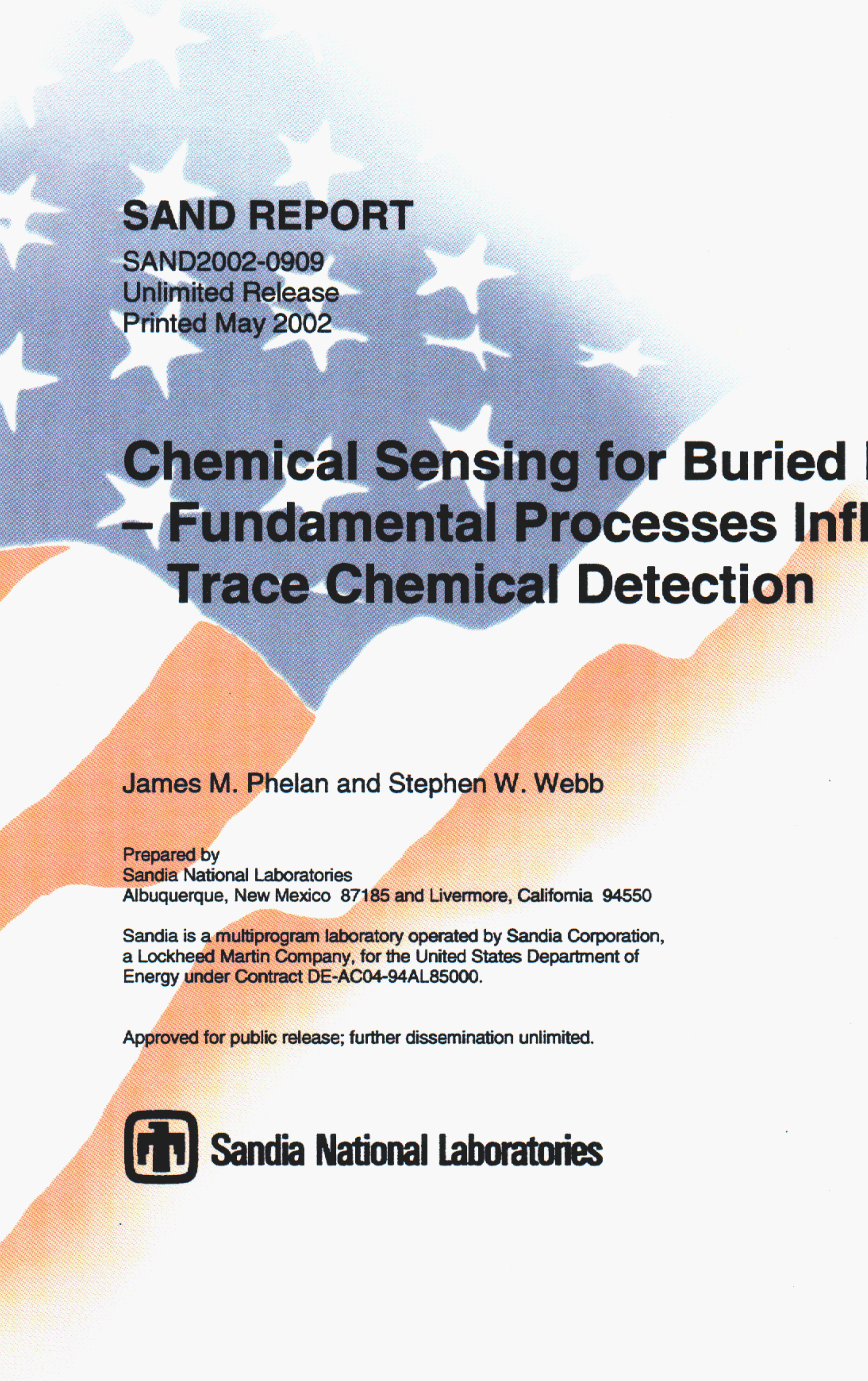


SAND REPORT

SAND2002-0909
Unlimited Release
Printed May 2002

Chemical Sensing for Buried Landmines – Fundamental Processes Influencing Trace Chemical Detection

James M. Phelan and Stephen W. Webb

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/ordering.htm

SAND2002-0909
Unlimited Release
Printed May 2002

Chemical Sensing for Buried Landmines – Fundamental Processes Influencing Trace Chemical Detection

James M. Phelan and Stephen W. Webb
Environmental Technology Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0719

Abstract

Mine detection dogs have a demonstrated capability to locate hidden objects by trace chemical detection. Because of this capability, demining activities frequently employ mine detection dogs to locate individual buried landmines or for area reduction. The conditions appropriate for use of mine detection dogs are only beginning to emerge through diligent research that combines dog selection/training, the environmental conditions that impact landmine signature chemical vapors, and vapor sensing performance capability and reliability. This report seeks to address the fundamental soil-chemical interactions, driven by local weather history, that influence the availability of chemical for trace chemical detection. The processes evaluated include: landmine chemical emissions to the soil, chemical distribution in soils, chemical degradation in soils, and weather and chemical transport in soils. Simulation modeling is presented as a method to evaluate the complex interdependencies among these various processes and to establish conditions appropriate for trace chemical detection. Results from chemical analyses on soil samples obtained adjacent to landmines are presented and demonstrate the ultra-trace nature of these residues. Lastly, initial measurements of the vapor sensing performance of mine detection dogs demonstrates the extreme sensitivity of dogs in sensing landmine signature chemicals; however, reliability at these ultra-trace vapor concentrations still needs to be determined. Through this compilation, additional work is suggested that will fill in data gaps to improve the utility of trace chemical detection.

Acknowledgements

This work was sponsored by the Geneva International Center for Humanitarian Demining (GICHD), under the technical direction of Havard Bach. 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.

Contents

List of Figures

List of Tables

1.0 Introduction

Landmines contain energetic chemicals that emit odors (chemical signatures) that are barely perceptible by humans. However, dogs can be specially trained to scent and indicate the presence of explosive chemical odors. The first records of the effect of environmental factors on landmine odors occurred during World War II, where the Finnish Armed Forces describe the importance of soil conditions on successful mine dog detection work (unknown author, circa 1940s, P. Soderburg translation).

The external physical conditions that affect explosive vapors in soils can now be described in much detail with advances in knowledge from agriculture, chemistry, soil physics, meteorology and computer science. There have been many contributions from basic research, applied research, and field anecdotes. The environment is complex, and the impact of the environment on the chemical odors from buried landmines is even more complicated. Individual phenomena have been explored in various levels of detail. The combination of external physical conditions (the environment), soil-chemical interactions, individual landmine characteristics are now being explored with computer simulation tools for comparison to trace chemical detection methods including mine detection dogs.

This report seeks to bring together the current state of knowledge for each of the important individual phenomena and demonstrate the utility of computer simulation as a tool to evaluate the complex combination of environmental factors affecting the chemical signature from buried landmines. Computer simulations can explore the impacts on the chemical vapors from specific environmental situations for comparison to the vapor sensing thresholds of mine detection dogs. With this knowledge, mine action programs can establish optimal operating conditions for the performance characteristics of mine detection dogs within their program. This analysis may establish marginal conditions based on environmental factors, landmine type and/or dog performance to limit field activities. However, one must recognize the limitations of computer simulation results and monitor actual environmental effects on mine dog detection performance.

This report is a compendium of relevant material on the nature of the chemical signature from buried landmines with emphasis on how individual and interdependent soil chemodynamic processes affect the ability of the dog to locate buried landmines. Each chapter discusses a single topic, with subsequent chapter contributing more information resulting in a comprehensive analysis of landmine trace chemical detection. Each chapter introduces the topic and is followed by key information in bullet form that is described in more detail in the balance of the chapter.

2.0 Numbers in Chemistry

Introduction. The intent of this report is to summarize information on the chemical properties of the explosive compounds in landmines that affect detection by mine detection dogs. Our analysis seeks to identify environmental factors that impact the dogs' ability to recognize landmine chemical odors. Thus, the amount or level or concentration becomes important, and we must lay a foundation for analysis in quantitative terms.

Key Information.

- Chemical sensing for landmines involves extremely small quantities that require specialized notation when discussing quantitative values.
- Terms used to describe the concentration of chemicals in soil, water and air have special units and one must have consistent units when comparing values.

Scientific Notation. Because of the extremely large range in the numbers found with this problem, one must use scientific notation to describe quantities. Table 1 shows the scientific notation, decimal notation, name and symbols for the most common values used in this report.

Table 1. Scientific Notation

Scientific Notation	Decimal Notation	Name	Symbol
10^6	1,000,000	mega	M
10^3	1,000	kilo	k
10^1	10	deca	d
10^0	1		
10^{-3}	0.001	milli	m
10^{-6}	0.000001	micro	µ
10^{-9}	0.000000001	nano	n
10^{-12}	0.000000000001	pico	p
10^{-15}	0.000000000000001	femto	f

Concentrations. Organic chemicals in the environment can dissolve or partition into the air, water and soil. Vapor is the term used to describe a chemical in air. Solute is the term used to describe a chemical in water. Residue is the term used to describe a chemical in soil. A chemical, such as TNT found in landmines, can transfer between the air, water and soil until it reaches equilibrium – a condition where all forces are balanced and change is minimal. A more detailed description of how landmine chemicals partition between air, water and soil particles in a soil system is presented in Chapter 5 – Chemical Distribution in Soils.

The term concentration is used to describe how much chemical is present in a given amount of air, water or soil. In water, the units are typically given as mass of chemical per volume of water (m/v) because the density of water (mass per unit volume, about 1 g/mL) is relatively constant. The most common units are milligram of chemical per liter of water (mg/L) or microgram of chemical per liter of water (µg/L). In soil, the units are typically given as mass of chemical per mass of soil (m/m), because the density of soil (1 to 2 g/mL) changes slightly depending on the compaction of the soil. The most common units are microgram of chemical per gram of soil (µg/g). However, for explosive residues in soil from landmines, the values are much lower and we more often use nanograms of chemical per gram of soil (ng/g). For air, the units are typically given as mass of chemical per volume of air (m/v). In our work, we typically use units of nanograms of chemical per liter of air (ng/L).

There are several other terms used to describe the concentration of a chemical in air, water or soil. These use the units of moles, which is a measure of the number of molecules. There are a constant number of molecules per mole, that is 6E23 (i.e. $6*10^{23}$), and is termed Avogadro's number. Most often, moles are used in the context of water concentration, such as moles of chemical per liter of water (moles/L).

The most common term used to express concentration is the "parts per" notation, but it is frequently misused. For soil, a ng/g is parts per billion (ppb) because a nanogram is 1 billion (10^9) less than a gram. For water, a mg/L is parts per million (ppm) because water has a density of about 1 g/mL, so a mg/L can be converted to µg of chemical per gram of water (µg/g) and a micro is 1 million (10^6) less than a gram.

For air, the conversion is more complicated because air is usually measured in volume, and part per notation for air is on a volume of chemical/volume of air basis. Fortunately, molecules of gas or vapor occupy a known volume – about 22.4 L/mole at 1 atmosphere pressure and 0°C (24.5 L/mole at sea level (1 atm) and 25°C). However, now you must know the atmospheric pressure, temperature and molecular weight of the chemical of interest. Equation [1] shows how to convert ng of chemical per liter of air (ng/L) to parts per trillion for TNT (molecular weight of 225 g/mole) - the vapor unit we will be using the most frequently in this report.

$$ppt = \frac{ng}{L} \cdot \frac{24.5L}{mole} \cdot \frac{mole}{225g} \cdot \frac{g}{10^9} \cdot 10^{12} \qquad [1]$$

This calculation shows for TNT (at sea level atmospheric pressure of 1 atm and 25°C) that 1 ng/L ≈ 110 ppt. For DNT at sea level and 25°C, 1 ng/L ≈ 135 ppt because the DNT molecular weight is 182 g/mole. Table 2 shows the most common units of concentration for water and soil for easy reference. Table 3 shows the sequence in "parts per" notations to describe lower and lower concentrations.

Table 2. Water and Soil Concentration Units

		parts per million (ppm)	parts per billion (ppb)
water	mass/volume	mg/L	µg/L
soil	mass/mass	µg/g	ng/g

Table 3. "Parts per" Notation

Scientific Notation	Decimal Notation	Term	Symbol
1 in 10^6	1 in 1,000,000	parts per million	ppm
1 in 10^9	1 in 1,000,000,000	parts per billion	ppb
1 in 10^{12}	1 in 1,000,000,000,000	parts per trillion	ppt

For these extremely low concentrations, one needs to be mindful that there must be at least one whole molecule per amount of air, water or soil for the concentration numbers to be detectable for a specified sample size. For example, with TNT one molecule weighs only 4E-22 ($4*10^{-22}$) grams. Thus, a 1 g soil sample with 1 ng/g TNT residue will have one trillion (10^{12}) molecules of TNT. And, a 100 mL volume of air with 1 ppt (0.01 ng/L) will have one billion (10^9) molecules of TNT. Table 4 shows these values for soil, water and air. Conversely, Table 5 shows the concentrations for only 1 molecule in a specified volume of soil, water and air.

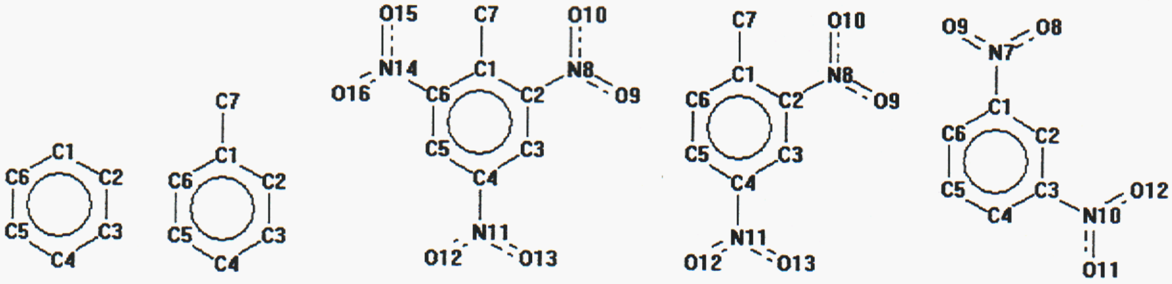
Table 4. Number of Molecules in Soil, Water and Air Samples

Media	Sample Size	Concentration	Number of Molecules
Soil	1 gram	1 ng/g	One trillion (10^{12})
Water	1 mL	1 µg/L	One trillion (10^{12})
Air	100 mL	1 ppt	One billion (10^9)

Table 5. Concentration of 1 Molecule of TNT in a Sample of Soil, Water and Air

Media	Mass Units	"parts per" Units
1 molecule per gram of soil	10^{-13} ng/g	10^{-13} ppb
1 molecule per mL of water	10^{-13} µg/L	10^{-13} ppb
1 molecule per 100 mL of air	10^{-12} ng/L	10^{-10} ppt

Molecular Structure and Formulas. This report will also discuss the names of several important chemicals linked to the chemical odor signature from military grade TNT. Figure 1 shows some of these important chemical structures with numbering schemes for the atoms in each molecule. For example, TNT is known specifically as 2,4,6-trinitrotoluene. There is a nitro group (NO_2) at the carbon 2, 4 and 6 positions of the toluene molecule. Chapter 3 will present more information on the types and names of the many chemicals involved in the manufacture of TNT.



benzene toluene 2,4,6-~~trinitro~~toluene 2,4-~~dinitro~~toluene 1,3-~~dinitro~~benzene

Figure 1. Chemical Structures for Compounds Important to Landmine Chemical Sensing

3.0 Target Chemical Compounds

Introduction. The observation that dogs can detect buried landmines by odor recognition has been described by many demining personnel. Whether the odor recognition comes from a single chemical or a mixture, or whether it comes from the explosives in the landmine or from the plastic case or the paint of a metal mine, is not known with certainty. Much of the evidence, however, points to the dog recognizing a chemical signature from the explosive main charge of the landmine. This chapter presents information on the complex mixture of chemicals in TNT, as TNT represents the main charge explosive in the majority of landmines in the world.

Key Information.

- TNT manufacturing processes vary around the world, which produce a variety of impurities at various levels.
- The three most important vapor constituents of military grade TNT include: 2,4,6-TNT; 2,4-DNT; and, 1,3-DNB.

TNT Manufacturing Impurities. TNT is manufactured by nitration of toluene with a nitric acid solution. The toluene is derived from the distillation of crude oil, and may have impurities such as benzene. The synthesis process favors the production of 2,4,6-trinitrotoluene, but other isomers (chemicals with same molecular formula, but with different structures) can be formed in smaller quantities. Different TNT production and purification processes will produce different amounts of isomeric impurities. Table 6 shows the impurities present before and after purification for the American continuous countercurrent treatment of TNT with anhydrous sodium sulfite (Kaye, 1980).

Table 6. 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 (DNB)	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

Vapor Signature Above Bulk TNT. Impurities present in solid phase TNT are only the starting point in the analysis of which chemicals are target odors for the dogs. Release of the chemical odors may follow several paths including dissolution into water that penetrates into the landmine and permeation through the plastic case into the soil. Permeation is a vapor driven process that makes the identification of vapor phase compounds from TNT very important. Table 7 shows a comparison of the solid and vapor phase impurities of TNT and DNT measured in military grade TNT. While the majority of the solid phase contains the 2,4,6 isomer of TNT, there are still small amounts of the other isomers of TNT as well as the many isomers of DNT. This demonstrates that military grade TNT vapor contains a mixture of compounds that dogs can use as cues to recognize buried landmines.

Table 7. 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 et al., 1971

In an evaluation of eight US and fourteen foreign military-grade TNT samples, headspace vapor analysis quantified the prevalence of the various isomers of TNT and DNT (Leggett et al., 1977). There were also two unknowns that were found, which could not be identified. This work showed that each TNT source material contained a variable mixture of these isomers. In some samples, certain isomers of TNT or DNT were not detectable. This work also showed that upon average, the 2,4-DNT was about 10 to 30 times greater in vapor concentration than 2,4,6-TNT.

Table 8 shows more recent work with similar results for 2,4-DNT, but also showed a compound not previously looked for or measured - 1,3-DNB (Jenkins et al, 2001). The vapor concentration of 1,3-DNB was present at levels near or exceeding that of 2,4-DNT, indicating that this compound may also be important in the chemical signature for mine detection dogs.

Table 8. Equilibrium Headspace Vapor Concentrations Above Military Grade TNT

	Headspace Vapor Concentration (ng/L) at 22°C		
Source of Explosive	1,3-DNB	2,4-DNT	2,4,6-TNT
US Military 1966 (TNT)	0.35	0.55	0.070
Yugoslavian PMA-1A (TNT)	4.6	1.4	0.078
Yugoslavian PMA-2 (TNT)	9.7	0.28	0.077

from: Jenkins, 2001

This effort also examined the influence of temperature (-12 to 31°C) on the headspace vapor concentrations. Seven compounds were found: 1,4-DNB; 1,3-DNB; 2,5-DNT; 1,2-DNB; 2,4-DNT, 3,5-DNT; and, 2,4,6-TNT. Of the impurities, all were found to increase exponentially with temperature (as expected), and the 1,3-DNB and the 2,4-DNT were always found at the greatest concentration.

Summary. The solid phase composition of TNT has been shown to be a mixture containing mostly 2,4,6-TNT with a large number of trace impurities. The headspace vapor composition of TNT also contains this mixture of compounds, but the concentrations of some of the impurities exceed that of TNT by a factor of 10 to 100. What cues the dogs may use to recognize buried landmines may involve one or many of these chemical compounds, but if recognition is concentration dependent, then what we understand about the environmental impacts to the levels of 2,4,6-TNT (i.e. TNT), 2,4-DNT (i.e. DNT) and 1,3-DNB (i.e. DNB) in soils will provide a guide on the impacts to the entire bouquet of odors.

4.0 Landmine Chemical Emissions

Introduction. In Chapter 3, chemical analytical tests showed that there were many chemicals derived from the TNT manufacturing processes that might be used as cues by mine detection dogs. In this chapter, the evaluation will focus on the three most prevalent explosive chemical signature compounds (TNT, DNT and DNB) found in the vapor form from military grade TNT. Presence in the vapor is important, because this is the main form that chemical emissions occur for most landmines.

Key Information.

- Transfer of landmine chemicals to soil involves both leakage and permeation (both together are termed landmine flux). Leakage occurs through openings in the case. Permeation occurs by vapor diffusion through the thickness of the plastic material.
- Composition of the plastic case material makes a significant impact on the leakage into soils – hard plastics (e.g. PVC) permeate less (at least 30 times) landmine signature chemicals than flexible materials (e.g. rubber).
- Higher temperatures cause higher flux – flux is exponential [$e^{0.11(\Delta°C)}$]; e.g. 1.7 times more for a change of 5°C, 3 times more for a change of 10°C, and 9 times more for a change of 20°C.
- Landmine flux is greater into water than into air (about 5 times more). Measurements are needed to determine how soil wetness impacts landmine flux.
- Painted steel landmines have surface contamination of landmine signature chemicals in the paint that is depleted over a short, but unknown, period of time. Permeation through the steel does not replenish the chemical signature preventing chemical sensing for these types of landmines.
- Whole landmine flux testing provides the best measure of landmine chemical signature release to soils; however, very few of these tests have been performed to date.

Leakage and Permeation. Landmine flux describes two principal methods on how explosive chemical signatures escape into the soil. Permeation describes the rate at which a gas or vapor passes through a polymeric material (plastic). Permeation does not occur through metals such as steel. Leakage is the rate at which gases or vapors pass through an opening or crack. For this analysis, data for the combined total transfer of chemical signature to the soil is needed, whether from permeation or leakage.

There are many types of landmines, with many materials and methods of construction that contribute to the overall chemical transfer rate. The explosive main charge may be open to the environment, such as the hinged box mine (Figure 2. PMA-1A) where mass transfer is mostly from leakage. For other landmines that are encapsulated in a plastic case (Figure 3. PMA2), permeation controls the mass transfer rate. Some mines have small holes (Figure 4. TMA-5), which allow vapors a direct escape path to the soil. These openings also provide a path for direct contact of the explosive main charge package with water, such as with an extended rainfall, which can release a large amount of chemical to the soil.

Figure 2. PMA-1A Landmine Hinged Box Style and Wax Paper Coating

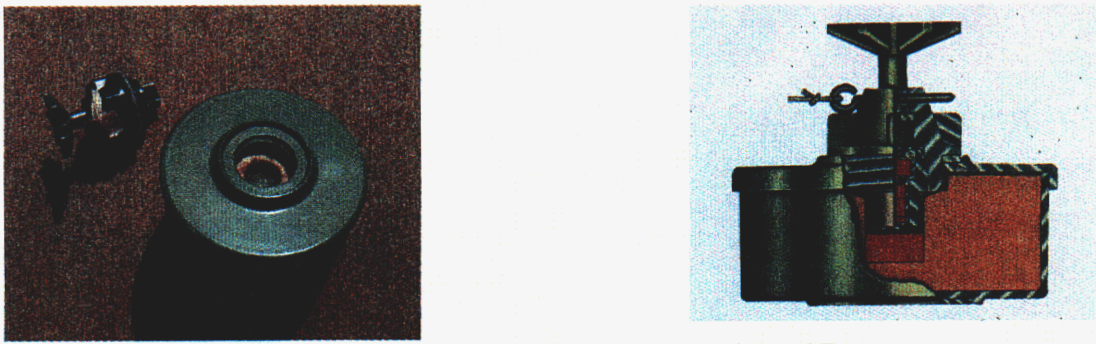


Figure 3. PMA-2 Antipersonnel Landmine and Fuse

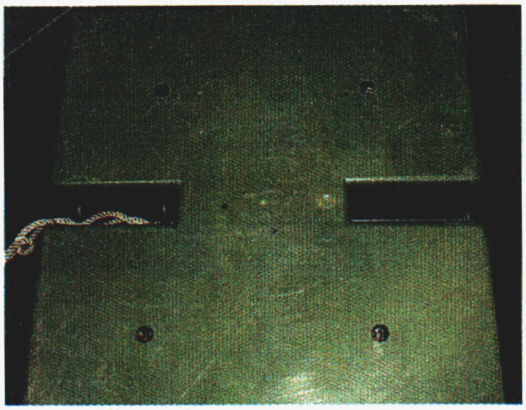


Figure 4. Base of TMA 5 Showing Holes

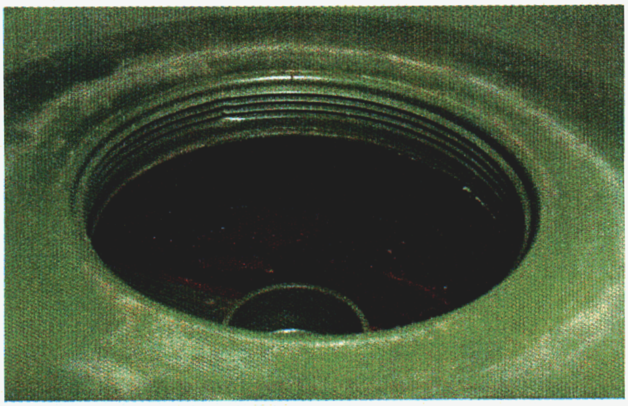


Figure 5. Coating on TMA-5 Main Charge Explosive

For the mines with such openings, the explosive main charge may be coated (Figure 5. TMA-5 with bitumen) or wrapped (Figure 2. PMA1-A with wax paper) to prevent gross damage to the explosive due to contact with soil water. The amount of chemical that can dissolve into water is much, much greater than the amount that can vaporize into the same volume of air (discussed in more detail in Chapter 5 – Chemical Distribution in Soils), so one must be mindful of both pathways in this analysis.

The explosive main charge that is encapsulated in a plastic case is not synonymous with being well sealed - plastics are permeable, allowing gases and vapors to migrate into and through the material. The factors that affect permeation include the type of polymer, physical state of the polymer, the nature of the penetrating gas or vapor, and the environmental conditions. Landmines are constructed from several types of plastics; however, the details on composition, additives and manufacturing processes are not known. Table 9 lists typical plastic materials used in the housings for landmines.

Table 9. Plastics used in landmines

Name	Acronym
Bakelite (phenolic)	BAK
Polyvinyl chloride	PVC
Polystyrene	PS
Polypropylene	PP
Polyethylene High density PE Low density PE	PE HDPE LDPE
Natural rubber	NR
Synthetic rubber	SR

Plastics are materials made from long threads of stable chemicals called polymers. The polymer threads can crosslink with other polymer threads, creating a web-like mat. Permeation of gases and vapors through this mat occurs by a process called vapor diffusion. On the inside of the landmine, the solid explosive main charge releases vapors, which become absorbed into the polymer mat. The amount of chemical that resides in the polymer is called the solubility (same term is used to describe the amount of chemical that dissolves in water). These molecules are pushed by new molecules released from the solid explosive. Eventually, the explosive vapor exits (evaporates) from the outside of the landmine into the soil system. The rate at which the molecules can move through the polymer is termed diffusivity. In the simplest example, permeation is a function of how much chemical is absorbed in the polymer (solubility) and the rate at which it can move through the polymer (diffusivity). The driving force is the difference in concentration from the inside of the mine compared to the outside (e.g. the diffusion gradient). The driving force increases with increased temperature, because at higher temperatures, the solid explosive produces a greater concentration of vapor.

The nature of the monomer (single unit of the polymer, e.g. vinyl chloride in PVC) used to build the polymer affects the permeability. A structural arrangement of a polymer that creates dense packing decreases permeability. The simpler the structure, the better the packing and the lower the permeability. Thus, PVC has a much lower permeability than LDPE. The permeability also increases with temperature - about 30 to 50% for every 5°C rise. Polymer formulations add to the complexity of the chemical mass transfer process because of the numerous combinations of polymer blends, copolymers, fillers, stabilizers and plasticizers (softeners).

Rubber materials also vary greatly depending on the source of natural latex used to make the rubber, or the chemical composition of the synthetic rubber (e.g. styrene butadiene rubber, SBR). Each plastic formulation (polymer material plus additives) has a characteristic void space that controls the rate of migration of gases and vapors – termed permeability or diffusivity, which is also a function of the size of the molecule permeating through the plastic. Figure 6 shows the relationship between molecular volume (size) and diffusion rate through two plastics with dissimilar pore structures (Mark and Kroschwitz et al., 1989). The diffusion coefficient for natural rubber is about 10^9 (1 billion) times greater than that of PVC, for a molecule of the size of TNT. The molecular volumes of TNT, DNT and DNB are similar, producing similar differences in the permeability of PVC and natural rubber. This is a key property that requires special notice. Mines made with rubber surfaces will permeate much, much larger amounts than PVC or other more dense plastics.

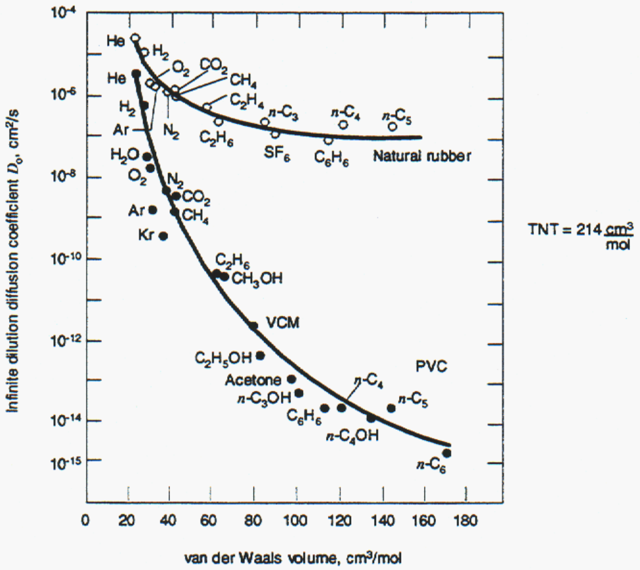


Figure 6. Diffusion Coefficients for Chemical Penetrants in Rubber and rigid PVC (Mark and Kroschwitz, 1985)

A metal mine (e.g. TMM1) is made from steel that has such a low permeability to landmine explosive vapors like TNT that permeation can be considered nil. This does not mean that metal mines do not leak, because there may be other pathways through poor construction seams or intentional openings, although threaded fittings would not be a likely leakage path as they typically create a very good vapor seal. However, metal mines may contain a short-term vapor signature from the paint. The paint is a polymer, which can be a reservoir for explosive chemical signatures that are derived from external sources, such as from storage in locations containing other explosive vapor sources (Bender et al., 1992).

With such a large number of factors contributing to landmine leakage, it may seem that mine specific leakage tests would be needed to accurately describe this process. However, this would be an enormous task, so we must be satisfied with a few mine-specific test results and use polymer coupon tests to make estimates for the others.

External Surface Contamination. One measure of the type and amount of explosive signature chemicals that leak from landmines is with an evaluation of the external surface contamination. This method measures the amount that is readily removable with a paper filter soaked in methanol. The chemical surface residue from the landmine is transferred to the paper filter, which is then analyzed quantitatively. These surface residues are derived from both chemical permeation through the plastic from the inside of the landmine and from chemical vapor deposition on the outside during handling and storage. Also, this represents an amount that is currently on the surface, without replenishment, and not a continuous leakage rate that is important for evaluating the likelihood of detection in the future.

Measurements of the surface concentration of two TMM1 metal cased mines prior to burial showed levels of TNT at 10 and 62 ng/cm^2 and DNT at 10 and 20 ng/cm^2 (Jenkins et al., 2000). After burial for 472 days, only a trace of TNT (0.4 ng/cm^2) was found on just one of the mines demonstrating that the paint reservoir had been nearly depleted of landmine signature chemicals. Measurements on the concentration of explosive signature compounds in paint scraped from unused US 60 and 81 mm mortars, and a 105 mm artillery projectile showed TNT and DNT levels that ranged from 1 to 45 µg/g – a considerable amount (Phelan et al, 2001).

A small set of Yugoslavian landmines acquired for emplacement at the Fort Leonard Wood, USA mine test facility were sampled before placement in the soil (Leggett et al., 2000). These landmines had been in storage since production 40-50 years prior and included: PMA1A, PMA2, TMA5 and TMM1. The results from this effort showed that TNT, DNT and DNB were found on each mine type, and RDX was found on the PMA-2, which uses an RDX booster. The levels varied considerably, but ranged from <2 ng/cm^2 (the method detection limit) up to near 400 ng/cm^2; however most were lower than 30 ng/cm^2. These results are very similar to the mean value for both foreign and USA landmines at 15 ng/cm^2, for tests using slightly different sampling and analysis methods (Hogan et al., 1992). Surface residues found on Soviet TM62-P anti-tank landmines contained 6 ng/cm^2 TNT and 28 ng/cm^2 DNT for a bakelite case; and, 3 ng/cm^2 TNT and 5 ng/cm^2 DNT for a polyethylene case (Chambers et al, 1998). Unfortunately, DNB was not quantified in this set of chemical analyses. The surface contamination confirms that the three signature chemicals, TNT, DNT and DNB are found on the outside of landmines, demonstrating that these compounds remain important as cues for detection by dogs.

Polymer Coupon Permeability. To evaluate the permeability differences of the plastics used in landmines, small pieces of a landmine plastic (e.g. polymer coupon) were allowed to absorb military grade TNT vapors (containing all of the chemicals described previously) in a glass bell jar for about six months (Leggett et al., 2002). The polymer coupons were then placed into tedlar bags (a very low permeability plastic) and allowed to exude chemical vapors for a set time period. The chemical vapors then deposit onto the interior tedlar bag surface. By washing the bag interior with a solvent and measuring the amount of chemical by quantitative analysis, a value that represents the release of vapors from the polymer coupon was determined. Other samples of these polymer coupons were placed into beakers of water, and also after a set time, samples of the water were obtained and analyzed for the signature chemicals. Figure 7 shows the results of these tests and demonstrate the effect of polymer type on release of chemical vapors. The flux of rubber is much, much greater than other polymers. Among the polymers, the higher density polymers (i.e. PVC) show a much reduced flux compared to low density polymers.

This work also indicated that the flux was greater into water than into air. Leggett et al. (2001) explains that with leakage into air, the explosive compounds are externally constrained by the limited vapor concentration in air. However, in water, the explosive compounds have a much greater solubility and mass transport is controlled by factors intrinsic to the polymer. Note that the differences in flux between water and air grows dramatically as the permeation rate of the polymer increases.

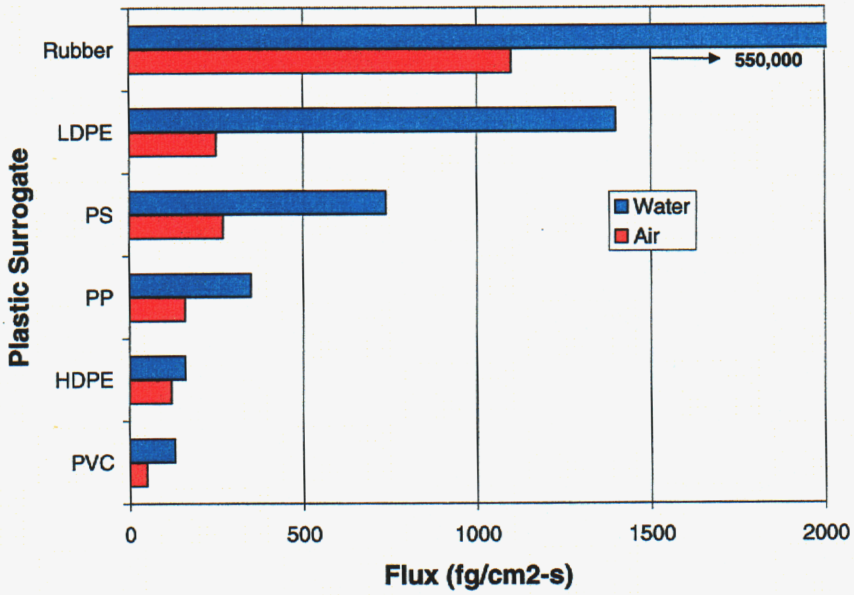


Figure 7. TNT Leakage Rate Dependence into Air or Water (Leggett et al., 2001)

TNT Solubility in Plastics. As noted earlier, the solubility of a chemical in a polymer contributes to the permeation rate. Leggett et al. (2002) obtained small samples of the polymer coupons, dissolved them in a chemical (solvent), and measured the amount of TNT. Figure 8 shows the results of these tests and indicates that lower density polymers contain a much greater resident concentration. These data also compare landmine specific materials with polymer coupons obtained from a commercial plastics supplier. A PMA2 is made from a polystyrene polymer, yet shows a slightly greater resident concentration than from a USA commercial product. The PMA1A case is made from PVC and has a slightly greater TNT load than PVC from a commercial supplier. It is not known whether these differences are significant or not, or represent that the PMA1A and PMA2 have had 40-50 years to accumulate compared to 6 months for the commercial polymer coupons. However, Figures 7 and 8 confirm that TNT (and speculatively for DNT and DNB) has greater permeation and solubility in low density polymers and rubbers than higher density materials.

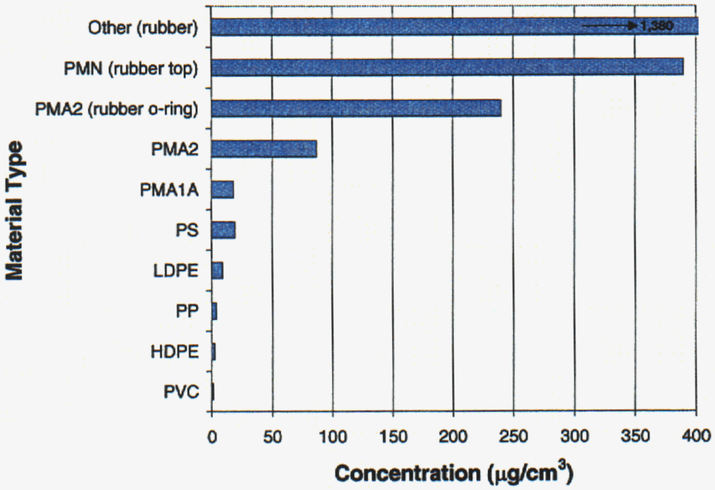


Figure 8. Resident Concentration of TNT in Various Plastics and Landmine Case Materials (Leggett et al., unpubl)

Landmine Flux Tests. In a similar set of experiments, five TNT filled and one RDX filled landmines were placed into tedlar bags for 2 to 7 days at temperatures from –3 to 34°C (Leggett et al, 2001). These tests found that the flux of the three principle chemicals (TNT, DNT and DNB) in the TNT mines were significantly different depending on the mine type and chemical (Table 10). The TMA5 had large fluxes most likely due to the holes on the bottom of the mine and the large surface area of this antitank mine. This will be found as soil residues underneath the mine, which may be more difficult to transport upward to the soil surface due to the presence of the mine itself. The PPM2 had the next highest flux. While the TMM1 mine appeared in this test to have a moderate flux of DNT, the chemical flux might diminish with time because of the limited reservoir of chemicals in the paint covering this metal mine. The PMA1A is a hinged box mine and it would be expected to have a much greater flux as the vapors can easily move out of the mine case. The PMA2 was shown to have the least flux due to the small size and low permeability of the PS case material.

Table 10. Landmine Flux into Air (20°C), ng/mine per day

Mine	Construction	TNT	DNT	DNB	RDX
TMA5	PS	1,380	15,100	4,500	
PPM2	unknown	128	12,800	3,480	
TMM1	Metal	740	1,720	282	
PMA1A	PVC	207	1,550	358	
PMA2	PS	24	282	332	
VS-50	unknown				14

From Leggett et al., 2001

This work also showed the temperature dependence of the flux into air was exponential, similar to the temperature dependence of vapor pressure. The data showed that regardless of the mine type or material of construction, the exponent remained the same at 0.11 [$y = a \cdot e^{0.11x}$, where x is temp (°C)]. Thus, for a 5°C change the flux changes by 1.7 times, for a 10°C change the flux changes 3 times, and for a 20°C change the flux changes 9 times.

When these mines were placed into water, the results showed a fast early time rise in solute concentrations followed by a steady increase with time. This initial rise is likely due to surface contamination dissolving into the water, followed by a steady permeation rate through the case materials. The flux values into water also followed that of the polymer coupon tests, showing a greater flux into water than into air (Table 11).

Table 11. Comparison of Mine Flux into Air and Water at 22°C (ng/mine per day)

Mine Type	Medium	TNT	DNT	DNB	RDX
PMA-2	air	21	240	240	
	water	1,270	720	1,300	
PPM2	air	2,040	2,110	460	
	water	4,640	6,690	1,000	
VS-50	air				8
	water				1,460

From Leggett et al., 2001

Leggett et al., 2001 also report preliminary test data that landmines placed into dry sand showed greater flux than into wet sand. Upon first inspection, this appears to confound the results above. However, if the sand was not sterilized, a wet soil has a much greater degradation rate, which might appear as a lower flux (see Chapter 6 – Chemical Degradation in Soils). More work is needed to resolve this discrepancy.

In work to evaluate the landmine flux into soil, Sandia National Laboratories created mine flux chambers from stainless steel and placed whole landmines into dry Sandia loam soil. Figure 9 shows the test apparatus with a PMN and a PMA-2 landmine. The landmines were allowed to leak into the soil for 12 to 33 days, then the entire mass of soil was extracted with acetonitrile (1:1) with ultrasonication (18 hr at 10°C) and the TNT, DNT and DNB measured by GC/ECD. Table 12 summarizes these flux test results. A comparison of these values to the polymer coupon tests was completed by assuming that only the top rubber surface of the PMN mine contributes to the soil residue (~ 80 cm^2), which corresponds to a TNT flux of 14,500 fg/cm^2-sec, which is similar to the rubber into air value of ~1000 fg/cm^2-sec (Figure 7). Completing the same comparison using the entire surface area of the PMA-2, the TNT flux is only 3 fg/cm^2-sec, which is much less than the polystyrene (PS)[300 to 750 fg/cm^2-sec] and closer to the PVC

[50 to 100 fg/cm^2-sec]. However, when one compares the PMA-2 results for TNT here (30 ng/day, Table 12) to that of Leggett above (21 ng/day, Table 11), the results are very similar.

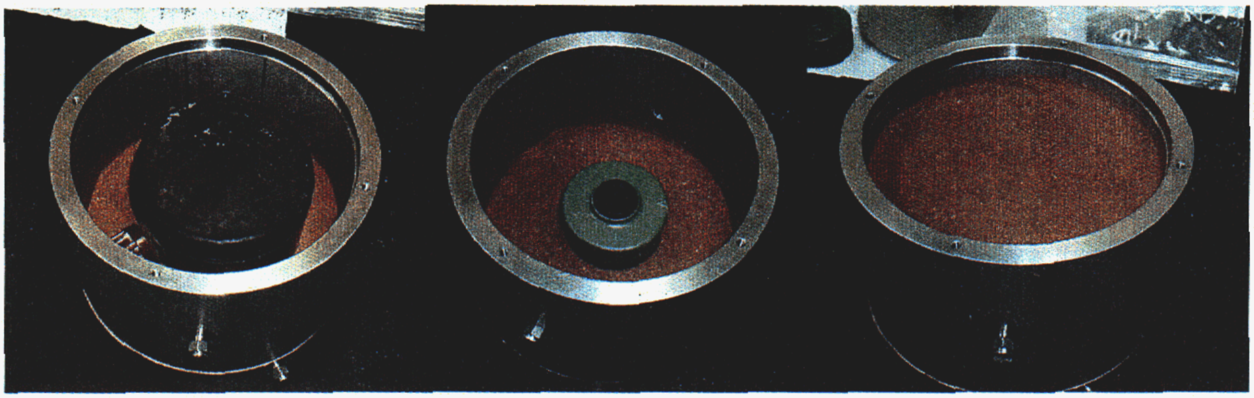


Figure 9. Whole Landmine Flux Tests in Soil

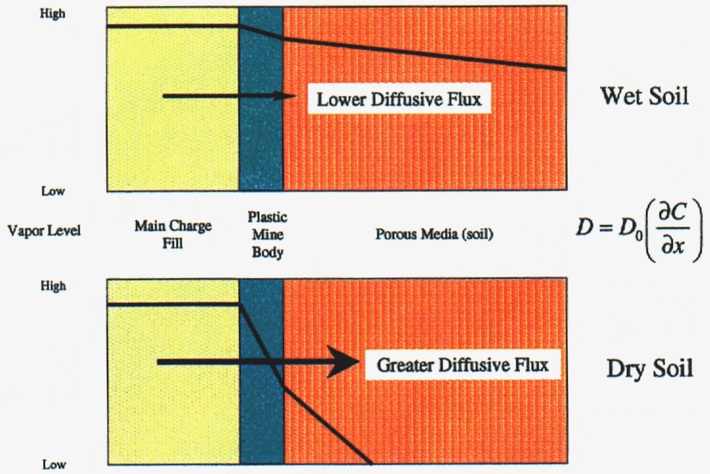
Table 12. Whole Landmine Flux Tests Results (µg/day)

Analyte	PMN	PMA-2
TNT	100 – 130	0.03
DNT	35 – 50	1
DNB	30 - 40	1
Soak time (days)	12 and 21	33

In earlier work, 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. These values are equivalent to 0.1 to 0.001 fg/cm^2-sec, which are much smaller than those found in the polymer coupon tests above. The low flux values determined by Spangler (1975) were likely a results of the preparation effort where the mine surface was cleaned and the small surrogate source inside contributed less mass for diffusion into the polymer.

An important, but yet unresolved issue is how much soil wetness impacts chemical permeation by changes in the diffusion gradient. One feature of dry soils is that chemical sorption is much greater depressing the vapor concentration in the soil (Chapter 5). Just like a temperature increase causes a greater gradient, depressing the vapor concentration in the soils also causes a greater gradient. Schematically, this is shown in Figure 10. Since landmines are placed in surface soils that undergo periodic wetting and drying, the flux rate from landmines may vary depending on soil wetness, which requires quantification for use in simulation modeling tools (Chapter 9).

Completion of this effort is complicated by the requirement to sterilize the soil before a wet soil flux test is initiated. Wet soil (except frozen) provides a microbiologically friendly environment. Most (if not all) soils contain microbes that become active when the soil becomes wet. In initial efforts to sterilize soils with radiation and chemicals, continued (yet reduced) TNT and DNT loss in soil slurry degradation tests demonstrated the difficulty in sterilizing soils.



$$D = D_0\left(\frac{\partial C}{\partial x}\right)$$

Figure 10. Diffusive Flux in Dry or Wet Soil

Summary. The results from landmine specific flux tests are critical to the understanding of which mine type contributes more or less chemical to the soil. This mine flux (or source term) is directly proportional to the amount of chemical made available to the ground surface as a cue for the dog (Chapter 7 – Chemical Transport in Soils). Much more work is needed to evaluate the chemical flux in to soil, specific to each landmine type and the effect of soil wetness on landmine flux.

5.0 Chemical Distribution in Soils

Introduction. In previous chapters, the three principal chemical signature compounds from military grade TNT (TNT, DNT and DNB) have been measured in the main charge explosive, in the vapor above the solid phase explosive, and in the air and water from mine leakage tests. Once these chemicals escape from the landmine into the soil, soil physical processes cause significant effects that dominate the amount of the chemical cue available for trace chemical detection.

Key Information.

- Landmine signature chemicals partition in the air, water and soil particles. Soil science can quantify these amounts and determine the concentrations in each.
- Soils with greater amounts of organic matter (agricultural or forest soils) or minerals (compared to desert sand) will sorb greater landmine signature chemicals, leaving less available for transfer to the air for vapor sensing.
- Soil moisture has a tremendous effect on soil-vapor sorption. Dry soils will sorb about 10,000 times more landmine signature chemicals than damp soils. This depresses the vapor levels the same amount. This process is reversible, so daily morning dew is valuable for vapor sensing, and afternoon drying is detrimental for vapor sensing.
- In damp soils, about 80 to 90% of the mass of TNT and DNT is found sorbed to the soil particles, about 10 to 20% is found in the soil water, and only $10^{-6}\%$ is found in the vapor.
- The soil acts as a temporary storage reservoir for the landmine signature chemicals, releasing them when dew or rain falls, and collecting more as soil water evaporates.

Background. Soils are a complex medium that contains air, water and soil particles. The landmine chemicals can exist in the air as a vapor, in the water as a solute and on soil particles as a residue. Fortunately, through many years of agricultural and industrial chemical research, the science of soil physics has provided quantitative means to describe how much of a chemical resides in the air, water and onto soil particles in a soil system (Jury, 1990). This is extremely valuable because the environment (soil type, temperature, rainfall, wind, sunlight intensity, etc.) changes due to geographic location and with local daily and seasonal weather cycles. In this chapter, information is presented on the steady state or equilibrium chemical phase partitioning processes. Then, in Chapter 9 – Landmine-Soil-Weather Systems Analysis, the complexity of time dependent weather cycles is combined with soil physics to provide a comprehensive systems analysis tool.

In the previous chapters, three chemical compounds were observed to the most likely cues used by dogs (TNT, DNT and DNB). As work was underway to measure the factors important for the distribution of chemicals in soils, information became available that DNB was infrequently found in soil samples obtained adjacent to landmines (Chapter 10 – Soil Residues from Landmines). Therefore, the work performed for chemical distribution in soils focused on TNT and DNT. If DNB becomes more prevalent in other landmine test programs, then methods described in this chapter can be employed to determine needed values for DNB.

Air and Water Solubility. There is a limit to the amount of chemical that can dissolve into air and water and sorb onto soils. The amount of chemical that dissolves into air is termed vapor pressure or vapor density, and is affected strongly by temperature. Figure 11 shows the vapor density of TNT and DNT (Pella, 1977) and reveals that DNT is always greater than TNT by about a factor of twenty (20) and that each increases about four-fold for every 10°C temperature rise. The amount of chemical that dissolves into water is termed water solubility, and is also affected by temperature (but not as much as for vapor). Figure 12 shows the water solubility of TNT and DNT (Phelan and Barnett, 2001) and reveals that DNT is also greater than TNT by about one and a half (1.5) and that each increases slowly up to 20°C, then increases much faster.

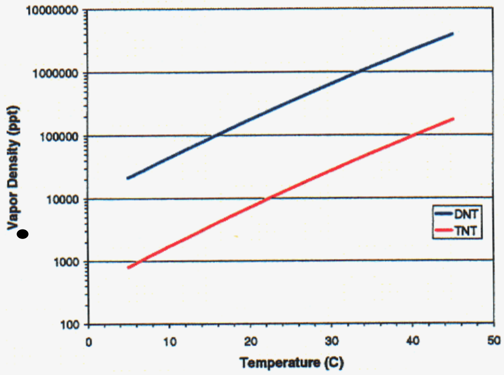


Figure 11. Vapor Density vs. Temperature

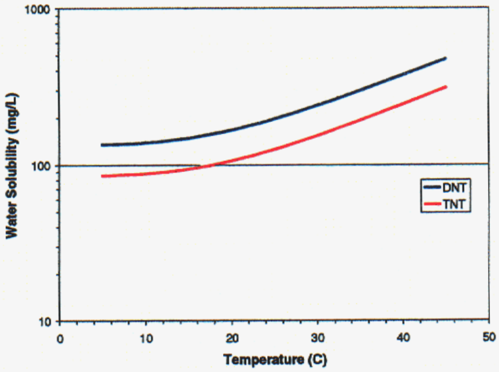


Figure 12. Water Solubility vs. Temperature

Air-Water Partitioning. In moist to wet soils, the pore space is filled partially with air and water. A measure of the amount of the chemical that exists in the gas phase to that in the aqueous phase, at equilibrium, is termed Henry's Law constant and is defined as

$$K_H = \frac{C_G}{C_L} \qquad [1]$$

where K_H is the Henry's Law constant (unitless) and C_G is the concentration in gas phase (g/cm^3 headspace) and C_L is the concentration in the liquid (aqueous or water) phase (g/cm^3 water). Henry's Law constant is also a function of temperature because both C_G and C_L are functions of temperature. A relationship for K_H as a function of temperature was developed with the relationships in Figures 11 and 12, and is graphically shown in Figure 13. This reveals that K_H for DNT is always greater than TNT by about a factor of twelve (12) and increases by about 2.5 for every 10°C rise in temperature.

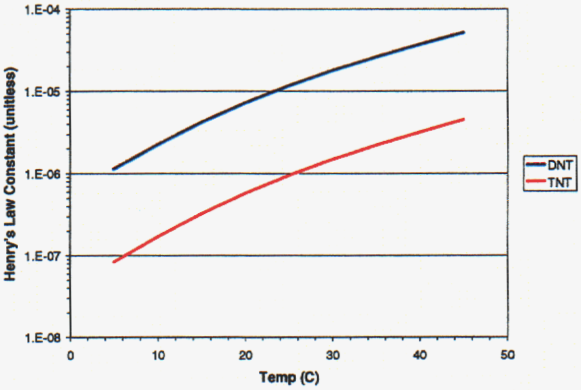


Figure 13. DNT and TNT Henry's Law Constant as a Function of Temperature

Soil-Water Partitioning. The amount of chemical that is taken up or held (sorbed) by soils is a complex topic, with much research that has analyzed the nature of the process and described which soil components (organic material, mineral phases) control the sorption processes (EPA, 1999). As with air/water partitioning, a measure of the amount of chemical in the water compared to the soil is used and is expressed as:

$$K_d = \frac{C_S}{C_L} \qquad [2]$$

where C_S is the sorbed concentration (μg/g), C_L is the aqueous phase concentration (μg/mL), and K_d has units of mL/g.

Past research efforts that have measured aspects of soil-water partitioning for TNT have shown large differences depending on soil type. Pennington and Patrick (1990) report that TNT sorption has a higher correlation to cation exchange capacity than the fraction of organic carbon, though Tucker et al. (1985) indicated the variation in K_d was correlated to both organic carbon (64%) and cation exchange capacity (78%). The desorption of chemicals from soils may not always be complete due to some permanent retention or degradation (biological or abiotic). Pennington and Patrick (1990) found with three sequential desorption steps that 88 to 93% of adsorbed TNT was desorbed. However, Comfort et al. (1990) found near permanent retention of TNT. In measurements of 14 different soil types from Army Ammunition Plants across the United States, the magnitude of the linear adsorption coefficients (K_d) ranged from 2.3 to 6.8 mL/g (mean of 4.0) (Pennington and Patrick, 1990). These values provide a good estimate of the range of K_d values for typical soils.

To better understand desorption, Xue et al. (1995) performed equilibrium and kinetic sorption studies for TNT and RDX. With a bentonite clay/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 mL/g, and for RDX at 1.6 mL/g for two soil types.

Very little work has been completed to measure the sorption of DNT on soils. Phelan and Barnett (2001) used Southwestern desert loam soil (Albuquerque, New Mexico) and found the K_d to be 1.8 mL/g for low DNT concentration solutions and 0.7 mL/g for the high concentration solutions. The decline in the K_d value implies that the sorption isotherm is not linear and more likely follows a Langmuir or Freundlich model than a linear one. These data are comparable to those measured for a Midwestern soil located at Fort Leonard Wood (Pennington et al., 1999) where the mean (std dev) K_d was 2.9 (1.4) mL/g.

Traditional standard methods to measure K_d are in batch equilibrium systems with a soil:water ratio of 1:4. This is convenient for testing, as the loss of analyte from the starting aqueous solution after contacting the soil for a standard time period (e.g. 24 hours) is assumed to be the amount transferred to the soil (EPA, 1989). The K_d value is determined as a linear fit of data based on variable starting solute concentrations. However, in unsaturated soils there are several factors that indicate that K_d values may vary as a function of soil saturation, causing potential increases and/or decreases in the K_d value.

With the pore space only partially filled with water, unsaturated soils have a smaller percentage of the total exchange sites in contact with the solute, which implies a potential decrease in the K_d value. Conversely, the water in unsaturated soil pores is closer to the soil particle surfaces, which implies a potential increase in the K_d value. Lastly, the ionic strength of unsaturated soil water increases due to the clay particle makeup of the small pores, which implies a potential increase in the K_d value (EPA, 1999). Since these factors imply both a potential increase and a potential decrease in the value of K_d, and without knowing which factor has the greatest impact, more research is needed with measurements for specific chemicals and soil types. One effort reported that soil-water partition coefficients were overestimated using batch equilibrium measurement methods (Burglsser et al., 1993) as a result of the particle concentration effect (solid-to-solution ratio and increased sorption capacity caused by particle separation during soil preparation).

In experiments with 2,4-DNT in a soil column breakthrough test, the K_d value was an important variable needed to improve data model comparisons (See Chapter 9). Batch equilibrium K_d measurements showed a linear K_d of about 1.7 mL/g; however, a much lower value of about 0.5 mL/g in a simulation model (T2TNT) improved the data model comparisons (Phelan et al., 2000). Also, in unsaturated soil vapor partitioning tests, parameter estimation results improved significantly if K_d was included as a fitting parameter (Phelan and Barnett, 2001). This work also showed that an unsaturated K_d value of 0.5 mL/g provided at better parameter fit. Since most soils are frequently in an unsaturated condition, more work is needed to define the soil-water partitioning coefficient as a function of soil saturation.

The importance of the soil-water partitioning coefficient will become evident later in the discussion of the interactions of these phase partitioning processes. Nevertheless, the data imply that TNT is sorbed slightly stronger to soils than DNT, the magnitude of the sorption is in the moderate range, and that in some soils there appears to be higher permanent retention (little is desorbed).

Soil-Air Partitioning. The amount of chemical that is held by soils has been shown to be strongly impacted by the soil moisture content (Ong and Lion, 1991a and 1991b; Petersen et al., 1994, 1995 and 1996; Ong et al., 1992). This appears to be a competitive displacement process where soils have a tremendous sorption capacity for organic chemicals when dry, but when wet, water is preferentially sorbed to the soil particle, displacing the chemical. The soil-air partitioning process is described in a similar way as with air-water and soil-water, with

$$K_{d'}(w) = \frac{C_S}{C_G} \qquad [3]$$

where C_S is the soil concentration (g/g), C_G is the vapor concentration (g/mL), *w* is the gravimetric moisture content (g/g), and $K_{d'}(w)$ has units of mL/g (same as for the soil-water partitioning coefficient, K_d). Figure 14 shows the impact of soil moisture content in the dry range of 1 to 11% on the soil-air partitioning coefficient ($K_{d'}$). This figure shows the $K_{d'}$ for TNT and DNT increase by about 10^8 as the soil dries. This is a tremendous change in a range of soil moisture contents that are typically found during weather cycles.

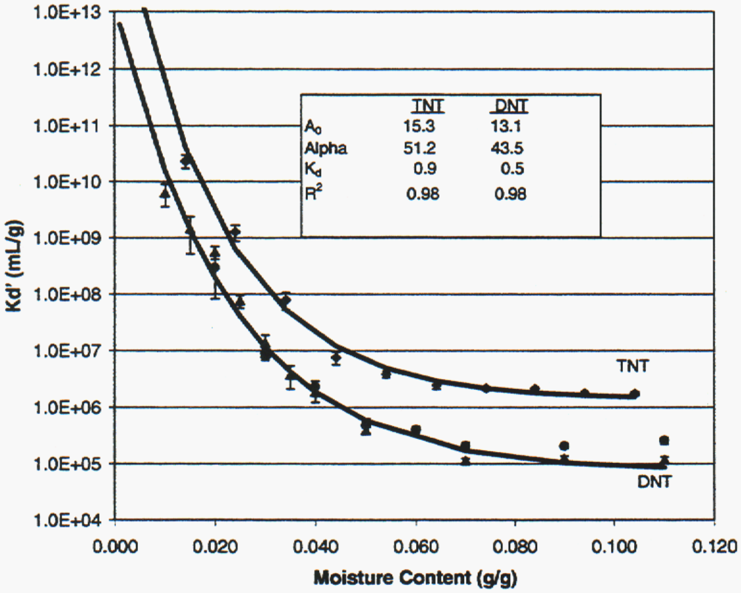


Figure 14. DNT and TNT Soil-Vapor Partitioning Coefficient versus Soil Moisture Content (Phelan and Barnett, 2001)

Integrated Soil Chemical Partitioning. The relationships described above can be assembled to show how chemicals partition between the air, water and soil sorbed phases. One can then evaluate shifts in these relationships due to changes in some of the key parameters. Jury et al. (1991) showed how the phase partitioning coefficients could be defined as phase mass fractions where f_S is the mass fraction sorbed to the soil, f_L is the mass fraction in the aqueous phase, and f_G is the mass fraction in the gas phase, and by definition,

$$f_S + f_L + f_G = 1 \qquad [4]$$

Table 13 shows a simplified spreadsheet with integrated equations for the phase partitioning of TNT. A similar table has been prepared for DNT (not shown). With only basic information of temperature, soil moisture content (or soil saturation), soil-water partitioning coefficient, and the total soil residue, this spreadsheet can be used to evaluate impacts of varying these parameters on the mass fractions and the vapor concentrations in air available as a cue for the dog.

Figure 15 shows an example of the soil solid and liquid phase mass fraction of TNT and DNT using typical values shown in Table 13. At all soil saturations, DNT always has a greater liquid mass fraction and a lower sorbed mass fraction when compared to TNT. For both chemicals, the liquid phase mass fraction rises as more water is present in the soil pore space. When the saturation drops below about eight percent, the impact of the soil-air partitioning process becomes evident. The liquid phase mass fraction becomes negligible with most of the mass fraction sorbed to the solid phase.

Table 13. TNT Phase Partitioning Estimation Spreadsheet

Parameter	Input (I)or Output (O)	Value	Units
soil moisture (grav) – w	I	0.15	g/g
soil temperature – T	I	23	°C
soil-water partition coeff – K_d	I	0.9	mL/g
Total Soil Concentration - C_T	I	1,000	ng/g
Total Solid Phase Concentration – C_S	O	0.86	$\mu g/cm^3$
Total Liquid Phase Concentration - C_L	O	0.94	mg/L
Total Vapor Phase Concentration - C_G	O	0.658	ng/L
Total Vapor Phase Concentration - C_G	O	70.347	ppt
Mass Fraction, Solid - f_S	O	0.86	
Mass Fraction, Liquid - f_L	O	0.14	
Mass Fraction, Gas - f_G	O	0.0000003	
Mass Fraction, Total	O	1.000000000	

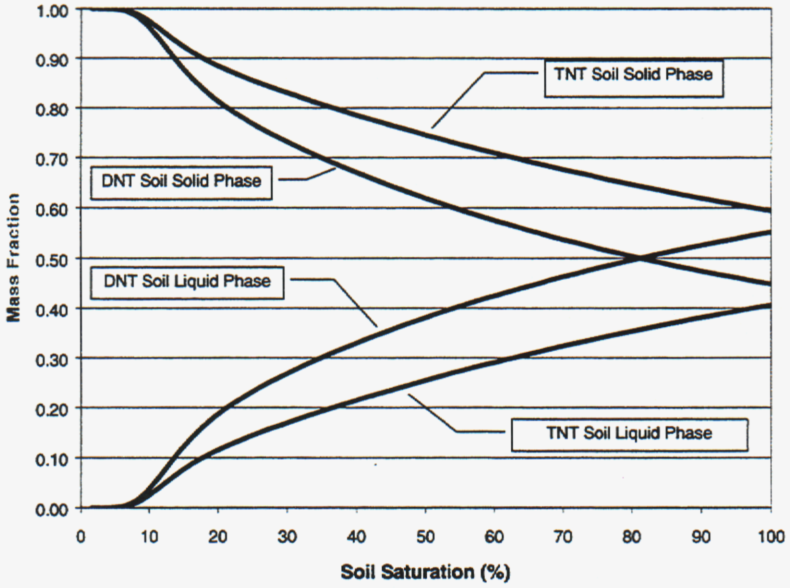


Figure 15. Soil Solid and Liquid Phase Mass Fractions

The effect of the soil-air partitioning process is more evident on the vapor mass fraction as shown in Figure 16. Below about ten percent saturation, the vapor mass fraction declines by a factor of about 10^5. At high saturation, the vapor mass fraction also declines because the remaining air filled voids become filled with water.

To evaluate the effect of the soil-water partitioning coefficient (K_d) on solid and liquid phase mass fraction, K_d was changed down to 0.5 mL/g and up to 3.0 mL/g as shown in Figure 17 for TNT. This range of K_d is likely typical for most soils; however, one can see that solid and liquid phase mass fraction is very sensitive to K_d. Figure 18 shows the effect of K_d on the vapor mass fraction. Since the vapor mass fraction is strongly controlled by K_H, which is affected by the liquid phase mass fraction, the effect of K_d on vapor phase mass fraction is approximately the same as for the liquid phase mass fraction in the range of 10 to 90 percent saturation. At the extremes, the effect of vapor-solid partitioning (low saturation) and diminished soil air porosity (high end) becomes prominent.

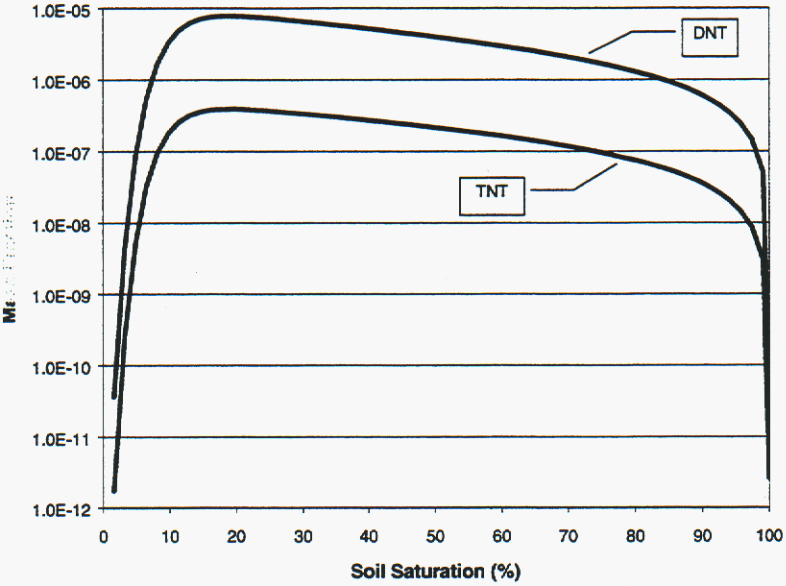


Figure 16. Soil Vapor Mass Fraction

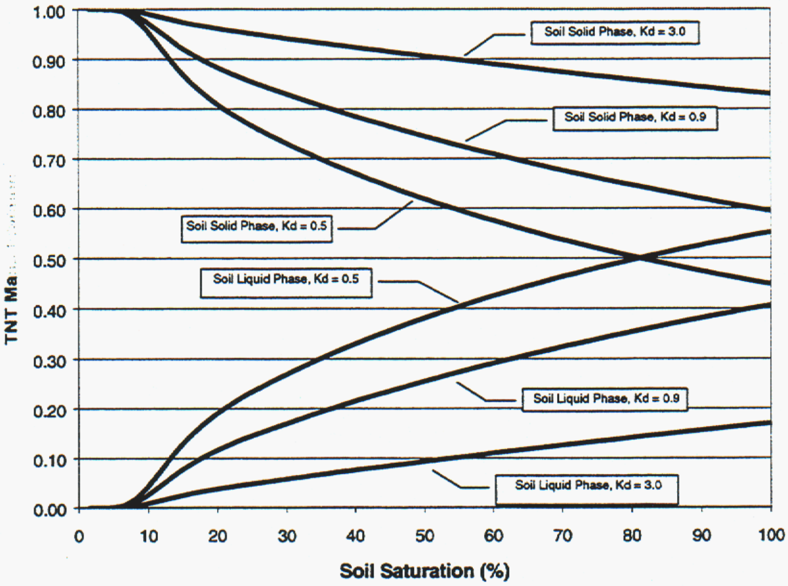


Figure 17. Effect of K_d on TNT Solid and Liquid Mass Fraction

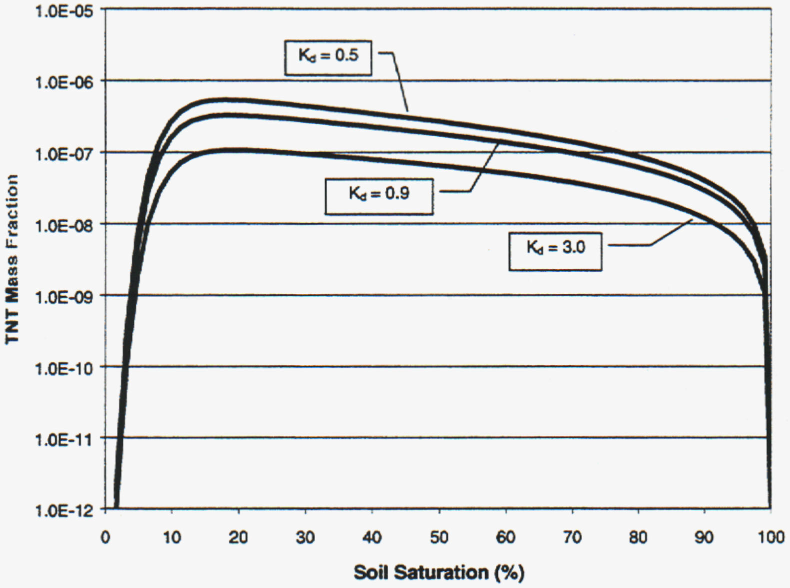


Figure 18. Effect of K_d on Vapor Mass Fraction

Temperature also has an effect because it affects both aqueous solubility and vapor pressure. Figure 19 shows the effect of increasing the temperature from 23°C to 45°C ($K_d = 0.9$ mL/g) and decreasing the temperature to 5°C ($K_d = 0.9$ mL/g) for the TNT vapor mass fraction. Decreasing the temperature to 5°C has the effect of decreasing the vapor phase mass fraction by a factor of 10, while increasing the temperature to 45°C has the effect of increasing the vapor phase mass fraction by a factor of about 5.

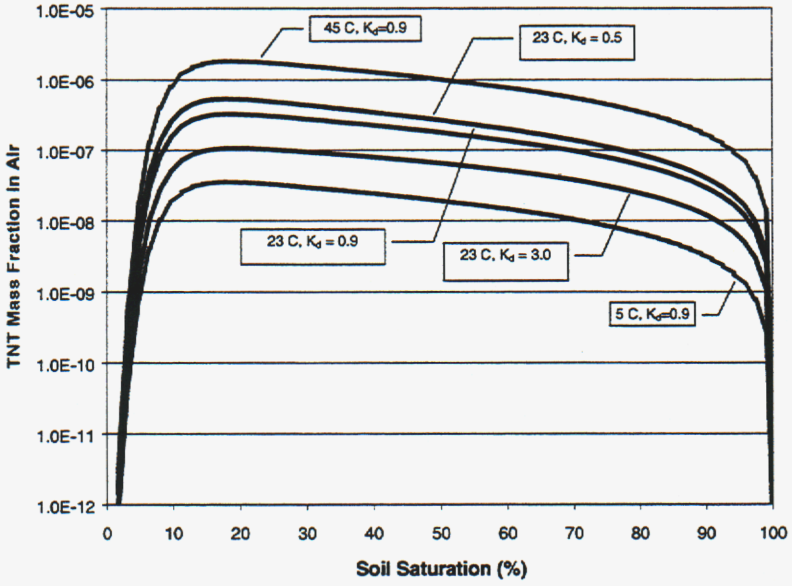


Figure 19. Effect of Temperature on TNT Vapor Mass Fraction

Summary. After several decades of agricultural and industrial chemical research and field application, soil chemical interactions are generally understood. For landmine signature chemicals (i.e. TNT and

DNT), laboratory test methods have defined the partitioning of these chemicals into soil systems. Soil phase partitioning relationships then define how much chemical is present sorbed to soil particles, dissolved in the water, and available in the headspace as vapor. The influence of temperature and soil moisture content can be accurately evaluated for any soil; however, the sensitivity of the soil-water partitioning coefficient demands that tests be completed for site-specific soils for improved accuracy. With these processes quantified, vapor concentrations can be derived (i.e. estimated) for use in mine dog vapor performance testing (Chapter 11) or from soil residues (Chapter 10) for comparison to mine dog vapor sensing thresholds.

6.0 Chemical Degradation in Soils

Introduction. Degradation of explosive residues in soils is a very complex phenomenon, occurring through combined natural biological and abiotic processes. The biological reactions occur by either fortuitous reactions or, less frequently, through metabolic breakdown for microbial energy utilization (Spain, 1995). Abiotic processes are chemical reactions with the soil components, typically iron bearing minerals that catalyze oxidation/reduction reactions (Hundal et al., 1997).

The degradation process involves a series of reactions that alter the original structure of the parent compound, forming many by-products that may be transient (quickly transformed) or become permanently bound to the soil organic matter. Both biotic and abiotic processes require the presence of water to induce these transformation reactions. Without sufficient water, the landmine signature chemicals can remain in soils for long periods of time. Understanding the factors that promote or suppress degradation are critical, because the rate of loss directly impacts the vapors available as cues for trace chemical detection.

Key Information.

- Landmine signature chemicals change form, chemical properties, and eventually become eliminated from soil systems by microbiological and soil mineral degradation reactions.
- The presence and amount of degradation by-products compared to parent compounds in soil samples is indicative of the degree of degradation that has occurred.
    - Degradation by products may be valuable vapor cues for dogs; however, there has been limited investigation on this matter.
- Both biologic and abiotic reactions require water for degradation reactions to proceed.
- Laboratory measurements of TNT, DNT and DNB found degradation rates to be dependent on soil type, soil moisture content and temperature.
    - Higher clay content and organic matter content soils have higher degradation rates.
    - Soil moisture contents greater than 1% cause very fast degradation rates (half the amount degrades over the period of one day)
    - Soil moisture contents less than 1% preserve landmine signature chemicals (half the amount degrades over the period of 3 years).
    - Only subzero (°C) conditions limit degradation. The greater the temperature, the greater the degradation rate.

Background. Both biological and abiotic chemical reactions produce similar degradation by-products due to the nature of the oxidation and reduction reactions. Table 14 indicates the principal degradation by-products for TNT, DNT and DNB. When found in soil samples, these compounds provide good evidence that degradation has occurred.

Table 14. Parent and Degradation By-Products of TNT, DNT and DNB

Parent Compound	Degradation By-Product (abbreviation)
2,4,6-TNT	4-amino-2,6-dinitrotoluene (4A-DNT)
	2-amino-4,6-dinitrotoluene (2A-DNT)
2,4-DNT	2-amino-4-nitrotoluene (2A-NT)
	4-amino-2-nitrotoluene (4A-NT)
1,3-DNB	3-nitroaniline (3-NA)

Chemical degradation information is important when included with landmine chemical emissions (Chapter 4) and distribution in soils (Chapter 5) to understand the amount of chemical available as cues for trace chemical detection. As is becoming evident, the environmental impacts to landmine chemical cues are becoming very complex. In order to fully account for all of these processes, computer simulation tools become necessary (Chapter 9). Biochemical degradation losses are an important parameter that offsets the gain from landmine chemical emissions.

Degradation processes are typically modeled as a simple first order or psuedo-first order process (Sawyer et al., 1994) that simplifies the simulation model input as a degradation rate constant, or half-life, that is independent of the chemical concentration. However, this simplification may lead to significant over or under estimates because the complex nature of explosive chemical degradation in soils is only beginning to be understood.

Very little information has been found on the intrinsic biodegradation rates of explosives in soils, because much of the literature reports data for active restoration methods such as composting or bioreactors where there is little correlation to natural conditions (Spain et al., 2000). More recent work on natural attenuation processes is a closer analogy, however, work has been limited to aquifer self cleansing and is not directly applicable to surface soils. However, reports from work on stability of analytes in soil samples, natural soil and post blast residue degradation studies have helped to define the nature of TNT, DNT and DNB degradation rates in soils.

Analyte stability studies. Past work that evaluated the maximum holding times (time before chemical analysis begins) for soil samples contaminated with trace levels of nitroaromatic compounds is one source for degradation rates of TNT and DNT (Maskarinec et al., 1991; Grant et al., 1993). Analysis of these reports shows a significant impact of the soil residue preparation method (aqueous or solvent enriched, or field contaminated), soil type, temperature, and data analysis method. The data from Maskarinec et al., 1991 were not used in this evaluation as this test used an excess solvent enrichment method (2 mL acetonitrile/2 g soil), not representative of landmine released chemical signatures.

Grant et al., 1993 prepared soils with aqueous enrichment (solute in water) with varied amounts of water held at room (22°C), refrigerator (2°C) and freezer (-15°C) temperatures. In addition, field contaminated soil from an Army production plant was tested. Water was added up to the maximum holding capacity of the soils (no visible freestanding water) and the temperature was held constant at room (22°C), refrigerator (4°C), and freezer (-15°C) temperatures. The moisture content was 4% (weight/weight or w/w) for the sandy loam, 20% (w/w) for the silty loam and clay soils, and 25% (w/w) for the field-contaminated soil. The nitroaromatic enriched soils showed a dramatic decline in concentration with time for TNT and DNT at room and refrigerator temperatures in all three soils. Only at freezer temperatures was the degradation limited. The effect of soil type was dramatic as well, as the clay soil induced significantly more loss than either the sandy or silty loam. However, the field-contaminated soil, at nearly the same initial concentration as the enriched soils, showed a much reduced degradation rate.

Because the data were used to define maximum holding times, Grant et al., 1993 did not report degradation rate constants. However, these data were re-evaluated to calculate degradation rates along with new data using soil from the Fort Leonard Wood minefield test site (Miyares et al., 2000). Miyares et al., 2000 prepared the soil with sieving to retain < 0.42 mm, moistened the soil to 20% (w/w) for 3 days to allow microbiological activity to become established, then added TNT, 2,4-DNT, 2,6-DNT and DNB and RDX in an aqueous solution, which increased the soil moisture content to 40% (w/w). Samples were held at 22, 4 and -4°C for up to 20 days. At 22°C, the TNT data did not show true psuedo or actual first order decay rates. In fact, there was an initial fast decline in the first day followed by a more moderate decline. Using the initial fast decline, an estimate of the half-life in the loam soils was estimated for TNT to be on the order of 1 day at 22°C. For the other chemicals and temperatures, the loss is properly described by a single first order process. Table 15 summarizes the results from these efforts for TNT, DNT and DNB.

Table 15. Degradation Half-Lives for Wet Soils

	Temp (°C)	Fort Leonard Wood (siltloam)	Silt	Sandy Loam	Clay	Aquifer
TNT	22	1	2	4	< 1	140
	2 or 4	17	17	20	1	
	-4	80				
	-15		520	5300	170	
2,4-DNT	22	26	50	53	2	
	2 or 4	53	180	230	13	
	-4	86				
	-15		1100	1100	144	
1,3-DNB	22	10				
	2 or 4	33				
	-4	84				
	-15					

from: Miyares et al., 2000

Natural Attenuation Studies. Cataldo (1993) incorporated 60 μg/g (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 (equates to a half-life of 2 days). Extractable parent compound and transformation products showed an 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 reached a greater level (~50%) and the extractable/unextractable fractions reached near steady-state much faster (about 10 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 that produce more water soluble compounds - which makes the transformation products less volatile and available for vapor phase collection, concentration and detection. Work with RDX showed that there was little transformation and most of the parent compound remained at 60 days.

Post-Blast Residue Degradation. In an evaluation of degradation rates of post-blast residue from detonated landmines, Phelan et al., 2002 (in prep.) detonated a PMA1A landmine and collected the post blast residue on long sheets of paper (30 m x 0.6 m). This material was combined, mixed well and split into 20 g aliquots (to help mitigate heterogeneity problems) for treatments at 5, 24 and 40°C, and 1, 5 and 10% (w/w) moisture content. To assess whether the nature of the post blast residue degradation was affected by other blast products (e.g. soot), a synthetic contaminated soil was prepared by solid phase enrichment methods at the same starting concentration of TNT found in the post blast residue (and also included DNT).

Results from this work showed that at soil moisture contents of 1% (w/w), the data were quite variable indicating that the combined post-blast residue was not uniform; however, there was virtually no loss of TNT. However, with soil moisture at 5% and 10% (w/w), the degradation proceeded very quickly. The degradation kinetics were not first order, with a fast initial phase followed by a much slower long term decline, similar to that found by Miyares et al., 2000.

In order to estimate the degradation half-life, the data was transformed (ln C/C_0), outlier data was removed, and the data were fitted with a linear equation. Where appropriate, only data from the first few days were used if there was an early time rapid decline followed by a slower rate. Table 16 reveals the results of this analysis and shows that a moisture content of 1 % (w/w) prevents significant degradation. At moisture contents of 5% and 10%, the degradation rates were very rapid. Unfortunately, this post-blast residue did not contain any measurable DNT or DNB to compare to the TNT.

Table 16. Post Blast Residue TNT Degradation Half-Life (Days)

	Temperature (°C)		
Soil Moisture Content (%, w/w)	5	24	40
1	1155	730	140
5	16	1	1
10	6	3	1

from: Phelan et al., 2002 (in prep)

Table 17 shows the results from the synthetic soil degradation study. The experimental design did not evaluate all of the temperature and soil moisture combinations; however, these results are similar to those in Table 16 and demonstrate that the post-blast residue degradation may be representative of landmine released chemicals in soils. Figure 20 shows a 3-d graphic of the impact of soil moisture content and temperature on the degradation half-life of TNT in post blast residue (Table 16).

Table 17. Synthetic Soil Residue Degradation Half-Life (Days)

	TNT			2,4-DNT		
	Temperature (°C)			Temperature (°C)		
Soil Moisture Content (%, w/w)	5	24	40	5	24	40
1	350			700		
5		1			1	
10			0.5			0.5

from: Phelan et al., 2002 (in prep)

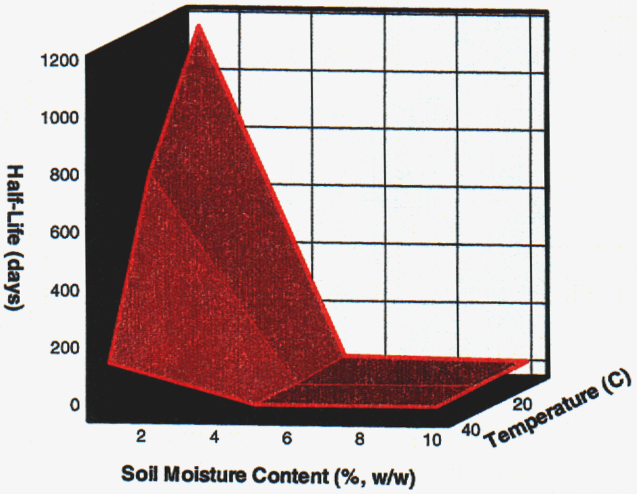


Figure 20. 3-d Plot of Post Blast Residue Degradation Half-Lives as a Function of Soil Moisture and Temperature

Summary. These results confirm that degradation rates are quite variable with major influences from soil type, temperature and soil moisture content; and, simple first order degradation kinetics do not often properly describe the loss process. However, it is clearly evident that above 1% moisture content (air dried soil), the degradation rate is extremely fast. This has significant implications for field samples collected wet, as only frozen conditions truly limit the degradation rate. Developing a complete set of quantitative values for use in simulation model analysis would take much more effort; however, the results presented above can be used to qualitatively compare regionally dry climates (e.g Afghanistan) versus wetter regions (e.g. Bosnia and Cambodia).

7.0 Chemical Transport in Soils

Introduction. Landmine signature chemical transport in soil is crucial to understanding the amount of vapor available as a cue to the dog. Landmine chemical leakage, soil chemical partitioning, chemical degradation, all play a role in how much chemical is present, but the chemical must move (be transported) from the proximity of the landmine to the ground surface to become available as a cue.

From Chapter 5, we described how landmine signature chemicals can exist in three phases: as a solute, as a vapor and sorbed to soil. In most circumstances, only vapor and solutes move through soils. There are two principal processes that contribute to chemical transport in soils, diffusion and convection. Diffusion is motion driven by differences in concentration (high to low) between locations, scaled by the internal energy of a molecule (diffusivity), which is affected by interactions with the soil. Diffusion can occur with both vapors in air and solutes in water.

Convection is the act of transporting chemicals in a stream of air or water. During infiltration of rainfall, solutes in water are convected downward. Evaporation convects solutes upward. Movement of air in soils induced by wind and barometric pressure can also convect vapors downward into and upward out of surface soils.

Key Information.

- Movement of landmine signature chemicals is controlled by chemical and soil properties, and driven mostly by the movement of water in soils.
- Water transports more TNT, DNT and DNB by convection than occurs by either vapor or solute diffusion.
- Conditions that cause upward evaporation of soil water in proximity to the landmine will be most beneficial for chemical sensing.

Diffusion. Over the last 30 years, researchers have explored diffusion of chemicals in soil. 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 that included vapor and liquid phase diffusion, soil-vapor partitioning, and soil-water partitioning. Vapor pressure, water solubility and phase partitioning coefficients were integrated to provide an effective diffusion coefficient for a given soil. The most widely used function for soil diffusivity is an adjustment of the diffusivity of a vapor in air based on the volumetric air content and porosity using the tortuosity model of Millington and Quirk (1961). Jury (1983) applied this same concept to the diffusivity of a solute in soil with the volumetric water content and porosity.

Combining the Millington and Quirk (1961) tortuosity model with phase partitioning functions, Jury (1983) 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 (i.e. soil saturation). Figure 21 shows the diffusivity of TNT in soil air, soil water and the sum of both – the effective diffusivity. This chart shows that solute diffusivity dominates vapor diffusivity at soil saturation values greater than about 20%. A soil saturation value of 20% is about 10% soil moisture by weight and is considered only damp. So during periods of moderate soil wetness, diffusive transport of TNT transport occurs mostly through the soil pore water. During dry periods, vapor diffusivity dominates, but is reduced by a factor of 10 – 100.

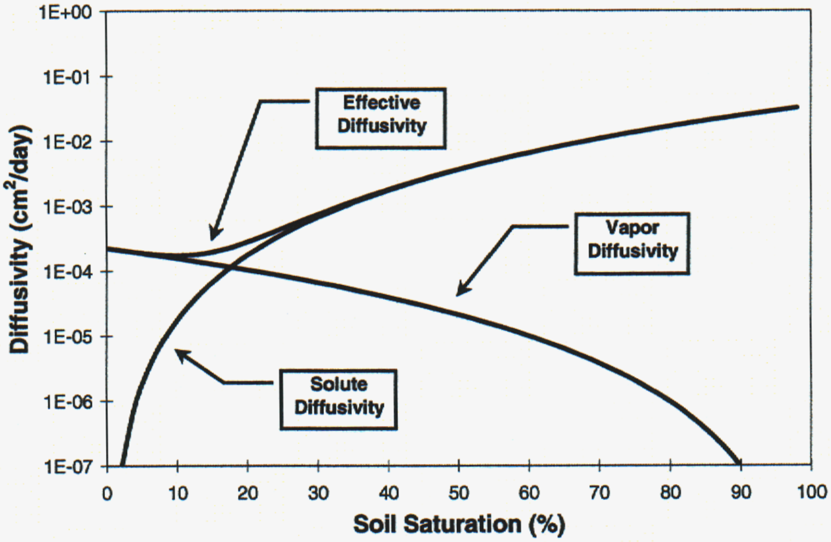


Figure 21. TNT Vapor, Solute and Effective Diffusivity (Phelan and Webb, 1997)

Figure 21 above is valid for soil saturation values greater than about 15% because below this value, soil-vapor sorption becomes significantly greater (see Chapter 5). The effect of soil-vapor sorption on the effective diffusivity of TNT, DNT and DNB was explored by Webb et al., 1999. Using the estimated chemical properties in Table 18 and vapor-solid partitioning values from Phelan and Barnett (2001), Figure 22 shows a dramatic decline in effective diffusivity below 15% saturation.

Table 18. Estimated Chemical Properties

	2,4,6-TNT	2,4-DNT	1,3-DNB
K_H (25°C)	5.9E-7	4.15E-6	9.6E-5
K_d (f_{oc} = 0.005)	2.5	1.2	0.17
D_l (cm^2/day)	0.580	0.632	0.686
D_g (cm^2/day)	5530.	5790.	6310.

This means that in dry soils, transport of landmine signature chemicals is essentially halted. However, when sufficient rainfall occurs, the chemicals that have accumulated on the dry soils can begin to move through combined vapor and solute diffusion.

Figure 22 shows some other very important differences between TNT, DNT and DNB. The effective diffusivity of TNT is much less than DNT, which is much less than DNB because of parallel trends in K_H, K_d, D_l and D_g. From Figure 22, one can see that TNT is dominated by solute diffusion and is always less than DNT and DNB. For DNT, vapor diffusivity starts becoming dominant at soil saturation less than 25% and for DNB, becomes dominant at soil saturations less than 55%. From Table 18, vapor diffusivity values for TNT, DNT and DNB are all about 10,000 times greater than solute diffusivity – meaning vapor diffusion is always much greater than solute diffusion. This means that in damp soils, the effective diffusivity of DNB does not decline as with DNT and TNT and remains 10 to 100 times greater until soil-vapor sorption becomes important.

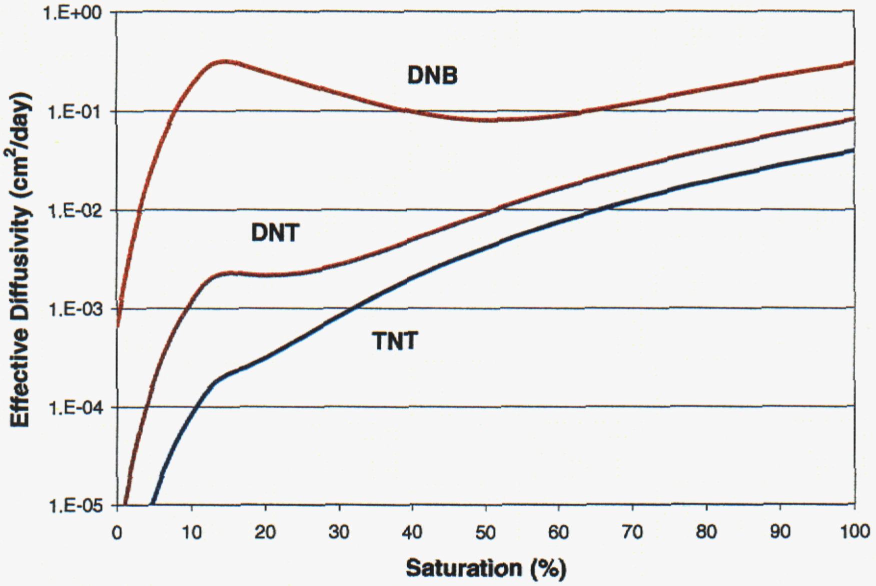


Figure 22. Effective Diffusivity for TNT, DNT and DNB with Soil Saturation

Convection. Convection describes the transport of a solute in a flowing soil solution. Chemical convection is the product of the solute concentration and the flux of water. Landmine signature chemicals held in stagnant soil pores will mix with infiltrating rainfall and be convected downward. The chemicals bound to soil particles will desorb until the soil-water partitioning relationship is satisfied. After rainfall ceases, soil water can move upward, pulled by evaporation from the ground surface. As described in Chapter 5, the mass fraction of TNT, DNT, and DNB are always much, much greater in water than in air. Thus, the optimal transport conditions are when water is moving upward through soils.

Vapor Transport Through Soils. In an effort to determine the effects of soil barriers on the transport of vapors from military-grade TNT, Jenkins et al. (1999) performed laboratory experiments that measured headspace vapor concentrations over time as a function of soil type, soil moisture content, and temperature. These tests used crystalline TNT (110 mg) buried below 2.5 cm of soil in 40 mL (27 x 95 mm) vials. Vapor samples were obtained at intervals up to 173 days. When terminated, the top 1 mm surface soil was collected and analyzed for residues of target analytes and soil-vapor partition coefficients were determined using the last vapor sample result.

These tests mimic only vapor transport because the vials were capped, which limits water movement and transport mechanisms. Figure 23 shows the results for TNT, DNT and DNB from one test series with silt soil at 23°C. For each chemical, the lowest soil moisture content (soil saturation) showed significantly reduced vapor concentrations (DNB vapor levels were below method detection limits) as a result of enhanced soil-vapor sorption. The increased vapor-solid sorption affects equilibrium partitioning between the surface soil residues and the headspace vapors (Figure 14), and the effective diffusion coefficient (Figure 22).

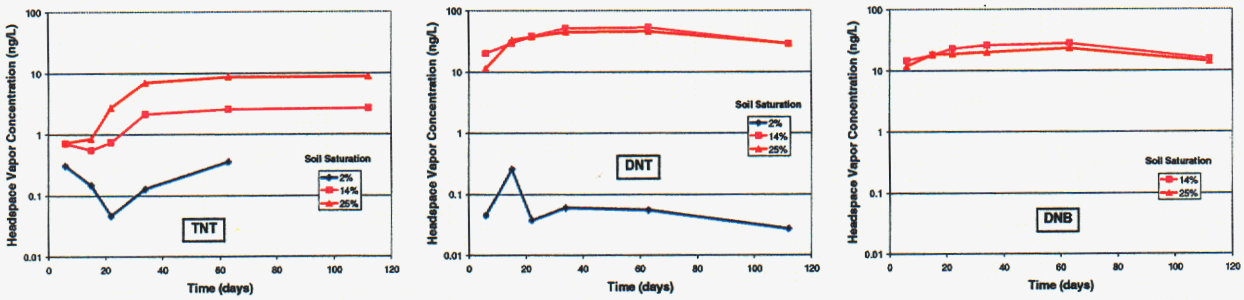


Figure 23. Vapor Transport Study Results (Jenkins et al., 1999)

If once assumes that at about day 60, the experiment has reached equilibrium where transport, repartitioning and degradation processes are all at steady-state, then one can qualitatively evaluate the magnitude of the headspace vapor concentration as an indicator of the magnitude of the effective diffusivity. From Figure 22, the effective diffusivity of TNT continuously rises as a function of soil saturation – and do the headspace vapor concentrations. However, the effective diffusivity of DNT rises from low saturation, but the values are similar at 14 and 25% saturation – and so are the headspace vapor concentrations. For DNB, the effective diffusivity declines from 14 to 25% saturation – and the headspace shows slightly lower headspace vapors at 25% compared to 14% saturation.

The work of Jenkins et al. (1999) demonstrates that vapor transport of landmine signature chemicals is affected by soil type, soil moisture content and temperature. They conclude that vapor concentrations were highest with sands, intermediate with silts and least with clays, consistent with a greater soil-water partitioning in the finer grained soil types. They conclude that dry soil conditions limit vapor transport, limiting headspace vapor concentrations to much lower levels than in moderately wet soils. Temperature was also important, where a change from 23°C to 4°C decreased vapor levels by a factor of at least 10, and at -12°C many of the headspace vapor samples showed non-detectable levels, more so in the clay and silt.

Summary. Transport of landmine signature chemicals in soils is necessary to move the landmine odor from the buried location to the soil surface. The driving forces for this movement, diffusion and convection, have been well studied providing a good understanding and mathematical representation for simulation modeling efforts. Since vapor and solute diffusion, and, air and water convection occur simultaneously, in variable amounts depending on the weather and soil conditions, it is mostly academic to evaluate how much chemical is transported by each mechanism.

However, since much more landmine signature chemical is present as a solute in soil pore water compared to that present in soil air, the movements of soil pore water control the transport of the landmine odor. Thus, processes that influence the upward evaporation of water between the landmine and the ground surface are important factors that increase the surface soil trace chemical residues. In locations where rain is infrequent, and evaporation from soils is minimal, vapor diffusion may become more important; however, the mass transport rates may be much reduced.

While a comparative analysis of mass transport by each mechanism may be academic, it would establish the magnitude for each process, and when one mechanism is absent (e.g. drought weather cycles), provide more understanding on the performance requirements for trace chemical detection.

8.0 Weather Factors Affecting Chemical Sensing

Introduction. Chemicals released from landmines undergo transport and degradation processes in the soil as discussed in earlier chapters. The chemical signature that reaches the soil surface is released into air currents near the surface, or the boundary layer, where it is rapidly diluted by the wind. The chemical signature above the boundary layer is essentially zero. This behavior is schematically shown in Figure 24. The chemical signature concentration is depicted by the concentration of red dots in the figure. Mine dogs sense the chemical concentration in the chemical boundary layer, and possibly on surface particles that are inhaled by the dog. The thickness of the chemical boundary layer is dramatically influenced by the weather conditions at the surface as is discussed in this chapter. In order to determine the best and worst times for chemical detection, the boundary layer behavior as influenced by weather conditions needs to be understood.

There has been a long history of research on the impacts of weather on near-surface soils for agricultural applications. The information needed to understand the heat and moisture balance for crop production and agricultural chemical (fertilizers and pesticides) efficacy can be used to understand the chemical transport in soils up to the ground surface. Some of the models developed for agricultural and chemical transport in the near-surface soils have been used for preliminary consideration of landmine chemical transport as discussed in Chapter 9, Landmine-Soil-Weather Systems Analysis.

In contrast, chemical transport in the air boundary layer above the soil surface has not been explored in detail. The boundary layer near the ground is driven by thermal processes and is a complicated

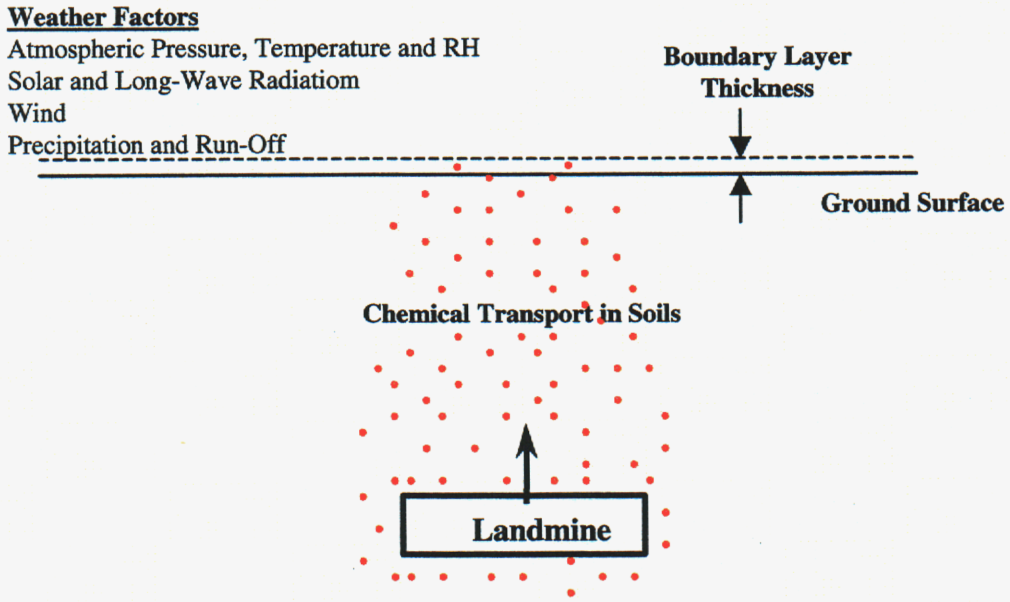


Figure 24. Depiction of Chemical Concentration Variation Including the Boundary Layer

interaction between thermal radiation gains and losses, evaporation of water, and the presence of low-growing plants (Gieger, 1957). Chemical transport in the air boundary layer is coupled with chemical movement in the soil and will be influenced by the weather and, in the present situation, by the actions of the dog.

This chapter introduces the key weather factors that influence the chemical concentration near the surface and in the boundary layer. An alliance of micrometeorology (weather near the ground) and soil physics (chemical transport in soils) is necessary to fully understand the impacts to the landmine chemical signature and the availability of vapors for chemical sensing. Chapter 9, Landmine-Soil-Weather Systems Analysis, begins to describe this alliance and presents tools to evaluate the complex interactions that weather induces on vapor concentrations at the soil surface. Much more work is needed to understand the impacts of weather on the chemical concentration in the boundary layer for the landmine scenario including the effect of dogs.

Key Information.

- The factors that affect chemical movement and concentration from the ground surface into the layer of air closest to the ground (i.e. the soil-atmosphere boundary layer) have not been thoroughly evaluated.
- Differences between the temperature of the soil and the air make a significant impact on localized vertical air movement that either dilutes or traps the vapors emanating from the soil.
    - Soil temperatures greater than air temperatures cause an unstable boundary layer with mini-thermals that dilute landmine signature chemical vapors - the greater the temperature difference, the greater the impact.
    - Soil temperatures less than air temperatures cause mini-inversions that trap landmine signature chemical vapors in the boundary layer
- Winds also impact the boundary layer – as the wind velocity increases, the boundary layer thickness decreases and the dilution increases.
- The influence of the dog's actions on the chemical boundary layer behavior has not been extensively considered.

Weather Factors. The weather factors that will be considered include:

✓ atmospheric pressure
✓ atmospheric temperature
✓ atmospheric relative humidity (vapor pressure)
✓ solar radiation (short-wave)
✓ long-wave radiation
✓ wind velocity
✓ precipitation
✓ plants

While not a weather factor *per se*, the effect of plants is generally to mitigate the influence of the weather at the ground surface. Each weather factor will be discussed including the impact on the air boundary layer thickness. For purposes of this discussion, some of the factors will be lumped together.

Atmospheric temperature, solar radiation, and long-wave radiation will all influence the soil surface temperature, which will be discussed in detail. The atmospheric relative humidity and precipitation determine the direction of water vapor and liquid water mass flux, which will be discussed together.

Atmospheric pressure. Atmospheric pressure variations generally have a minor influence on chemical vapor transport. As the pressure varies, such as when a weather system passes through, there will be a slight change in the convective transport of the chemical signature in the vapor phase out of the soil; this process is often referred to as barometric pumping (Auer, et al., 1996). The effect is generally small, however, compared to the other weather processes.

Soil surface temperature. The soil surface temperature is directly influenced by the atmospheric temperature, solar radiation, and long-wave radiation. The higher the atmospheric temperature, the higher the soil surface temperature.

The thermal radiation energy balance at the soil surface has three components. Solar (short-wave) radiation from the sun adds energy to the soil surface. Long-wave radiation emitted from the atmosphere also adds energy to the soil. The soil loses energy through long-wave radiation emittance to space.

Radiation from the sun is absorbed and reflected in the atmosphere and is influenced by the altitude, clouds, water vapor, and the presence of particles such as smoke and dust in the atmosphere (Arya, 1988). Clouds, water vapor, and particles all decrease the net solar radiation reaching the soil surface, while a higher altitude increases the net solar radiation. Solar radiation is obviously highly variable during the day and is generally a maximum in the early afternoon and is zero at night. The net solar radiation reaching the soil surface is partially absorbed by the soil and partially reflected. The fraction of incoming radiation that is reflected back to the atmosphere is called the surface albedo, or reflectivity. The lower the albedo, the higher the net incoming radiation absorbed by the soil surface. Darker and wetter soils tend to have a smaller albedo than lighter and dryer soils (Campbell and Norman, 1998); therefore, more solar radiation is absorbed in darker and wetter soils.

The net long-wave radiation added to the soil surface is the long-wave radiation added from the atmosphere minus the long-wave radiation lost to space. Long-wave radiation from the atmosphere to the soil is affected by the presence of clouds, and water vapor as well as the air temperature in the atmosphere. Long-wave radiation flux from the atmosphere to the surface is slightly higher for clouds than with a clear sky and increases with increasing air temperature. The amount of long-wave radiation lost into space is dependent on the temperature of the surface. Both long-wave radiation components are directly dependent on the emissivity of the soil surface. Darker soils and wetter would have a slightly larger emissivities than lighter and dryer soils. A darker soil increases the net long-wave radiation value. Whether the net long-wave radiation is positive or negative depends on the relative temperatures of the atmosphere and the soil, as well as the emissivity of the clouds. Generally, however, the net long-wave radiation is negative.

The thermal radiation energy balance is generally positive during the day due to solar radiation and is negative at night due to the net long-wave radiation. However, there are other processes that affect the heat balance of the soil surface. As mentioned earlier, heat is also added (or subtracted) to the soil surface due to the atmospheric temperature. Heat is also conducted to and from the surface in underlying the soil by heat conduction. During the day, the soil surface temperature is generally higher than the soil underneath, so heat is conducted into the underlying soil. Similarly, at night, the soil surface temperature is less than the underlying soil, so heat is added to the soil surface through conduction. Mass transfer also influences the soil surface temperature. Water evaporation and condensation, e.g., dew, also become heat sinks (evaporation) and heat sources (condensation) at the surface.

As seen from the above discussion, the soil surface temperature is a complex energy balance including the effects of the air temperature, radiation (solar, long-wave, and radiation to space), conduction in the soil, mass transport in the soil, and evaporation and condensation processes at the surface. The surface temperature of the soil affects the chemical signature at the surface. For example, at higher temperatures, the vapor-liquid partitioning coefficient, or Henry's coefficient, will be higher, meaning that more of the mass is in the gas phase. The local water vapor pressure will also be increased, possibly leading to higher evaporation rates, which will increase the chemical vapor flux rate into the boundary layer.

As an example of the variation of soil surface temperature, Figures 25 and 26 show the temperature of soil as a function of depth for high desert soil in Albuquerque, New Mexico, USA. A TM62P antitank mine was buried in the soil 4 inches below ground surface (to the top). These figures show the typical sinusoidal variations in soil temperatures caused by daytime net positive radiation (heating) and net negative nighttime radiation (cooling). These temperature cycles dampen out as the depth increases. Note the significant surface temperature variation during the day. In the winter, the surface temperatures vary about 5 to 20 °C during the day, while the temperatures at the top of the landmine vary by 4 °C or less. The highest temperatures are in the early afternoon due to solar radiation, while the minimum temperatures are in the early morning before solar radiation becomes significant. During the summer months, the variation is more dramatic due to the higher level of solar radiation. While the timing is similar to that in the winter, the surface temperature variation in the summer is much higher at about 40 °C, or about twice as large as during the winter. During the summer months, the temperature variation at the top of the mine, which is 4 inches below the surface, varies about 12 °C during the day compared to a variation of 4 °C during the winter.

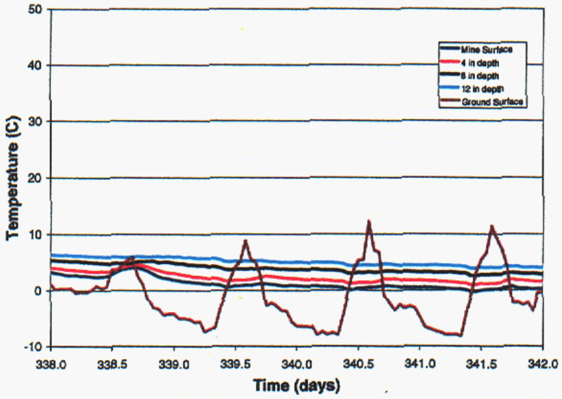


Figure 25. Winter Soil and Landmine Temperatures

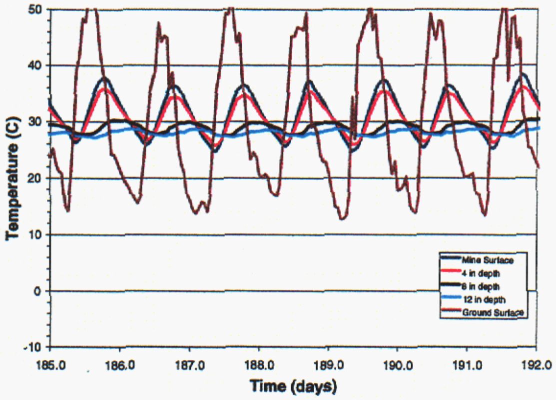


Figure 26. Summer Soil and Landmine Temperatures

Soil Water Content. Water mass transfer in the soil occurs through a balance of the water added to the soil through net precipitation (precipitation minus runoff), water evaporated at the soil surface, and water that flows through the system to the underlying soil units. Retention and transport of water in the soil is influenced by the soil characteristics, such as the amount of clay present, and by other properties such as the porosity and the unsaturated soil characteristic curves. Weather affects the soil water content dramatically through precipitation at the surface, and the atmospheric water vapor pressure, which directly influences evaporation. (The term relative humidity is often used that is simply the water vapor pressure divided by the saturated value). The saturated water vapor pressure increases with increasing temperature. If the atmospheric vapor pressure is higher, evaporation will be reduced. Therefore, evaporation is smaller for higher relative humidity conditions, which will increase the soil water content. If the soil surface temperature is increased, the evaporation rate will be higher, decreasing the soil water content.

The soil water content dramatically affects the chemical partitioning among the phases (gas, liquid, solid) including sorption, as well as the gas and liquid transport (convection plus diffusion). At low soil saturations (< 10%), the amount of chemical vapor available for sensing drops dramatically as discussed earlier in Chapter 5, Chemical Distribution in Soils.

There are competing effects between the soil surface temperature and the soil surface water content as illustrated by an increase in soil surface temperature. While this increase will lead to an increase in Henry's constant, which in turn leads to a higher gas-phase chemical concentration, the higher soil surface temperature also leads to a decrease in the surface moisture content due to evaporation, which would lower the gas-phase concentration for low liquid saturations where vapor-solid sorption becomes important. The net effect of an increased soil surface temperature on the gas-phase chemical concentration is dependent on the interaction between temperature and moisture content.

Air Boundary Layer. The air boundary layer, which is the air layer just above the soil surface, is a complicated function of weather and soil conditions. The dogs need to sniff in the chemical boundary layer in order to locate the chemical signatures emanating from buried landmines.

In reality, there are numerous boundary layers at the soil surface. There are boundary layers for momentum (wind), water vapor, and heat (thermal) as well as for the chemicals emanating from the buried landmines. The behavior of each of these boundary layers is a little different. Boundary layers develop and thicken with increasing distance from their origin. The wind, water vapor, and heat boundary layers are generally at equilibrium as the origin of the boundary condition may be at the edge of the field containing the landmines, which may be many 100s of meters away. In contrast, the origin of the chemical boundary layer is above the landmine, so the chemical boundary layer has had little opportunity to develop and thicken. Thus, the chemical boundary layer, which is of utmost importance for sensing, is probably thin relative to the other boundary layers. Chemical concentration is highest at the soil surface and is rapidly diluted in the boundary layer, going to zero at the edge or thickness of the chemical boundary layer. Thus, if the chemical boundary layer thickness were x cm, there will generally be no chemical signature x cm or more above the ground.

The dominant factors determining the boundary layer thicknesses are the wind speed, the air temperature, and the soil surface temperature. As the wind speed increases, the boundary layers become thinner. Conversely, for calm conditions, the boundary layer thicknesses are much greater than for windy conditions.

The air and soil surface temperatures strongly influence the boundary layer thicknesses. If the soil surface temperature is higher than the air temperature, which typically happens in the daytime due to solar radiation, the boundary layers are unstable as small thermal convection air currents are created. The net effect is that the average boundary layer thickness is reduced. However, these thermal convection air currents also have the potential to transport landmine signature chemical vapors upwards beyond the "average" boundary layer thicknesses. Settles and Kester, 2001, describe an example of intermittent thermals rising at speeds of 0.25 m/sec and at frequencies of about 4 per minute. With the unpredictable nature of these currents, chemical concentrations may vary considerably as a dog passes into an area containing landmine signature soil residues.

Conversely, when the soil temperatures are lower than the air temperature such as at night, a temperature inversion occurs and the boundary layers are stable. Wind velocities are often lower at night due to the stability of the boundary layers. Under these conditions, the boundary layer becomes thicker and dilution decreases, providing for optimum conditions for vapor sensing as far as the boundary layer thickness is considered.

Effect of Dogs. The chemical boundary layer thickness and the chemical concentration within this boundary layer will be affected by the actions of a sniffing dog as discussed by Settles and Kester (2001). For example, if the dog exhales prior to sniffing, he will disturb the local boundary layers, further diluting the signal. When the dog does sniff, it is not clear what air volume is sampled by the dog. For example, depending on the sniffing rate and the proximity of the dog's nose to the ground, the dog may only sniff the air from the boundary layer above the soil surface, or he may sample air above and below the soil surface, which would have a higher chemical concentration that that in the boundary layer. If the dog's nose is close to the ground and the sniffing rate is sufficient, small soil particles with potentially orders of magnitude higher chemical concentrations than in the vapor could be entrained by the sniffing action and sampled by the dog. With the moist conditions in the dog's nose, the potential for the release of sorbed chemicals exists, especially if the surface soil is dry. These interactions have not been studied at the present time.

Plants. The effect of plants was not included in the above discussion. The reason for this exclusion is that their impact on the chemical signature has not been evaluated. It is well known that the impact of plants will be to mitigate any variations of atmospheric conditions. For example, plants will shade the soil resulting in reduced solar radiation to the surface and lower surface temperatures. Plants act as a sink for water, which will affect the water content in the subsurface and surface soil. The impact of plants will be to increase the vapor pressure at the soil surface relative to the atmosphere resulting in reduced evaporation from the surface. Plants also act as a sink for landmine chemicals, possibly transporting them to their leaves. The influence of plants on detection of chemical signatures from landmines needs to be examined further.

Summary. The effect of weather conditions on the chemical concentration at the soil surface and in the boundary layer just above the surface is dynamic and very complex. The soil surface temperature and water content, which can dramatically influence the chemical vapor concentration at the surface, is a function of a number of dynamic parameters including solar radiation and precipitation. The boundary layers just above the soil surface, which control the dilution of the chemicals, are predominantly dependent on the wind speed and the temperature difference between the surface of the soil and the air temperature. The only way to thoroughly evaluate the dynamic influence of the weather conditions is through models and simulations, which are discussed in Chapter 9, Landmine-Soil-Weather Systems Analysis.

9.0 Landmine-Soil-Weather Systems Analysis

Introduction. Previous chapters in this report have described individual properties and the processes affecting the chemical signature from buried landmines including the effect of weather. Shown separately, these individual elements are complex. However, there are even more complex interdependencies among these elements that challenge our intuition to fully understand the impacts to the landmine chemical signature. For example, increased soil moisture releases sorbed landmine signature chemicals from soils causing significantly greater vapor levels. However, increased soil moisture also induces biochemical degradation that reduces the soil residues, which would decrease the vapor levels. If the increased soil moisture comes from an extended rainfall, soil chemical residues would be washed deeper into the soil profile, which also decreasing vapor levels. The interdependencies between the processes are complex and are difficult to evaluate *a priori*.

One method to understand these complex interdependencies is through the use of computer simulation tools. Computer simulations can efficiently evaluate numerous scenarios in a short time period and can also provide estimates for vapor or soil residue values that may be difficult to measure or are below analytical chemical detection limits. However, computer simulations require input data from all of the individual properties and processes, which is no simple task. There are landmine signature chemical properties, soil phase partitioning properties, mine-specific flux processes, degradation processes and weather factors. Fortunately, many of these have been determined, but only from a limited set of soils and mine types, and recent weather data can be unavailable or incomplete.

The computer solves the mass, momentum and heat conservation equations for the various components using a step-by-step problem solving procedure (an algorithm). With the large number of interdependent actions, the computer must be fast for the results to be obtained in a short duration. With today's computers, an annual weather cycle driven simulation may only take a few hours to evaluate the annual variation of the chemical signature. The computer simulation output has much to offer for analysis and evaluation. Vapor concentrations over time can be compared to dog vapor sensing thresholds to assess whether dogs may miss mines as a result of the conditions used in the simulation. In addition, other correlations can be determined that help define limits to certain conditions (e.g. rainfall, wind, temperature, season, time of day) that may be used to initiate or terminate mine dog work in the field.

While computer simulation results are extremely valuable in understanding these complex interdependencies, computer simulation results are not the truth. Simulation results provide estimates that are based on experimental data and soil-physics based computational science. Unknown errors may be found in our understanding of the fundamental soil-chemical processes, the interactions between these processes, and in the complex mathematics simulation tools required. However, when simulation results closely mimic experimental or field data from a system that combines several or many of these individual processes, our confidence grows that the simulation tools provide a reasonable representation of actual conditions.

As mentioned in Chapter 8, Weather Factors Affecting Chemical Sensing, the effect of plants has not been thoroughly examined. In the landmine-soil-weather systems analysis methods that are discussed below, bare soil has been assumed to date. In order to include the effect of plants, a methodology to include the impact of plants needs to be incorporated into the systems analysis approaches. Such an approach has been identified but not yet included as discussed later in this chapter.

Key Information.

- The complex interactions between landmine signature chemicals, soil and weather require advanced computer simulation tools to determine the changes in vapor concentrations available as a cue to the mine detection dog.
- Several soil physics based simulation models of varying complexity are available; however, advanced training is necessary to understand the appropriate model to use and to evaluate simulation results.
- Laboratory experiments combining multiple factors help to validate the accuracy of simulation model results. However, complete validation is nearly impossible because of the natural variability in all of the factors.
- Simulation models are best used to establish conditions appropriate for mine dog applications and those that should be avoided.
- Landmine signature chemical transport models have been developed that can now be used to assess situational scenarios for routine or troublesome field conditions.
  - Situation specific input data are needed for simulation models to produce realistic results.
    - Data needs: mine-specific flux, soil-water partitioning coefficient, degradation rates and weather history.
- The effect of plants has not been included in landmine chemical signature simulation models.

Complex interdependencies. Figure 27 shows a simplified diagram of the principal landmine soil chemical interactions described in previous chapters. Not included here are some of the complex soil hydraulic processes that influence soil moisture during precipitation and drainage such as hysteresis in the soil characteristic curves. These are important, but do not directly affect the soil-chemical processes included in this report. Most of these processes are included in the various simulation modeling tools to different degrees of sophistication.

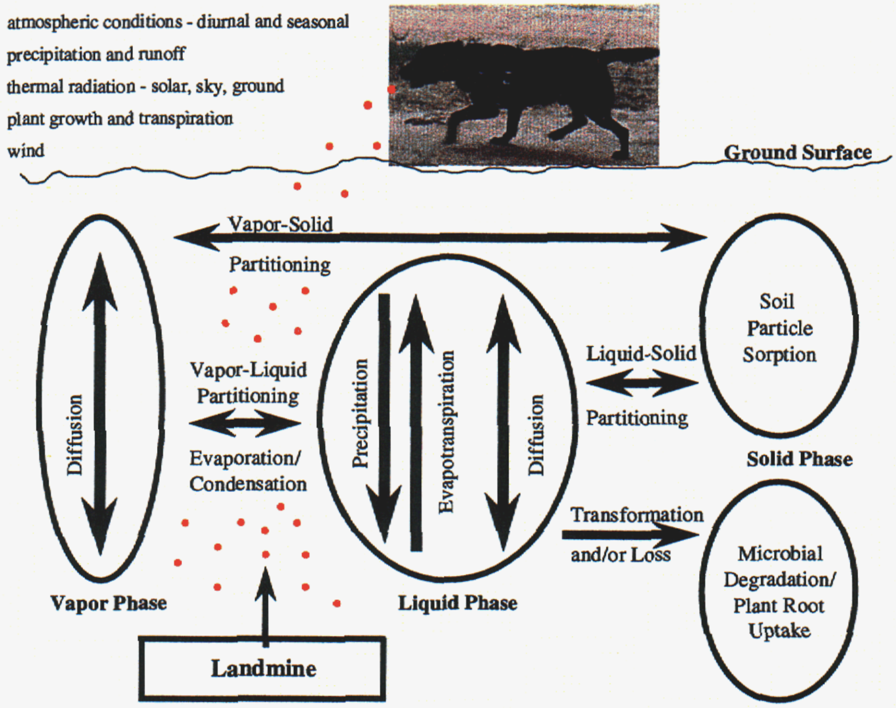


Figure 27. Complex Interdependencies Affecting Landmine Signature Chemicals in Soil

Simulation modeling tools. A number of soil physics based simulation models have been used to evaluate the soil chemical interactions described in this report. Our initial analyses used a one-dimensional screening model developed to compare the pollution potential of various agricultural chemicals. This model is termed the Behavior Assessment Model (BAM) (Jury et al., 1983a, 1984a,b,c), which was later modified to become the Buried Chemical Model (BCM) (Jury et al., 1990). These models used simplified approaches such as constant and uniform soil saturation and temperature, constant water flux, and a constant boundary layer thickness. As discussed in Chapter 8, Weather Factors Affecting Chemical Sensing, many of these parameters are highly variable in reality.

The BAM and BCM models were very useful in categorizing the relative mobility, volatility and persistence of TNT, DNT and DNB chemicals in relation to other well-characterized agricultural chemicals. This initial analysis only required a simple set of input parameters: soil-water partitioning coefficient (K_d), soil-air partitioning coefficient (Henry's constant, K_H), diffusion coefficient in air (D_G), and the bio-chemical half-life ($T_{1/2}$).

The Buried Chemical Model was used to evaluate the effect of differing soil properties, water flux conditions and sequences on the behavior of TNT, DNT and DNB (Phelan and Webb, 1977). The surface vapor flux was evaluated because this parameter was considered to be the principal pathway for detection of buried landmines by dogs. This sensitivity analysis was presented in three conference proceedings

(Phelan and Webb, 1998a; Phelan and Webb, 1998b; Webb et al., 1998) and in a project report from Dr. Jury (Jury and Guo, 1998). Table 19 shows the parameters evaluated and a summary of the impacts.

Table 19. Sensitivity Analysis Summary

Parameter	Impact on steady state surface flux
Soil Bulk Density	Inversely proportional
Henry's Law Constant	Directly proportional
Soil-Water Partition Coefficient	Inversely proportional
Source Flux	Insignificant compared to initial surface concentration
Initial Concentration	Directly proportional
Burial Depth	Increases lag time (very sensitive)
Water Flux (Precipitation or Evaporation)	Evaporation enhances, precipitation depresses
Biochemical Half-life	Insensitive if > 1 year, very sensitive if < 60 days

Jury also performed a 2-dimensional analysis (Jury and Guo, 1998) to evaluate the surface soil spatial variation in vapor flux using similar assumptions to those in his BAM and BCM approaches. The results showed that the surface vapor flux was greatest directly above a source with a small halo up to twice the width of the buried source. The surface flux drops off exponentially with increasing lateral distance from the edge of the mine.

While the Buried Chemical Model was valuable for an initial assessment, the assumptions of constant and uniform liquid content and temperature, as well as a single boundary layer thickness, are obviously great simplifications. In order to address these and other issues, a multidimensional mechanistic code was modified for application to this problem. This code, which is based on the TOUGH code from Lawrence Berkeley Laboratory (Pruess, 1987, 1991), considers air, water vapor, and explosive chemical mass transport and heat flow in a porous media and is able to address many of these questions. This code has been named T2TNT (Webb et al., 1999).

Modifications to TOUGH2 to produce T2TNT included the following:

Chemical Components – Landmines typically emit TNT, DNT, and DNB vapors. The behavior of each of these chemicals is different (vapor pressure, vapor/liquid, liquid/solid, and vapor/solid partitioning), so each component is modeled separately with unique properties specified for each chemical.

Gas Diffusion – Gas diffusion can be an important transport mode for explosive vapors in the subsurface, especially for low moisture content conditions. In order to mechanistically model gas diffusion in a porous medium, the Dusty Gas Model (Webb, 1996) has been implemented.

Liquid Diffusion – Liquid diffusion can be a dominant transport mode for explosive vapors in the subsurface, especially for moderate and high moisture content conditions. Liquid diffusion was not present in the original version of TOUGH2. Liquid diffusion using Fick's Law has been included because of the significant chemical concentration in the liquid phase.

Liquid-Solid Sorption – The solid-liquid partition coefficient was determined to be a fairly sensitive parameter for soil partitioning and transport (Phelan et al., 1999). Laboratory determined values showed that the sorption isotherm is not linear and followed more of a Freundlich relationship (Phelan and Barnett, 2001). In addition, liquid-solid sorption may vary with soil moisture content (EPA, 1999). Thus, in T2TNT, options for a linear sorption isotherm and a Freundlich sorption isotherm have been included. Modification of sorption as a linear function of liquid saturation is also an option.

Vapor-Solid Sorption - Vapor-solid sorption is significant for explosive vapors at low soil moisture contents. The experimental data are well described by the Petersen et al. (1995) function, which was originally developed for volatile organic compounds. The Petersen et al. (1995) expression has been incorporated into T2TNT with chemical specific parameters.

Biodegradation – A simple first-order constant half-life approach has been implemented to model biodegradation of the explosive vapors. From Chapter 6, degradation has been shown to be a function of the soil moisture content and temperature. This function will be incorporated in a future version of T2TNT

Surface Boundary Conditions – Due to the shallow burial depth of many landmines, the fluid conditions surrounding the landmine are strongly influenced by the surface conditions. The parameters necessary to adequately model the surface boundary conditions include: solar and long-wave radiation, the surface boundary layer that is a function of wind speed and soil-air temperature differences, precipitation and evaporation at the surface, plants and their root systems, and the diurnal and seasonal variation of these parameters.

The effect of surface boundary conditions including the boundary layer thicknesses and the effect of plants is complex. For inclusion into T2TNT, a number of existing models have been evaluated. As a result, the SiSPAT model developed by Braud et al. (1995, 1996) has been selected for inclusion into T2TNT with the kind permission of M. Vauchlin of LTHE in Grenoble, France. Subroutines from SiSPAT are included directly into T2TNT as necessary. SiSPAT has been successfully applied to a number of field studies as documented by Braud et al. (1995, 1996), and Boulet et al. (1997), and more are in progress. Therefore, SiSPAT provides a well-documented and tested approach for modeling the soil-plant-atmosphere interface in the T2TNT code.

At the present time, the surface boundary conditions for a bare soil have been implemented, including the surface boundary layer, solar and long-wave radiation, precipitation, and other conditions including the diurnal and seasonal variation of the parameters. Incorporation of the plant portion of the SiSPAT model into T2TNT is planned for a future version.

Capillary Pressure Curve - The typical representation of the capillary pressure curve breaks down at low liquid saturations. The curve asymptotes to a liquid residual saturation where the capillary pressure goes to minus infinity. Below this residual saturation, the capillary pressure is undefined causing computational problems. In order to alleviate this situation, a methodology has been developed to extend the capillary pressure curve to include the dry region down to zero liquid saturation (Webb, 2000). This technique results in a finite value of the capillary pressure below liquid residual saturation, which agrees with the available data.

Calculation of the boundary layer thickness is a considerable task involving turbulence modeling and meteorological conditions in the atmosphere above the boundary layer. Due to this complex behavior, simplified techniques are usually employed based on similarity functions (Arya, 1988). The solution of these equations gives the total boundary layer resistance from the surface to a reference level, which is typically 10 m for wind and 2 m for temperature (Braud, 1996). Most of the resistance is in the first few cms directly above the soil surface. For simplicity, a stagnant boundary layer thickness is often defined, which is simply the boundary layer resistance divided by the appropriate diffusivity or thermal conductivity neglecting turbulent transport. This stagnant boundary layer thickness is much less than the physical value and is a lower bound on the physical boundary layer thickness.

Based on simplified turbulence profiles, most of the mixing and dilution takes place in a physical boundary layer thickness ten times the stagnant value. Thus, if the stagnant boundary layer thickness is 1 cm, the physical boundary layer thickness is approximately 10 cm. Of this thickness, about half the mixing and dilution takes place in the lower 10% of the boundary layer, or in the lower 1 cm in this example.

Based on the implementation in SiSPAT, Figure 28 shows the impact of the wind speed and soil-atmosphere temperature difference on the stagnant boundary layer thickness for water vapor. Under neutral conditions, where soil and air temperatures are equal, wind speeds greater than 1 m/s cause the stagnant boundary layer to diminish to less than 1 cm. Thus, the physical boundary layer for water vapor mass transfer is on the order of 10 cm. The chemical boundary layer thickness is smaller than the water vapor value due to the differences in transport coefficients (Webb and Phelan, 2000) and the fact that the chemical boundary layer is developing. Thus, the chemical boundary layer is certainly much less than 10 cm for these conditions. Dogs must sniff for landmine signature chemicals well within the chemical boundary layer or risk missing a mine vapor cue.

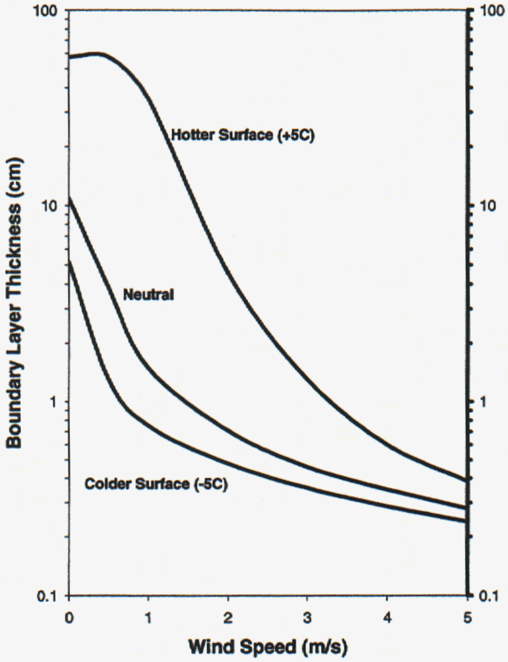


Figure 28. Boundary Layer Thickness

Model Validation. In order evaluate the physics and to gain confidence in the T2TNT model, laboratory-scale soil column experiments were conducted. Laboratory-scale soil column experiments were designed after those of Petersen et al. (1996) and Spencer and Cliath (1973). Both methods used headspace measurements to estimate flux of organic chemical from the soil surface. We used the soil suction control apparatus of Spencer and the soil moisture measurement approach of Petersen et al. (1996) in our experiment. Figure 29 shows a picture of the soil column test apparatus. Details of the experimental methods, parameter estimation and model formulation are described in Phelan et al, 2000.

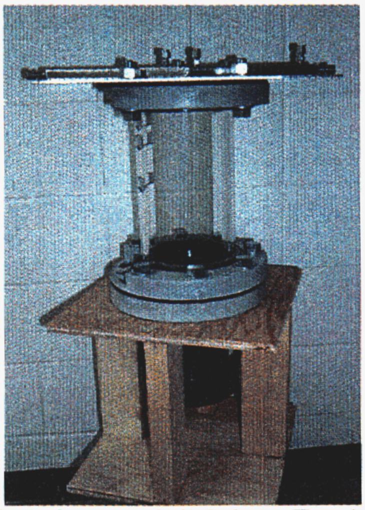


Figure 29. Laboratory Soil Column Test Apparatus.

In the design of this test, soil moisture of about 0.25 cm^3/cm^3 was desired to maintain the soil pore space at about 50% liquid saturation. Thus, vapor-solid sorption is not a factor in these test results. Data from the water content reflectometers showed that the soil moisture distribution remained relatively constant over the test duration and showed an expected gradient with higher moisture contents at the bottom of the soil column.

DNT was added to the soil column 3.5 cm below the soil surface. The surface flux of DNT was measured in the experiment using Solid Phase Micro Extraction (SPME) fibers. The flux of DNT into the plenum increased by about a factor of 10^4 over the duration of the test (Figure 30). The experiment was sacrificed on day 29 and samples were collected for soil moisture and DNT residues. Simulation results from T2TNT were compared to the data and are also shown in Figure 30. Based on the soil-water partitioning coefficient data the low range liquid-solid sorption coefficient, K_d, of 1.5 mL/g was selected for the initial simulations to compare to the data. As shown in Figure 30, while the surface flux as a function of time has the right shape, the values are an order of magnitude or more below the experimental data.

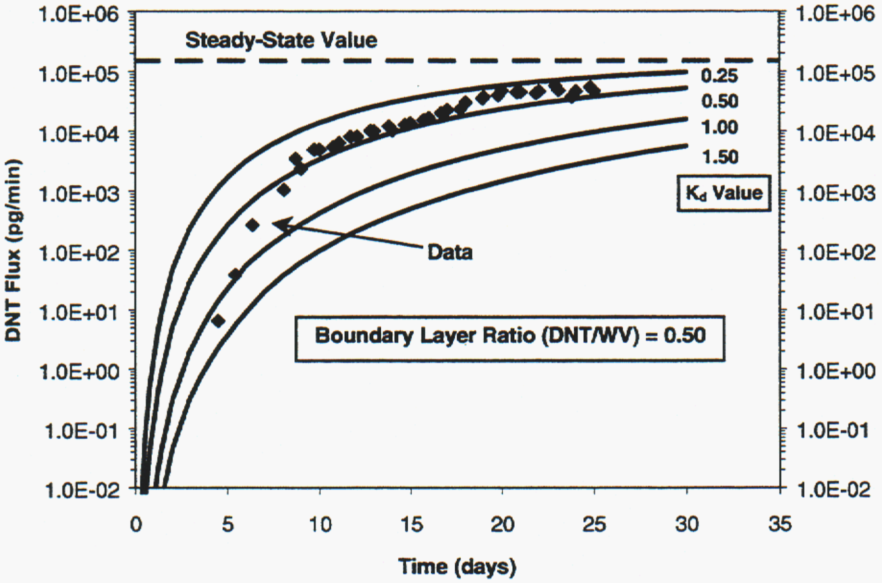


Figure 30. Data Model Comparisons - Effect of K_d Value

The sensitivity of the K_d factor is readily apparent in Figure 30. At this stage of the project, the Fruendlich soil-water partitioning isotherm had not been incorporated into T2TNT. Another factor causing the discrepancy in values obtained from measured K_d versus data-model comparisons is in how the measured K_d is obtained. The low soil:water ratio in the batch equilibration K_d method allowed for near complete contact of the soil particle surface to the DNT in the water and allowed for migration into secondary porosity of soil minerals. In a soil column test this is not the case. Some proportion of soil surface area is not in contact with the water (and DNT) due to partial liquid saturation and surface-to-surface contact of soil particles. Because of the uncertainty in the value of K_d in the soil column test it was decided to vary the value of K_d until a reasonable match to the data was found as given in Figure 30. The final value of K_d that matches the data reasonably well is ~0.5 mL/g. The results from this initial test indicated that K_d may be influenced by partial saturation of the soils and that this should be considered in T2TNT. This phenomena has been previously recognized (EPA, 1999); however, there have been mixed results to define the relationship of soil-water partition coefficient to soil saturation.

A second test was performed using the same apparatus and operating conditions. This test evaluated the effects of wetting and drying phenomena on the vapor flux of DNT at low liquid saturation, which include vapor-solid sorption phenomena. Details of the materials, methods and results are given in Phelan et al., 2001.

The data and model comparison for the surface flux of DNT is shown in Figure 31 that reflect the variation in soil column conditions. The initial relative humidity of the air was ~50%. At Day 35, the relative humidity was changed to 0%, which increased the evaporation rate and the DNT vapor flux. At Day 44, a drying event was imposed that dramatically lowered the soil saturation and the DNT vapor flux. A wetting event at Day 69 significantly increased the DNT vapor flux and the soil saturation. Another wetting-drying cycle was imposed after Day 69 as can be clearly seen.

Unlike the prediction given by Phelan et al. (2000) in Figure 30, no soil-water partitioning parameters were varied to try to improve the data-model comparison. However, T2TNT now includes a Freundlich isotherm for the soil-water partition coefficient, which is also weighted linearly as a function of soil saturation. The simulation results show excellent agreement with the data, especially considering the three order-of-magnitude variations during wetting-drying cycles. The initial surface flux out to 35 days is very close to the data including the transient variation up to that point. Up through Day 35, surface flux results from Test 1 and 2 were very consistent demonstrating good control of fixed experimental parameters. In Test 2, the increase in the surface flux due to the change in the inlet air relative humidity at Day 35 is seen in the model predictions, although the magnitude of the increase is under predicted. The dramatic change in the surface flux data of about three orders of magnitude caused by the wetting and drying events is also reflected in the model predictions, including the timing. The maximum differences are about a factor of 3, which is excellent considering the 5000-fold change in DNT surface flux.

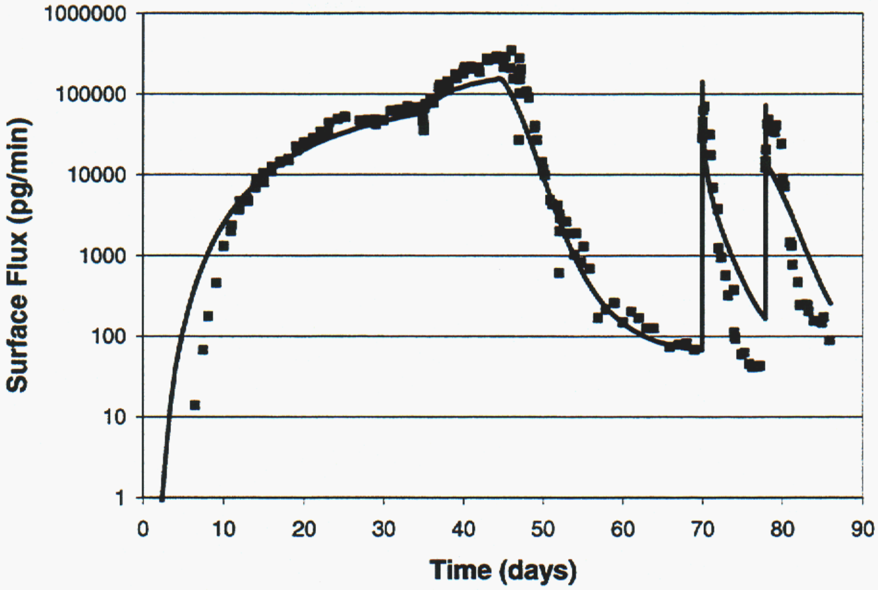


Figure 31. T2TNT Data Model Comparisons

The data-model differences that occurred during the wetting and drying cycles may be due to hysteresis in the soil moisture characteristic curves. Hysteresis causes differences in the soil moisture content at a given soil tension during wetting and drying periods (Hillel, 1982). At low moisture contents, this can cause significant differences in model estimates (which uses a drying soil moisture characteristic curve) compared to experimental data. Unfortunately, measurement of wetting and drying soil-moisture characteristic curves would be laborious and may be unnecessary for this application.

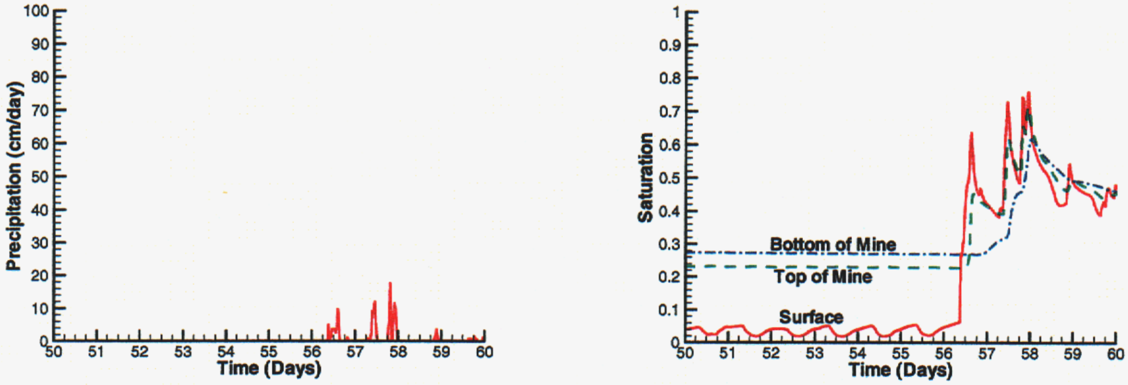
The results from this test show how important soil-vapor partitioning can be to the vapor released by surface soils as indicated by the dramatic rise in the surface flux after wetting. In addition, the soil-water partition coefficient must be modeled with a Freundlich isotherm rather than a linear one, and the soil-water partition coefficient must be weighted for soil saturation. These test results give confidence in the predictive capability of the T2TNT code.

Demonstration Calculations. In order to estimate the influence of weather conditions, demonstration calculations have been performed. These calculations assumed a constant chemical source flux and a constant biodegradation rate for each chemical and used actual weather data. The results indicate the variability in the chemical concentrations on the soil surface over the long-term (1 year) and the short-term (daily). Details on the input data requirements and simulation results can be found in Webb and Phelan (2000). The weather data from a standard weather station consisted of the following: atmospheric pressure, air temperature, relative humidity, solar radiation, precipitation, wind speed and wind direction at four elevations. In addition to these parameters, the long-wave radiation from the atmosphere must be included. Because it was not measured, long-wave radiation was estimated from measured weather parameters.

Figures 32 (a) through (h) show the diurnal variation in T2TNT simulation results showing key factors of precipitation and resulting soil saturation, surface radiation balance and resulting soil temperatures at several depths, as well as the chemical concentrations of TNT, DNT and DNB expressed as total concentrations and as separate solid, liquid and gas phase concentrations. Of note is the dramatic increase in surface gas-phase concentrations of all three chemicals following a rainfall event.

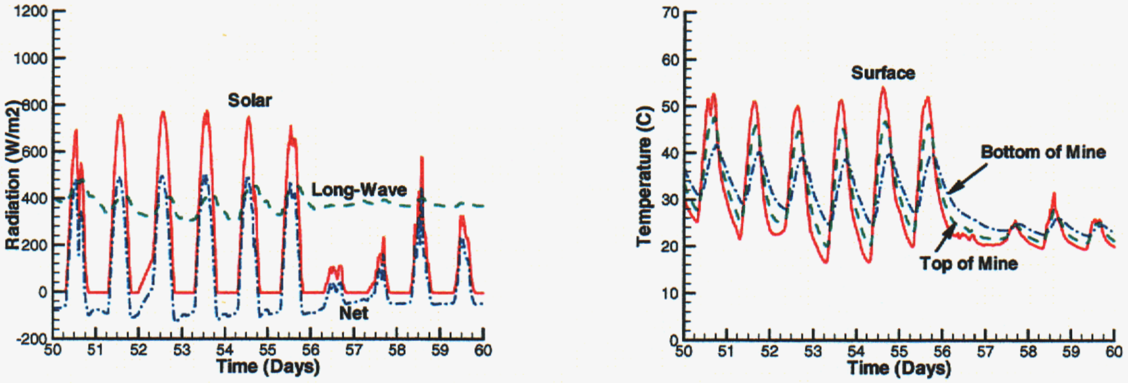
Figures 33 (a) through (f) show the seasonal variation in T2TNT simulation results showing the surface soil liquid and gas phase concentrations of TNT, DNT and DNB. The seasonal variations in the liquid phase are impacted by changes in soil moisture due to precipitation and the gas phase variations are impacted by changes in the liquid phase concentrations and temperature effects on the vapor-liquid partitioning coefficient (Henry's Law Constant). Of note is the near uniformity of the maximum and minimum values indicated in Figure 33 (a) through (f). This is likely due to the fact that the source release rate and the degradation rate for each chemical are held constant over time, which is a significant simplification.

These demonstration calculations show the capabilities of T2TNT in expressing numerous interdependent input data and output results that are extremely valuable in understanding the complex phenomena in this problem. One aspect that requires yet more refinement is the variability of the degradation rate as a function of soil moisture and temperature, scaled according to soil type. In addition, the effect of plants on the results should be added to T2TNT.



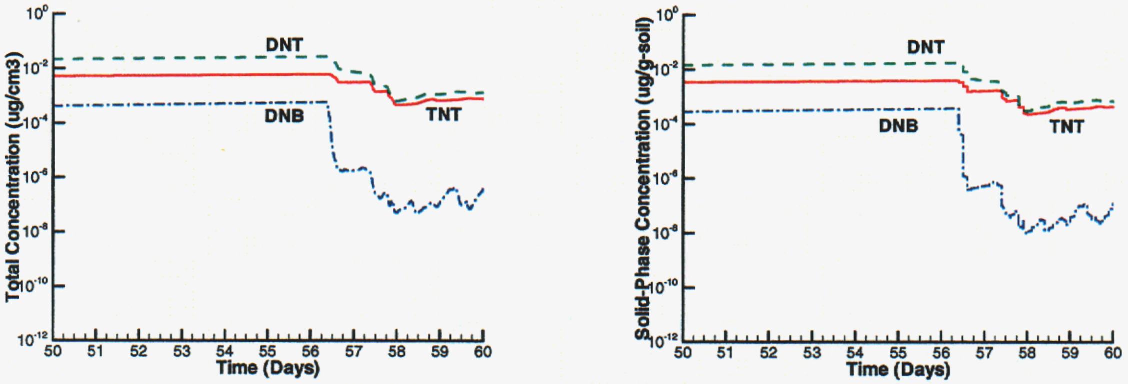
(a) Precipitation

(b) Saturations



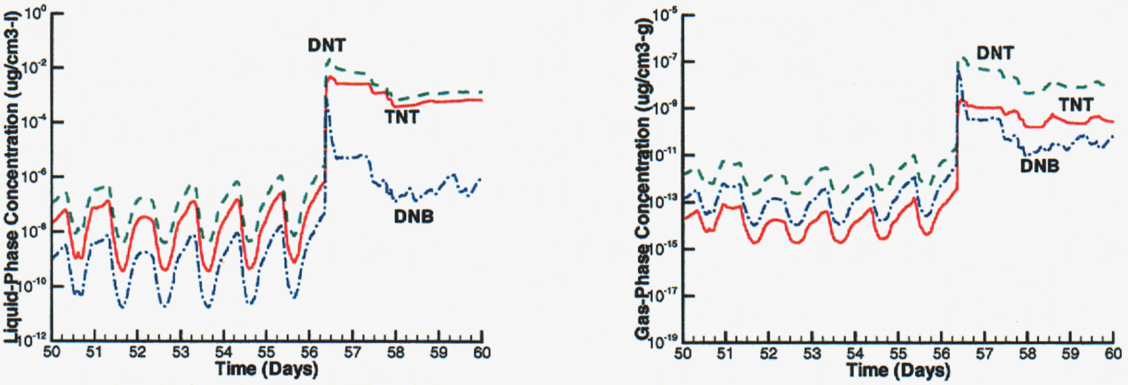
(c) Surface Radiation Balance

(d) Temperatures



(e) Surface Total Concentration

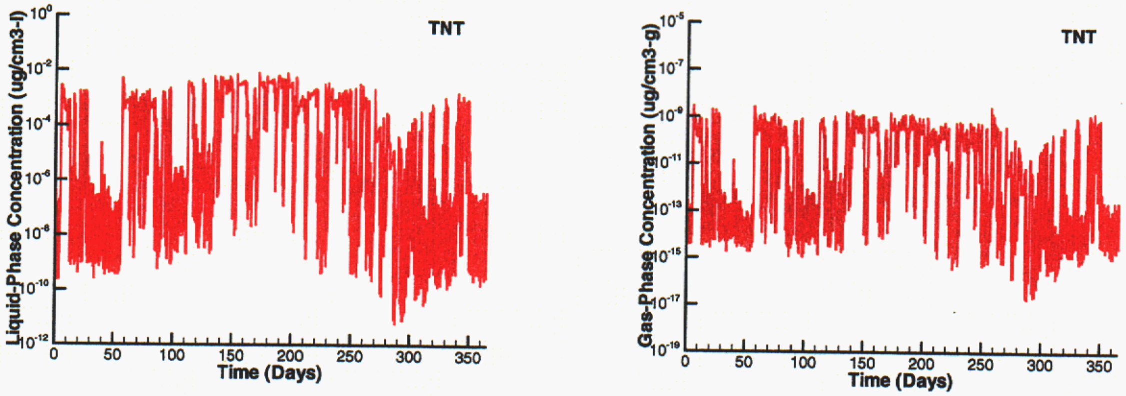
(f) Surface Solid-Phase Concentration



(g) Surface Liquid-Phase Concentration

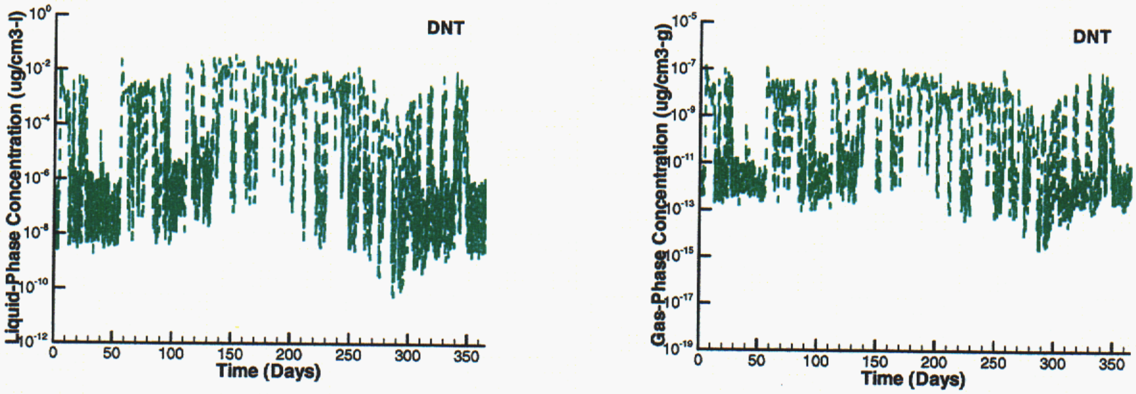
(h) Surface Gas-Phase Concentration

Figure 32. Diurnal Variation of Various Parameters for the Period 50-60 Days



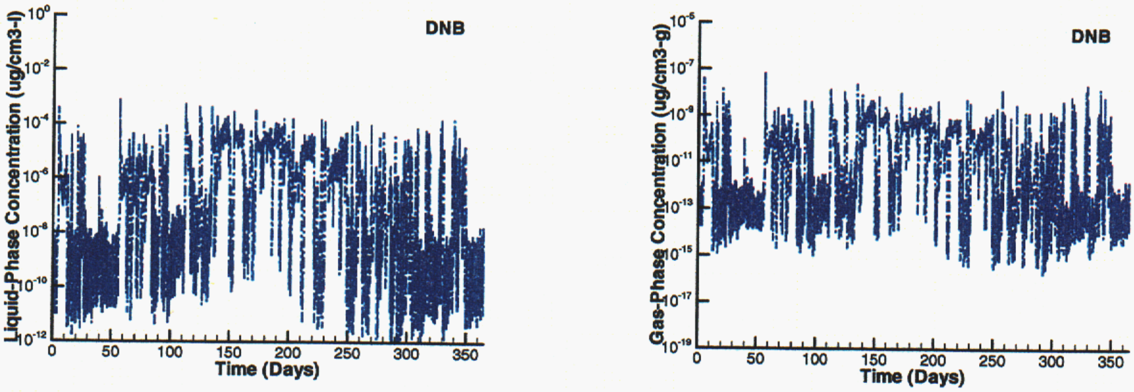
(a) Surface Liquid-Phase Concentration of TNT

(b) Surface Gas-Phase Concentration of TNT



(c) Surface Liquid-Phase Concentration of DNT

(d) Surface Gas-Phase Concentration of DNT



(e) Surface Liquid-Phase Concentration of DNB

(f) Surface Gas-Phase Concentration of DNB

Figure 33. Seasonal Variation of Surface Liquid- and Gas-Phase Concentrations

Summary. In this chapter, the individual soil-chemical interactions were combined into a complete landmine-soil-weather systems evaluation tool. This tool provides for the complex interdependent interactions that occur in the soil and produce estimates of the vapor concentrations and surface soil residues for comparison to mine dog performance capabilities. The effect of plants is currently not included in T2TNT. This tool can now be used to evaluate various scenarios – certain combinations of particular mine types (leakage), soil properties, and weather patterns. Differences in soil vapor emanations for scenarios in regional areas (Afghanistan, Cambodia, Mozambique, Angola) may demonstrate the critical nature of maintaining optimal mine dog performance or the futility of certain situations where vapor levels are well below typical mine dog vapor sensing capabilities.

10.0 Soil Residues from Landmines

Introduction. Sampling and chemical analysis of soils (and vapor above soils) provides direct evidence of the type and magnitude of landmine signature chemicals available as cues for the dog. These measurements are valuable in understanding the true variations in soil residues and vapor concentrations as a function of mine type, soil type, and weather history. One unfortunate problem encountered, however, is that even with optimized sample collection, sample preparation and highly sensitive laboratory analytical chemistry methods, the net soil residue is often below method detection limits. This problem is even more acute for vapor sampling and analysis, as there is much less chemical in the vapor phase compared to the soil (Chapter 5). However, when vapor levels are below detection limits but soil residues are detected, vapor concentrations above the soil can be estimated using the phase partitioning relationships described in Chapter 5. These vapor levels, whether measured or estimated, can be compared with vapor sensing thresholds of individual mine detection dogs to evaluate the probability of detection for conditions specific to the mine type, soil type and weather history.

Key Information.

- Chemical analysis of soil sample provides evidence of the actual amount of landmine signature chemicals from a landmine.
- Soil sample results have found TNT, DNT, 4A-DNT and 2A-DNT as the most prevalent landmine signature chemicals.
- Surface soil residues found are low, typically less than 100 ng/g.
- Soil sample method detection limits of 1 – 10 ng/g limit the measurement of lower concentrations that may still be useful in generating vapor cues for dogs.
- Soil residue values can be translated into vapor concentrations in the air boundary layer above soils for comparisons to dog vapor sensing thresholds.

Soil Sampling and Analytical Methods. Modern methods for soil sampling and chemical residue analysis developed for environmental pollution assessments (EPA SW846, 2002) can be used for landmine soil residue assessments. Sampling strategies have been developed that emphasize location specific (grab samples) or area specific (composite samples) with many recommendations for sample sizes compared to the area of interest. Composite samples combine several subsamples that provide an average over an area. The variation in soil residue values surrounding the landmine is lost in preference for an average over a larger area. For field landmine soil sampling, a grab sample is desired that provides a point value at that particular time while still leaving undisturbed areas for sampling at later dates. This method generates more samples, but at the same time provides a better description of the variation of soil residues surrounding the landmine. However, once a sample is collected degradation can still proceed. Options to halt the degradation process include processing the sample immediately (impractical for most field situations), storing the sample as cold as possible (on ice the temperature is 2-4°C, which can still allow degradation to occur), or air drying the sample (which causes a minor loss of ~10-15%, Cragin et al, 1985).

Several laboratory chemical analysis methods are available to quantify the chemical residues in soils. After careful mixing, aliquots of soil (1 to 20 grams) are removed from the sample container, mixed with acetonitrile or acetone (1:4 ratio up to 1:1 ratio, weight/volume) and placed into a temperature controlled (10°C) ultrasonicator for up to 18 hours (Walsh and Ranney, 1999). Quantification can be performed via high-pressure liquid chromatography (EPA SW846 Method 8330), or by gas chromatography with either a electron capture detection (EPA SW846 Method 8095), thermionic detector (Hewitt et al, 2001), nitrogen/phosphorus detector (Hewitt et al, 1999; Kjellstrom and Sarholm, 2000), or mass spectroscopy.

The analytical method detection limit is an important concept in landmine soil residue evaluations because frequently the analysis finds no chemical residue. This does not mean that no residue exists – it means that if there is any, it is below the detection limit for the chemical analysis method. Method detection limits vary with the soil, extraction method, and sensitivity of the instrumental method. Typical method detection limits for TNT and DNT are about 1 to 10 ng/g.

Soil Residues. Several studies have evaluated specific mine types on single occasions; however, due to the large time and resource commitment necessary to monitor soil residues over time, there have been few studies that have evaluated seasonal variations in soil residues. Chambers et al (1998) report soil residues after 150 days since burial of a TM62-P antitank mine. Surface soil values for TNT were very large (2030 ng/g) and DNT was below the method detection limit (<10 ng/g). Subsurface values ranged from 20 to 160 ng/g TNT and 20 to 2,700 ng/g DNT from above and to the side of the mine. Desilets et al. (1998) measured soil residues from unspecified antitank mines 10 months after burial and found TNT residues of 2 to >8 ng/g using a prototype soil-solvent extraction ion mobility spectroscopy analyzer.

Kjellstrom and Sarholm (2000) reported on soil samples obtained from antitank and antipersonnel mines in Bosnia that had been buried for three months and three years in both a deciduous forest and a gravel road. Selected sample results are shown in Table 20.

Table 20. Soil Residues from Bosnia (Kjellstrom and Sarholm, 1998)

Analyte	PMA2*	TMA4*	TMA4**
TNT (ng/g)	720	96	160
2,4-DNT (ng/g)	110	380	5,400
1,3-DNB (ng/g)	83	-	600
2A-DNT (ng/g)	160	16	1,600
4A-DNT (ng/g)	210	28	690

* gravel road
** deciduous forest

The only multi-season landmine soil residue data set came from a long-term monitoring project at the DARPA developed Fort Leonard Wood Site. Jenkins et al. (2000) reports on about 1000 soil residues taken over four sampling events spanning 16 months since burial. Over this time period, soil samples were obtained surrounding the following landmines: TMA5, TMM-1, PMA-1A, PMA2, Type 72. Some very important observations were found through this effort:

- Surface soil samples did not always show detectable residues at every sample location. In some cases, detectable residues were more frequently found beyond the boundary of the landmine than directly above it.
- The three most prevalent compounds were 2,4,6-TNT, 2,4-DNT and both 4A-DNT and 2A-DNT (degradation by-products of TNT).
- The frequency that surface samples detected a specific analyte at a specific landmine type was typically less than 50% (i.e. less than half of samples taken had detectable residues).
- Over the five sampling events, the frequency of detection typically increased (i.e. more samples found detectable residues as time progressed)
- Table 21 presents a summary of the surface soil residues showing
  - Frequency of detection ranges from 10 to 48% over a large number of samples
  - TNT residues are much lower than DNT
  - DNB residues were generally absent (faster degradation, lower soil sorption, greater volatility)
  - 2A-DNT and 4A-DNT typically show much greater values
    - Phase partitioning parameters for these compounds have not been compiled or measured; however, vapor pressure values for these compounds have been reported to be 1000 times less than TNT, implying that these compounds will have minimal vapor concentrations compared to TNT or DNT.
  - Median values (half of the sample set are greater and half less than this value) are very low for all compounds.

Table 21. Summary of Surface Soil Residues (ng/g) Collected Near Mines in August 1998 and April, July, November 1999 (Jenkins et al., 2000)

Chemical	Analyses	Detections (%)	Maximum	Mean	Median
TMA 5					
2,4,6-TNT	172	33 (19)	44	8	4
2,4-DNT	172	37 (22)	248	34	16
2A-DNT	172	48 (28)	685	62	17
4A-DNT	172	48 (28)	586	60	17
PMA-1A					
2,4,6-TNT	95	10 (11)	2	4	4
2,4-DNT	95	25 (26)	227	8	32
2A-DNT	95	27 (28)	600	109	44
4A-DNT	95	31 (33)	459	112	44

Figure 34 shows unpublished data on the surface soil spatial distribution of 2,4-DNT surrounding a TMA-5 and PMA1A landmine (T. Jenkins). Soil residues varied greatly in the vicinity of the landmine, but also showed a directional vector downslope. This has been attributed to surface water runoff transport of soil residues as particles or redeposition of DNT as a solute.

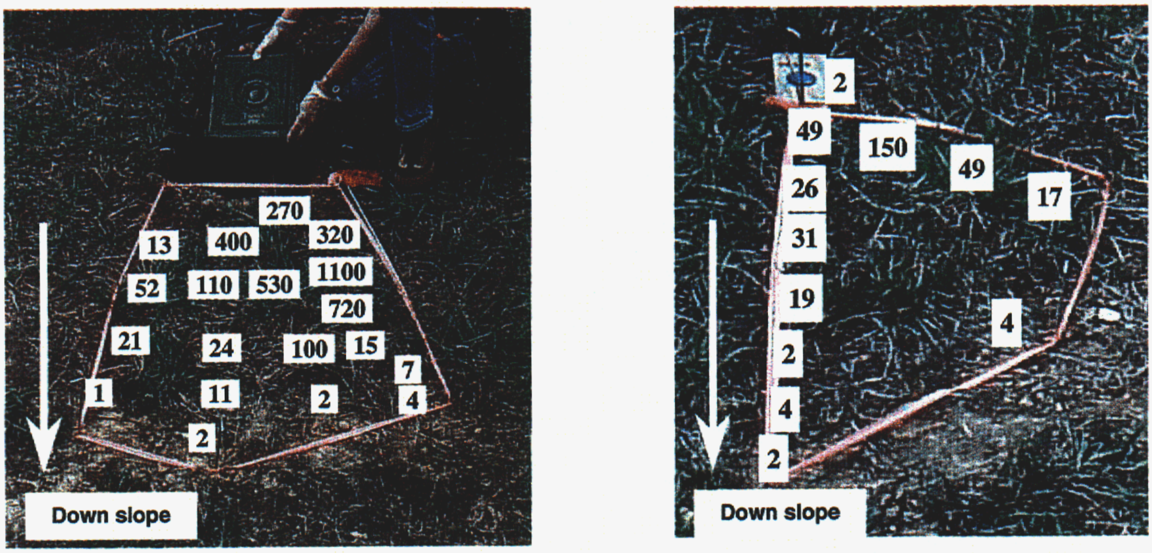


Figure 34. Spatial Distribution of 2,4-DNT (ng/g) in Surface Soils Near TMA-5 (left) and PMA1A (right) (Jenkins, unpublished data)

Vapor Concentration Estimates. Reports on vapor samples from landmines in the field are rare. The probability of detecting a landmine signature vapor with current equipment is low because the vapor concentrations are extremely small. Jenkins et al. (2000) used higher soil residue samples from the Fort Leonard Wood mine site and sampled the headspace in a small vial. Soil/air partition coefficients ($K_{s/a}$) were calculated using the ratio of the soil residue to the vapor concentration. These coefficients are equivalent to the $K_{d'}$ coefficients described in Chapter 5. Calculated $K_{s/a}$ values for TNT and DNT at soil moisture contents of 10 to 19% (wet weight) are very similar to the $K_{d'}$ values shown in Figure 14. In addition, values tabulated for 2A-DNT and 4A-DNT are only 15 to 18 times greater than for 2,4-DNT, indicating that these compounds may be another vapor available as a cue for the dog. Using median surface soil concentrations and median $K_{s/a}$ values, Jenkins et al (2000) estimated vapor concentrations in the air boundary layer above landmines and are shown in Table 22.

Table 22. Estimated Vapor Concentrations in the Air Boundary Layer from Surface Soils Residue Data and $K_{s/a}$ Values

Chemical	TMA5		PMA1A	
	ng/L	ppt	ng/L	ppt
2,4,6-TNT	9.4×10^{-4}	0.1	8.5×10^{-4}	0.1
2,4-DNT	1.5×10^{-1}	20	3.0×10^{-1}	40
2A-DNT	9.0×10^{-3}	1	2.3×10^{-2}	3
4A-DNT	1.1×10^{-2}	1	2.0×10^{-2}	2

Summary. Soil residues from samples obtained at the ground surface in close proximity to a landmine provide the best direct evidence on the amount of chemical signature available as a cue for a dog.

Unfortunately, many of these measurements are found to be below the chemical analysis method detection limit. Nevertheless, soil residue values help tremendously in defining conditions promising for mine dog detection work. Summary statistics for one minefield (Fort Leonard Wood, USA) show that the principal landmine chemical signature compounds are TNT, DNT, 2A-DNT and 4A-DNT. The absence of DNB confounds much of the previous work (Chapters 3 through 6) that indicated DNB should be a target compound. More work is needed to evaluate the reason for the absence of DNB in soils near landmines.

The two primary degradation by-products of TNT, 2A-DNT and 4A-DNT, have been frequently disregarded as unimportant vapor signatures for landmine detection on the judgement that the vapor pressure could be about 1000 times lower than that of DNT. However, soil residues of 2A-DNT and 4A-DNT were frequently higher than that of either TNT or DNT, and laboratory headspace soil-air partition coefficient determinations indicate that 2A-DNT and 4A-DNT may be at higher vapor concentrations than previously considered. More work is needed to evaluate the significance of 2A-DNT and 4A-DNT as a contributor to the landmine chemical vapor signature.

11.0 Vapor Sensing Threshold of Dogs

Introduction. Observation of the dogs' ability to locate hidden objects (lost people, contraband, and explosives) by vapor sensing has occurred over the last century. However, very little work has been completed that describes how the dog can accomplish these amazing tasks. Only recently has work been performed that has explored the chemical compounds dogs use to recognize landmines (Johnston et al, 1998), the aerodynamics of how the dog inhales vapors and aerosols (Settles and Kester, 2001), and compared the performance of dogs to laboratory instrumentation and detection thresholds for narcotics and other non-energetic materials (Furton and Meyers, 2001).

Key Information.

- Vapor sensing thresholds of trained mine detection dogs are difficult to determine because the dogs' capabilities are so much greater than laboratory chemical measurement instrumentation.
- The psychology of dog testing is very important because the dog can find alternative methods to achieve a reward and confound the testing regime.
- Some dogs that were trained only on TNT could also find DNT.
- Some dogs could not recognize even the highest vapor standards.
- Some dogs could sense down to the limits of one molecule per sniff, but not all dogs could reach this level.
- Variations in training history and operational methods also translated into differing capabilities.

Vapor Sensing Threshold Screening Tests. In an initial effort to determine the lower vapor sensing thresholds for landmine detection dogs, Phelan and Barnett (2002) prepared soil samples containing known residues of TNT or DNT and, by ten-fold dilution (decade), produced soil residues over a wide dynamic range. By using the phase partitioning relationships (Chapter 5), the headspace vapor concentrations present adjacent to these soils were estimated.

Table 22 shows the typical soil residues measured before presentation to the dogs. In order to determine the extremely low sensing thresholds of the dogs, the soil samples were diluted below the soil analytical method detection limit. Because the soil dilutions demonstrated a linear decade decline, values below the method detection limit were extrapolated from the last measurable value. Also, the reader must be cautioned in the accuracy of the estimated headspace vapor concentrations, because small variations (1%) in soil moisture in dry soils creates larger variations (~ 100 fold) in headspace vapor concentrations. Nevertheless, this method was successful as a screening tool to determine the vapor sensing threshold of trained mine detection dogs. Figures 35 and 36 show the headspace vapor concentrations of the TNT and DNT as a function of soil moisture content for the soil residues shown in Table 23.

Table 23. Decade Dilution Soil Residues (ng/g)

Jar	TNT	DNT
T-1	98,320	
T-2	11,060	
T-3	1,080	
T-4	100	
T-5	11	
T-6	1	
T-7	<MDL	
T-8	<MDL	
D-1		6,850
D-2		650
D-3		61
D-4		6
D-5		<MDL
D-6		<MDL
D-7		<MDL
D-8		<MDL

MDL – minimum detection limit

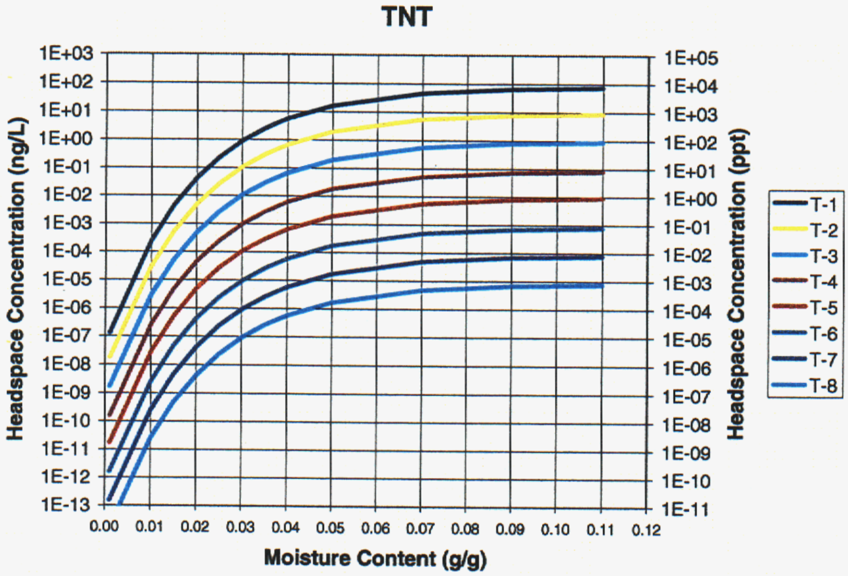


Figure 35. TNT Soil Headspace Concentrations as a Function of Soil Moisture Content

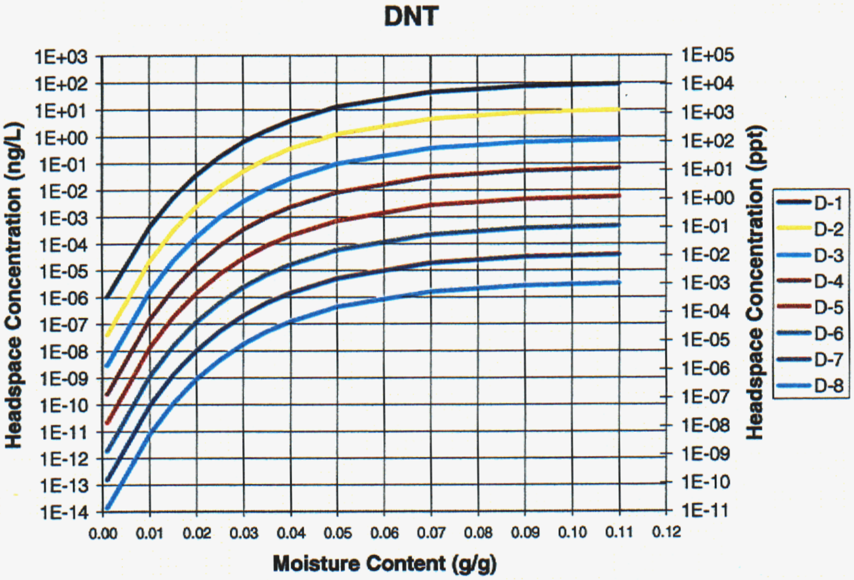


Figure 36. DNT Soil Headspace Concentrations as a Function of Soil Moisture Content

Three groups of mine detection dogs trained by different means were presented these vapors on four different occasions and with different methods. Each dog training organization expressed the importance of presenting the test samples to the dogs in a manner in which they are accustomed, so that they are not distracted by the novelty of a new item or require additional training specific to the test sample. Figures 37 through 40 show the soil vapor standards in the various test configurations. Observations from this work showed:

- Some dogs that were trained only on TNT could also find DNT.
- Some dogs could not recognize even the highest vapor standards.
- Some dogs could sense down to the limits of one molecule per sniff (10^{-10} ppt, see Table 5), but not all dogs could reach this level.
- Variations in training history and operational methods also translated into differing capabilities.
- The psychology of dog testing becomes very important as the dog can find alternatives methods to achieve a reward and confound the testing regime.

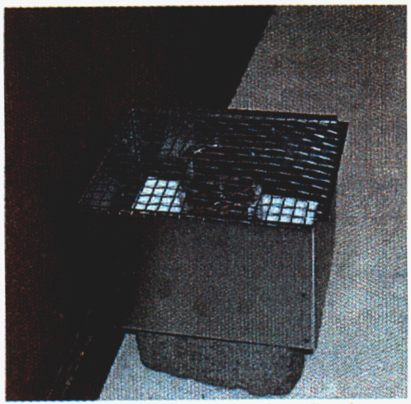


Figure 37. Jar in Testing Station

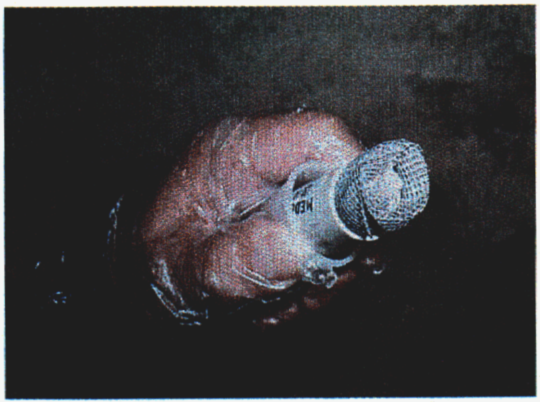


Figure 39. MEDDS Filter Soil Vapor Generator

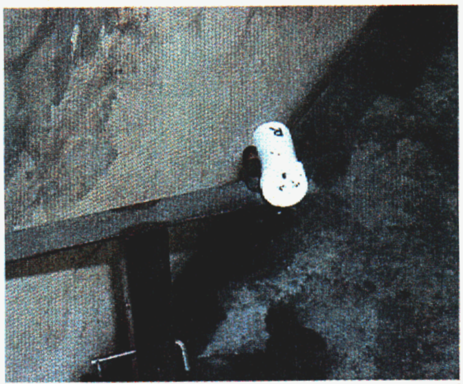


Figure 38. MEDDS Vapor Sample Presentation Method

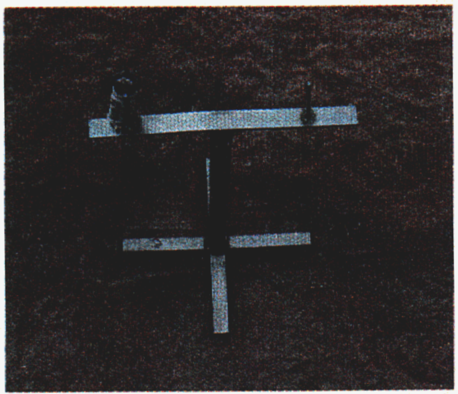


Figure 40. REST Sample Presentation Method

Sensing by Soil Particle Inhalation. The initial focus of the vapor sensing threshold testing was to determine if soil particle inhalation was a significant mechanism in the dogs' ability to detect buried landmines. Soil particles containing trace amounts of TNT or DNT produce extremely trace vapor levels. Wetting dry soil particles displaces the TNT or DNT, producing large increases in vapor levels (~ 10^5). TNT and DNT soil residues were created to produce a vapor level below which the dogs could not identify. If upon inhalation of these dry soil particles, the dogs could recognize the odor, then this implies moisture in the dogs' nose releases sorbed vapors and inhalation of dry soil particles becomes an important mechanism contributing to the low detection capability. Figure 41 shows the original planned testing regime that would allow headspace vapor levels to span almost ten orders of magnitude. However, the higher range of headspace chemical signature vapor levels under wet conditions was abandoned after the first set of mine detection dogs were found to be able to recognize the low concentration vapors from the dry soils. While landmine detection by inhalation of soil particles containing sorbed TNT or DNT may be another mechanism for successful recognition, it is not necessary, because of the excellent trace vapor detection capabilities of the dogs.

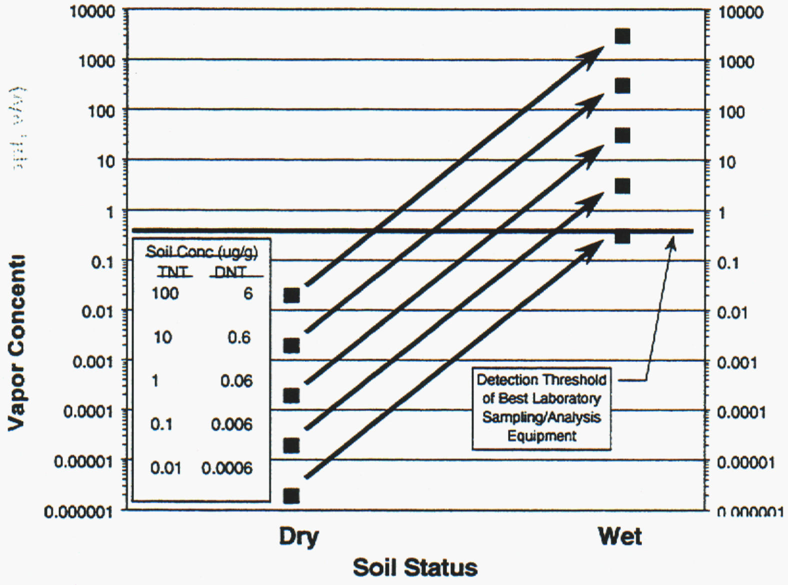


Figure 41. Initial Testing Strategy

Comparison to Vapor Estimates from Field Landmine Soil Residues. At the end of Chapter 10, a summary of surface soil samples from buried landmines was presented. Surface soil residues of landmine signature chemicals were not always measurable, but when detectable, were typically found in the range of 1 to 100 ng/g (Table 21). For TNT, this translates into a T-4 to T-6 dog testing level (Table 23). For DNT, this is about a D-3 to D-5 level. This suggests that dogs need to be consistently working at the T-6 or D-5 level to be successful in detecting landmines in dry soil conditions. However, in wet soil, this may be relaxed to a T-4 or D-3 levels as more vapor is present with wet soils compared to dry soils.

We must recognize that these are generalities and mine dog vapor sensing performance must ultimately be linked to the specific mine flux, soil type and weather cycle combination for a particular mine action problem. Much more work is needed to correlate landmine soil residues and mine dog vapor sensing performance to establish minimum mine dog qualification standards.

Summary. The vapor sensing capabilities of dogs are almost universally undisputed; however, measuring the dogs' performance at ultra-trace vapor levels is difficult because the sensitivity of chemical measurement technology is far inferior compared to that of the dog. Initial screening methods to determine the vapor sensing threshold of dogs were developed using soil headspace vapor sources that were quantified by extrapolation beyond measurable levels in soils and estimation methods that correlate soil residues to vapor concentrations. Even with the uncertainty in this initial screening method, the method does confirm the ultra-trace vapor sensing capabilities of the dog. However, there were differences noted in the sensitivity of different dogs, in the sensitivity in a single dog on sequential days, and in the reliability of an individual dog at a given vapor level. Much more work is needed to establish the probability and reliability of detection as a function of training and working history, breed, and other factors, yet to be determined.

12.0 Summary

Trace chemical detection of buried landmines is a complex subject; however, when carefully analyzed, the complexities can be separated into individual elements for study, comparison and evaluation. This report has summarized the data, information, and conclusions from previous research efforts in analytical chemistry, soil physics, and computational simulation.

The principal objective of this effort is to communicate the nature of the landmine chemical signature, the impact of environmental conditions on this signature, and methods to compare expected chemical concentrations available as a cue to the performance capabilities of a trace chemical detector, such as the trained mine detection dog. To meet this objective, this report has focused on quantitative analysis, demanding much of the reader in understanding the world of small numbers, scientific notation, and units of measure not normally encountered outside of scientific and engineering literature.

After an introduction to numbers and nomenclature in chemistry, we examined the odor of landmines and which chemicals contribute to the vapor signature of military grade TNT. Three target compounds comprise the majority of the vapor signature - TNT, DNT and DNB. However, DNT and DNB, which are manufacturing impurities, are found in greater vapor concentrations than TNT due to the greater vapor pressure of each. The possibility that other chemicals in ultra-trace quantities contribute significantly to the odor signature cannot be discounted. Thus, we have focused attention on the major vapor components until such time that new target odors become identified.

Landmines are constructed in an endless variety of materials and methods of assembly. Chemical emission from landmines is the first step in the movement of the chemical signature through soils. Measurements of landmine emissions have shown that the nature of the casing material makes a significant difference on the chemical emission rate. Landmines with rubber casing parts release significantly greater landmine chemical signatures than those with dense plastic casings such as PVC. The amount of chemical released by many landmines is surprisingly large; however, before reaching the ground surface, much of the chemical is lost in sorption and degradation processes. Many more measurements of the unique, individual landmine chemical emissions are needed for comparative analysis of the ease or difficulty of detection.

Once released from the landmine, the chemical signature engages in a complex exchange, distributing the mass of chemical between the soil air, soil water and onto soil particles. Each landmine chemical behaves differently, which affect the mobility and concentration available as a cue for the dog. The most dramatic effect observed is during a transition of soil moisture from very dry conditions to slightly damp. Dry soil has few water molecules sorbed to the surface. The very large surface area of soils provides a tremendous surface for sorption of landmine signature chemicals from the vapor phase. Dry soil containing landmine signature residues will have very low vapor concentrations due to this vapor-solid sorption phenomenon. However, when wetted, the water displaces the landmine signature chemicals, increasing the vapor concentrations a tremendous amount (e.g. 10,000 to 100,000 fold). We are only beginning to understand how this impacts mine dog performance in the field. For example, in perennially dry soil conditions such as Afghanistan, why are the mine detection dogs so successful in finding buried landmines? Instead of vapors, the dogs may inhale suspended soil particles containing landmine signature chemicals. When these dry particles contact wet surfaces inside the dogs' nose, the landmine signature chemicals may be displaced providing the cue for the dog. In contrast, many deminers have expressed that landmines can be found much easier in the early morning hours before the nightly dew and surface soil moisture has been lost to evaporation.

The benefit of soil moisture in releasing sorbed landmine signature chemicals is apparent as described above. However, soil moisture also initiates the degradation process, which can cause rapid loss of the valuable landmine signature chemicals. With dry soil conditions, the loss is not measurable, and the soil can be considered an excellent storage media. However, when the soil becomes just damp, the biological and abiotic degradation processes begin working fast, where the half-life (the time where half the mass is lost) is measured in just a day or slightly more. Without constant landmine chemical emissions, a wet soil would consume the majority of the chemical stored on the soil in a matter of days. The complex nature of degradation has challenged many research projects, and the conventional environmental engineering descriptors poorly describe the nature of this process. As such, much more work is needed to better describe these processes.

Up to this point, this report has described individual processes occurring in the landmine and the soil. However, the local weather conditions are the principal drivers for moving the chemical signature through the soils. Rainfall, evaporation, solar radiation, heat, cold, and wind contribute to complex processes near the soil surface. Because the landmine is in the near surface soils and the mine detection dog is sniffing for chemical signatures from the air, these interactions are very important. Of all of the knowledge on landmine chemical sensing, this topic is the least well understood. The sharp contrast between soil physics processes and atmospheric physics in the layers closest to the ground, with a driving force of weather that affects both, creates a very complex interacting process with few applications from similar problems (e.g agricultural chemical emissions). Chemical mass transport from the landmine to the soil surface and into the air is a very localized process, where averaging over larger scales does not make sense. Much more research is needed with specialized expertise to improve our knowledge in this critical area.

Chemical transport in soils has been a well studied aspect of soil physics. Chemical diffusion in vapor and water in soil are well described from gas and solute diffusivity, air and water filled porosity, and soil-water and soil-vapor sorption. Chemical convection combines the mass transport of water, through precipitation downward and evaporation upward, and the temperature dependent solubility of each chemical in water.

As the story of trace chemical detection of buried landmines unfolds, we find there are many individual complex processes along the way. Understanding each one individually is a challenge; however, the combination of all of these is an even greater challenge. We begin to lose our intuitive ability to judge the impact of the summation of all of these processes. Therefore, we have engaged the use of simulation modeling tools, which can combine most of the processes and provide a wealth of insight into the amount of landmine chemical signature available as a cue for trace chemical detection. These simulation models require sophisticated computers with high speed to complete an analysis of an annual weather cycle. The coupling of simulation models for soil transport and atmospheric transport of chemicals has yet to be made. When available, this will provide a key tool, because the processes for atmospheric dispersion of the landmine signature chemicals emitted from the soil surface is key to understanding the probability of detection for under specific landmine-soil-weather conditions.

The measurement of soil residues from actual landmines in the field provides us with an understanding of the variability inherent in natural processes. The heterogeneous nature of soils and the variability in each of the unit processes described in the report, create a reality that is nearly impossible to model. Efforts to characterize the actual soil residues from landmines have also been challenged, because the ultra-trace nature of these soil residues is frequently below advanced technology's most capable method detection limits. However, when measurable, the results indicate that the soil residues are not uniform, and the greatest concentrations are not directly over the landmine. Surface runoff after a rain, can move the landmine chemical signature downslope, creating a smear of soil residue some distance from the actual landmine. The importance of measurement of actual soil residues can not be underestimated. This provides the reality check for simulation modeling, for comparison to the performance and vapor sensing threshold of mine detection dogs, and for situational analysis to understand what combinations of mines, soil and weather will provide sufficient chemical for trace chemical detection.

Since dogs are actively engaged in mine detection work, one would assume that the vapor sensing thresholds and performance capabilities have been carefully measured. This is not the case. Only recently have we begun to measure the vapor sensing thresholds of trained mine detection dogs. This has been difficult, because the dogs' vapor sensing capability far surpasses the capability of modern measurement techniques. Even so, with extrapolation and estimation techniques, we find that the dog is capable of sensing at extraordinary low levels, levels that approach that of one molecule per sniff. More research is needed to measure the vapor sensing performance of a greater numbers of individual dogs, including the reliability at these extremely low concentrations.

This report demonstrates the complex physics involved in chemical transport from buried landmines, including the interdependencies between the various processes. While much knowledge has been obtained in the last few years, additional information is needed to improve our ability to predict chemical movement from buried landmines.

We hope that this report provides a resource for those seeking to understand the fundamental processes that affect chemical sensing for buried landmines, and those seeking to fill in needed information to improve our understanding of trace chemical detection of buried landmines. The current numbers of buried landmines that need to be found is astounding, providing decades of work for mine action centers worldwide. This problem is not of short duration. With the placement of new buried landmines from new and renewed conflicts more resources are needed to improve the currently working demining tool of trace chemical detection.

References/Bibliography

Arya, S.P., 1988, Introduction to Micrometeorology, Academic Press, San Diego.

Auer L.H., N.D. Rosenberg, K.H. Birdsell, and E.M. Whitney, 1996. "The effects of barometric pumping on contaminant transport," J. Contaminant Hydrology, 24:145-16

Bender, E.A., A. Hogan, D. Leggett, G. Miskolczy, and S. MacDonald, 1992. Surface contamination by TNT. Journal of Forensic Sciences, 37(6):1673-1678.

Boulet, G., I. Braud, and M. Vauclin, 1997, "Study of the mechanisms of evaporation under arid conditions using a detailed model of the soil-atmosphere continuum. Application to the EFEDA I experiment," J. Hydrology, 193:114-141.Braud, I., 1996, SiSPAT User's Manual – **Simple Soil Plant** Atmosphere Transfer Model, Version 2.0, LTHE, Grenoble, France.

Braud, I., A.C. Dantas-Antonino, M. Vauclin, J.L. Thony, P. Ruelle, 1995. A simple soil-plant-atmosphere transfer model (SiSPAT) development and field verification. Journal of Hydrology 166 (1995) 213-250.

Burglsser, C.S., M. Cernik, M. Borkovec and H. Sticher. 1993. Determination of Nonlinear Adsorption Isotherms from Column Experiments: An Alternative to Batch Studies. Environ. Sci. Technol., Vol. 27, No. 5, 943-948.

Campbell, G.S., and J.M. Norman, 1998, An Introduction to Environmental Biophysics, Second Edition, Springer-Verlag, New York.

Cataldo, D.A., S.D. Harvey, R.J. Fellows. 1993. The Environmental Behavior and Chemical Fate of Energetic Compounds (TNT, RDX, Tetryl) in Soil and Plant Systems. Pacific Northwest Laboratory, Richland, WA. PNL-SA-22362. Presented at the 17th Annual Army Environmental R&D Symposium and 3rd USACE Innovative Technology Transfer Workshop, June 22-24, 1993. Willamsburg, VA.

Caton, J.E., C. Ho, R.T. Williams, and W.H. Griest. 1994. Characterization of insoluble fractions of TNT transformed by composting. J. Environ. Sci. Health A29:659-670.

Cebeci, T., and P. Bradshaw (1984), Physical and Computational Aspects of Convective Heat Transfer, Springer-Verlag, New York.

Chambers, W.B., P.J. Rodacy, E.E. Jones, B.J. Gomez and R.L. Woodfin, 1998. Chemical sensing system for classification of mine-like objects by explosives detection. in *Proceedings of the SPIE 12th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets III,* April 13-17, 1998, A.C. Dubey, J.F. Harvey, J.T. Broach eds.

Comfort, SD and Shea, PJ et al. 1995. TNT Transport and Fate in Contaminated Soil. Journal of Environmental Quality, v.24, pp.1174-82, Nov/Dec.

Cooper, P., 1996. Explosives Engineering. Wiley-VCH. New York, NY.

Cragin, J.H., D.C.Leggett, B.T. Foley and P.W. Schumacher, 1985. TNT, RDX and HMX explosives in soil and sediments – Analysis techniques and drying losses. U.S. Army Cold Regions Research and Engineering Laboratory Report 85-15. 1985.

Culver, T.B., C.A. Shoemaker, and L.W. Lion. 1991. Impact of vapor sorption on the subsurface transport of volatile organic compounds: A numerical model and analysis. Water Resour. Res. 27:2259-2270.

Desilets, S., L.V. Haley and U. Thekkadath, 1998. Trace explosives detection for finding land mines. in *Proceedings of the SPIE 12th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets III,* April 13-17, 1998, A.C. Dubey, J.F. Harvey, J.T. Broach eds.

Dionne, B.C., D.P. Rounbehler, E.K. Achter, J.R. Hobbs, and D.H. Fine. 1986. Vapor Pressure of Explosives. Journal of Energetic Materials, Vol 4, 447-472 (1986).

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

Ehlers W., J. Letey, W. F. Spencer, and W.J. Farmer. 1969a. Lindane Diffusion in Soils: I. Theoretical Considerations and Mechanism of Movement. Soil Sci. Soc. Am. Proc., 33, 501-504 (1969).

Ehlers, W., W.J. Farmer, W. F. Spencer, and J. Letey. 1969b. Lindane Diffusion in Soils: II. Water Content, Bulk Density, and Temperature Effects. Soil Sci. Soc. Am. Proc., 33, 505-508 (1969).

EPA, 1989. Code of Federal Regulations, Subpart C – Transport Processes, §796.2750 Sediment and soil adsorption isotherm, 50 FR 39252, Sept 27, 1985, as amended at 52 FR 19058, May 20, 1987; 54 FR 29715, July 14, 1989.

EPA, 1999. Understanding Variation in Partition Coefficient, K_d, Values. United States Environmental Protection Agency, Office of Air and Radiation, EPA 402-R-99-004A, August 1999.

EPA, 2002. Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, On-Line. United States Environmental Protection Agency, Office of Solid Waste.

Falta, R.W., K. Pruess, S. Finsterle, and A. Battistelli. 1995. T2VOC User's Guide, LBL-36400, Lawrence Berkeley Laboratory.

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

Furton, K. G. and L.J. Myers, 2001. The scientific foundation and efficacy of the use of canines as chemical detectors for explosives. Talanta 54 (2001) 487-500.

Geiger, R., 1957. The Climate Near the Ground. Harvard University Press, Cambridge, Massachusetts.

George, V., T.F. Jenkins, D.C. Leggett, J.H. Cragin, J. Phelan, J. Oxley and J. Pennington, 1999. Progress to date on determining the vapor signature of a buried landmine. in *Proceedings of the SPIE 13th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets IV,* April 5-9, 1999, Vol 3710, pp 258-269, A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.

George, V., T.F. Jenkins, J.M. Phelan, D.C. Leggett, J. Oxley, S.W. Webb, P. H. Miyares, J. H. Cragin, J. Smith, T.E. Berry. 2000. Progress on determining the vapor signature of a buried landmine. In *Detection and Remediation Technologies for Mines and Minelike Targets V,* A.C. Dubey, J.F. Harvey, J. T. Broach, R.E. Dugan, Editors, Proceedings of SPIE Vol. 4038 (2000)

Gibbs, T.R. and A. Popolato, eds. 1980. LASL Explosive Property Data. University of California Press, 1980.

Grant, C.L., T.F. Jenkins, S.M. Golden. 1993. Experimental Assessment of Analytical Holding Times for Nitroaromatic and Nitramine Explosives in Soil. U.S. Army Cold Regions Research and Engineering Laboratory Special Report 93-11, Hanover, New Hampshire. June 1993.

Hamaker, J.W. 1972. Diffusion and Volatilization. In Organic Chemicals in the Soil Environment. Ed. By Goring and Hamaker. Volume 1. Marcel Dekker, Inc. New York. 1972.

Hewitt, Alan D., and Thomas F. Jenkins (1999) On-site method for measuring nitroaromatic and nitramine explosives in soil and groundwater using GC-NPD: feasibility study. U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory Special Report 99-9.

Hewitt, Alan D., Thomas F. Jenkins, and Thomas A. Ranney (2001) Field gas chromatography/thermionic detector system for on-site determination of explosives in soils. U.S. Army Corps of Engineers, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory Technical Report ERDC/CRREL TR-01-9.

Hillel, D. 1982. Introduction to Soil Physics. Academic Press, Inc. San Diego, California.

Hogan, A. W., D. C. Leggett and J. Lacombe, 1990. Environmental Influences on Mine Detection. U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory. Special Report 90-31. August 1990.

Hogan, A., D. Leggett, T. Jenkins, and P. Miyares, 1992. Surface Contamination of Depot-Stored Landmines: Results from Preliminary Analyses. Memorandum to Defense Advanced Research Projects Agency (June 23, 1992).

Hundal, L.S., J. Singh, E.L. Bier, P.J. Shea, S.D. Comfort and W.L. Powers, 1997. Removal of TNT and RDX from Water and Soil Using Iron Metal. Environmental Pollution, Vol. 97, No. 1-2, pp. 55-64, 1997.

Howard, P.H. 1990. Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Volume II, Solvents. Lewis Publishers, Michigan. 1990.

Jenkins, T.F., W. F. O'Reilly, R. P. Murrmann and C.I. Collins. 1974. Detection of Cyclohexanone in the Atmosphere Above Emplaced Antitank Mines. U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire. Special Report 203. April 1974.

Jenkins, T.F., D.C. Leggett, R.P. Murrmann, 1974. Preliminary Investigation of the Permeability of Moist Soils to Explosive Vapor. In Spangler, 1974.

Jenkins, T.F., D.C. Leggett, and T.A. Ranney, 1999. Vapor signatures from military explosives: Part 1. Vapor transport from buried military grade TNT. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 99-21. December, 1999.

Jenkins, T.F., M.E. Walsh, P.H. Miyares, J. Kopczynski, T. Ranney, V. George, J. Pennington, and T. Berry, 2000. Analysis of Explosives-Related Chemical Signatures in Soil Samples Collected Near Buried Landmines. U.S. Army Corps of Engineers, Engineer Research and Development Center, Report ERDC TR-00-5. August 2000.

Jenkins, T.F., D.C. Leggett, P.H. Miyares, M. E. Walsh, T. A. Ranney, J. H. Cragin and V. George, 2001. Chemical signatures of TNT-filled land mines. Talanta 54 (2001) 501-513.

Johnston, J.M., M. Williams, L.P. Waggoner, C.C. Edge, R.E. Dugan, and S.F. Hallowell, 1998. Canine Detection Odor Signatures for Mine-Related Explosives. Proc. SPIE, Detection and Remediation Technologies for Mines and Minelike Targets III, Vol 3392, p 490-501, 1998.Jury, W.A. and L. Guo, 1998. One Dimensional Transport of Vapor From A Buried Landmine. Project report. University of California, Riverside. July 20, 1998.

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

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

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

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

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

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

Jury, W.A., W.R. Gardner and W.H. Gardner, 1991. Soil Physics, Fifth Edition. John Wiley and Sons.

Jury, W.A. and L. Guo, 1998. Two Dimensional Transport of Vapor From A Buried Landmine. Draft project report. University of California, Riverside. September 1, 1998.

Kaplan, D.L. and A.M. Kaplan. 1982. 2,4,6-trinitrotoluene-surfactant complexes: Decomposition, mutagenicity and soil leaching studies. Environ. Sci. Technol. 16:566-571.

Kaye, S.M. 1980. Encyclopedia of Explosives and Related Items, Volume 9. US Army Armament Research and Development Command, Large Caliber Weapon Systems Laboratory. Dover, New Jersey.

Keller, H.B. 1970. A new difference scheme for parabolic problems. In <u>Numerical Solution of Partial-Differential Equations</u>, J. Bramble, ed., Vol. II, Academic Press, New York.

Kenaga, E.E. and C.A.I. Goring. 1980. Relationship between Water Solubility, Soil Sorption, Octanol-Water Partitioning, and Concentration of Chemicals in Biota. Aquatic Toxicology, ASTM STP 707, J. G. Eaton, P.R. Parrish, and A.C. Hendricks, Eds., American Society for Testing and Materials, 1980 pp. 78-115.

Kjellstrom, A.H. and L.M. Sarholm, 2000. Analysis of TNT and related compounds in vapor and solid phase in different types of soil. in *Proceedings of the SPIE 14th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for*

Mines and Minelike Targets V, April 24-28, 2000, A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.

Leggett, D.C., T.F. Jenkins and R.P. Murrmann. 1977. Composition of Vapors Evolved from Military TNT as Influenced by Temperature, Solid Composition, Age, and Source. U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory. SR 77-16/AD A040632.

Leggett, D.C., T.F. Jenkins, A. Hogan, T.A. Ranney, P.H. Miyares, 2000. External Contamination on Landmines by Organic Nitro-Compounds. U.S. Army Engineer Research and Development Center - Cold Regions Research and Engineering Laboratory, ERDC-CRREL Technical Report TR-00-2, Hanover, NH. March 2000.

Leggett, D.C., J.H. Cragin, T.F. Jenkins, T.A. Ranney, 2001. Release of Explosive-Related Vapors from Landmines. U.S. Army Engineer Research and Development Center - Cold Regions Research and Engineering Laboratory, ERDC-CRREL Technical Report TR-01-6, Hanover, NH. February 2001.

Leggett, D.C. and J.H. Cragin, 2002. Diffusion and Flux of Explosive-Related Compounds in Plastic Mine Surrogates. U.S. Army Engineer Research and Development Center - Cold Regions Research and Engineering Laboratory, ERDC-CRREL Technical Report ERDC-TR-33, Hanover, NH.

Lenchitz, C. and R.W. Velicky. "Vapor Pressure and Heat of Sublimation of Three Nitrotoluenes," J. Chem. Eng. Data, 15(3):401-403 (1970).

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1990. Handbook of Chemical Property Estimation Methods, Environmental Behavior of Organic Compounds. American Chemical Society, Washington D.C. 1990.

Mark, H.F. and J.I. Kroschwitz, 1985. Encyclopedia of polymer science and technology. John Wiley & Sons, Inc. 1985.

Maskarinec, M.P., C.K. Bayne, L.H. Johnson, S.K. Holladay, R.A. Jenkins and B.A. Tompkins. 1991. Stability of explosives in environmental water and soil samples. Oak Ridge National Laboratory Report ORNL/TM-11770, Oak Ridge, Tennessee, 37831.

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

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

Miyares, P.H. and Jenkins, T.F. 2000. Estimating the Half-Lives of Key Components of the Chemical Vapor Signature of Land Mines. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Technical Report ERDC/CRREL TR-00-17, September 2000.

Murrmann, R.P. and Nakano, Y. 1971. Influence of Soil on Detection of Buried Explosives and Tunnels by Trace Gas Analysis. Report No: RR 288/AD 727667.U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory.

Murrmann, R.P., T.F. Jenkins, D.C. Leggett, 1971. Composition and Mass Spectra of Impurities in Military Grade TNT Vapor. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 158, Hanover, NH.

Ong, S.K. and L.W. Lion. 1991a. Mechanisms for trichloroethylene vapor sorption onto soil minerals. J. Environ Qual. 20:180-188.

Ong, S.K. and L.W. Lion. 1991b. Effects of soil properties and moisture on the sorption of trichloroethylene vapor. Water Res. 25:29-36.

Ong, S.K., T.B. Culver, L.W. Lion, and C.A. Shoemaker, 1992. Effects of soil moisture and physical-chemical properties of organic pollutants on vapor-phase transport in the vadose zone. Journal of Contaminant Hydrology, 11(1992) 273-290.

O'Reilly, W.F., T.F. Jenkins, R.P. Murrman, D.C. Leggett and R. Barrierra, 1973. Exploratory Analysis of Vapor Impurities From TNT, RDX and Composition B. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 194, Hanover, NH. October 1973.

Pella, P.A. 1977. Measurement of the vapor pressures of TNT, 2,4-DNT, 2,6-DNT and EGDN. J. chem. thermodynamics, 1977, 9, 301-305.

Pennington, J.C. and W.H. Patrick. 1990. Adsorption and Desorption of 2,4,6-Trinitrotoluene by Soils. J. Environ. Qual. 19:559-567 (1990).

Pennington, Judith C., Paul H. Miyares, David B. Ringelberg, Mansour Zakikhani, C.Michael Reynolds, Debra Felt, Richard B.Coffin, Douglas Gunnison, Luis Cifuentes, Herbert L. Fredrickson and Thomas F. Jenkins, 1999. Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Final Report. US Army Corps of Engineers, Technical Report SERDP-99-1, July 1999.

Pennington, J.C., C.A. Hayes, S.L. Yost, P.Miyares, T.Jenkins. 1999. Partitioning Coefficients on Fort Leonard Wood Soils. Draft Report, U.S. Army Corps of Engineers, Waterways Experiment Station, September 1, 1999.

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

Petersen, L.W., P. Moldrup, Y.H. El-Farhan, O.H. Jacobsen, T. Yamaguchi, and D.E. Rolston, 1995. The Effect of Moisture and Soil Texture on the Adsorption of Organic Vapors. J. Environ. Qual. 24:752-759 (1995).

Petersen, L.W., Y.H. El-Farhan, P. Moldrup, D.E. Rolston and T. Yamaguchi. 1996. Transient Diffusion, Adsorption and Emission of Volatile Organic Vapors in Soils with Fluctuating Low Water Contents. J. Environ. Qual. 25:1054-1063 (1996).

Peterson, M.S., L.W. Lion, and C.A. Shoemaker. 1988. Influence of Vapor-Phase Sorption and Diffusion on the Fate of Trichloroethylene in an Unsaturated Aquifer System. Environ. Sci. Technol., Vol. 22, No. 5, p. 571-578. 1988.

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

Phelan, J.M. and S.W. Webb, 1998a. Chemical Detection of Buried Landmines. Proceeding 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," in *Proceedings of the SPIE 12th Annual Conference on Detection and Remediation Technologies for Mines and Minelike Targets III, Orlando, FL, April 13-17, 1998.*

Phelan, J.M. and S.W. Webb, 1999. Chemical Soil Physics Phenomena for Chemical Sensing of Buried UXO. Proceedings of UXO Forum 1999, May 25-27, 1999. Department of Defense Explosive Safety Board and United States Army Environmental Center.

Phelan, J.M., Gozdor, M., Webb, S.W., and M. Cal. 2000. "Laboratory Data and Model Comparisons of the Transport of Chemical Signatures From Buried Landmines/UXO" in *Proceedings of the SPIE 14th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets V,* April 24-28, 2000, A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.

Phelan, J.M., J.L. Barnett, and P.J. Rodacy, 2000. Post-Blast Residue from Antipersonnel Landmines. SAND2000-1651, Sandia National Laboratories, Albuquerque, NM. July, 2000.

Phelan, J.M. and J.L. Barnett. 2001. Phase Partitioning of TNT and DNT in Soils. Sandia National Laboratories Report SAND2001-0310, Albuquerque, New Mexico. February 2001.

Phelan, J.M. and J.L. Barnett. 2001. Solubility of 2,4-Dinitrotoluene and 2,4,6-Trinitrotoluene in Water. J. Chem. Eng. Data, Mar/Apr 2001.

Phelan, J.M., P.J. Rodacy and J.L. Barnett, 2001. Explosive Chemical Signatures from Military Ordnance, Sandia National Laboratories Report SAND2001-0755, Albuquerque, New Mexico. April 2001.

Phelan, J.M., S.W. Webb, M. Gozdor, M. Cal and J.L. Barnett, 2001. Effect of Wetting and Drying on DNT Vapor Flux – Laboratory Data and T2TNT Model Comparisons. in *Proceedings of the SPIE 15th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls,* *Detection and Remediation Technologies for Mines and Minelike Targets VI*, April 16-20, 2000, Orlando, FL. A.C. Dubey, J.F. Harvey, J.T. Broach, V. George, eds.

Phelan, J.M. and J.L. Barnett, 2002. Chemical Sensing Thresholds for Mine Detection Dogs. in *Proceedings of the SPIE 16th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets VII*, April 1-5, 2002, Orlando, FL. A.C. Dubey, J.F. Harvey, J.T. Broach, eds.

Phelan, J.M. and J.L. Barnett, 2002. Degradation of Post-Blast Residue from Antipersonnel Landmines. Sandia National Laboratories Report (in preparation).

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

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

Pruess, K. 1995. Proceedings of the TOUGH Workshop '95. Berkeley, CA. LBL-32700, Lawrence Berkeley Laboratory, March 20-22, 1995.

Ro, Kyoung S.; Venugopal, Asha; Adrian, D. Dean; Constant, D.; Qaisi, Kamel; Valsaraj, Kalliat T.; Thibodeaux, Louis J.; and, Roy, Dipak. Solubility of 2,4,6-Trinitrotoluene in Water. J. Chem. Eng. Data 1996, 41, 758-761.

Rosenblatt, D.H.; Burrows, E.P.; Mitchell, W.R.; and, D.L. Parmer. 1991. Organic Explosives and Related Compounds. In *The Handbook of Environmental Chemistry*; Hutzinger, O. Ed.; Springer-Verlag: New York, 1991; Volume 3, Part G.

Sawyer, C.N., P.L. McCarty, G. F. Parkin. 1994. Chemistry for Environmental Engineering. Fourth Edition. McGraw-Hill, Inc.

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

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

Settles, G. S. and D. A. Kester, 2001. Aerodynamic sampling for landmine trace detection. Proceedings of SPIE Vol 4394, Detection and Remediation Technologies for Mines and Minelike Targets VI, A.C. Dubey, J. F. Harvey, J. T. Broach, V. George, Eds.

Spain, J.C., 1995. Biodegradation of Nitroaromatic Compounds. Annual Review of Microbiology, V.49, pp523-555.

Spanggord, R.J.; Mabey, W.R.; Mill, T.; Chou, T.W.; Smith, J.H.; Less, S.; and D. Robert. 1983. Environmental Fate Studies on Certain Munitions Wastewater Constituents. LSU-7934, AD-A138550; SRI International: Menlo Park, CA, 1983.

Spangler, G.E.. 1974. Physical Model for the Subterranean Movement of Explosive Vapors from Mines. Report No: MERADCOM-R-2095

Spangler, G.E.. 1975. Measurements on the Availability of TNT Vapor from Antitank Mines. U.S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia. Report No: MERADCOM-R-2159

Spain, J.C., J. B. Hughes and H. Knackmuss, eds. 2000. Biodegradation of Nitroaromatic Compounds and Explosives. Lewis Publishers, CRC Press, Boca Raton, Florida.

Spencer, W.F. and M.M. Cliath, 1973. Pesticide volatilization as related to water loss from soil. J. Environ. Qual. 2:284-289.

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

Stephen, H. and T. Stephen. 1963. *Solubilities of Inorganic and Organic Compounds;* MacMillian Co.; New York, 1963; Vol.1 Part 1.

Taylor, C.A. and W.H. Rinkenbach, 1923. The Solubility of Trinitrotoluene in Organic Solvents. J. Am. Chem. Soc. 1923, 45, 44-59.

Tucker, W.A., E.V. Dose, G.J. Gensheimer, R.E. Hall, C.D. Pollman, and D.H. Powell. 1985. Evaluation of critical parameters affecting contaminant migration through soils. Final Report for the U.S. Army Toxic and Hazardous Materials Agency. ESE, Gainesville, FL

U.S. Army, 1971. Engineering Design Handbook: Explosives Series. Properties of Explosives of Military Interest. AMPC 706-177, Headquarters, U.S. Army Material Command, January 1971.

U.S. Environmental Protection Agency. 1992. *SW846, Chapter One – Quality Control, Revision 1, July 1992*. Washington D.C.: GPO.

Urbanski, T. 1964. *Chemistry and Technology of Explosives*; MacMillian Co.; New York, 1964; vol I.

Verschueren, K.. 1983. *Handbook of Environmental Data on Organic Chemicals*, 2nd ed.; Van Nostrand Reinhold Co.; New York, 1983.

Walsh, M.E. and T.A. Ranney, 1999. Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Soils Using GC-ECD. U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Special Report 99-12. August 1999.

Webb, S.W. 1996. Gas Phase Diffusion in Porous Media - Evaluation of an Advective-Dispersive Formulation and the Dusty-Gas Model Including Comparison to Data for Binary Mixtures. SAND96-1197. Sandia National Laboratories.

Webb, S.W. and J.M. Phelan, 2000. Effect of Diurnal and Seasonal Weather Variations on the Chemical Signatures from Buried Landmines/UXO. in *Proceedings of the SPIE 14th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets V,* April 24-28, 2000, A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.

Webb, S.W., 2000. A simple extension of two-phase characteristic curves to include the dry region. Water Resourc. Res., Vol 36, No. 6, 1425-1430, June 2000.

Webb, S.W., K. Pruess, J. M. Phelan and S. Finsterle, 1999. Development of a Mechanistic Model for the Movement of Chemical Signatures from Buried Landmines/UXO. in *Proceedings of the SPIE 14th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets IV,* April 5-9, 1999, A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.

Webb, S.W., S.A. Finsterle, K. Pruess, and J.M. Phelan, 1998. Prediction of the TNT Signature from Buried Landmines. Proceedings of the TOUGH '98 Workshop. Berkeley, CA.

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

Distribution:

1	MS0719	S.M. Howarth, 6131
30	MS0719	J.M. Phelan, 6131
10	MS0719	S.W. Webb, 6131
1	MS1452	B.W. Marshall, Jr.2552
1	MS1452	P.J. Rodacy, 2552
1	MS1452	J.L. Barnett, 2552
1	MS0892	R.J. Simonson, 1764
1	MS1188	V. George, 15311
1	MS9018	Central Technical Files, 8945-1
2	MS0899	Technical Library, 9616
1	MS0612	Review and Approval Desk, 9612 for DOE/OSTI

3 Havard Bach
Geneva International Center for Humanitarian Demining
Av. de la Paix 7 bis, PO Box 1300
1211 Geneva 1, Switzerland

3 Ian McLean
Geneva International Center for Humanitarian Demining
Av. de la Paix 7 bis, PO Box 1300
1211 Geneva 1, Switzerland