VAPOR PHASE TRANSPORT OF EXPLOSIVE RELATED COMPOUNDS THROUGH UNSATURATED SANDY SOILS

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ABSTRACT

Chemical detection of buried explosives devices through chemical sensing is influenced by factors affecting the transport of chemical components associated with the devices. Explosive-related chemicals (ERCs), such as 2,4-Dinitrotoluene (DNT) and 2,4,6-Trinitrotoluene (TNT), are somewhat volatile and their overall transport is influenced by vapor-phase diffusion. Gaseous diffusion depends on environmental and soil conditions. The significance of this mechanism is greater for unsaturated soil, and increases as water content decreases. Other mechanisms, such as sorption, which affect the overall fate and transport, may be more significant under diffusion transport due to the higher residence time of ERCs in the soil system.

Vapor transport in soil of DNT and TNT was analyzed using one-dimensional physical model (1-D column). Experiments were conducted at different soil water contents and temperatures. Variation of the vapor phase concentrations were analyzed spatially and temporally. Vapor samples were obtained from the columns using Solid Phase Microextraction (SPME) and analyzed using Gas Chromatography. In addition, soil samples were extracted and analyzed using High Performance Liquid Chromatography. Measured data was modeled using the HYDRUS 1-D code, in order to determine the most important transport parameters affecting the vapor transport.

Results suggest that DNT and TNT overall vapor transport is influenced by diffusive and retention processes, water content, source characteristics, and temperature. Vapor concentrations of DNT and TNT at a given temperature tend to increase with increasing water contents at very dry conditions ($\theta_w < 8\%$), reach a maximum value, and decrease with further increase in water contents at the higher water content regime. Higher temperatures induced higher vapor concentrations, principally, due to increments of the explosive source volatilization. Vapor sorption was more dominant at low water contents (< 1%) and decreases several orders of magnitude (3) with increments in water contents. This sorption process was rate-limited. Vapor fluxes were higher near the explosive source than further away. Results suggest that the main parameter affecting the vapor transport is the soil water content and temperature.

RESUMEN

La detección química con censores para encontrar dispositivos explosivos enterrados, es influenciada por factores que afectan el transporte de los componentes químicos asociados con los dispositivos. Los compuestos químicos relacionados con explosivos, como lo son el 2,4-Dinitrotolueno (DNT) y el 2,4,6-Trinitrotolueno (TNT), son un poco volátiles y el transporte general es influenciado por la difusión en la fase de vapor. La difusión gaseosa depende de factores tales como condiciones ambientales y propiedades de los suelos. La importancia de estos mecanismos es mayor en los suelos no saturados e incrementa a medida que el contenido de agua disminuye. Otros mecanismos, como la adsorción, los cuales afectan el destino y transporte general de los contaminantes, pueden ser más significativos bajo el transporte difusivo debido al mayor tiempo de residencia de los químicos explosivos en el suelo.

El transporte de vapores de DNT y TNT en suelos fue analizado utilizando un modelo físico de una dimensión (columna de 1-D). Los experimentos fueron realizados a diferentes contenidos de humedad y temperaturas. Las variaciones de las concentraciones en la fase de vapor fueron analizadas espacialmente y temporalmente. Muestras de vapor fueron obtenidas de las columnas utilizando Microextracción en la Fase Sólida y analizada utilizando Cromatografía de Gases. En adición, muestras de suelo fueron extraídas y analizadas utilizando Cromatografía de Líquidos de Alto Desempeño. La data medida fue modelada utilizando el código HYDRUS 1-D, para así poder determinar los parámetros de transporte más importantes que afectan el transporte de vapores.

Los resultados sugieren que el transporte general de DNT y TNT es influenciado por procesos difusivos y de retención, contenidos de humedad, características de la fuente, y por la temperatura. Las concentraciones de vapor de DNT y TNT a una temperatura dada y bajo condiciones del suelo extremadamente secas ($\theta_w < 8\%$), tuvieron la tendencia a incrementar con aumentos en el contenido de humedad del suelo. Una vez las concentraciones de vapor alcanzan un máximo estas comienzan a disminuir a medida que el contenido de humedad del suelo continua incrementado. Altas temperaturas indujeron mayores concentraciones de vapores, principalmente, debido a los incrementos en la volatilización de la fuente de explosivo. Mientras tanto, la adsorción de vapores fue dominante a contenidos de humedad bajos (< 1%) y decreció algunas ordenes de magnitud (3) con incrementos en el contenido de humedad. Estos procesos de adsorción ocurrieron a una razón limitada. Los flujos másicos fueron mayores cerca de la fuente de explosivo (la mina) en comparación con los flujos medidos distante de la fuente. Los resultados sugieren que el parámetro principal que más afecta el transporte de vapores es el contenido de humedad de los suelos y la temperatura.

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LIST OF SYMBOLS AND ABBREVIATIONS

A = Area

A_{iA} = Air-Water Interfacial Area
<i>alpha</i> = First-order Kinetic Rate Constant
$A_N =$ Avogadro's Number
BET = Brunauer-Emmett-Teller
BC = Boundary Condition
C = Liquid, Gas or Solid Concentration
C_A = Gas Phase Concentration
C_{eq} = Equil. Conc. in Gas or Liquid Phase
C_{NPC} = Concentration without Porous Cup
C_0 = Initial Gas Phase Concentration
C_{PC} = Concentration using Porous Cup
C_S = Solid Phase Concentration
$C_S^{\ k}$ = Soil Conc. Sites with Kinetic Sorption
C_u = Uniformity Coefficient
C_W = Liquid Phase Concentration
C_{W-0} = Initial Solution Concentration
C_{WS} = Conc. in Solid and Liquid Phases
D = Effective Diffusion in Gas or Water
D_A = Effective Diffusion in Gas Phase
D_{A-M} = Molecular Air Diffusion Coefficient
DNT = 2,4 Dinitrotoluene
D_W = Effective Diffusion in Liquid Phase
D_{W-M} = Molecular Water Diffusion
ERCs = Explosive Related Compounds
erfc = Complementary Error Function
f = Fraction of Sites with Direct Sorption
F = Vapor or Water Flux
$F_A =$ Vapor Flux
$f_{\rm OC}$ = Fraction of Organic Carbon
$f_{\rm OM}$ = Fraction of Organic Matter

GC = Gas Chromatograph HPLC = High Performance Liquid Chrom. °K = Kelvin Degrees K_{BET} = BET Sorption Coefficient K_d = Water to Soil Partition Constant K_d ' = Air to Dry Soil Partition Constant K_d " = Air to Wet Soil Partition Constant K_{Fr} = Freunlich Sorption Coefficient K_H = Henry's Law Constant k_{iA} = Interface-Air Distribution Coefficient K_L = Langmuir Sorption Coefficient K_{OC} = Organic Carbon Distribution Coeff. K_{OM} = Organic-Matter Distribution Coeff. L = Straight Line Length *LBC* = Lower Boundary Concentration *Le* = Real Length of the Flowpath m_{air} = Average Molecular Mass of Air MA_W = Area of Water Molecule $m_{\rm g}$ = Molecular Mass of the Chemical m_T = Mass Transfer Term *MNLs* = Monolayers of Water M_P = Eluted Mass M_S = Mass of Dry Soil M_W = Mass of Water *MW*= Molecular Weight MW_W = Molecular Weight of Water M&Q= Millington and Quirk Model M_0 = Zero Moment M_1 = First Moment n = PorosityNAPLs = Non-aqueous Phase Liquids

LIST OF SYMBOLS AND ABBREVIATIONS

n_m = Number of Moles	UXOs = Unexploded Ordnance
OD = Outer Diameter	UV = Ultraviolet
OM = Organic Matter	V_A = Volume of Air
P = Gas Phase Pressure	v_{air} = Average Molar Volume of Air
ppb = Parts per Billion	v_{gas} = Average Molar Volume of the Gas
ppm = Parts per Million	VOCs = Volatile Organic Compounds
Q_D = Diffusive Vapor Flow	VP = Vapor Pressure
R = Retardation Factor	V_S = Volume of Solids
R^2 = Coefficient of determination	V_T = Total Soil Volume
$R_g = \text{Gas Constant}$	$V_V =$ Volume of Pores
RH = Relative Humidity	V_W = Volume of Water
RMSE = Root Mean Square Error	<i>w</i> = Gravimetric Water Content
$r_s = \text{Reactions}$	z = Distance in the Z Axis
S = Water Solubility	θ_A = Volumetric Air Content
S_A = Specific Surface Area of Soil Particle	θ_W = Volumetric Water Content
SPME = Solid Phase Microextraction	$ \rho_b $ = Soil Bulk Density
T = Temperature	$ \rho_p = \text{Particle Density} $
t = Time	$\rho_w =$ Water Density
t_m = Mean Arrival Time	τ = Tortuosity Coefficient
TCE = Trichloroethylene	$\eta =$ Water Viscosity
TNT = 2,4,6 Trinitrotoluene	γ = Aqueous Activity Coefficient
<i>UBC</i> = Upper Boundary Concentration	

CHAPTER 1: INTRODUCTION

One of the most common problems associated with territories implicated in warfare, and others used as firing ranges is the presence of landmines and unexploded ordnances (UXOs). The majority of explosives found in antipersonnel and antitank landmines contain trinitrotoluene (TNT) [Phelan and Barnett, 2001b]. Military grade TNT often contains a number of impurities, including 2,4-dinitrotoluene (DNT) and other isomers of dinitrotoluene and trinitrotoluene [Jenkins et al., 1999]. This study refers to these compounds as explosives related compounds (ERCs). In addition to the risk of explosion, there are others risks associated with human health and the environment. Long-term exposure to some ERCs (such as DNT and TNT) is associated with liver and blood damage, anorexia, anemia, and is classified as possible human carcinogens [ATSDR, 1995; ATSDR, 1998]. The threats to the human health and the environment drive the scientific community to develop new technologies for detection and remediation of ERCs in the environment.

Technologies for ERC detection include mine-sniffing dogs, biological, and chemical sensing [MacDonald et al., 2003]. Detection of ERCs from buried explosives using these technologies requires the presence of ERCs near the soil-atmospheric surface. The presence of ERCs associated with buried explosive devices near this surface is controlled by source characteristics and on the fate and transport processes that affect their movement in the soil. Similarly, the efficiency of remedial technologies to clean up ERC-contaminated soil is strongly influenced by these processes. Accurate chemical detection of land mines and efficient remediation techniques of contaminated sites, thus, requires good understanding of the factors affecting the fate and transport of ERCs in soils.

Fate and transport processes control the direction and magnitude of ERC movement in soils. These processes are affected by environmental conditions, soil characteristics, and ERCs physical and chemical properties [Phelan and Webb, 1999]. Environmental conditions include: rainfall frequency and intensity, solar radiation,

temperature, atmospheric relative humidity and barometric pressure. Soil characteristics include: soil chemistry, organic matter content, grain size, gradation, compaction, water content and biological activity. ERCs chemical properties affecting the transport are: molecular composition, molecular weight, vapor pressure, solubility, and sorption characteristics. Because TNT and DNT are somewhat soluble in water and show some vapor pressure, they can be transported in the aqueous and gaseous phases. Their principal mode of transport, as well as its direction and magnitude, depend on environmental conditions and soil properties. These compounds can move through the soil with the flowing water in a rain event or by volatilization and gas-phase diffusion during dry seasons, as illustrated in Figure 1.



Figure 1. Illustration of the environmental fate and transport processes within the unsaturated zone for detection of ERCs emanating from buried landmines

Landmines and UXOs are found near the soil surface, in the unsaturated zone. This zone is exposed to variable amounts of rain, infiltration, and heat condition; which induce changes in the water content, water flux, and subsequent transport characteristics of ERCs in soils. Transport of ERCs under wet conditions is dominated by advection and dispersion in the water phase. Meanwhile, under dry conditions or limited water flow the vapor-phase transport mechanism are gas advection induced by pressure changes and diffusion.

Diffusion occurs as chemicals are transported under concentration gradients from regions of high to low concentrations. It can occur in the soil-water and soil-gas phases, depending on soil characteristics, water contents, and chemical properties. Diffusion in the water phase is an important transport mechanism for water- soluble chemicals, high soil-water contents, and low water flow or stagnant conditions. Water-phase diffusion, for instance, is an important transport mechanism for contaminants in clay soils of low hydraulic conductivity, such as impermeable layer in landfills. Diffusion in the gas-phase is an important transport mechanism for volatile (high vapor pressure) or semi-volatile (some vapor pressure) compounds, low water contents, and permeable soils.

Vapor-phase transport has been identified as one of the most important processes affecting biological and chemical detection of many ERCs near the soil surfaces [Leggett et al., 2001]. It is generally controlled by gas-phase diffusion, but is also influenced by retention, mass transfer, and degradation processes [Miyares and Jenkins, 2000; Phelan and Webb, 2002; Price et al., 2002; Ravikrishna et al., 2002]. Retention mechanisms may involve a series of equilibrium and non-equilibrium interactions and include: sorption to mineral surfaces, soil organic matter, and air-water interfaces, and dissolution into the bulk water phase [Pennington and Patrick, 1990; Costanza and Brusseau, 2000; Erikson and Skyllberg, 2001; Ravikrishna et al., 2002]. Sorption processes are responsible for concentrating ERCs around landmines [George et al., 1999; Jenkins et al., 2000], but it depends on water contents, water flow, and other environmental factors. Although diffusive flux through the soil may be a major process controlling the movement of ERCs to the soil surface, experimental work has focused on measuring surface emission flux

from ERC-contaminated soils. Most research on vapor transport in the unsaturated zone has focus on volatile organic compounds (VOCs), while vapor diffusion of ERCs through the soil has only been addressed through simplified numerical models (Phelan and Webb, 2002). A need, thus, exist to experimentally assess the diffusive behavior of ERC vapors at different distances from the ERC source under different environmental and soil conditions.

This research evaluates the principal factors affecting the vapor transport of ERCs in unsaturated soil. The overall goal of the research is to characterize the diffusive transport behavior of DNT and TNT vapors under different environmental and soil conditions. In particular, this research addressed the effect of soil water content and temperature on vapor diffusion, mass transfer, and retention mechanisms. The research work involves: (i) developing a physical model to experimentally determine the diffusive vapor transport behavior of TNT and DNT at different spatial and temporal scales; (ii) conducting vapor transport experiments at different soil-water contents and temperatures; and (iii) analyzing the experimental data using analytical and numerical methods to determine vapor-phase transport parameters as a function of imposed conditions.

CHAPTER 2: LITERATURE REVIEW

Fate and transport of ERCs vapors near soil-atmospheric surfaces depend on the physical and chemical properties of the chemicals, soil properties and conditions, and environmental conditions. This chapter presents a review of the physicochemical properties, soil characteristics, and fate and transport processes affecting the mobility of DNT and TNT in unsaturated soil. It also presents a review of previous research reported on factors and processes affecting the movement of ERC vapors in soils.

2.1 Physicochemical Properties of the ERCs

The transport of ERCs in soils is strongly influenced by the physicochemical properties of the compounds. These properties, which are related to the chemical composition and structure, include: molecular diffusion, aqueous solubility, vapor pressure, and partitioning characteristics. Molecular diffusion affects the rate of movement of the chemical within a fluid and controls their movement under conditions of negligible fluid flow. The solubility influences the capacity of water to transport chemicals, where as vapor pressure influence the transport in the gas phase. Partitioning characteristics influence the distribution of chemicals among the different environmental compartments (e.g., water, air, soil, organic matter). They are generally described by distribution constants, such as Henry's Law constant and the soil-water distribution constant.

2.1.1 Chemical Formula

TNT and DNT belong to a group of organic nitroaromatics compounds consisting of toluene and nitrogroups in its structure (Figure 2). The nitrogroups consist of two different elements, Nitrogen (N) and Oxygen (O), which are both highly electronegative. Because oxygen is more electronegative than the nitrogen atom, the N-O bond is slightly polarized.



Figure 2. Chemical formula and structure of 2,4,6-Trinitrotoluene and 2,4-Dinitrotoluene (Walsh et al., 1995)

2.1.2 Molecular Gas and Liquid Diffusion

An important physical characteristic affecting the transport of TNT and DNT is their molecular diffusion. Molecular diffusion reflects the random movement of molecules caused by Brownian motion through the medium of interest [Schwarzenbach et al., 2003]. Diffusion is function of the compounds' molecular size, as well as the viscosity and temperature of the fluid media [Brown et al., 2000]. Molecular diffusion is generally greater for compounds with lower molecular weights than for the heavier molecular weight compounds. Because air is much less densely packed and viscous than water media, molecular diffusion for a particular compound tends to be much greater in air than in water. Higher temperature results in lower fluid viscosity and in greater molecular diffusion [Schwarzenbach et al., 2003].

Molecular diffusion results in the movement of chemicals from regions of high to low concentrations (Figure 3). The flux (F) caused by this movement is proportional to the concentration (C) gradient and is described by the Fick's First Law:

$$F = D \frac{\partial C}{\partial z} \tag{1}$$



Figure 3. Conceptualization of the diffusive transport mechanism

where, *D* is the molecular diffusion coefficient, *z* is distance, and $\partial C/\partial z$ is the concentration gradient. The molecular diffusion coefficient is a function of the molecular properties of the compound, fluid characteristics, and temperature [Brown et al., 2000].

The molecular diffusion coefficient in air (D_{A-M}) for organic molecules can be estimated using the Fuller-Schettler-Giddings empirical correlation [Schwarzenbach et al., 2003]:

$$D_{A-M} = \frac{10^{-3} T^{1.75} \sqrt{1/m_{air} + 1/m_g}}{P(v_{air}^{1/3} + v_g^{1/3})^2} \qquad (\text{cm}^2/\text{s})$$
(2)

where, *T* is the absolute temperature (°K), m_{air} is the average molecular mass of air (28.97 g/mol), m_g is the molecular mass of the diffusing chemical (g/mol), *P* is the gas phase pressure (atm), v_{air} is the average molar volume of the gases in air ($\approx 20.1 \text{ cm}^3/\text{mol}$), and v_g is the molar volume of the chemical of interest (cm³/mol). The molar volume of the chemical (v_g) can be estimated with Table 1. Using this table and the molecular formula of the compounds, the v_g was estimate for TNT (175.35 cm³/mol) and DNT (160.68 cm³/mol). With the molar volume, molecular weight, and ambient pressure ($\approx 1 \text{ atm}$), the air-phase molecular diffusion coefficients can be estimated as function of temperature using Equations 3 and 4.

Atom or structural segment	$v_g (cm^3/mol)$
Carbon (C)	16.5
Hydrogen (H)	1.98
Oxygen (O)	5.48
Nitrogen (N)	5.69
Chlorine (Cl)	19.5
Sulfur (S)	17
Aromatic and heterocyclic rings	-20.2

Table 1. Estimation of diffusion volumes of organic molecules(Schwarzenbach et al., 2003)

$$D_{A-M_{TNT}} = 0.24647 \cdot T(^{\circ}K)^{1.75} \qquad (\text{cm}^2/\text{day})$$
(3)

$$D_{A-M_{DNT}} = 0.25983 \cdot T(^{\circ}K)^{1.75}$$
 (cm²/day) (4)

Molecular diffusion in liquids strongly depends on the interactive forces between the molecules of water and solute [Schwarzenbach et al., 2003]. Consequently, the water viscosity is one of the principal factors affecting water-phase molecular diffusion. Molecular diffusion coefficient in water (D_{W-M}) can be estimated using an empirical correlation [Chatwin, 1998]:

$$D_{W-M} = \frac{13.26 \times 10^{-5}}{\eta^{1.14} \cdot v_g^{0.589}} \qquad (\text{cm}^2/\text{s})$$
(5)

where, η is the water viscosity in centipoises at the temperature of interest, and v_g is the molar volume of the chemical calculated using Table 1. Based on Equation 5, the molecular-water diffusion coefficients as function of temperature can be estimated for TNT and DNT as:

$$D_{W-M_{TNT}} = 38.113 \times 10^{\frac{282.492}{140-T}(^{\circ}K)} \qquad (\text{cm}^2/\text{day}) \tag{6}$$

$$D_{W-M_{DNT}} = 40.126 \times 10^{\frac{282.492}{140-T}(^{\circ}K)} \qquad (\text{cm}^2/\text{day}) \tag{7}$$

Molecular diffusion for DNT and TNT in gas and water phases were estimated from Equations 3,4,6, and 7 for 22°C and 35°C (Table 2). This table indicates much higher values in the gas phase than the water phase. Higher values are also observed at higher temperatures. Slightly higher diffusion coefficients for DNT in the gas and water phases indicate that molecular diffusion for DNT is supposed to be slightly higher than TNT under the same conditions and gradients.

	Temperature: 22°C		Temperature: 35°C	
	TNT	2,4-DNT	TNT	2,4-DNT
Water-Molecular Diffusion (cm ² /day)	0.5758	0.6063	0.7963	0.8383
Gas-Molecular Diffusion (cm ² /day)	5,180	5,461	5,586	5,889
Solubility (mg/L)	112.7	181.2	200.5	307.1
Vapor Pressure (mg/L)	5.911E-05	1.451E-03	3.439E-04	7.188E-03
K _H (-)	5.243E-07	8.011E-06	1.715E-06	2.341E-05
Molecular Weight (g/mol)	227.133	182.1354		

Table 2. Values of the TNT and DNT physicochemical properties used in this study

2.1.3 Solubility

Aqueous solubility (*S*) of ERC is an important factor affecting solute transport in subsurface environments. It influences the capacity of a compound to dissolve and to be transported in water. Solubility is function of the molar structure of compounds as it affects their polarity. In general, organic compounds are less polar than water, since they are chiefly constructed from atoms having comparable electronegativities resulting in evenly spaced electronic distribution [Schwarzenbach et al., 2003]. Generally, more polar compounds have greater solubilities. The polarity of organic molecules is influenced by several factors, including the number and type of functional groups and the size of the organic molecules. Larger organic molecules tend, in general, to have lower solubility than similar molecules of smaller size. However, in the case of DNT and TNT, DNT shows a higher solubility than TNT, which is a larger molecule with higher molecular weight than DNT (Table 2). Reported solubilities of DNT at 20°C averages 189 mg/L (\pm 54.6), while for TNT the average is 106 mg/L (\pm 20.2). These differences result in a higher capacity of DNT for aqueous transport when compared with TNT.

Temperature also influences the aqueous solubility of chemical compounds. Increments in temperatures could decrease the solubility of some liquid compounds (e.g., dichloromethane and superheated bromomethane), whereas other compounds show a solubility increase with increments in temperature (e.g., trichloroethylene and subcooled naphthalene) [Schwarzenbach et al., 2003]. In the case of TNT and DNT, higher temperatures result in higher solubilities. Several studies have reported solubility values for TNT and DNT at different temperatures (see Figures 4 and 5). The data, however, shows some variability and generates some degree of uncertainty in the actual values. Temperature-dependent solubility models for TNT and DNT (Figures 4 and 5) were, therefore, developed for this study. The models, which were developed using regression analysis of the published data, predict the average solubility of TNT (Eq. 8) and DNT (Eq. 9) as a function of temperature. Estimated solubility values for TNT and DNT at 22°C and 35°C are given in Table 2. These estimates indicate that DNT is slightly more soluble in water than TNT.

$$S_{TNT} = 17.7407 + 31.4089 \cdot (1.0516)^{T(\circ C)}$$
 (mg/L) (8)

$$S_{DNT} = 23.9662 + 58.0766 \cdot (1.0463)^{T(^{\circ}C)}$$
 (mg/L) (9)

2.1.4 Vapor Pressure

The vapor pressure of a compound dictates its capacity to volatilize into the gaseous phase, and its capacity to move as a vapor. Vapor pressure (*VP*) is defined as the pressure of the vapor of a compound at equilibrium with its pure condensed phase, be it liquid or solid [Schwarzenbach et al., 2003]. The higher the vapor pressure of a compound, the greater is its capacity to volatilize, attain greater concentrations, and move in the vapor phase. At equilibrium, the vapor concentrations in the gas phase can be estimated from the Ideal-Gas Equation as [Brown et al., 2000]:

$$MW\left(\frac{n_m}{V_A}\right) = \frac{VP}{R_g T}$$
(10)



Figure 4. Published data and proposed model for determination of TNT water solubilities at different temperatures



Figure 5. Published data and proposed model for determination of DNT water solubilities at different temperatures

where, MW is the molecular weight, n_m is the number of moles, V_A is the gas volume, R_g is the gas constant (0.0823 atm-L/mol-°K), T is temperature (°K), and VP is the vapor pressure of the compound at a given atmospheric pressure.

The vapor pressure of a compound is strongly influenced by temperature. Figures 6 and 7 illustrate the increment of TNT and DNT vapor pressures with increasing temperature. These figures illustrate the published data and different models reported in the literature for the prediction of the TNT and DNT vapor pressures. Unfortunately, these figures show a lot of variability, principally for DNT data which has a variability of about one order in magnitude. This study applies the empirical models from Dionne et al. [1986] and Pella [1977], for the prediction of the vapor pressure of TNT and DNT, respectively. These models were selected because their predicted data is closer to the central tendency of all data and models. Selected models are represented by the solid red lines in Figures 6 and 7. The equations for the Dionne-model and Pella-model described by Equations 11 and 12, respectively.

$$LOG VP_{TNT}(ppb) = 19.37 - \frac{5481}{T(^{\circ}K)}$$
 (11)

$$LOG \ VP_{DNT}(torr) = (13.08 \pm 0.19) - \frac{(4992 \pm 59)}{T(^{\circ}K)}$$
(12)

According to these models, the vapor pressure for TNT and DNT are 6.30×10^{-9} and 1.93×10^{-7} atm, respectively, at 22°C, and 3.83 x 10⁻⁸ and 9.97 x 10⁻⁷ atm, respectively at 35°C. Therefore, TNT and DNT are semi-volatile organic compounds because their vapor pressures are in the range of 10⁻¹¹ to 10⁻⁴ atm. It also reflects that DNT vapor pressures are higher than those for TNT, indicating the greater volatility of DNT.



Figure 6. Published data and empirical models for determination of the TNT vapor pressures at different temperatures



Figure 7. Published data and empirical models for determination of the DNT vapor pressures at different temperatures

2.1.5 Henry's Law Constant

At any particular temperature the movement of molecules from the liquid to the gas phase goes on continuously [Brown et al, 2000]. However, as the number of gasphase molecules increases, the probability that a molecule in the gas phase will strike the liquid surface and be recaptured by the liquid increases. Eventually, the rate at which molecules return to the liquid is exactly equal to the rate at which they escape. When these processes are occurring simultaneously at equal rates then the system is in dynamic equilibrium. The compound's abundance in the gas phase to that in the aqueous phase at equilibrium is referred as the Henry's Law constant (K_H). This constant quantifies the relative escaping tendency of a compound existing as vapor molecules as opposed to being dissolved in water [Schwarzenbach et al., 2003]. Henry's Law constant is described using the following equation:

$$K_{H} = \frac{C_{A}}{C_{W}} = \frac{VP}{S} \quad \text{(dimensionless)} \tag{13}$$

where, C_A and C_W are the concentrations of the compounds in the air and water phases, VP is the vapor pressure, and S is the aqueous solubility of the compound, respectively. Because K_H is a function of vapor pressure and solubility, it is also a function of temperature. Figures 8 and 9 show the values of K_H that were available in the literature as a function of temperature for TNT and DNT, respectively. In addition, values of K_H calculated (red line) from the temperature-dependent vapor pressure functions (Eqs. 11 and 12) and solubility models (Eqs. 8 and 9) are presented in these figures. The error bars in Figures 8 and 9 represent the range of minimum and maximum values found in the literature for a given temperature. The K_H variability could be as high as two orders in magnitude for DNT, while for TNT the values range is smaller.

Low K_H values (< 2.5 x 10⁻⁵) of TNT and DNT (Table 2) indicate that these compounds have higher tendency to get dissolved in water than to volatilize. Although characterized by low aqueous solubility (ppm range), at equilibrium a greater fraction of

the mass would consequently be in the water than in the gas phase. Higher values at higher temperature reflect a greater fraction of the compounds in the gas phase at higher temperatures. Higher values of DNT reflect at both temperatures the greater volatility over TNT.



Figure 8. Calculated and published Henry's Law constant (K_H) values for TNT as function of temperature and the range of possible values (error bars)



Figure 9. Calculated and published Henry's Law constant (K_H) values for DNT as function of temperature and the range of possible values (error bars)

2.2 Unsaturated Soil System

Subsurface soil environments are comprised of solid soil particles and pore spaces in between the particles. The solid phase is comprised of minerals of different sizes, shapes and chemical compositions, as product of the weathering of the parent rock or materials. In addition, the solid phase may have an organic fraction which is composed by plants and animals in different stages of decomposition. Pore spaces are generally filled with water and/or gas, except in cases where non-aqueous phase liquids (NAPLs) are present in the subsurface. If all pore spaces are filled with water the system is considered water-saturated.

Most subsurface environments are comprised of an unsaturated zone, also known as the vadose zone and a saturated zone (Figure 10). It is in the unsaturated zone that most landmines and UXOs are found in land environments. Water in the unsaturated zone



Figure 10. Soil subsurface system (Source: USGS, 2006)

is characterized by negative soil-water pressures; whereas water in the saturated zone below the water table is subjected to positive pressures. The capillary fringe which comprises the region between the saturated and unsaturated zone, is considered nearly saturated but subjected to negative soil-water pressures.

Pore spaces in the unsaturated zone contain liquid and gas phases, as depicted in Figure 11. The liquid phase is mostly comprised of water (except in the presence of NAPLs) and dissolves solutes. The gaseous phase occupies the volume of the pores that is not occupied by the liquid phase, and is comprised principally by a mixture of gases of O_2 , CO_2 , water vapor, and contaminant vapors.



Figure 11. Graphic conceptualization of the unsaturated soil system

The total soil volume (V_T) is expressed as the sum of the contribution of the different phases;

$$V_T = V_S + V_W + V_A \tag{14}$$

where, V_S , V_W , and V_A are the volumes of solid, water, and gas, respectively. The volume of pores (V_v) between the solid particles constitutes the volume occupied by water and air (provided that no other fluid exist in the soil). It is generally described by the soil porosity (n), which is defined as the ratio of the pore volume to the total volume of the soil ($n=V_v/V_T$). Porosity is related to the bulk (or packed) density of the soil (ρ_b = mass of soil/total volume) and the soil particle density (ρ_p = mass of soil particle/volume of soil particle) by:

$$n = 1 - \frac{\rho_b}{\rho_p}$$
 (dimensionless) (15)

Soil in the vadose (unsaturated) zone can be comprised of variable fluid contents. The amount of water and gas in the pores influences many processes, including gas exchange with the atmosphere, diffusion of nutrients to plant roots, soil temperature, and the speed at which solutes and vapors move through the vadose zone [Jury and Horton, 2004]. The amount of water and air in soil are commonly described by the gravimetric water content (w), volumetric water content (θ_W), and volumetric air content (θ_A):

$$w = \frac{M_W}{M_S} \tag{16}$$

$$\theta_W = \frac{V_W}{V_T} = w \left(\frac{\rho_b}{\rho_W} \right) \tag{17}$$

$$\theta_A = \frac{V_A}{V_T} \tag{18}$$

where, M_W and M_S are the mass of water and mass of dry soil, respectively, and ρ_w is the density of water.

Water in unsaturated soil can be characterized as pellicular, pendular, and funicular water (Figure 12) [Charbeneau, 2000]. Pellicular water contains water layers strongly held by physical forces and commonly occur at very low soil-water contents. Pendular water (Figure 12a) is held in pores by capillary forces caused by surface tension between water and air. Funicular water (Figure 12b), which occurs at relative high water contents, is subjected to gravity drainage at atmospheric conditions. The amount of water sorbed to the soil particle under the pellicular water regime can be described in terms of monolayers.

A monolayer is formed when a group of bound water molecules occupies a total area identical to the soil surface area, as illustrated in Figure 13. The number of soil monolayers (*MNLs*) could be determined using the following equation:

$$#MNLs = \frac{w \cdot MA_W \cdot A_N}{S_A \cdot MW_W}$$
(19)


Figure 12. Distribution of water as: (a) pellicular and pendular water at small soil water contents, and (b) as funicular water at higher water contents (Source: Charbeneau, 2000)



Figure 13. Graphic conceptualization of the water monolayers covering the soil particle

where, w is the gravimetric water content (g/g), MA_W is the molecular area of water equal to 10.8 x 10⁻²⁰ m²/molecule [Livingston, 1949], A_N is the Avogadro's number (6.02 x 10²³ molecules/mole), S_A is the specific surface area of the soil particle (m²/g), and MW_W is the molecular weight of water (18 g/mol).

2.3 Chemical Transport in the Unsaturated Zone

The fate and transport of chemicals in subsurface environments are controlled by advective, dispersive, mass transfer, and reactive processes [Brannon et al., 1999; Anava et al., 2007; Phelan and Webb, 2002]. Advective and dispersive processes relate to the movement of chemicals with and within the bulk fluids (water or air). Advective transport causes the chemicals to move with moving fluid, such as when infiltrating water induce water flow in the soil. Dispersive transport results in the movement of chemicals from region of high concentration to low concentration and spreading of the chemicals. Dispersive transport is generally caused by two mechanisms: mechanical dispersion and molecular diffusion [Fetter, 1999]. Mechanical dispersion result from velocity variation within a moving fluid and dominate dispersion transport processes under advective conditions. Molecular diffusion results from the random movement of molecules caused by Brownian motion in the medium of interest [Schwarzenbach et al., 2003]. It is a significant transport mechanism under limited flow conditions. Mass transfer processes influence the movement of chemicals between environmental components (e.g., water, air, solid, organic matter). Reactive processes, which include sorption, chemical precipitation and transformation, affect the overall transport of chemicals and result in chemical retardation, greater spreading, and the disappearance or production of chemicals.

The dynamics of ERC movement in soils is complex, involving multiple, interrelated processes that vary with environmental conditions [Anaya et al., 2007]. Advection, dispersion and diffusion in the water phase dominate transport during wet conditions. At low soil-water contents during dry conditions, water flow is limited and transports of chemicals occur through water diffusion and/or vapor transport. Volatile or semi-volatile chemicals, such as TNT and DNT, would be subjected to both forms of transport. Because, the diffusion coefficients in air for TNT and DNT are much greater than those in water (i.e., $D_{A-M}/D_{W-M} > 10^4$), vapor phase transport is expected to control the movement of these chemicals at low water contents.

2.4 Vapor Transport in Soils

Vapor transport in the unsaturated zone could be induced by air flow or by gaseous diffusion. Air flow in the unsaturated zone is present near the soil surface where significant convective flow occur, for example, as a result of turbulence-induced air pressure fluctuations [e.g., Tillman et al., 2002] and changes in mean air temperature or barometric pressure [Choi et al., 2002]. Advective transport in the vapor phase is also important during air sparging techniques and vapor extraction activities used for remediation of sites contaminated with volatile organic compounds (VOCs) [Hutzler et al., 1989]. However, under normal environmental conditions, vapor transport in soil occurs predominantly by molecular air-diffusion.

Air-diffusion or gaseous diffusion is considered to be the most important process causing gaseous interchange between the soil and the atmosphere [Troeh et al., 1982]. Gaseous diffusion renews the oxygen supply and removes excess of carbon dioxide from soil [Troeh et al., 1982]. Also, significant amounts of water vapor reach the soil surface by diffusion and escape into the atmosphere. Gaseous diffusion is considered a predominant vapor transport process for VOCs in the unsaturated zone [Petersen et al., 1994]. The significance of vapor diffusion of semi-volatile compounds such as TNT and DNT has yet to be explored. A need, thus, exists to advance knowledge on vapor diffusive transport in the unsaturated zone.

2.4.1 Effective Gas-Phase Diffusion in Soils

In soils, air diffusion cannot proceed as fast as it can in air because the compounds must follow longer pathways as they travel around mineral grains and water [Jury and Horton, 2004]. To account for this, an effective diffusion coefficient in air (D_A) must be used:

$$D_A = \frac{D_{A-M}}{\tau(\theta_W)} \tag{20}$$

where, $\tau(\theta_W)$ is the saturation dependent tortuosity coefficient. If *L* is the straight-line distance between the ends of the tortuous flow path and L_e is the real distance through the flow path, the tortuosity factor can be defined as $\tau = L_e/L$. Tortuosity values are always greater than 1. This factor increases with increasing soil-water content because there are more restrictions for the air diffusion of the compounds. Similar to diffusion in soil-air, molecular diffusion in soil-water is restricted by the presence of soil minerals and air. An effective diffusion coefficient in water (D_W) is, therefore, used to characterize diffusion in soil-water.

$$D_W = \frac{D_{W-M}}{\tau(\theta_W)} \tag{21}$$

The tortuosity factor has been shown to be a function of soil water content [Jury and Horton, 2004]. In general, the tortuosity factor is assumed to increase with increasing water content for gas-phase diffusion in soils, and to increase with decreasing water contents for aqueous-phase diffusion. The general trend describing the effect of water content on τ has been for long a subject of debate, and it is likely dependent on the system and chemicals being analyzed.

Empirical equations have been used to relate the effective gas diffusion with the molecular gas diffusion as function of the air content. Some function apply a linear model of the form $D_A/D_{A-M} = a(\theta_A-b)$, and others have used the exponential model $D_A/D_{A-M} = s \cdot \theta_A^{m}$ (*a*, *b*, *s*, and *m* are parameters determined empirically) (Table 3). Many models have been established using tracers as diffusing compounds [Costanza and Brusseau, 2002; Werner and Höhener, 2003]. The most commonly used models for describing the effective diffusion coefficient of gases were developed by Penman [1940] and Millington and Quirk [1961].

The Millington and Quirk (M&Q) model has been used in several studies, showing in some circumstances good agreement with the laboratory measured data.

Karimi et al. [1987] used the M&Q model for benzene (C_6H_6) gas transport and proved the applicability of this model for the prediction of effective diffusion in porous media of low molecular weight compounds. Gierke et al. [1992], using toluene and methane as tracer, successfully estimated the effective gas diffusion coefficient using the M&Q model. Werner and Höhener [2003], using some volatile compounds and SF₆ as tracer, determined that the effective diffusion coefficients in the soils are better described by the M&Q when compared to the Penman model.

Although the M&Q model has shown a considerable improvement over other models, it still failed to accurately predict the gas phase diffusivity at higher relative saturations [Fuentes et al., 1991]. For instance, M&Q model does not predict the termination of gaseous diffusion at relative saturations less than one [Schaefer et al, 1997]. Peterson et al. [1988], using the M&Q model for vapor transport of TCE, observed deviations of the effective diffusion coefficients as high as 39%. Sallam et al. [1984], Petersen et al. [1994], and Batterman et al. [1996], determined that the effective diffusion coefficients were generally larger than the values predicted by the M&Q model, and lower than the values predicted by the Penman model. According to Jin and Jury [1996], Penman and M&Q relationships often defined a lower and an upper limit of the effective diffusion coefficients values.

Effective diffusion coefficients of undisturbed soils and sieved-repacked soils often differ greatly [Moldrup et al., 1997, 2000]. Penman models largely overestimates, while the M&Q model underestimated the effective diffusion coefficients in sieved, repacked soils [Moldrup et al., 2000]. For this reason, Moldrup et al. [2000] derived a model to determine the effective diffusion coefficients in repacked soils. This model was based on the Marshall [1959] model for completely dry porous media, and included a reduction term (θ_A/n) to describe the increased tortuosity, compared with a dry soil at the same air-filled porosity, resulting from interconnected water films. Therefore, the Moldrup [2000] model gives better predictions for repacked soils compared with the Penman and the M&Q models.

Equation	Parameter Values	Material Tested	Air Porosity (θ_A)	References ^a
$\frac{D_A}{D_{A-M}} = s \cdot (\theta_A)^m$	s=1, m=2	sand, soils	$0.16 < \theta_A < 0.61$	Buckingham, 1904
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.66, b = 0	sand, glass spheres	$0.15 < \theta_A < 0.93$	Penman, 1940
$\frac{D_A}{D_{A-M}} = a \cdot (\theta_A - b)$	a = 1.3, b = 0.1 a = 0.71, b = -0.01	brookston clay paulding clay	$0.10 < heta_A < 0.30$ $0.05 < heta_A < 0.33$	Blake and Page, 1948
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.668, b = 0 a = 0.97, b = 0.09	loam sand	$0.10 < heta_A < 0.45$ $0.10 < heta_A < 0.45$	Taylor, 1949
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.58, b = 0		$\theta_A = 0.355$	Van Bavel, 1952
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.37, b = 0.17	soils at different depths	$0.20 \le \theta_A \le 0.40$	Runkles, 1956
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.66, b = 0.1	soils	$0.14 \le \theta_A \le 0.39$	Call, 1957
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.60, b = 0 a = 0.68, b = 0	dry materials wetted materials		Rust et al., 1957
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.90, b = 0.14	soils	$0.15 < \theta_A < 0.60$	Wesseling and Van Wijk, 1957
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	0.73 < a < 0.90, b = 0		$0.2 < \theta_A < 0.4$	Dye and Dallavalle, 1958
$D_A / D_{A-M} = (\theta_A)^{4/3}$		porous solids	$0.25 < \theta_A < 0.50$	Marshall, 1959
$\frac{D_A}{D_{A-M}} = s \cdot (\theta_A)^m$	s = 1.9, m = 1.4	dry sand, glass spheres	$0.17 < \theta_A < 0.43$	Curie, 1960
$\frac{D_A}{D_{A-M}} = s \cdot (\theta_A)^m$	s = 1.75, m = 2.1	wet sand, glass spheres	$0.30 < \theta_A < 0.40$	Curie, 1961
$\frac{D_A}{D_{A-M}} = s \cdot (\theta_A)^m$	s = 0.49, m = 1.5	silt loam topsoil	$0.02 < \theta_A < 0.40$	Gradwell, 1961
$D_{A}/D_{A-M} = \frac{(\theta_{A})^{10/3}}{n^{2}}$		sandy clay	$0.10 < \theta_A < 0.50$	Millington and Quirk, 1961
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.90, b = 0.11	soils	$\theta_A > 0.10$	Wesseling, 1962
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.88, b = 0.16	soils	$0.25 < \theta_A < 0.52$	Ritchie, 1964
$\frac{D_A}{D_{A-M}} = s \cdot (\theta_A)^m$	s = 0.85, m = 2	soils		Bakker et al., 1970
$D_A / D_{A-M} = a \cdot (\theta_A - b)$	a = 0.53, b = 0.05	disturbed Soils	$0.07 < \theta_A < 0.30$	Ayres et al., 1972
$\frac{D_A}{D_{A-M}} = \frac{(\theta_A)^{3.1}}{n^2}$		yolo silt loam	$0.05 < \theta_A < 0.15$	Sallam et al., 1983.
$D_{A/D_{A-M}} = \left(\frac{\theta_{A} - 0.12}{1 - 0.12}\right)^{1.23}$		yolo loam soil		Petersen, 1994
$\frac{D_A}{D_{A-M}} = \frac{(\theta_A)^{2.5}}{n}$		sieved and repacked soils		Moldrup et al., 2000
$\frac{D_A}{D_{A-M}} = \frac{\left(\theta_A\right)^{2.5}}{\left(\theta_A + \theta_W\right)^{1.3}}$		undisturbed soil		Bartelt-Hunt et al., 2002

Table 3. Available models in the literature to determine the effective gas-phase diffusion coefficients (D_A) in different porous media as function of air content (θ_A) , molecular gas diffusion (D_{A-M}) , and/or soil porosity (n)

^a Some data was collected from Troeh et al., 1981

2.5 Sorption of Organic Compounds into the Unsaturated Soils

Sorption processes involve physicochemical interactions between compounds in fluid matrices and other energetically-favorable phases. In solute and vapor transport literature, the term *sorbent* refer to the soil or any other solid material, and interfacial surface. Meanwhile, the term *sorbate* refers to the solute or vapor sorbed onto the soil particles [Schwarzenbach, 2003]. Sorption of chemicals (i.e., solutes and/or vapors) to the soil is a general term referring to the absorption, adsorption, ion exchange, and chemisorption. Adsorption is the process by which the sorbate is held at the soil-particle surfaces or interfaces (e.g., gas-liquid, gas-solid, and liquid-solid) by van der Waals forces. Absorption is the process by which the sorbate penetrates the sorbent (e.g., soil particle, organic matter). Ion exchange refers to a process by which positively and negatively charged ions (cations and anions, respectively) in bulk water are exchanged with ions in the diffuse double layer surrounding soil particles [Schwarzenbach, 2003]. The ions are held near the soil surface by electrostatic forces, which depend on the chemical properties, the presence of the ions, and the soil properties. Ion exchange is a process which affects mostly charged compounds and is not expected to affect TNT and DNT. Chemisorption occurs when the solute is incorporated to soil by a chemical reaction. Because at times it is difficult to identify which mechanism is responsible for the sorbate-sorbent interaction, sorption is a loose term used to describe the overall result of these processes.

Sorption processes involve equilibrium and non-equilibrium interaction between the sorbate and sorbents. If the sorptive process is slow compared with the rate of contaminant transport in the porous media, sorption will not reach equilibrium and must be described by a kinetic sorption model. On the other hand, if the sorptive process is rapid compared with the contaminant transport, sorption reaches an equilibrium condition and could be described by equilibrium sorption models. Sorption models describe the equilibrium relationship between solute or vapor concentration in the water or gas phase, respectively, and the concentration at the sorbent (e.g., soil, air-water interface). These models are commonly referred to as sorption isotherms because the relationship only applies at a constant temperature. The simplest and most commonly used soil sorption model is the linear isotherm, which relates solute (C_W) or vapor (C_A) concentration linearly to the sorbed concentration on the soil (C_S) as expressed in Equations 22 and 23.

$$Cs = K_d'C_A \tag{22}$$

$$Cs = K_d C_W \tag{23}$$

where, K_d ' and K_d are the air-soil and water-soil distribution constants, respectively. Commonly used nonlinear sorption models include the Freundlich (Eq. 24), Langmuir (Eq. 25), and Brunauer-Emmett-Teller (BET) (Eq. 26) isotherm [Chatwin, 1998]:

$$C_s = K_{Fr} C_{eq}^{\frac{1}{n}}$$
(24)

$$C_{S} = \frac{K_{L}C_{S_{MAX}}C_{eq}}{1 + K_{L}C_{eq}}$$
(25)

$$C_{s} = \frac{K_{BET} C_{S_{MAX}} C_{eq}}{(C_{sat} - C_{eq}) [1 + (K_{BET} - 1) C_{eq} / C_{sat}]}$$
(26)

where, C_s denotes the soil concentration, K_{Fr} is the Freundlich sorption coefficient, C_{eq} is the equilibrium concentration in aqueous or vapor phase, 1/n is an empirical exponent, K_L is the Langmuir sorption coefficient, Cs_{max} is the maximum sorbate concentration, and K_{BET} is the BET sorption coefficient. Langmuir and BET isotherms were developed originally to characterize the adsorption of gases by solids.

ERCs in unsaturated soil media can be sorbed to soil organic matter, the soil mineral surface, or to the air-water interface. The degree to which the chemicals are sorbed to each of these compartments depends on chemical physicochemical properties, the amount and nature of organic matter, soil properties, and the air-water interfacial areas [Schwarzenbach et al., 2003], and environmental conditions [Torres et al., 2007].

Sorption to soil organic matter (OM) is the predominant sorption mechanism for non-ionic organic compounds [Schwarzenbach et al., 2003] in wet soils containing relatively high fraction of organic matter (f_{om} = mass of organic matter/mass of soil > 1%) [Fetter, 1999]. It is often quantified using the organic-matter distribution coefficient (K_{OM}) and the organic carbon distribution coefficient (K_{OC}):

$$K_d = f_{OM} K_{OM} \tag{27}$$

$$K_d = f_{OC} K_{OC} \tag{28}$$

where, f_{oc} is the weight fraction of organic carbon in the soil. Values of K_{OC} are measured or often estimated using linear free energy relationships with solute solubility (*S*) and the solute distribution constant between octanol and water (K_{OW}):

$$\log K_{oc} = a \log K_{ow} + b \tag{29}$$

$$\log K_{oc} = -c \log S + d \tag{30}$$

where, a, b, c, and d are empirical constants derived to different groups of homologous organic compounds [Schwarzenbach et al., 2003]. Considering TNT and DNT homologous to alkylated and chlorinated benzenes, a, b, c, and d are assumed to be 0.74, 0.15, 0.70, and 0.59, respectively. Applying these values to the respective log K_{OW} and S values for TNT and DNT yield log K_{OC} values ranging between 1.778 and 2.854 (Table 4) for TNT, and between 1.615 and 2.647 for DNT. The estimated values are within reported *log* K_{OC} values for TNT (1.6-2.7; Eriksson and Skyllberg, 2001) and DNT (-0.6 - 2.3; Hernandez et al., 2006; Phelan et al., 2000) for various soils. Using calculated *Koc* values and the fraction of organic carbon in soil (f_{oc} =0.07%), the water-soil distribution constant (K_d) was estimated from 0.042 to 0.500 L/kg for TNT, and from 0.029 to 0.310 L/kg for DNT.

Sorption to mineral surface can be a dominant mechanism for soils with low f_{oc} [Karimi-Loftbad et al. 1996] and low water contents. Under natural conditions, soil particles are preferentially sorbed with water because the polar nature of water and the

Ľ	Junit	$\mathbf{n}(\mathbf{n}_{OC})$									
		log Kow	Solubility mol/L (25°C)	log Koc ^d	log Koc	e					
	TNT	2.2 - 2.7 ^a	5.646 x 10-4	1.778 - 2.148	2.854						
	DNT	1.98 ^b	1.120 x 10-3	1.615	2.647						
L	ATSDF	R, 1995									
)	ATSDR, 1998										
l	Using Equation 29										
;	Using Equation 30										

Table 4. Determination of the organic carbon distribution coefficient (K_{OC})

0 1

charge characteristics of most soils [Shoemaker et al., 1990]. As a result the sorption of organic chemicals to soil, which is mostly through relatively week van deer Waals forces, is limited in the presence of water [Petersen et al., 1994].

The amount of chemicals sorbed to soils has been shown to be impacted by the soil water content [Petersen et al., 1994, 1995]. Generally, soils have a high sorption capacity for organic chemicals when dry, but significantly lower when wet. Sorption constants of gases or vapors (K_d) have been shown to be substantially greater than the solute sorption constants (K_d) [Phelan and Barnett, 2001b]. Peterson et al. [1988] determined that unsaturated partition coefficients for relatively dry porous solid can be over two orders of magnitude greater that coefficient measured under saturated conditions for trichloroethylene (TCE). Phelan and Webb [2002] show that K_d ' for TNT and DNT increases about 5 orders of magnitude (10^8) as the soil dries from 11 to 1% gravimetric water content. These results indicate that, although sorption to organic matter continues to be significant for soils with organic matter, the mineral surface is the main contributor to the overall sorption capacity of organic chemicals for soil with very low water contents. In fact, variation in vapor sorption coefficients for dry soils has been explained by their surface areas rather than their organic content [Rhue et al., 1988; Ong and Lion, 1991], indicating that the adsorption reaction at the mineral phase dominates vapors uptake under oven-dry conditions [Ong and Lion, 1991].

Ong and Lion [1991] studied the mechanism for trichloroethylene (TCE) vapor sorption onto the soil minerals. Initially, vapor-soil (K_d) partition coefficient decreased exponentially 2 to 5 orders of magnitude with increments in water content, reached a minimum, and then had a slight increase (Figure 14). They divided the vapor sorption graph in three regions. Region 1 is designated as extending from an oven-dried surface to moisture content corresponding to a single monolayer of water coverage. In this region, vapor-soil partition coefficients are several orders of magnitude greater than at greater water contents, and soil surface area is proportional to the magnitude of the sorptive partition coefficient. This region is associated with sorption onto the soil surface bound water and direct sorption to the soil surface because there is not enough water to surround the soil particle. Region 2 is a transitional zone, including moisture contents corresponding from a single monolayer to about 8 monolayers coverage (calculated using the N₂-BET method). This region is characterized by a steep reduction in the soil sorption capacity until reaching a minimum sorption. Vapor sorption in this zone is dominated by adsorption onto the surface of bound water with a limited dissolution, caused by the "salting out" effects as the results of the well-structure pattern of the initial hydrating water layers. Direct sorption to the soil surface could be occurring in this region since soil surface coverage by water molecules may not be uniform. Region 3, corresponds to the region from 8 monolayers coverage to field capacity. This region is characterized by the increase uptake of vapor on the soils with the increment of moisture content, since there is sufficient water in the system that the vapor must first partition into the soil-water prior to partitioning onto the soil particle. The slight increasing in sorption into this region is the result of the dissolution of vapor into the sorbed-bound water, sorption of vapors at the liquid-vapor interface, and/or sorption at the liquid-solid interface. Finally, Ong and Lion [1991], determined that the Henry's Law could be applied only when the soil moisture correspond to more than 8 monolayers coverage of water on the solid surface because at this point water molecules start acting as a solvent.



Moisture Contents (%)

Figure 14. Designated regions for vapor-phase sorption phenomena as a function of soil moisture contents (Source: Ong and Lion, 1991)

The high sorptive capacity of dry soils may increase the vapor uptake of organic chemicals, causing greater capacity for their retention and storage [Ong et al., 1992]. One would expect this phenomenon to greatly retain these compounds and restrict the volatilization from dry soil to the atmosphere. However, they would be released as soon as water molecules are reintroduced to the soil surface [Petersen et al., 1996].

Sorption of organic chemicals to the air-water interface in unsaturated soils has been documented for VOCs [Hoff et al., 1993; Constaza and Brusseau, 2000]. Padilla [1998] attributed enhance retardation (R_{iA}) of TCE at low water contents to this sorption mechanisms and related it to the saturation-dependent specific air-water interfacial area (L^2/L^3_{Total}) of the soil (A_{iA}):

$$R_{iA} = 1 + \frac{A_{iA}k_{iA}}{\theta_W} \tag{31}$$

where, k_{iA} is the interface-air distribution coefficient of the chemical. Values of k_{iA} are dependent on chemical properties and temperatures [Hoff et al., 1993; Bruant and Conklin, 1998]. Air-water interfacial areas vary with soil water content. They tend to increase with water contents to a maximum value, and then decreasing with further

increase in saturation [Padilla, 1998]. For a given surface-active chemical, accumulation at the air-water interface is, therefore, expected to increase as water contents increases at low water contents, and decrease at high water contents.

Air-water interfacial sorption of ERCs has not yet been reported in the literature. Visual inspection of solutions following the addition of TNT and DNT crystals has shown visual accumulation at air-water interfaces (Figure 15).

Studies have shown that desorption of ERCs from soils may not always be complete due to some permanent retention (chemisorption) or degradation [Pennington and Patrick, 1990; Comfort et al., 1995; Phelan and Webb, 2002]. General data suggest that TNT is sorbed slightly stronger than DNT [Phelan and Webb, 2002].



Figure 15. Accumulation of TNT crystals at air-water interface

2.6 Diffusive Vapor Transport Equations

One dimensional transport of chemicals in unsaturated soils having negligible air or water advection can be described by:

$$\theta_{A} \frac{\partial C_{A}}{\partial t} + \theta_{W} \frac{\partial C_{W}}{\partial t} + \rho_{b} \frac{\partial C_{S}}{\partial t} = \theta_{A} D_{A} \frac{\partial^{2} C_{A}}{\partial z^{2}} + \theta_{W} D_{W} \frac{\partial^{2} C_{W}}{\partial z^{2}} - r_{S} + m_{T}$$
(32)

where, C_A is the concentration in air, C_W is the concentration in water, C_S is the concentration in soil, r_s refers to applicable chemical and biological reactions, m_T is the mass transfer term, ant t and z are the time and distance, respectively. The air-phase diffusion coefficient is much higher than the water-phase diffusion coefficient (approximately by a factor of 10,000), and the water-diffusion term in the equation (32) can be neglected. For non-reactive compounds (i.e., no reaction and $r_s = 0$) the 1-D vapor diffusive transport can be described by:

$$\frac{\partial C_A}{\partial t} \left(1 + \frac{\theta_W C_W}{\theta_A C_A} + \frac{\rho_b C_S}{\theta_A C_A} \right) = D_A \frac{\partial^2 C_A}{\partial z^2}$$
(33)

Soil-water concentrations can be related to vapor concentrations in air at equilibrium using the Henry's Law Constant (K_H , Equation 13). This relationship is applicable only when the soil-water content is enough to allow that water behaves as a solvent [Ong and Lion, 1991]. Soil concentrations can be related to vapor concentrations using soil-air (K_d ') and soil-water (K_d) distribution coefficients (Equations 22 and 23). Diffusive vapor transport can, therefore, be described by:

$$\frac{\partial C_A}{\partial t} \left(1 + \frac{\theta_W}{\theta_A K_H} + \frac{\rho_b f K_d'}{\theta_A} + \frac{\rho_b (1 - f) K_d}{\theta_A} \right) = D_A \frac{\partial^2 C_A}{\partial z^2}$$
(34)

where, f represents the fraction of soil sites where vapors are directly sorbed. The previous equation (34) can be rewritten using an effective instantaneous retardation factor (*R*):

$$\frac{\partial C_A}{\partial t} = \frac{D_A}{R} \frac{\partial^2 C_A}{\partial z^2}$$
(35)

where, R is the term in parenthesis in Equation 34.

If the soil is initially free of chemical and then exposed to a constant concentration at the bottom and a zero concentration at the top of the soil, the vapor concentration $C_{Ai}(z,t)$ at some distance z from the contamination source and some time t after the chemical source is placed, can be determined from the following analytical solution [Fetter, 1999]:

$$C_{A}(z,t) = C_{0} \operatorname{erfc}\left[\frac{z}{2\sqrt{\frac{D_{A}}{R}t}}\right]$$
(36)

where, C_0 is the initial constant source concentration at the bottom of the soil, and *erfc* is the complementary error function.

Vapor flux (F_A , mass/length²) at a distance z from the source can be estimated using [Cussler, 1997]:

$$F_A = C_0 \sqrt{\frac{D_A}{\pi \cdot t}} \left[e^{-z^2/4tD_A} \right]$$
(37)

2.7 Transport Models for the Vadose Zone

During the last three decades there have been significant developments on subsurface transport models. Initially, these models were developed for agricultural applications for the understanding of the nutrients and pesticide transport. Later, as significant contamination was identified in many sites, models were developed and modified to predict the fate and transport of hazardous contaminants (e.g., VOCs). Some models, such as HYDRUS 1D [Šimůnek et al., 1995] and T2TNT [Webb et al., 1999], have been adapted to work with fate and transport of ERCs in soils.

Commonly, models based on saturated-zone transport concepts are applied for the prediction of transport in unsaturated zone. This practice is not completely appropriate, as the behavior of contaminants in the unsaturated zone is very dependent on the soil-water content. Many models describing the behavior and fate contaminants in unsaturated porous media, for instance, assume that sorption of vapors can be adequately described by the saturated partition coefficients. However, simply replacing the saturated partition coefficient with a vapor-phase partition coefficient in a transport model is not adequate since both liquid- and vapor-phase sorption occur simultaneously [Shoemaker et al., 1990], and the degree at which they happen vary with water content.

There are many environmental factors and important transport mechanisms that must be incorporated in unsaturated zone transport models. These transport mechanisms include: gas and water advection; gas and water diffusion or dispersion; gas-water, gassolid, water-solid partitioning; chemical and physical non-equilibrium, mass transfer limitations between phases, and chemical and biological reaction. Many of these mechanisms may occur concurrently, making difficult to distinguish their relative impact to the overall transport.

Ong et al. [1992] published a complete summary of some of the principal models developed for the vapor transport and their respective physical-chemical and biological features (Table 5). Although many models of vapor transport are available, information is

limited on physical-chemical processes affecting the movement of organic vapors, such as the rate of vapor-phase partitioning and/or mass transfer of vapors.

In addition to these models, Brusseau [1991] developed a chemical and physical non-equilibrium organic-vapor transport model. They used a first-order mass transfer between the gas and water phases and rate-limited sorption equilibrium between water and soil. Gierke et al. [1990] derived a model for unsaturated transport with the presence of gas and water flow. They determine the effects that gas and liquid diffusion, gas-water equilibrium and mass transfer, and solute sorption had on vapor transport. Their model includes physical non-equilibrium to account for as gas-water mass transfer, film transfer, and intra-aggregate diffusion, but chemical non-equilibrium was not considered.

References		Features *													
		2	3	4	5	6	7	8	9	10	11	12	13	14	15
Mohsen et al., 1980	2		Х	Х									Х		Х
Weeks et al., 1982	1		Х	Х			Х	Х					Х		
Jury et al., 1983	1		Х		Х	Х	Х	Х			Х				
Stephanatos, 1985	2		Х	Х	Х	Х	Х					Х	Х		
Abriola and Pinder, 1985	1	Х	Х		Х	Х	Х					Х	Х	Х	Х
Pinder and Abriola, 1986	2	Х	Х		Х	Х	Х					Х	Х	Х	Х
Springer, 1986	3		Х				Х	Х							
Corapcioglu and Baehr, 1987	1	Х	Х		Х	Х	Х	Х			Х		Х	Х	Х
Baehr, 1987	2	Х	Х		Х	Х	Х	Х					Х	Х	
Hutzler et al., 1989	1		Х	Х	Х	Х	Х	Х		Х					
Metcalfe and Farquhar, 1987	2		Х	Х		Х	Х						Х		Х
Sleep and Skyes, 1989	2		Х	Х	Х	Х	Х			Х		Х	Х	Х	Х
Shoemaker et al., 1990	2		Х		Х	Х	Х	Х	Х		Х				
Culver et al., 1991	2		Х		Х	Х	Х	Х	Х			Х	Х		

Table 5. Physical-chemical and biological features of various vapor transportmodels (Source: Ong et al., 1992)

* 1 = number of dimensions; 2 = multicomponent (pollutant); 3 = diffusion, vapor phase; 4 = advection, vapor phase; 5 = diffusion, aqueous phase; 6 = advection, aqueous phase; 7 = dissolution (Henry's law); 8 = sorption at solid-liquid interface; 9 = vapor sorption other than 7 and 8; 10 = non-equilibrium mass-transfer effects; 11 = biodegradation; 12 = temporal variability in moisture contents; 13 = spatial heterogeneity; 14 = immiscible phase; 15 = density-dependent gas behavior

Pruess [1991] developed the code TOUGH2. This code is used to simulate heat transfer and fluid flow in porous media. TOUGH2 was modified by Webb et al. [1999] for the landmine application and was renamed as T2TNT. The modifications to the TOUGH2 code were: to include the physicochemical properties of the ERCs, to change the use of the Fick's Law by the Dusty Gas Model for gas diffusion, to include the liquid diffusion, to add the water-solid and vapor-solid sorption using the Petersen et al. [1995] model, to calculate the boundary layer at the soil surface, to include the atmospheric boundary conditions, and to incorporate biodegradation and the presence of plants [Phelan and Webb, 1999; Webb et al., 1999].

Some of the developed models are analytical solution to the advection-diffusion equation (e.g., Jury et al., 1984; Pinder and Abriola, 1986; Corapcioglu and Baehr, 1987). However, these models were limited by assuming homogenous porous medium, linear equilibrium adsorption between all phases, no mass transfer limitations, and homogenous distribution of water contents. Other models using finite element (e.g., Stephanatos, 1985; Sleep and Sykes, 1989), have the suitability of applying non-linear and non-equilibrium partition coefficients, the use of mass transfer rate, and the evaluation of spatial and temporal variations of heterogeneous porous media.

This study uses HYDRUS-1D code [Šimůnek et al., 1995] for the vapor transport modeling. This Windows-based numerical model is one of the most widely used for unsaturated flow and solute transport modeling [Scanlon, 2004]. HYDRUS-1D has the following features: one dimensional variably-saturated flow (using Richard's Equation), root water uptake, heat transport, pedotransfer functions (to determine soil hydraulic properties), and solute transport. The solute transport module includes: nonlinear sorption, two-site non-equilibrium sorption (including mass transfer), mobile-immobile, water zero-order production, sequential transformation reactions, fixed and time variable boundary conditions. Moreover, HYDRUS-1D facilitates the spatial distribution of materials and water contents using an interactive graphics-based interface for data input and, also, for viewing the simulation results. This code is a useful tool for estimating soil hydraulic parameters, solute transport and reaction parameters, and heat transport parameters through the use of inverse modeling. Inverse methods have become the standard in soil science to identify solute transport parameters, and have been shown to be very successful [Casey and Šimůnek, 2001].

2.8 TNT and DNT Transport from Buried Explosive Devices

Recent efforts to develop and electronic dog's nose have prompted a careful evaluation of the transport of explosive related compounds signatures from buried landmines through the soil to the ground surface [Phelan and Barnett, 2001b]. Extensive documentation exists on the fate and transport of explosives residues from contaminated soils and groundwater under saturated conditions [McGrath, 1995]. However, processes controlling the migration of ERCs through soil under unsaturated conditions are poorly understood [Ravikrishna et al., 2002]. There are only few studies concerning to ERCs vapor transport. The most important ERCs studies during the last decade will be described next.

In 1999, Jenkins and collaborators analyzed the vapor signature from buried explosives. They had the objective of measuring the headspace vapor concentration of TNT, DNT, and 1,3-dinitrobenzene (1,3-DNB) above a 2.5 thick soil covering 110 mg of solid TNT. Three different soils (silica sand, silt loam, and clay) were investigated at three different water contents: air dry ($\approx 2.1\%$ -3.1 %), low moisture ($\approx 5.8\%$ -10%), and high moisture ($\approx 15\%$ -33%). Every set of experiments were conducted in 40-mL amber vials containing TNT beneath the soil. Vials were held at three temperatures (23°C, 4°C, and -12°C) for up to 173 days. Soil headspace was sampled using polyacrylate solid phase microextraction (SPME), using sorption periods time between 5 to 20 minutes. Vapor samples were analyzed using gas chromatography. At the end of the experiments the top 5 mm (≈ 2 to 4 grams) of soil were collected, extracted with acetonitrile and analyzed using high-performance liquid chromatography (HPLC). Experimental results showed that vapor concentrations above air dried soils were about an order of magnitude lower than over moist soils. For example, at day 63, 2,4-DNT vapor concentration over

sandy soil were 34.9, 168, 211 pg/mL, for 0%, 2.1% and 3.1% soil water contents, respectively. Furthermore, concentrations of the nitroaromatics were about an order of magnitude higher over sand than silt and about two orders of magnitude higher for clay. In regard to the soil temperature effects on the vapor concentrations, results showed that at low temperatures vapor concentrations were significantly smaller than the concentrations at 23°C. Another important result was the change in soil sorbed concentration as function of temperature and moisture content. Soil concentration of 2,4-DNT in sand at 23°C was reduced from 1.52 to 0.992 mg/kg, when moisture content was changed from air-dried to high. Also, these concentrations were reduced from 1.14 to 0.769 mg/kg with a decrease in temperature from 23°C to 4°C. However, TNT behavior was slightly different when the soil concentrations were evaluated at different water contents. TNT soil concentration at 23°C increased with moisture content from 1.23 to 1.82 mg/kg of sand. Jenkins et al. [1999] also determined the soil-air partition constants (K_d) for the different compounds, soil types, and temperatures. Soil-air partition constants decreased with temperature, and were higher for clay and dry soils, and lower for sand and wet soils. Determined K_d values of sandy soil at 23°C ranged from 5.5 x 10³ to 4.4×10^4 L/kg for 2,4 DNT; and from 1.6 x 10^4 to 3.9 x 10^5 L/kg for TNT for wet soil and dry soil, respectively.

The following year (2000), Jenkins and collaborators published results on the signature of explosive-related chemical signatures in soil samples collected near buried landmines. They established a minefield where eight different types of mines were buried with TNT as a main charge. Samples of soil (silt loam) near the landmines at 41, 111, 270, 368, and 472 days from the burial were collected. These samples were extracted using acetonitrile and aliquots were analyzed using HPLC. Also, from sorption isotherm experiments they determined that soil-water partition constant (K_d) ranged non-linearly from 1.9 to 16.2 L/kg for TNT and 1.2 to 6.4 L/kg for DNT. Moreover, they performed studies about the soil-air partitioning coefficients. Contaminated soil near the mines was extracted, equilibrated in closed vials, and measured the headspace concentrations above soils. Their results shown that the soil-air partition constant (K_d) ranged from 3.9 x 10⁴ to 7.0 x 10⁶ L/kg (averaging 8.6 x 10⁵ L/kg) for DNT, and 1.3 x 10⁶ to 3.1 x 10⁷ L/kg

(averaging 9.6 x 10^6 L/kg) for TNT, all in the range of 10% to 19% of gravimetric water contents. They determined that, although TNT and 1,3-DNB are important components of landmines fluxes, they do not accumulate in the soil to the same degree as DNT, and attributed this to the higher environmental stability of DNT. Finally, they estimated the concentrations in the atmospheric boundary layer above a landmine in 0.85 pg/L and 300 pg/L for TNT and DNT, respectively.

Leggett and collaborators (2001) studied the release of explosive-related vapors from landmines. They analyzed five landmines containing TNT as the main explosive charge. Experiments used Tedlar plastic bags, where the landmines were inserted and sealed. Vapor fluxes emanating from the mines (inside of the bags) were continuously monitored using SPME technique as a sampling method. These experiments ran from 2 to 7 days at different temperatures, ranging from -3°C to 34°C. Results showed that DNT fluxes emanating from mines to the air at 20°C ranged from 0.6 to 30.3 ng/cm²-day (determined using the mean flux values and the surface area of the mines); and from 0.2 to 3.0 ng/cm²-day for TNT fluxes. A second type of experiments was conducted at 22°C, they submerged the mines in water to evaluate the release of ERCs from landmines into surrounding water. Experiments results showed that DNT was the predominant contaminant vapor emitted by the TNT-filled mines. Emissions of vapors from mines in water occurred very rapidly at the beginning of the experiments and tended toward a constant flux rate at the end of the experiments. Fluxes from mines in water were about 3 times larger than mines in Tedlar plastic bags.

Phelan and Barnett (2001b) studied the phase partitioning of TNT and DNT in soils. Their research includes laboratory measurements of water solubility, soil-water partitioning, and soil-vapor partitioning of TNT and DNT. They determined values of K_d for DNT equal to 1.8 mL/g for low solution concentrations (0.3 to 1.3 µg/mL), and 0.72 mL/g for high solution concentrations (20 to 130 µg/mL). This reduction in the partition constant at high solution concentration proved that sorption follows a Freundlich isotherm. Using this type of isotherm, they determined that the soil concentration (C_s in µg/g) as function of water concentrations (C_W in µg/mL) could be determined using

 $C_S=2.1C_W^{1.3}$. Soil-vapor partition coefficients were measured as function of soil water content. In the study, about 1 gram of DNT was placed into 5 dram vial. Water was added through the septum top in 5 to 20 µL increments into the soil. Vapor samples in the soils headspace were taken using SPME fibers. They found that at dry soil conditions, DNT vapors were marginally detectable using SPME sampling. However, when the soil was wetted, the headspace vapor concentrations were larger. They explained this observation with the fact that at low water contents the soil-vapor partitions are higher. Values of soilvapor partition constants increase exponentially by a factor of 100,000 as the soil moistures decreased below the ten (10) monolayers water coverage instead of the eight (8) monolayers, as suggested by Ong and Lion [1991]. Finally, they developed an empirical correlation, based on Petersen's model [Petersen et al., 1995], to describe the DNT soil-vapor partition coefficients (K_d) as function of water contents (w):

$$K_{d}' = 10^{\left\{ \left[13.1 - \log\left(\frac{w + 0.53}{8.72 \times 10^{-6}}\right) \right] e^{-43.5 \cdot w} + \log\left(\frac{w + 0.53}{8.72 \times 10^{-6}}\right) \right\}}$$
(38)

In 2002, Ravikrishna and collaborators reported a study on the vapor phase transport of unexploded ordnance compounds through soils. They analyzed the vapor flux emanating from a 2-cm thick soil layer contaminated with 2,4-dinitrotoluene, 2,6-dinitrotoluene, and 1,3-dinitrobenzene. This study measured the vapor flux above the soil, when subjected to sweeping air above the soil. They trapped air samples using stainless-steel tubing containing 0.2 grams of Tenax[®]. Experiments were conducted in three different soils (sandy loam, clay loam, and clay). Each soil was analyzed using three different combinations of soil moisture and relative humidity (RH) of the sweeping air passing above the soil layer (5%-soil moisture with 100%-RH, 20%-soil moisture with 0%-RH, and 5%-soil moisture with 0%-RH). They also studied the variation in vapor flux as function of temperatures, conducting experiments at 24°C and others at 14°C. In general, their research showed that vapor fluxes of the three compounds were reduced with time, especially for the experiments at 5%-soil moisture with 0%-RH. They suggested that this behavior was caused by a reduction of the moisture content during the experiments, which increase the vapor-soil sorption and consequently reduced the vapor

concentration. Another hypothesis was that reduction of soil moisture content produced a surface reaction (e.g., oligomerization) that degraded these compounds. They modeled collected data using an analytical solution for the vapor transport equation. The model was calibrated using the soil-air partition constant as the fitting parameter. Modeled K_d constants were compared with those estimated using water-soil sorption constant and the Henry's Law constant because direct measurements of K_d was not performed. Discrepancies between modeled and estimated K_d were about one order of magnitude. Soil-air partition constants were in the range of 8.9×10^4 to 1.7×10^6 L/kg and model-fitted constants were in the range of 1.1×10^5 to 4.2×10^7 L/kg. Finally, they evaluated the effects of soil temperature on vapor fluxes, and found that fluxes at 24°C were uniformly higher than those obtained at 14°C. Fluxes of 2,4-DNT at 14° C were in the range of 0.11 to 0.51 ng/cm²-hr, while fluxes at 24°C were in the range of 1.43 to 6.63 ng/cm²-hr.

Cragin and Leggett [2003] worked in the determination of diffusion and flux of ERCs through plastic mine surrogates. They evaluated five different types of plastic mine surrogates (low- and high-density polyethylene, polypro-pylene, polystyrene, and polyvinyl chloride). The first part of the experiments was using a circular piece of the plastic surrogates, and doped them with 200-g of TNT in a desiccators jar for several months. Then, specimens were placed in Tedlar plastic bags for a week at different temperatures and air concentration samples were taken. They found that TNT fluxes $(ng/cm^{2}-day)$ emanating from the different plastic surrogates ranged from 0.4 to 1.2 μ g/cm²-day at -4°C, from 2.0 to 7.5 μ g/cm²-day at 9.2°C, and from 4.0 to 23.3 μ g/cm²day at 21.5°C. In the second part of the experiment, they repeated the same procedure of the fist part, and then plastic surrogates were placed in jars containing water in order to desorb them. Water samples were taken periodically for two months. Following desorption in the water, specimens were removed and extracted with acetonitrile for two weeks. Using this procedure they corroborate the ERC air fluxes for a second time, determined the diffusivities in the plastics, and measured the plastic-air partition coefficients. Measured fluxes of DNT at 21.5°C ranged from 7.5 to 51.8 ng/cm²·day, and from 5.1 to 19.4 ng/cm²·day for TNT. Meanwhile, the ERC diffusivities in plastic mine

surrogates at 21.5°C ranged from 0.66 x 10^{10} to 28 x 10^{10} cm²/s for DNT, and from 2.9 x 10^{10} to 30 x 10^{10} cm²/s for TNT. Finally, plastic-air partition coefficients (V_{air}/V_{plastic}) were determined in the range of 1.3 x 10^{-3} to 54 x 10^{-3} for DNT, and 15 x 10^{-3} to 290 x 10^{-3} for TNT.

Table 6 presents a summary of some transport parameter values presented in this section and from others studies not described herein. Soil-water distribution constants reported in the literature were higher than the ranges of values determined in this study (0.042-0.500 L/kg for TNT, 0.029-0.310 L/kg for DNT) using equations 29 and 30. It is postulated that the type of soil and the lower fraction of organic carbon reduce the soil sorption of these compounds.

	Soil Headspace Vapor	Vapor Fluxes	Soil-Water Distribution	Soil-Vapor Distribution
	Concentration (pg/mL)	(ng/cm ² -day)	Constant (L/kg)	Constant (L/kg)
	34.9 to 211 (23°C) ^a	0.6 to 30.3 (20°C) ^c	1.2 to 6.4 (silt loam) $^{\rm f}$	5.5×10^3 to 4.4×10^4 (sand) ^a
DNT	275 to 1,840 (22°C) ^b	34.32 to 159.1 (24°C) ^d	0.72 to 1.8 (sandy loam) $^{\rm g}$	$3.9 \text{ x } 10^4 \text{ to } 7 \text{ x } 10^6 \text{ (sandy loam)}^{\mathrm{f}}$
		0.828 to 10.3 (23°C) $^{\rm b}$	0.67 (sandy loam) d	8.9×10^4 (sandy loam) ^d
TNT	3.19 to 96.8 (23°C) ^a	0.344 to 2.58 x 10 ³ (25°C) ^h 0.2 to 3.0 (20°C) ^c 4 x 10 ³ to 23.3 x 10 ³ (21°C) ^e .322 to 1.05 (23°C) ^b	1.9 to 16.2 (silt loam) $^{\rm f}$	1.6×10^4 to 3.9×10^5 (sand) ^a 1.3×10^6 to 3.1×10^7 (sandy loam) ^f

Table 6. Summary of the transport parameters of DNT and TNT reported in the literature

References:

^a Jenkins et al., 1999

b George et al., 1999

c Leggett et al., 2001

^d Ravikrishna et al., 2002

e Cragin and Leggett, 2003

f Jenkins et al., 2000

^g Phelan and Barnett, 2001b

h Phelan et al., 2001

CHAPTER 3: MATERIALS AND METHODS

Vapor transport experiments were conducted in soil columns packed with sandy soil by placing DNT and TNT crystals beneath the soil, and monitoring vapor-phase concentrations with time at different distances from the source. Vapor transport above the source was monitored at different environmental and soil conditions. Two temperatures (22°C and 35°C) and different water contents below soil-water field capacity were analyzed. Details on the materials and methods used in the experiments are presented herein. Pictures of the materials and equipments used in the experiments are provided in Appendix A.

3.1 Physical System

The physical system used to simulate vapor transport above landmines consisted of three stainless-steel soil columns connected to a sweeping line at the top (Figure 16). The columns were placed inside an environmental chamber to control the temperatures. The sweeping lines were set to deliver a flow of humidified air (breathing quality) across the top of the column at a rate of 80 mL/minute. They were used to quickly remove ERCs from the soil headspace to maintain a zero-concentration boundary condition at the soil surface. Air flow in the sweeping line was delivered from compressed air cylinders (Linde Gas, PR) and controlled using a flow meter and a mass flow controller (Cole-Parmer, A-32505-00). Air was humidified to 70% relative humidity using a gas washing bottle (ACE Glass, Inc.) to reduce water evaporation in the columns.

3.1.1 Environmental Chamber

Soil columns during experiments were placed inside an environmental chamber (Figure 17) designed to maintain constant temperatures ($\pm 0.1^{\circ}$ C) from 4°C to 45°C. The



Figure 16. Schematic of the experimental system



Figure 17. Environmental chamber and soil columns

plexiglass chamber has dimension of 90x60x60 cm (wide, height, depth). Temperature was controlled using a recirculation water bath (Thermo Scientific, Neslab RTE 10), a high performance fan (Flex-a-Lite), and two oils cooler at the front of the fans. Cooled or heated water circulates through copper tubing (1/4-inch OD). Insulating bubble rap was adhered to the chamber walls in order to reduce heat losses.

3.1.2 Soil Columns and Sampling Ports

Three customized stainless steel columns were used for the experiments, with the dimension illustrated in Figure 18. Columns 1 and 3 were fabricated by Swagelok®, while column 2 was fabricated by a local seller (Añasco Precision, Inc., PR). All columns consisted of a flat bottom cap, a long main tube, and an upper cap with an internal conical shape. Both caps in each column were hold tightly to the main tube with two sanitary clamps. Teflon gaskets were placed between the cap and the tube to prevent leaks at the cap-tube connection. The upper cap has included an aperture of 0.6-cm, through which the sweeping line was connected. Each column contained three sampling ports at the distances illustrated in Figure 18. These sampling ports consisted of cylindrical porous cups (0.6-cm OD, 1.6-cm long) welded to 0.32-cm stainless steel tubes and a VICI® end cap containing a syringe guide with a Teflon septum (Figure 19). The pore size of the porous cups has an average of 100-µm, according to manufacturer specifications (Mott Metallurgical, NJ).



Figure 18. Soil columns and sampling ports dimensions



Figure 19. Vapor sampling port

3.2 Column Packing and Water Content Analysis

The sandy soil used in the experiments was collected from Isabela, Puerto Rico. Physical and chemical characteristics of the soil are presented in Table 7. More details of soil characteristics are given by Rodriguez et al. [2006] and Molina et al. [2006]. This soil is classified as a well sorted because de uniformity coefficient ($C_u = 3.57$) is less than 4 [Fetter, 2001]. The sand was sieved using a No. 10 mesh (2 mm openings). Prior to the column packing, distilled water was added to the oven-dried (105°C for 24 hours) sand and thoroughly mixed with a spoon to achieve the homogeneous distribution of preselected water contents for each column. Selected water contents were below the soil field capacity to prevent water drainage and non-uniform water content throughout the column. Field capacity has been defined as the water content near soil surface profile (i.e., root zone) at which drainage becomes negligible [Jury and Horton, 2004]. Field capacity for the sand used in these experiments was estimated to be near 13%. Water contents in the experiments were thus set below this value. Once, soils were wetted, samples of each soil were taken and placed in an oven to analyze their initial water contents. Water contents were determined gravimetrically [Jury and Horton, 2004] by measuring soil weights prior to and after drying a given soil mass.

Table 7. Physical and chemical characteristics of the soil (Source: Molina et al., 2006)

USCS	Fraction Organic	Organic	pН	Specific	Specific Surface	Mineralogy	Sieve A	analysis	d_{50}^{a}	<i>C</i> _{<i>u</i>} ^b
Classification	Carbon	Matter		Gravity (g/cm [°])	Area (m ⁻ /g)		% Sand	% Fines		
SP	0.07%	0.47%	8.83	2.83	1.687	Quartz/Calcite	92.6	7.4	0.4 mm	3.57

^a Particle size diameter smaller than 50% in a grain-size distribution curve

^b Uniformity coefficient ($C_u = d_{60}/d_{10}$)



Figure 20. Columns packing: (a) packing equipments, (b) inserted sampling port, and (c) explosive source on the bottom cap

Soil columns were packed on increments of 1-cm and tapping about 20 times with a Teflon piston (Figure 20a). Porous cups were inserted into the columns once the sand levels were near the sampling port elevation, as shown in Figure 20b. Soil packing densities (bulk) were determined by weighting the columns (with all accessories) prior to and after packing.

Experiments were conducted by placing TNT and DNT crystals (Chem Service, Inc.), 100-mg each, beneath the soil and monitoring vapor-phase concentrations at sampling ports along the column for a period of time. TNT and DNT crystals were spread along the bottom of the column prior to packing (Figure 20c). In two experiments (Sets 1 and 2; Table 8), the explosive source was distributed about 1.5-cm diameter on the center of the bottom cap. The explosive source was distributed over the whole cap (about 3.4-cm diameter) for other experiments (Sets 3, 4, and 5; Table 8). A total of five vapor transport sets of experiments were conducted in soil (Table 8). Vapor transport behavior of DNT and TNT in soils under different water contents was analyzed at 22°C and 35°C. Three different targeted water contents were evaluated at each set of experiments.

Several vapor transport experiments were also conducted in the stainless steel columns with no soils. This was done to determine the diffusive vapor transport behavior in bulk air in the column system. The no-soil vapor transports experiments were conducted by placing the explosive source (TNT and DNT crystals) at the bottom of the column. These experiments were all conducted at 22°C.

Set	Column	Source Area	Targeted Water	Experimental		
561	Column	(cm ²)	Content (cm ³ /cm ³)	Period (days)		
	1	1.8	1%	80		
1	2	1.8	5%	80		
	3	1.8	10%	80		
	1	1.8	1%	50		
2	2	1.8	4%	50		
	3	1.8	9%	50		
	1	9.1	3%	80		
3	2	9.1	5%	80		
	3	9.1	11%	80		
	1	9.1	15%	50		
4	2	9.1	12%	50		
	3	9.1	5%	50		
	1	9.1	14%	80		
5	2	9.1	9%	80		
	3	9.1	3%	80		

Table 8. Target experimental conditions

At the end of each experiment, columns were removed from the environmental chamber. Samples of soil were collected from the columns at locations closer to the sampling ports. These samples were used to determine the final water contents and soil concentrations.

3.3 Vapor-Phase Sampling and Analysis

After column packing, vapor sampling began periodically (about a sample every two days). Vapor sampling was performed in a passive mode, in which ERCs vapors diffuse through the sample collectors (sampling ports). Active sampling, by which the vapor is withdrawn, could not be applied because of its potential to induce vapor flow. The sample collector consisted of a Solid Phase Micro-Extraction (SPME) fiber inserted into the sampling ports for a predetermined time. The procedure for the vapor sampling consisted of inserting a SPME syringe into the sampling port for 4 minutes, as shown in Figure 21. The SPME stationary phase used was polydimethylsiloxane/divinylbenze with 65-µm of film thickness (Supelco®). A sampling (SPME sorption) time of 4 minutes was determined from calibration curves obtained for different exposure SPME (sorption) times. Although the sorption time was not the optimal (~15 minutes) recommended by Mayfield [2006]; the 4-minutes exposure time provided sensitive detection (to ng/L), reduced the sampling time, and provided a linear calibration curves (Figure 22).



Figure 21. Column sampling using SPME



Figure 22. SPME calibration curves for DNT and TNT solution headspace

After each sample collection, the SPME fiber was inserted into the injection port of the gas chromatograph (GC) and desorbed for 5 minutes. Analytes were desorbed in that period of time, showing no carry-over on the successive desorption. It is recommended that the SPME fiber be used no more than 100 times to avoid inconsistent measurements from damaged fibers that were observed at the end of the experiments. The gas chromatograph used in this study was an SRI 8610C equipped with a micro-electron capture detector and a 0.25-mm x 15-m RTX XLB column (Restek Corporation). Injector and detector temperatures were set at 265°C and 300°C, respectively. The oven was initially set at 160°C for 30 seconds, ramped to 175°C at 3°C/min, and ramped again to 195°C at a rate of 7°C/min. Measured sample areas from the GC were converted to vaporphase concentrations using SPME calibration curves.

Calibration of SPME was done by sampling the headspace of a known solution concentration for 4 minutes. Calibration standards of DNT and TNT were made in 25-mL amber vials with Teflon septum and screw caps. Each standard was prepared injecting a known volume of a reference standard of 1,000 mg/L (Restek Corporation) into 8-mL of distilled water. Calibration standards were placed on a vortex mixer for 30 seconds, and left for five days at 22°C in order to equilibrate the vapor and water phases. After equilibrium was reached, standards headspace were sampled and analyzed using the same SPME sorption and desorption times. Headspace concentrations in the vials were calculated as:

$$C_{A} = \frac{C_{W-0}}{\left(\frac{1}{K_{H}} + \frac{V_{A}}{V_{W}}\right)}$$
(39)

where, C_{w-0} is the initial solution concentration, K_H is the Henry's Law constant (Table 2), and V_A and V_W are the gas (17-mL) and water (8-mL) volumes, respectively.

3.4 Soil Extractions

After completion of the experiments, and immediately after the last gas sample was taken, soil samples around each sampler were collected, extracted, and analyzed for DNT and TNT concentrations. Soil extractions were conducted with the same procedure used by Jenkins et al. [2000]. Two grams of soils were placed in a 22-mL vial and 5-mL of acetonitrile was added. Then, vials were placed on a vortex mixer for 30 seconds and placed in an ultrasonic bath for 18 hours at the room temperature (22°C). After that, vials were removed and allowed to stand undisturbed for 30 minutes. The supernatant was filtered and 1.5-mL of the filtered aliquot was collected in a clean autosampler vial. Extractions were analyzed in a S200 high performance liquid chromatograph (Perking Elmer) with UV detector at 254 nm. A 25-cm HPLC column (Supelco®, Ascentis C18) was used to separate the analytes using water: methanol (30:70) as the mobile phases at a flow rate of 1 mL/min. HPLC standards were prepared in acetonitrile using Restek reference standards.

3.5 Sampler Efficiencies

The efficiencies of the porous samplers were determined at 22°C using empty columns (i.e., no soil). Similar to vapor transport experiments, one experiment was conducted using a column connected to the air-sweeping system in the environmental chamber. Another experiment was conducted with the column completely closed to the atmosphere. Efficiencies were determined by placing the ERC source at the bottom of the columns (100 mg of TNT and DNT crystals) and measuring vapor concentrations in the sets of samplers. Each sampler set was placed in the same location and included a stainless steel tube fitted to a porous sampler and another with no porous sampler (i.e., only the tube). Vapor concentration samples were measured at the same time in both samplers using two SPME fibers. Both SPME were calibrated previous to sampling.

3.6 Data Analysis

The fate and transport experiments generated spatial and temporal concentration data. Temporal concentration distributions, also known as breakthrough curves for DNT and TNT vapors were analyzed comparatively and analytically to determine the transport behavior of these vapors under the imposed conditions. Analytical assessment involved using of analytical equations, temporal concentrations differentials, and the method of moments for temporal concentration distribution. Temporal concentration differentials and analytical equations were used to estimate vapor fluxes. Breakthrough curves were also analyzed numerically using HYDRUS 1-D [Šimůnek et al., 1995]. The numerical modeling method is described in Chapter 5.

The method of moments was used to estimate diffusive flow and eluted masses. It characterizes the measured breakthrough data of DNT and TNT. Experimental absolute moments, M_n , are obtained through integration of the breakthrough data using the trapezoidal rule [Padilla el al., 1999]. Using this method, the zero (M_0) and first (M_1) moment are calculated.

$$M_n = \int_0^\infty t^n C(z, t) dt$$
(40)

$$M_{0} = \int_{0}^{\infty} C(z,t) dt = \sum \left(\frac{C_{i} + C_{i+1}}{2} \right) (t_{i+1} - t)$$
(41)

$$M_{1} = \int_{0}^{\infty} tC(z,t)dt = \sum \left(\frac{C_{i}t_{i} + C_{i+1}t_{i+1}}{2}\right)(t_{i+1} - t)$$
(42)

The first normalized absolute moment of the effluent concentration signal is used to estimate the mean arrival time of the vapors (t_m) [Padilla et al., 1999]. The mean arrival time is used in conjunction with the volume of air (V_A) to calculate the diffusive flow. Finally, the eluted mass (M_P) is determined using the diffusive flow and the zero moment.

$$t_m = \frac{M_1}{M_0} \tag{43}$$

$$Q_D = \frac{V_A}{t_m} \tag{44}$$

$$M_P = Q_D * M_0 \tag{45}$$

CHAPTER 4: EXPERIMENTAL RESULTS AND DISCUSSION

Transport experiments were conducted to characterize the vapor diffusive behavior of TNT and DNT in low water content soils at different temperatures and water contents. This chapter describes and discusses: the soil and environmental conditions attained for the experiments; vapor explosive signatures and temporal distribution concentrations at different distances from the source; the vapor transport behavior of TNT and DNT at different experimental conditions; soil concentrations and vapor retention (retardation); and TNT and DNT diffusive vapor fluxes. It also addresses the efficiencies of the passive sampling techniques used during the experiments.

4.1 Soil and Environmental Experimental Conditions

The vapor transport behavior of DNT and TNT in sandy soil was analyzed at different water contents, temperatures, and source distribution, as summarized in Table 9. This table shows the experimental conditions attained during the experiments. It shows that soil bulk densities range from 1.54 to 1.69 g/cm³ for all columns, averaging 1.60 g/cm³ (\pm 0.04). Soil porosity averaged 43.41% (\pm 1.50%). The data shows that over 73% of the bulk density and porosity data fall within one standard deviation, and reflect that soil packing properties are statically similar for most columns.

Measured water contents prior to (initial) and at the end of the experiments (final) indicate some water content variations during the experimental period (Table 9). In most experiments (73%), average soil water contents decreased during the experiments indicating water evaporation losses. Relative humidity of the flowing (sweeping) air above the soil columns were measured in 32% and 68% for the experiments at 35°C and 22°C, respectively. The water vapor deficit in the air stream could have induced water evaporation from the soil. Water evaporation was greater at the upper port because it is closer to the soil surface where the air was flowing. Generally, greater water looses are observed for soils with higher initial water contents ($\theta_{w-initial} > 8\%$). This is attributed to
S	Calana	Temp.	Bulk Density	Denseiter	Soil	$\theta_{W\text{-INITIAL}}$	$\theta_{W\text{-}FINAL}$ - Port 1	$\theta_{W\text{-}FINAL}$ - Port 2	$\theta_{W\text{-}FINAL}$ - Port 3	Average	Averg. Water	Experimental
Sei	a Column	(°C)	(g/cm ³)	Porosity	Depth (cm)	(cm ³ /cm ³)	$\theta_{W\text{-}FINAL}(cm^3\!/cm^3)$	Monolayers #	Period (Days)			
	1	22	1.61	43.29%	6.926	1.87%	*	1.28%	Ť	1.28%	17	79
1	2	22	1.59	43.97%	6.891	4.92%	*	4.09%	÷	4.09%	55	79
	3	22	1.55	45.41%	6.944	9.53%	*	8.36%	Ť	8.36%	116	79
	1	35	1.62	42.81%	6.926	0.99%	0.39%	0.57%	ŧ	0.48%	6	51
2	2	35	1.64	41.89%	6.891	3.55%	3.71%	3.45%	Ť	3.58%	47	51
	3	35	1.57	44.71%	6.944	8.08%	7.67%	7.10%	Ť	7.39%	101	51
	1	22	1.64	42.00%	12.7	2.52%	0.66%	0.66%	0.66%	0.66%	9	80
3	2	22	1.59	43.67%	13.07	4.91%	5.28%	5.27%	4.98%	5.18%	69	80
	3	22	1.59	43.93%	12.728	10.92%	11.96%	10.34%	9.83%	10.71%	144	80
	1	35	1.55	45.18%	12.7	15.21%	14.75%	12.83%	11.39%	12.99%	179	43
4	2	35	1.54	45.61%	13.07	12.60%	10.66%	9.84%	9.67%	10.06%	140	43
	3	35	1.64	42.19%	12.728	4.89%	5.25%	5.12%	4.96%	5.11%	67	43
	1	22	1.63	42.33%	12.7	16.78%	14.55%	13.60%	12.32%	13.49%	177	63
5	2	22	1.59	43.91%	13.07	7.83%	8.63%	7.84%	7.40%	7.96%	107	63
	3	22	1.69	40.29%	12.728	2.65%	2.42%	2.48%	2.33%	2.41%	30	63

Table 9. Conditions used in the experiments

* Values were not determined

† Sampling ports without soil

Estimated using a water molecular area of 10.8 x 10⁻²⁰ m² (Livingston, 1949) and the specific surface area of the soil (1.687 m²/g)

the greater amount of water available for evaporation at higher water contents, since the water is held with weaker capillary forces. Some columns, mostly those with initial water contents between 3.5% and 7.8%, showed an increase in average water contents during experiments. This can be potentially attributed to water condensation (i.e., uptake from flowing air sweeping stream) in the soil. The reason for this uptake and why it occurs around the same water contents is unknown, but may be caused by differences in soil-water content tension around the soil particles. Greater final water contents in the bottom ports could reflect some drainage from the upper soil portions.

4.2 Vapor Signatures in Soil

Crystals of TNT and DNT were used in the experiments as the explosive source. Figure 23 shows a GC chromatograph with peaks and retention times of the different compounds detected in a gas sample collected with SPME. Two peaks located next to the DNT peak were observed from the beginning of the experiments. These peaks were also observed in samples collected from DNT source vials. Therefore, these peaks must correspond to some impurity in the production of the DNT, possibly to 2,5-DNT and 3,5-DNT.



Figure 23. Vapor signatures within the soil Column 2 of experimental Set 5 held for 63 days

4.3 Trinitrotoluene Vapor Transport

TNT vapor concentrations were very low in comparison with the DNT gas concentrations (Figure 24). This is attributed to the higher vapor pressures and Henry's Law constants, and the lower sorption characteristics of DNT compared to TNT. Trinitrotoluene vapor concentrations were not observed in Port 2 or Port 3, indicating that the low vapor concentrations emanating from the source were sorbed or degraded in the first layers of soil.

Measured TNT vapor concentrations at the bottom port, close to the ERC source (Figure 25) show significant differences on transport behavior as a function of temperature. Higher measured vapor concentrations reflect the higher vapor pressures at higher temperatures. Higher temperatures also reflect faster diffusive transport, shown by earlier vapor breakthrough. TNT vapor concentrations were detected at the bottom port (about 3-cm from the explosive source) 9 days after starting the experiment at 35°C, and at 36 days for 22°C (Figures 25a and b).



Figure 24. DNT and TNT vapor concentrations for Port 1 and water content (initial) of 15.21% at 35°C (Col. 1, Set 4; Table 9)

The faster vapor transport at higher temperatures is attributed to faster diffusion resulting from greater Brownian movement (greater diffusion coefficients) and concentration gradients. Greater concentration gradients are established by the higher vapor pressures at the source at higher temperatures and, possibly, to greater vaporization rates. It is postulated that measured concentrations near the source (\approx 3-cm) after 40 days had not achieved equilibrium (i.e., continue to increase) and are less than 6% and 2% of the TNT's vapor pressure at 22°C and 35°C, respectively. Although lower than vapor-pressure concentrations are expected away from the source in a diffusive system, the low concentrations attained relative to the respective vapor pressures, and the inability to reach equilibrium after 40 days suggest rate limited mass transfer processes affecting the transport of TNT vapor in low water content soils. Mass transfer limitations may occur by slow rates of: vaporization (solid to gas), dissolution (solid to water), volatilization (water to gas), and/or sorption and desorption processes.



Figure 25. TNT gas concentrations measured at Port 1 for the different soil water contents (initial) at temperatures of 35°C (a) and 22°C (b)

TNT soil-vapor concentrations at different water contents (Figure 25) show soil water content to be a dominant factor on the TNT vapor transport in unsaturated soils. TNT vapor concentrations were observed only in columns with water contents higher than about 4%. This suggests strong retention and mass transfer limitations into the gas phase at these low water contents. Generally, when detectable, vapor phase concentrations were lower for soils with lower water contents. TNT gas concentration measured close to days 45 and 65 for 35°C and 22°C, respectively, were compared with their average water contents in Figure 26. This figure shows higher vapor concentrations at 35°C than at 22°C. It also shows that at water contents less than 9%, TNT vapor concentrations increase with higher water contents (i.e., higher concentrations are measured at higher water content). These results support those by Jenkins et al. [2000] and Leggett et al. [2001], which indicate higher vapor concentration at higher water contents. Lower vapor concentrations at lower water contents are attributed to greater retention and lower mass transfer processes. Greater retention at soil surfaces is expected at very low water contents because of the lower amounts of water covering the surface and lower competition for sorption sites.

Maximum TNT vapor concentrations as a function of water contents is achieved at about 9% water content, suggesting that at this amount of water, the gas-solid sorption capacity of TNT is limited. At water contents higher than 9% TNT concentrations tend to decrease with increasing water content (Figure 26). This is attributed to greater retention in the water phase and air-water interface, which is expected to increase with increasing water contents at this water content regime.



Figure 26. Variations of TNT gas concentrations with soil water content (final) at 35°C (collected on day 45) and 22°C (collected on day 65)

Measured vapor concentrations of TNT were compared with those reported by Jenkins et al. [1999]. Vapor concentration reported at 23°C for sand measured on day 63 ranged from 3.19×10^{-3} to $1.01 \times 10^{-1} \mu g/L$ for dry soil and 2.10% water content, respectively. TNT concentrations measured in air for the current study ranged from 1.10 x 10^{-3} to $3.09 \times 10^{-3} \mu g/L$ for soils having a water content of 4.50% and 7.89%, respectively. These results show the proximity between both measurements; however, Jenkins et al. [1999] reported values that are slightly higher. This discrepancy is attributed to the fact that in their study the vapor concentrations were measured in the soil headspace in closed vials, and these concentrations tend to reach equilibrium (i.e., higher vapor concentrations).

4.4 Dinitrotoluene Vapor Transport

In addition to TNT, vapor concentrations of DNT were monitored in the different sampling ports for each experiment. DNT vapor concentrations were greater near the explosive source (Port 1) than further away (Port 3). Figure 27 shows the variation of vapor concentration with time measured at an initial water content of 12.60% and a temperature of 35°C (Set 4, Col. 2; Table 9). It is observed that DNT vapor concentration breakthrough curves show later arrival at farther distances from the source because the vapor must travel a longer distance. The data collected from other experiments showed similar trends as presented in Appendix B-1.

DNT gas concentrations never achieved constant concentrations during the experimental period for any column, indicating that vapor transport is very low and takes more than 80 days to achieve steady state conditions. Increasing DNT concentrations gradients with time (Figure 28) support the postulation that the transport processes had not achieved steady-state conditions. At equilibrium, concentration gradients should be constant and not change with time.

Measured concentrations are slightly lower than the values reported by Jenkins et al. [1999]. They measured concentrations ranging from 3.49 x 10^{-2} to 2.11 x 10^{-1} µg/L, for dry soil and for a water content of 3.10%, respectively. The research presented herein measured concentrations in Port 1 ranging from 5.20 x 10^{-2} to 9.54 x 10^{-2} µg/L, for water contents of 1.57% and 4.50%. However, measured concentrations in both studies are about one or two orders of magnitude lower than the vapor pressure concentration of DNT (1.45 µg/L).

Similar to TNT, DNT vapor concentrations are highly influenced by variations in temperature (Figure 29). Generally, higher temperatures result in higher vapor concentrations and concentration gradients. The ratio of concentrations at 35°C and 22°C, after 40 days is approximately 3.82 in Port 1 and 7.78 in Port 3. The ratio at Port 1 is closer to the ratio of vapor pressures (4.95) at 35°C and 22°C. This indicates that higher



Figure 27. Variations of DNT at different distances from the explosive source for a water content (initial) of 12.60% and temperature at 35°C (Col. 2, Set 4; Table 9)



Figure 28. Variations of DNT vapor concentration gradients (dC_A/dz) between the different sampling ports of the soil columns with $\theta_{Wavg.}$ =2.41% at 22°C (Col. 3, Set 5; Table 9)

vapor concentration at high temperatures is due to the higher vapor pressures of the explosives source at distances closer to the source. Greater concentrations gradients at higher temperatures also indicate higher vapor pressures at the source at higher temperature. It is postulated that at farther distances from the source, vapor concentrations is controlled to a greater extent by diffusive transport, than mass-transfer processes from the source. This results in lower concentrations gradients away from the source than near the source (Figure 28). Higher temperatures also seem to influence the rate of vapor transport with distance. For instance, vapor concentration at Port 1 was 7.8 times higher than that at Port 3 after 40 days of transport at 22°C, but was only 3.8 higher at 35°C (Figure 29). The higher vapor concentration and concentration gradients near the source than away, at lower temperatures, suggests that diffusive and mass transfer limitations influence vapor concentrations away from the source to a lesser extent at 35°C than 22°C. Faster rate of increase in DNT vapor concentrations with temperature indicates faster diffusive transport at higher temperatures.



Figure 29. DNT gas concentrations in the different sampling ports at 35°C for a water content (initial) of 15.21% (Col. 1, Set 4; Table 9) and at 22°C for a water content (initial) of 16.78% (Col. 1, Set 5; Table 9)



Figure 30. Changes in DNT vapor concentrations at different distances from the source in Column 2 and 3 of Set 2 when temperature was reduced from 35° C to 27° C

The effects of temperature variations in vapor transport can also be observed in the DNT breakthrough curve (Figure 30) resulting from an experiment in which the columns were subjected to variable temperatures during the experiments. The temperature in experimental Set 2 (Table 9) was initially set to 35°C, but was reduced to 27°C from day 6 to 7 and from day 14 to 15 after some equipment malfunction. These reductions in temperatures caused a decrease in DNT vapor concentrations in the sampling port located closest to the source (Figure 30). This is attributed to the reduction of DNT vapor pressure with the reduction in temperature.

In Figure 30, the soil column with a lower initial water content of 3.55% (Col. 2, Set 2) showed a reduction in vapor concentration almost immediately after the temperature was changed (reduced), however, the one with an initial water content of 8.08% (Col. 3, Set 2) showed a response only after the first temperature variation. Changes in concentration trends due to temperature variations were not as noticeable at

sampling ports away from the source (Port 2). At greater distance from the source, vapor concentrations continued to increase after temperature variation (reduction). After the second phase of temperature variations, the increasing concentrations trend was only slightly changed and then increase rapidly to concentrations higher than at the port closer to the source. This behavior was observed to a much greater extent in the column with lower water content (Column 2). It is suspected that this behavior may be related to relative variation in vapor pressure at the source and diffusive transport away from the source as temperature varied, but a definite explanation is not known.

DNT vapor concentrations also show to be influenced by water content (Figure 31). The effect of water content on DNT vapor concentration, however, is influenced by the distance from the source and the temperature (Figure 31). In Figure 32, DNT vapor concentrations tend to increase with increasing water contents (below 5%-8%). At higher water contents, DNT vapor concentrations for experiments conducted at 22°C continue to increase slightly with increasing water contents for distances further away from the source (i.e., Port 3), but shows a tendency to decrease or remain constant for distances closer to the source (Port 1 and 2). For experiments at 35°C, vapor concentration for soils at the higher water contents regime (>8%) tend to decrease or remain constant with increasing water contents (see Appendix B-2 for larger graphs).



Figure 31. DNT vapor concentration variations with water contents (initial) in the Ports 1, 2 and 3 at 22°C and 35°C



Figure 32. Variation of DNT gas concentrations (collected on day 35) with soil water contents (final) in the different sampling ports

Increasing vapor concentrations with increasing water content at the low water content regime is associated with decreasing sorption capacity as water content increases. In general, decreasing capacity of reversible sorption (non permanent sorption caused by weak physical forces), result in earlier elution of chemicals. In theory, the equilibrium concentrations at a particular distance should be the same for all conditions, provided that the source concentrations (vapor pressure) is the same and that sorption is reversible (see Figure 33).

The difference in vapor concentrations at the same location for the different conditions used indicate that vapor transport has not reached equilibrium or that non-reversible sorption is occurring (Figure 33b). Soil extraction data (discussed later in Section 4.5) indicate that sorption is reversible (Figure 33a), and support the hypothesis that the concentrations have not yet reach equilibrium. It is, therefore, postulated that higher sorption capacity at low water contents retains DNT (and TNT) vapors for a long period of time (>80 days) before the sorption capacity is exceeded and the vapor can breakthrough. At higher water contents, the sorption capacity for DNT is reduced by competition with water, and vapor breakthrough begins at earlier times (is not retarded as much) than at the lower water contents. Indeed, earlier initial breakthrough is generally observed for the experiments conducted at higher water contents.



Figure 33. Theoretical elution of chemicals influenced by (a) reversible and (b) non-reversible (or degradation) sorption

At the higher water content regime (>5%-8%) decreased vapor concentrations with increasing water contents suggest increasing retardation. The increase retardation at these water contents is attributed to dissolution in the water phase and potential adsorption at the air-water interface (if interfacial areas are increasing in the pellicular or pendular water regimes).

The increase retention capacity of DNT vapors at very low water contents is also supported by the results on temporal vapor concentration in the soil columns with lowest water contents at 35°C (Col. 1, Set 2; Table 9) and 22°C (Col. 1, Set 3; Table 9). DNT vapor concentrations were never detected in the soil column with lowest water content and the highest temperatures (Col. 1, Set 2; Table 9). The initial water content in this column was established at 0.99%, but decreased during experiments to 0.39%. Average water content in this column results in an average water monolayers of 6 (Table 9). Ong and Lion [1991] reported that at a water content corresponding to less than 8 layers of water coverage (calculated using N₂-BET method), the gas-solid partition coefficient increases about one to two orders in magnitude. This high sorption capacity could be the responsible for the absence of concentrations.

The soil column with the lowest water content at 22°C (Col. 1, Set 3; Table 9) showed a normal behavior of DNT vapor concentrations during the first 45 days but a steep reduction afterward (Figure 34). The initial water content in this column was established at 2.52%, but it was reduced to 0.66% during the experiments by evaporation. The final water content for this setup corresponds to 9 layers of water coverage, which is close to the boundary established by Ong and Lion [1991]. In experiments conducted by Ravikrishna et al. [2002] was observed a similar downward gradient when the soil water content decreased from 5% to 0.1%. They suggested the hypothesis that the soil was dry enough to cause surface reaction to degrade the DNT (i.e., oligomerization). Karimi-Lotfabad et al. [1996] observed this phenomenon for polyaromatic hydrocarbons on dry soils with very low organic carbon.



Figure 34. Reduction of DNT vapor concentrations at different distances from the explosive source when soil water content reduced from 2.52 to 0.66% in Column 1 of Set 3

4.5 Soil Extractions

Results from the soil extractions conducted at the end of the experiments reflect the overall amount of ERCs sorbed into the soil and partitioned to soil water at the time when the last gas-phase sample was taken because soil extractions were performed on the wet soil. HPLC chromatographs (Figure 35) indicate that both TNT and DNT were found in the soil extractions. Results of the soil extractions are presented numerically in Table 10. Although, concentrations in the water could be determined using the equilibrium partition coefficient K_H , a bulk term was used because the mass transfer rate between gas and water phases is not well understood at low water contents. Therefore, the equilibrium partition constant (K_d) between gas phase concentration (C_A) and wet-soil (C_{WS} , i.e., grouping water and solid phases as a single phase) was determined using K_d =Cws/C_A.



Figure 35. Representative HPLC chromatograph for soil extractions

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Table Tu	. 5011	extract	ion results of each ex	periment in th	e different sampling ports
		Final	DNT		TNT

10 0

		Final DNT				TNT			
Set	Column	Sampling	Water	Final Vapor Conc.	Final Water & Soil	Kd"	Final Vapor Conc.	Final Water & Soil	Kd"
		Port	Content	(mg/L)	Conc. (mg/kg)	(L/Kg)	(mg/L)	Conc. (mg/kg)	(L/Kg)
		1	1 280/	5 202E 05	5 570	105 054	0.000E±00	0.000	
	1	2	1.28%	5.502E-05	3.570	220 594	0.000E+00	0.000	
		2	1.20/0	1.030E-05	5.590	220,394	0.0001.000	0.000	
1	2	1	4.09%	9.969E-05	7.093	71,152	1.478E-06	0.080	54,381
-	_	2	4.09%	5.150E-05	5.037	97,801	0.000E+00	0.000	
	2	1	8.36%	9.039E-05	8.330	92,162	2.773E-06	0.146	52,582
	3	2	8.36%	5.398E-05	6.022	111,557	0.000E+00	0.000	
	1	1	0.39%	3.092E-07	2.727	8,818,862	9.269E-07	8.913	9,616,611
	1	2	0.57%	3.092E-07	0.386	1,246,954	9.269E-07	4.118	4,443,171
		1	3.71%	1.367E-04	11.274	82,499	1.585E-06	0.574	361.902
2	2	2	3.45%	3.959E-04	8.351	21,093	0.000E+00	0.340	- ,
		1	7 670/	1 647E 04	14 720	<u>80</u> 400	2 101E 06	0.271	116 112
	3	1	7.0770	1.04/E-04 1.527E-04	0 500	61,999	5.191E-00	0.371	110,115
		2	7.1070	1.537E-04	9.509	01,007	0.00011+00	0.130	
	1	1	0.66%	1 811E-05	7 593	419 343	0.000E+00	0.258	
		2	0.66%	7 722E-07	2.527	3 272 406	0.000E+00	0.125	
		-	5.000/	0.5200.05	5.021	(0, (00	1.624E.06	0.120	070 (00
	2	1	5.28%	8.520E-05	5.931	69,608	1.634E-06	0.457	279,602
3		2	5.27%	4.029E-05	2.367	58,740	0.000E+00	0.000	
		3	4.98%	4.084E-00	0.334	80,707	0.000E+00	0.000	
		1	11.96%	1.216E-04	6.927	56,948	3.335E-06	0.669	200,485
	3	2	10.34%	3.677E-05	3.589	97,614	0.000E+00	0.000	
		3	9.83%	9.510E-06	1.063	111,733	0.000E+00	0.000	
		1	14 750/	1 2715 04	15 709	115 204	4.961E.06	0.720	152.070
	1	1	14./5%	0.222E 05	15./98	P0 264	4.801E-00	0.739	152,079
	1	2	12.85%	9.525E-05 2.004E-05	7.465	87 202	0.000E+00	0.038	
		3	11.3970	5.774E-05	5.491	07,393	0.0001.000	0.000	
Ι.		1	10.66%	1.237E-04	14.868	120,150	5.904E-06	0.987	167,094
4	2	2	9.84%	7.104E-05	7.914	111,405	0.000E+00	0.000	
		3	9.67%	3.022E-05	2.590	85,718	0.000E+00	0.000	
		1	5.25%	2.927E-04	8.729	29,825	1.174E-06	0.123	104,674
	3	2	5.12%	1.326E-04	4.158	31,364	0.000E+00	0.000	
		3	4.96%	3.228E-05	2.235	69,236	0.000E+00	0.000	
					0.015		1.0.415.0.6	0.000	
	1	1	14.55%	5.295E-05	0.817	15,435	1.344E-06	0.088	65,790
	1	2	13.00%	4.908E-05	0.725	14,001	0.000E+00	0.030	
		3	12.3270	1.044E-05	0.289	17,380	0.000E+00	0.000	
_		1	8.63%	1.606E-04	2.151	13,393	2.478E-06	0.681	274,990
5	2	2	7.84%	4.041E-05	0.728	18,010	0.000E+00	0.116	
		3	7.40%	1.043E-05	0.168	16,103	0.000E+00	0.000	
		1	2.42%	9.589E-05	4.071	42,459	0.000E+00	0.037	
	3	2	2.48%	3.247E-05	3.386	104,275	0.000E+00	0.000	
		3	2.33%	3.417E-06	0.852	249,438	0.000E+00	0.000	

Soil extraction results (Table 10) show that the concentrations of TNT retained in the wet soil were generally lower than those measured for DNT under same conditions, except for the soil with the lowest water content at 35°C (Col. 1, Set 2). Lower TNT soil concentrations relative to DNT are attributed to lower TNT concentrations in the vapor phase. Sorbed (retained) concentrations in wet soil are, thus, related to the concentrations in the vapor phase. Results of DNT soil extractions show that sorbed concentrations (Figure 36) follow similar trends to vapor concentrations (Figure 32) with changes in water contents. In most cases, both retained and vapor concentrations increase as water contents at higher water contents regimes. These results suggest that DNT sorption processes were not necessarily controlling the vapor phase concentrations and that sorbed concentrations are more affected by the vapor transport, except, at the lower water contents.

TNT retained concentrations in the wet soil as a function of water content (Figure 37) follow similar behavior as the vapor phase concentrations (Figure 26). TNT sorbed concentrations initially increase as water content increases from very dry conditions, reach a maximum value, and show a tendency to decrease with further increase in water contents at the higher water content regime.

TNT and DNT concentrations extracted from wet soil were always higher for soil closer to the ERC source (Port 1) than further away (Ports 2 and 3). This is also attributed to the higher vapor concentrations closer to the source. It is important to note that TNT was detected in the wet soil extracts from Port 2 in several occasions, even when no-vapor concentrations were detected from these ports. No detection of TNT vapors is attributed to the vapor concentrations below detection limits (0.9 ng/L). Plots of vapor concentrations versus extracted concentrations for TNT (Figure 38) and DNT (Figure 39) show that, in general, extracted concentrations tend to increase with increasing vapor concentrations. Changes in extracted concentration with vapor concentrations depend, however, on the temperature and water content regime. At 22°C, TNT soil extracts concentrations show a more scattered data in relation to the vapor-phase concentration



Figure 36. Retained DNT mass in soil and water as function of the soil water content for each sampling port at $22^{\circ}C$ (a) and $35^{\circ}C$ (b)



Figure 37. Retained TNT mass in soil and water as function of the soil water content for Port 1 at the different temperatures

and appear to be influenced by the water content of the soil (Figure 38a). Except for the soil with the lowest water content (Col. 1, Set 2; Table 9), TNT concentrations on the wet soil at 35°C increased linearly with increasing vapor concentrations, independent of water content (Figure 38b).

Plot of DNT vapor concentrations versus extracted concentrations at 22°C shows that the relationship do not follow a linear behavior for soils with high retained mass (Figure 39a). Linear relationships at this temperature are generally observed for soils with low retained mass and often associated with higher water contents regimes. At 35°C extracted concentrations show a linear relationship with vapor concentrations for similar water content conditions, but this relationship varies for different water contents (Figure 39b). In general, at 35°C the slopes of the relationship is higher for the soil with lower water contents, decrease, and then tend to increase with higher soil water contents.



Figure 38. Soil and water concentrations as a function of TNT vapor concentrations for the different average final water contents at 22° C (a) and 35° C (b)



Figure 39. Soil and water concentrations as a function of DNT vapor concentrations for the different average final water contents at 22°C (a) and 35°C (b)

Linear equilibrium distribution coefficients of wet-soil (K_d "= C_{WS}/C_A) for DNT at 22°C were generally higher for distances further away from the source (Port 3) suggesting non-equilibrium conditions. This was not the case at 35°C, in which K_d " values were generally lower at farther distance.

Higher retention capacity is generally observed for low water content soils (Figure 40). This behavior has been reported previously by several authors (e.g., Petersen et al., 1994; Petersen et al., 1995; Ong and Lion, 1991; Phelan and Barnett, 2001b). Values of gas to water-soil partition constants (K_d ") increases from 2 to 3 orders of magnitude when the water contents are lower because direct sorption to the solid surface is taking place. Ong and Lion [1991] have reported this increment when the water monolayers are less than 8. Meanwhile, Phelan and Barnett [2001b] concluded that the increments should be observed below 10 monomolecular layers of water. This research determined that the exponential rise begins at a value of about 17 water layers (Figure 41). K_d " values of DNT and TNT as function of water content (Figure 42), were very close and show a similar behavior for both compounds. TNT K_d " values were, however, slightly higher. This behavior might be explained with the higher sorptive capacity of TNT.



Figure 40. Variation of the air to water-soil DNT distribution constants (K_d) at different temperatures with increments in water contents



Figure 41. Variation of the air to water-soil DNT distribution constants (K_d) at different temperatures as function of monolayers of water



Figure 42. K_d " values of DNT and TNT at different temperatures as function of water content

4.6 DNT and TNT Fluxes

Measured gas concentrations in the experiments, with and without soil, were used to determine the vapor fluxes. Measured vapor fluxes (F_A) were calculated using the following equation [Hutchinson and Livingston, 2002]:

$$F_{A} = \left(\frac{V_{A}}{A}\right) \frac{dC_{A}}{dt}$$
(46)

where, V_A is the volume of air and A is the circular area of the column. Moreover, vapor fluxes can be estimated from the empirical model presented in Equation 37. Figures 43 and 44 show the fluxes of DNT and TNT calculated using the empirical model and those measured (i.e., determined using Equation 46) for experiments conducted at 22°C using the open column without soil. Modeled data was fitted to the measured data by finding the C_0 value of Equation 37 that minimizes the root mean square error (*RMSE*),

$$RMSE = \sqrt{\left(\frac{1}{n}\sum_{i=1}^{n} \left(F_{Measured} - F_{Estimated}\right)^{2}\right)}$$
(47)

where, n is the number of data points.

Modeled DNT vapor fluxes in Figure 43 show a good fit with the measured data with a RMSE of 4.236 x 10^{-4} . Modeled initial concentration (C_0) was 1.11 x $10^{-2} \mu g/L$, which is two orders of magnitude lower than the equivalent vapor pressure of DNT at 22°C (1.451 $\mu g/L$). Modeled fluxes for all ports are identical thus in Figure 43 is showed only one curve. Measured fluxes show differences between the ports, lower maximum fluxes and later arrival were observed at ports away from the source. This suggests that mass transfer from the source (volatilization / dissolution / vaporization) is rate-limited.

DNT vapor fluxes as a function of time increase initially, reach a maximum, and then decrease. Maximum fluxes are reached relatively rapidly (>2 days), and tend to arrive earlier and reach higher values at distances closer to the source. Higher maximum fluxes at closer distances from the source indicate transient vapor transport. Decreases

fluxes with time toward a constant value indicate that flux is reaching equilibrium with time. The higher vapor flux of DNT measured in the empty column at 22°C was 1.031 x $10^{-3} \,\mu\text{g/cm}^2$ -day and the equilibrium flux was 6.05 x $10^{-5} \,\mu\text{g/cm}^2$ -day.

TNT vapor fluxes were measured in only few times, since gas concentrations were almost undetectable. Measured data was compared with the modeled data in Figure 44. The highest measured vapor flux was $5.432 \times 10^{-6} \,\mu\text{g/cm}^2$ -day and the equilibrium flux was $8.8 \times 10^{-7} \,\mu\text{g/cm}^2$ -day. However, modeled data did not fit well with the measured data because TNT concentrations took some days in becoming detectable and the model predicted higher fluxes at the earlier times, as illustrated the red dashed curve in Figure 44. Therefore, modeled flux was lagged to begin about 2.8 days later (represented by the green solid line) and the data fitted better. The best C_0 fit that minimized the RMSE (= 3.335×10^{-7}) was $6.12 \times 10^{-5} \,\mu\text{g/L}$, which is about three orders of magnitude lower than TNT vapor pressure at 22° C (5.911 x $10^{-2} \,\mu\text{g/L}$). These facts indicate that the volatilization or sublimation of the explosive source is not instant and do not correspond to the vapor pressure, indicating mass transfer limitations at the source.



Figure 43. DNT vapor fluxes modeled and measured in the empty columns at different distances from the explosive source, using a temperature of 22°C



Figure 44. TNT vapor fluxes modeled and measured in the empty columns at different distances from the explosive source, using a temperature of 22°C

Measured vapor fluxes in soil columns show greater variation than column without soil because of the sensitivity of the estimation method to variations in measured concentrations (see vapor fluxes in soils for all other experiments in Appendix C-1). In general, (and similar to the results from the columns without soil) the measured fluxes in soils tend to increase with time to a maximum flux and then decrease (Figure 45). Although similar in behavior to the results from the columns without soil, variations of vapor fluxes in soils with time are significantly lower than in free air. Furthermore, vapor fluxes in soils show much lower maximum values than in free air, and do not decrease to constant value. This behavior indicates that diffusive vapor transport in soils is influenced by, not only air porosity, but by retention and mass transfer mechanisms.



Figure 45. Measured vapor fluxes of DNT in the packed column with sand at different distances from the source, for the experiment conducted at 22°C and 4.89% of water content (Col. 3, Set 3; Table 9)

Soil water content was an important factor affecting the magnitude of the vapor flux in soils. Figures 46 and 47 show DNT fluxes as function of water content measured at the same distance from the source (\approx 6.5-cm). Vapor fluxes as function of water content show similar behavior to vapor concentrations. Vapor fluxes tend to increase, reach a maximum, and then decrease with further increase in water contents. Maximum fluxes correspond to water content of about 7%. In addition, vapor fluxes were measured first in wet soils than in dry soils, indicating less retarded transport. It is possibly due the less sorption and/or mass transfer limitations. Drier soils also show lower overall fluxes than the soils with higher water contents. Comparing Figures 46 and 47, vapor fluxes at 35°C are about 4 times higher than at 22°C. This is due the higher mass transfer from the explosive solid source to vapor and faster diffusion. Vapor fluxes for TNT measured in Port 1 show similar behavior, but are much lower than for DNT. Their temporal variations tend to also be much slower compared with the values of DNT. This is attributed to the lower TNT vapor concentrations, potential greater sorption, and greater mass transfer limitations of TNT.



Figure 46. Measured vapor fluxes of DNT in Port 2 (\approx 6.5-cm from the source) at 22°C as function of the soil-water content (final-average)



Figure 47. Measured vapor fluxes of DNT in Port 2 (\approx 6.5-cm from the source) at 35°C as function of the soil-water content (final-average)

In summary, measured vapor fluxes in the columns with soil were in the range of 10^{-5} to $10^{-6} \ \mu g/cm^2$ -day for DNT, and ranged from 10^{-7} to $10^{-8} \ \mu g/cm^2$ -day for TNT. Meanwhile, vapor fluxes in the columns without soil ranged from 10^{-3} to $10^{-5} \ \mu g/cm^2$ -day for DNT, and from 10^{-6} to $10^{-7} \ \mu g/cm^2$ -day for TNT. Therefore, the presence of soil reduces the vapor flux from 2 to 3 orders of magnitude comparing with the measured fluxes in the empty columns. This reduction is due the distribution of the ERCs through the different soil phases and by restrictions of the free air space within the soil.

Comparing measured values in columns with soil with those reported in the literature, we found that only two studies have evaluated vapor fluxes of DNT through soils. The first was developed by Ravikrishna et al. [2002] and they found that DNT vapor fluxes ranged from 10^{-1} to 10^{-5} µg/cm²-day, for the different types of soil and water contents at 24°C. The second, developed by Phelan et al. [2001], determined that the DNT vapor fluxes ranged from 10^{0} to 10^{-4} µg/cm²-day, after periods of soil drying and wetting at 25°C. These studies report higher vapor flux values than the measured in this study. Ravikrishna et al. and Phelan et al. are using aqueous-phase DNT as the explosive source, however, this study is using the source in the solid-phase. It is, therefore, postulated that greater mass transfer limitations exist when the explosive pass from solid to vapor phase than from liquid to vapor. This fact could be explained by the thermochemistry of DNT. The enthalpies of the solid and liquid states of DNT are 94.2 and 75.3 kJ/mol, respectively, at 72°C [Rittfeldt, 2001]. Therefore, the solid-phase has stronger intermolecular attractions and requires more energy for the transition to the vapor-phase. This thermodynamic restriction is the responsible of the limited production of vapors at the source.

Two studies were found that measured fluxes of landmines without soil. The first was from Leggett et al. [2001], whom reported vapor fluxes of DNT and TNT emanating from five types of landmines placed in Tedlar plastic bags. They measured vapor fluxes at 20°C ranged from 10^{-2} to $10^{-4} \,\mu\text{g/cm}^2$ -day and from 10^{-3} to $10^{-4} \,\mu\text{g/cm}^2$ -day for TNT (calculated using the surface area of the mines). The second study was conducted by Spangler [1975]. They placed landmines in vapor collection chambers and measured

TNT concentration increase over time. According to Phelan and Webb [2002], the TNT flux rates measured by Spangler were from 10^{-6} to $10^{-8} \,\mu\text{g/cm}^2$ -day. The latter results are very similar to the measured vapor fluxes in this research.

Diffusive flows (Q_D) and eluted masses (M_P) of DNT were estimated using moment analysis (Table 10-5). Diffusive flow represents the diffusive velocity of the vapors in the system. This flow was changing temporally and spatially (Figure 48). Earlier and faster initial flow of DNT is observed near the ERCs source and was decreasing toward a constant value. At farther distances the diffusive flow was lower indicating that the diffusive transport is not at equilibrium. Comparing the diffusive flow at different temperatures (Figure 49) was determined that the trends are very similar; however, at 35°C the flow was observed earlier than at 22°C. This behavior indicates that the increments in temperature generate a faster diffusion and less retention, principally, at earlier times and closer distances from the source.

Water content was affecting the mean diffusive flow as shown in Figure 50. Increments in soil water content were reducing the diffusive flow. This is explained by the larger availability of soil-air space at lower water contents for the vapor transport. Thus, increments in water content reduce the velocity of the vapor because the contaminant is retained by the water. Figure 50 also shown that the mean diffusive flow is slower closer to the source. This suggests that the mass transfer from the solid-state source to the gas-state (i.e., sublimation) is slower compared with the transport processes in the soil.

The amount of DNT mass eluted at the end of the experiments was estimated (Figure 51). It is generally higher near the source than away from the source, indicating that the system was not reached equilibrium. Higher mass was eluted at soil water contents of about 8%. This behavior was observed previously in other analysis; and could be indicating that 8% of water content is the soil condition where the transport processes are more effective, there are less sorption / retention / rate-limited processes, and a higher source volatilization is occurring.

Column	Port	T (°C)	$\theta_{W (\text{Final})}$	Q_D (L/day)	M_P (µg)			
1	1	22	1.28%	2.413E-04	6.199E-04			
1	2	22	1.28%	4.351E-04	1.902E-04			
2	1	22	4.09%	1.555E-04	7.527E-04			
2	2	22	4.09%	3.470E-04	5.480E-04			
2	1	22	8.36%	2.121E-04	8.776E-04			
3	2	22	8.36%	3.779E-04	6.156E-04			
			Set 2					
2	1	35	3.71%	2.887E-04	6.987E-04			
2	2	35	3.45%	8.207E-04	3.246E-04			
2	1	35	7.67%	3.221E-04	1.303E-03			
3	2	35	7.10%	5.804E-04	1.778E-03			
	Set 3							
1	1	22	0.66%	4.530E-04	2.711E-04			
1	2	22	0.66%	7.619E-04	4.113E-05			
	1	22	5.28%	1.367E-04	3.818E-04			
2	2	22	5.27%	3.663E-04	3.092E-04			
	3	22	4.98%	5.083E-04	3.789E-05			
	1	22	11.96%	2.040E-04	7.326E-04			
3	2	22	10.34%	3.873E-04	3.233E-04			
	3	22	9.83%	5.375E-04	5.988E-05			
			Set 4					
	1	35	14.75%	3.433E-04	1.190E-03			
1	2	35	12.83%	6.351E-04	1.168E-03			
	3	35	11.39%	8.584E-04	4.361E-04			
	1	35	10.66%	2.481E-04	8.511E-04			
2	2	35	9.84%	6.396E-04	6.498E-04			
	3	35	9.67%	1.037E-03	1.646E-04			
	1	35	5.25%	4.352E-04	4.286E-03			
3	2	35	5.12%	7.420E-04	1.896E-03			
	3	35	4.96%	9.750E-04	3.573E-04			
			Set 5					
	1	22	14.55%	2.390E-04	2.665E-04			
1	2	22	13.60%	4.177E-04	3.518E-04			
	3	22	12.32%	5.241E-04	1.149E-04			
	1	22	8.63%	1.557E-04	6.418E-04			
2	2	22	7.84%	3.855E-04	3.180E-04			
	3	22	7.40%	5.777E-04	7.133E-05			
	1	22	2.42%	2.517E-04	6.649E-04			
3	2	22	2.48%	5.123E-04	1.800E-04			
	3	22	2 33%	6 548E-04	3 192E-05			

Table 10-5. Diffusive flows (Q_D) and eluted masses (M_P) estimated using moment analysis



Figure 48. Estimated diffusive flows at different distances from the source in the column with water content (initial) of 2.65% at 22°C (Col. 3, Set 5; Table 9)



Figure 49. Estimated diffusive flows in the different sampling ports at 35°C for a water content (initial) of 15.21% (Col. 1, Set 4; Table 9) and at 22°C for a water content (initial) of 16.78% (Col. 1, Set 5; Table 9)



Figure 50. Variations of the mean diffusive flow with soil water content for the experiments conducted at 22°C



Figure 51. Variations of the eluted masses with soil water content for the experiments conducted at 22°C

4.7 Sampler Efficiencies

DNT vapor concentrations were measured in empty columns using samples fitted with and without porous cups at different distances from the source. Higher vapor concentrations in the sampling ports without porous cups were measured compared with concentrations measured in the sampling ports with porous cups (Figure 52). This indicates that passive vapor sampling using porous samplers does not necessarily represent the concentrations at the source at the time of sampling. Diffusion and possibly sorption processes through the porous sampler influence the measured concentration and reduce their efficiency.

Comparison of measurements made in the open column (connected to airsweeping system) with those in the close column show that vapor concentrations in the closed column were higher than in the open column (Figure 53). The difference is due to the boundary conditions established at the top of the column. The open column had a zero-concentration boundary at the top of the column, thus establishing a spatial gradient from the source to the column exit. Even at equilibrium, this would require concentrations to decrease away from the source. The closed column had a no-flow boundary at the top of the column, which would cause the column to eventually reach vapor pressure concentration everywhere; as a consequence, concentrations in the close column would eventually reach higher concentration than in the open column.

Using the results of the previous experiments, porous cups efficiencies were determined using the following equation:

$$Efficiency(\%) = \left[1 - \left(\frac{C_{PC} - C_{NPC}}{C_{PC}}\right)\right] * 100$$
(48)



Figure 52. Comparison of the DNT gas concentrations measured in the sampling ports with porous cups vs. without porous cups at different distances from the explosive source in the open column



Figure 53. Comparison of the DNT gas concentrations at different distances from the explosive source measured in the sampling ports without porous cups of the open column and close column
where, C_{PC} and C_{NPC} are the concentrations with porous cup and concentration without porous cup, respectively. Figure 54 shows the porous cups efficiencies at each sampling port of the open and close columns. Porous cups efficiencies are function of the distance from the explosive source. Sampling ports near the explosive source (Port 1) are more efficient with an average efficiency of 29.26%. Meanwhile, the average efficiency of the middle ports (Port 2) is 27.03%. The upper ports (Port 3) are less efficient with an average efficiency of 17.74%. This is probably due to the lower concentration gradients for passive (diffusive) sampling at the ports further away from the source.

It was concluded that measured concentrations during the experiments were, therefore, higher than measured, and were corrected. Vapor concentrations for modeling purpose were corrected using the average porous sampler efficiencies. The others data were not corrected because they are comparative in nature and the efficiencies increase all concentrations by the same percentage.

Padilla et al. [2006] showed that porous samplers (same as the ones used in this study) were 100% efficient for DNT samples in aqueous phase. Lower efficiencies were measured for TNT. Much lower efficiencies were obtained for DNT and TNT passive sampling in the vapor phase in this study. This indicates that: (1) vapors were being retained in the larger surface area of the stainless steel porous medium; and/or (2) diffusive transport across the porous medium was rate-limited.



Figure 54. Porous cups efficiencies at each sampling port of the experiments ran in open and close columns

CHAPTER 5: NUMERICAL ANALYSIS RESULTS AND DISCUSSION

Vapor transport from an explosive source within the unsaturated soil was analyzed using the HYDRUS-1D code [Šimůnek et al., 1995]. Vapor concentrations of DNT were modeled and compared with the collected data in the experiments. Particular environmental and soil conditions used in each experiment were reproduced numerically by fitting transport parameters until differences between measured and model-calculated temporal concentrations were minimized. TNT vapor concentrations were not modeled because of the limited amount of data collected in the experiments.

5.1 HYDRUS Modeling Description

HYDRUS-1D [Šimůnek et al., 1995] was originally developed to describe the transport of solutes in unsaturated media subjected to advective, diffusive, mass transfer, sorption, and reactive processes in the aqueous phase. Gas-phase transport was assumed to occur only through diffusive transport, and subjected to sorptive and reactive processes. Rate-limited processes in the vapor-phase were, however, not considered.

The results obtained in this research indicated that DNT and TNT vapor transport is subjected to rate-limited processes which influence significantly the transport. Because the transport equations are basically the same for vapor and solute transport, it was decided to simulate vapor transport as a solute and vice versa (i.e., solute as a vapor) in HYDRUS. This allowed the use of rate-limited processes in the vapor phase.

HYDRUS uses Equation 49 as the base equation for the solute transport with linear sorption and nonequilibrium transport. Some of the parameters in this equation were altered to obtain an equation that simulates vapor transport, as shown Equation 50.

where, f is the fraction of exchange sites assumed to be at equilibrium, α (alpha) is the first-order kinetic rate constant, and C_s^k is the soil concentration in sites with kinetic sorption. Table 11 presents a summary of the parameters identified in HYDRUS-1D and what they represented in the simulations performed in this research. "HYDRUS" parameters are those used by HYDRUS-1D if it is modeling solute transport. Parameters under "This Research" are those entered to the program in order to model the vaporphase as liquid-phase.

entered to	o the H	YDRUS code
HYDRU	S	This Research
θ_{W}	\rightarrow	θ_{A}
C_W	\rightarrow	C_A
C_A	\rightarrow	C_W
D_W	\rightarrow	D_A
D_A	\rightarrow	D_{W}
K_H	\rightarrow	K_{H}^{-1}
K_d	\rightarrow	K_{d} '

Table 11 Transport parameters

HYDRUS-1D software has an interface where the model parameters are entered. These parameters include: soil properties, chemical characteristics, and model settings. Table 12 presents the main settings used in this code. These conditions were fixed for all simulations.

-

Main Processes		Time Step Control	
General Solute Transport:	Ŋ	Lower Optimal Iteration Range:	3
Inverse Solution:	V	Upper Optimal Iteration Range:	7
		Lower Time Step Multiplication Factor:	1.3
Inverse Solution		Upper Time Step Multiplication Factor:	0.7
Solute Transport Parameters:	\checkmark		
Resident Concentrations:	\checkmark		
No internal Weighting of Inversion Data:	\checkmark	Internal Interpolation Tables	
Max Number of Iteration:	30	Lower Limit of the Tension Interval:	1.E-06
Number of Data Points in Objective Function:	40	Upper Limit of the Tension Interval:	1.E+04
Geometry Information			
Length Units:	cm	Soil Hydraulic Model	
Number of Soil Materials:	2	Single Porosity Models:	\checkmark
Number of Layers for Mass Balances:	1	van Genutchen - Mualem:	\square
Decline from Soil Profile:	1	No hysteresis:	Ŋ
Time Information		Water Flow Boundary Conditions	
Time Units:	days	Upper BC - Constant Pressure Head:	V
Initial Time:	0	Lower BC - Constant Pressure Head:	\checkmark
Final Time:	80		
Initial Time Step:	1.E-03	Initial Condition	
Minimum Time Step:	1.E-05	In the Water Content:	V
Maximum Time Step:	5		
		Solute Transport	
Print Information		Crank-Nicholson Scheme:	V
T-Level Information:	1	Galerkin Finite Elements:	\checkmark
Screen Output:	\checkmark	Use Tortuosity Factor:	\checkmark
Hit Enter at End:	\checkmark	Mass Units:	μg
Number of Print Times:	40	Absolute Concentration Tolerance:	1.E-07
		Relative Concentration Tolerance:	1.E-07
Iteration Criteria		Maximum Number of Iterations:	30
Maximum Number of Iterations:	30	Stability Criterion:	2
Water Content Tolerance:	1.E-04	Number of Solutes:	1
Pressure Head Tolerance:	1	Pulse Duration:	80

Table 12	Fixed main a	settings used	in HVDRUS	for all ev	nerimental	conditions
TADIC 12.	FIXCU Main S	settings useu	III III DKUS	101 all Ca	permentar	conultions

HYDRUS modeling was performed using the solute transport module. This module was used with inverse optimization to estimates the transport parameters. HYDRUS optimization minimizes the squared deviation between the modeled and experimental concentrations that minimized the objective function by the Levenberg-Marquardt nonlinear minimization algorithm [Casey and Šimůnek, 2001]. The two-sites sorption model was used in the solute transport module to consider the chemical nonequilibrium. One fraction of the contaminant was assumed to have instant sorption, while the remaining fraction was considered to be a first-order kinetic rate process. Partitions to the solid phase were assumed to be linear, thus the K_d " was used.

HYDRUS code has the option of using or not using the tortuosity factor. The default model of the code is the Millington and Quirk [1961] to determine the tortuosity factor. Although the applicability of this relationship is questioned at higher water contents, it is used in the modeling assuming its applicability at the experimental water contents.

Unsaturated soil hydraulic properties in the HYDRUS code were determined using Rosetta Lite v. 1.1, which was independently developed by Marcel Schaap at the U.S. Salinity Laboratory. Rosetta uses pedotransfer functions to predict soil hydraulics parameters from basic soil data. The inputs to this program are: the soil textural class, the soil textural distribution, bulk density, and one or two water retention points. The soil textural distribution and bulk densities were used in the simulations. Water retention points were not relevant since there was not flow in the experiments, but if it was, it would have been used to present relative permeability in the gas phase.

The soil materials, water contents, number of nodes, and observation points were entered in HYDRUS-1D using an interactive graphics-based interface. Water contents were those measured experimentally at the end of the experiments. Meanwhile, the observations points were located at the same distances of the sampling ports where the experimental concentrations were measured.

HYDRUS modeling consisted of enters all parameters required by the code, and includes the measured vapor concentrations for the inverse simulation. Values of the general parameters used for each column condition are given in Table 13. These values, which remain constant during the modeling, include: geometry information, water flow parameters, solute transport and reaction parameters, and profile information. Some of these do not represent the HYDRUS parameters value because they represent the values for the vapor-phase as established in Table 11. The solute transport boundary conditions used in the model were constant concentrations. The upper boundary concentration (*UBC*) was equal to zero. Meanwhile, the lower boundary concentrations (*LBC*) were determined for each experiment and port.

n		Set 1		as	t 2		Set 3			Set 4			Set 5		11
r at attracts	Col. 1	Col. 2	Col. 3	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	UIIIS
Geometry Information															
Depth of the Soil Profile:	6.926	6.891	6.944	6.891	6.944	12.7	13.070	12.728	12.700	13.070	12.728	12.700	13.070	12.728	cm
Water Flow Parameters															
Residual soil water content (Qr) :	0.4201	0.3987	0.3705	0.3818	0.3704	0.4134	0.3839	0.3197	0.3043	0.3495	0.3690	0.2778	0.3528	0.3787	cm ³ /cm ³
Saturated soil water content (Qs) :	0.4329	0.4397	0.4541	0.4189	0.4471	0.4200	0.4367	0.4393	0.4518	0.4561	0.4219	0.4233	0.4391	0.4029	cm^3/cm^3
Parameter a in the soil water retention function:	0.0367	0.0366	0.0365	0.0371	0.0365	0.0371	0.0366	0.0366	0.0365	0.0365	0.0370	0.0370	0.0366	0.0375	cm ⁻¹
Parameter n in the soil water retention function (ns) :	3.2404	3.2605	3.2813	3.1845	3.2754	3.1893	3.2528	3.2596	3.2804	3.2813	3.1972	3.2033	3.2596	3.1069	[-]
Saturated hydraulic conductivity (Ks):	505.6	531.0	584.9	453.7	558.9	457.6	520.3	529.7	577.2	592.6	464.2	469.5200	529.7	395.3	cm/day
Tortuosity parameter in the conductivity function (I):	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	[-]
Solute Transport and Reaction Parameters															
Bulk Density $(\rho$):	1.605	1.586	1.545	1.644	1.565	1.641	1.594	1.587	1.551	1.539	1.636	1.632	1.587	1.690	g/cm ³
Water Diffusion (D_{WM}) : *	5,461	5,461	5,461	5,889	5,889	5,461	5,461	5,461	5,889	5,889	5,889	5,461	5,461	5,461	cm ² /day
Gaseous Diffusion $(D_{A,M})$: *	0.606	0.606	0.606	0.838	0.838	0.606	0.606	0.606	0.838	0.838	0.838	909'0	0.606	0.606	cm ² /day
Henry's Law Constant (K_H) : *	124,822	124,822	124,822	42,724	42,724	124,822	124,822	124,822	42,724	42,724	42,724	124,822	124,822	124,822	[-]
Profile Information															
Number of Nodes:	60	60	60	09	60	80	80	80	80	80	80	80	80	80	
Top Water Contents (θ_W): *	0.4201	0.3988	0.3705	0.3845	0.3761	0.4134	0.3868	0.3410	0.3379	0.3594	0.3723	0.3001	0.3651	0.3796	cm^3/cm^3
Bottom Water Contents (θ_W): *	0.4201	0.3988	0.3705	0.3818	0.3704	0.4134	0.3839	0.3197	0.3043	0.3495	0.3694	0.2778	0.3528	0.3787	cm^3/cm^3
Observation Point 1 (Distance from the Source):	6.410	6.571	6.494	6.571	6.494	9.527	10.732	9.680	9.527	10.732	9.680	9.527	10.732	9.680	cm
Observation Point 2 (Distance from the Source):	3.120	2.315	3.157	2.315	3.157	6.410	6.571	6.494	6.410	6.571	6.494	6.410	6.571	6.494	cm
Observation Point 3 (Distance from the Source):						3.12	2.315	3.157	3.12	2.315	3.157	3.12	2.315	3.157	cm
Observation Point 1 (Node Number):	5	4	5	4	5	21	15	20	21	15	20	21	15	20	
Observation Point 2 (Node Number):	33	40	33	40	33	40	40	40	40	40	40	40	40	40	
Observation Point 3 (Node Number):						61	99	60	61	66	60	61	66	60	

Table 13. Values of general parameters used for HYDRUS modeling of each experimental condition

* Values of these parameters repesent those for the gas-phase as was established in Table 11.

Once the main settings and general parameters are entered to HYDRUS, the following parameters were determined inversely from the model: fraction of exchange sites assumed to be at equilibrium (*f*), first order coefficient for nonequilibrium adsorption (*alpha*), and the lower boundary concentration (*LBC*). These parameters were changed until a combination that produce higher coefficient of determination (\mathbb{R}^2) for each experiment was obtained.

5.2 HYDRUS Results and Discussion

HYDRUS modeling was conducted using DNT concentration modified by the sampling ports efficiencies. These concentrations are summarized in Appendix D-1. Initially, modeled parameters of *LBC*, *f*, and *alpha* were fixed for all sampling ports at the same time. However, the measured concentrations could not be fitted with the model using the same transport parameters for all ports. Therefore, each sampling port was modeled individually. Figure 55 shows the measured and modeled concentrations for the Column 2 of Set 4, where the three ports were fitted independently. These graphs illustrated the difference between the measured and modeled concentrations when the best fitted parameters for each port were used to model the three ports at the same time. These results show that parameters required to best simulate transport at the distance closest to the source (Port 1) would significantly under estimate concentrations at greater distances. Parameters that best represent the transport at the sampling distance further away from the source (Port 3) would significantly over estimate concentrations at closer distances.

Parameters estimation was performed by changing one parameter at the time and looking for the higher coefficient of determination (R^2) between modeled and measured data. All iterations conducted for each experiment are presented in Appendix D-2. The final values of the parameters that better describes the vapor transport are summarized in Table 14. In addition, graphs of the final model prediction for each experiment are presented in Appendix D-3.



Figure 55. Measured and modeled values of vapor concentrations for the Column 2 of Set 4; (a) fitting Port 1, (b) fitting Port 2, and (c) fitting Port 3

						Samp	ling Port	1						
Demonstrate		Set 1		Se	et 2		Set 3			Set 4			Set 5	
rarameters	Col. 1	Col. 2	Col. 3	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3
* Kd (cm ³ /g):	30,739	20,819	26,967	24,139	26,187	122,700	20,367	16,663	33,709	35,156	8,727	4,516	3,919	12,424
f:	0.311	0.407	0.199	0.348	0.134	0.094	0.428	0.206	0.049	0.134	0.041	0.744	0.838	0.600
Alpha (day ⁻¹):	1.13E-02	5.88E-03	9.77E-05	1.27E-03	1.56E-03	2.30E-03	1.51E-01	4.88E-05	1.56E-03	6.01E-04	3.91E-04	2.62E-03	4.88E-07	1.58E-07
LBC (µg/L):	0.75	0.75	0.75	1.00	1.00	0.75	0.75	0.75	1.00	1.00	1.00	0.75	0.75	0.75
R ² :	0.982	0.986	0.911	0.792	0.880	0.974	0.957	0.968	0.988	0.988	0.961	0.955	0.863	0.961

Table 14.	Final values of the trans	sport parameters us	ed in the model for	each experiment
1 4010 1 10	I mai faides of the trans	por c parameters as	ca in the model for	cach caper mene

Domoniotomo		Set 1					Set 3			Set 4			Set 5	
Farameters	Col. 1	Col. 2	Col. 3	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3
* Kd (cm ³ /g):	59,627	26,436	30,154	5,701	16,728	884,531	15,877	26,385	21,695	30,113	8,478	3,947	4,868	28,186
f:	0.170	0.189	0.130	0.750	0.172	0.008	0.363	0.102	0.053	0.071	0.229	0.382	0.735	0.224
Alpha (day ⁻¹):	1.95E-05	4.77E-10	3.91E-04	1.56E-03	6.10E-08	3.59E-04	1.24E-04	1.18E-03	1.69E-03	2.03E-03	7.29E-03	2.58E-05	3.81E-07	7.81E-04
LBC (µg/L):	1.45	1.45	1.45	7.19	7.19	1.00	1.00	1.00	3.00	3.00	3.00	1.00	1.00	1.00
R ² :	0.985	0.927	0.894	0.922	0.946	0.927	0.964	0.966	0.996	0.995	0.982	0.992	0.983	0.968

Sampling Port 2

Sampling Port 3

Panamotore		Set 1					Set 3			Set 4			Set 5	
rarameters	Col. 1	Col. 2	Col. 3	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3	Col. 1	Col. 2	Col. 3
* Kd (cm ³ /g):						74,391	15,393	19,821	15,504	15,206	12,282	3,120	2,857	44,250
f:						0.184	0.395	0.157	0.108	0.139	0.270	0.449	0.988	0.143
Alpha (day ⁻¹):						1.95E-05	4.77E-10	5.44E-05	1.06E-04	5.78E-05	2.20E-04	1.26E-07	3.05E-06	1.56E-03
LBC (µg/L):						1.45	1.45	1.45	7.19	7.19	7.19	1.45	1.45	1.45
R ² :						0.434	0.915	0.955	0.989	0.996	0.990	0.984	0.964	0.969

* Values of these parameters where substituted by the modified parameters as was established in Table 11

Initially, the lower boundary concentrations used in the modeling corresponded to the vapor pressure. However, simulated concentrations were much higher than measured, thus lower concentrations were necessary as *LBC*, especially for the ports closer to the explosive source. Modeled values of *LBC* at 22°C were increasing from 0.75, 1.00, and 1.45 μ g/L, for Port 1, 2, and 3, respectively. Meanwhile, at 35°C the values of *LBC* increased from 1.00, 3.00, and 7.19 μ g/L, for Port 1, 3 and 3. These values indicate that at higher temperatures the source is emanating higher gas concentrations. In addition, indicate that sublimation is not an instant process. Therefore, the *LBC* must be represented using a kinetic source that changes its concentration during the time. This kinetic effect is observed more in the sampling ports closer to the source because they are more affected by the conditions of the source and not by the transport characteristics as the case of the distant ports.

Upper ports were modeled using *LBC* values equivalent to the vapor pressure. These higher values of *LBC* at the upper ports could be caused by the accumulation of vapors above the soil. During the first and second set of experiments, gas concentrations above the soil surface were measured. Those concentrations were increasing through the time, indicating that the upper boundary conditions not necessarily were equal to zero. Figure 56 shows how the concentrations of both ports can be fitted at the same time using the same parameters but using the upper boundary condition (*UBC*) equal to the experimental measured concentration above the soil. This fact could be verified only for Sets 1 and 2 because the columns were packed up to the middle and vapor samples were taken above the soil. However, data of vapor concentrations above the soil in Sets 3, 4 and 5 was not obtained, thus the model was set with an *UBC* of zero. Constant values of *UBC* different to zero could not be used in the model because this could represent a downward transport.



Figure 56. Variation of the model prediction for the Column 2 (Set 1) when the upper boundary concentration (UBC) is zero or is equal to the measured concentration above the soil

The partition coefficients between the gas and wet soil measured experimentally and modified by the sampling ports efficiencies were used in the models. These values were modeled using a fraction with kinetic sorption and results agree very well with the measured data. The average fraction of sites assumed to be at equilibrium was about 0.30 (\pm 0.24) (Figure 57), indicating that about 70% of sites are influenced by kinetic sorption. The values seemed to increase, reach a maximum, and then decreased with increasing water content, but showed no major influence between different temperatures and sampling distances. The average value of the first order coefficient for kinetic sorption (*alpha*) was 0.005 day⁻¹. These values of *alpha* were extremely variable for all experiments, and could not be associated directly to any soil condition or transport parameter. Therefore, the results shown that a large portion of the sites have nonequilibrium sorption. This could be produced by the mass transfer limitations of the source. Like the sources concentrations are changing with time, this is affecting the sorption rate and could be responsible of the sorption nonequilibrium.



Figure 57. Fraction of sites with instant sorption as function of water contents for the different sampling ports and temperatures

5.3 Sensitivity Analysis

Estimated parameters in the model were evaluated using sensitivity analysis. First, the contribution of the Henry's Law constant was evaluated. Figure 58 shows the variation of modeled vapor concentrations when the partition constant among the gas and water phase is used or not used. The use of the Henry's Law has the same effects of the sorption mechanism because is reducing and retarding the breakthrough curve of the gas concentrations. The changes in the modeled concentrations are, however, not significant.

The second parameter evaluated was the lower boundary concentration. As shown in Figure 59, higher *LBC* will increase the vapor concentration. For this reason it is very important to know the behavior of the solid explosive source to the appropriate modeling of the vapor transport. The model seems to be highly sensitive to this parameter.



Figure 58. Changes on modeled vapor concentration with and without the use of the Henry's Law constant (K_H)



Figure 59. Changes of modeled vapor concentrations with variations in the lower boundary concentrations (*LBC*)

Figure 60 shows the relative effect of the gas to wet soil distribution constants (K_d) in the model. It shows that if the partition constant is zero (i.e., no sorption), modeled vapor concentrations increase instantaneously and achieved equilibrium. As the partition constants increases, vapor concentration breakthrough curves are retarded or moved to the right side in the time scale. In addition, those high sorption capacities have the effect of reducing the vapor concentrations. In the case that the partition constants were higher than 350,000 L/kg, the vapor concentrations could not be measured during the first 80 days.

Another parameter analyzed was the fraction of sites (f) with equilibrium sorption. Figure 61 shows the changes in the modeled vapor concentrations with different fraction of sites with instant sorption. Variations on these fractions have a similar effect in the vapor concentration as the K_d ". Increments of f represent higher direct sorption and more retardation of the vapor transport. Meanwhile, lower f indicates that a greater part of the sorption is kinetic, but these do not have greater effect in the vapor concentrations.



Figure 60. Variations on the vapor concentration with changes in the gas to wetsoil partition constants $(K_d")$



Figure 61. Changes of modeled vapor concentrations with variations in the fraction of sites with equilibrium sorption (f)

Variations on nonequilibrium sorption rate (*alpha*) values tend to influence the total sorption capacity of the wet-soil (Figure 62). No-significant retardation of the breakthrough curve is observed when *alpha* is increased. This parameter has more effect at later times in the breakthrough curve and its effects are noticeable principally on the maximum gas concentration achieved by the model.

The sensitivity analysis for variations in the soil water contents (simulated air content) for this research indicates that when the water contents are lower, there are more empty pores for vapor diffusion and thus vapor concentrations are higher (Figure 63). This analysis is not completely true because in this research the partition constants are higher at low water contents which could reduce the vapor transport.

Another parameter evaluated was the gas diffusion constant (D_g) . Figure 64 illustrates the changes on vapor concentration with variations on D_g and its respective temperatures. The sensitivity analysis does not show large variations in the vapor concentrations with different soil temperatures. It is, thus, postulated that the principal effects of the changes in temperatures are on the volatilization rate of the explosive source and not in the diffusive vapor transport. Water diffusion constants (D_w) does not show large effects on the vapor transport (Figure 65). This is because it is several orders of magnitude lower than D_g .



Figure 62. Changes of modeled vapor concentrations with variations in the first order coefficient for nonequilibrium adsorption (*alpha*)



Figure 63. Variations on the vapor concentration with changes in the soil water contents (θ_W)



Figure 64. Changes of modeled vapor concentrations with different gas diffusion constants (D_g) as a consequence of variations in temperatures



Figure 65. Changes of modeled vapor concentrations with variations in the water diffusion constants (D_w)

CHAPTER 6: SUMMARY AND CONCLUSIONS

Landmine detection and remediation of sites contaminated with explosive-related chemicals (ERCs) have become a great challenge for the scientific and military community. Accurate chemical detection of landmines and efficient remediation techniques require good understanding of the factors affecting the fate and transport processes of ERCs in soils. These processes are influenced by environmental conditions, soil characteristics, and ERCs physical and chemical properties. This research focuses on determining the effect of water content and temperature on the vapors transport of TNT and DNT through the unsaturated soil. It involves (i) developing a physical model to experimentally determine the diffusive vapor transport behavior of TNT and DNT at different spatial and temporal scales; (ii) conducting vapor transport experiments at different soil-water contents and temperatures; and (iii) analyzing the experimental data using analytical and numerical methods to determine vapor-phase transport parameters as a function of imposed conditions.

Vapor transport experiments were conducted in soil columns packed with sandy soil by placing DNT and TNT crystals beneath the soil, and monitoring vapor-phase concentrations through the time at different distances from the source. Vapor concentrations were monitored thorough passive sampling of soil air using Solid Phase Microextraction (SPME) technique. This technique involves exposing the SPME fiber to soil-air for 4-minutes, and 5-minutes desorption into a gas chromatograph equipped with an electron capture detector. The technique provided very high sensitivity of TNT and DNT, detecting down to the low nano-grams per liter.

Experimental results show that TNT and DNT vapor concentrations are highly influenced by soil-water contents, temperature, and source characteristics. This postulation is supported by the following observations and conclusions:

• TNT vapor concentrations are much lower than DNT due to TNT's much lower vapor pressure, higher retention mechanism, and slower mass transfer.

- TNT and DNT vapor concentrations at given water content are higher at higher temperatures, reflecting the higher vapor pressures at higher temperature. It is postulated that higher temperatures also induce higher rates of mass transfer from the source and faster diffusive transport. Faster diffusive transport at high temperatures is reflected in earlier vapor breakthrough, and result from a higher molecular diffusion and higher concentrations gradients imposed by the higher vapor pressure at the source.
- Vapor concentrations of DNT and TNT at a given temperature tend to increase with increasing water contents at very dry conditions, reaching a maximum value, and then decreasing with further increase in water content at the higher water content regime. Vapor concentrations were undetectable at very low water contents (less than 0.48%), corresponding to 6 water layers or less of coverage. Increasing vapor concentration with increasing water content at the low water content regime is associated with decreasing sorption capacity at water content increase. It is, therefore, postulated that higher sorption capacity at low water contents retains DNT (and TNT) vapors for a long period of time (>80 days) before the sorption capacity is exceeded and the vapor can breakthrough. At higher water contents, the sorption capacity for DNT is reduced by competition with water, and vapor breakthrough begins at earlier times (is not retarded as much) than at the lower water contents. At the higher water content regime (>5%-8%), decreased vapor concentrations with increasing water contents suggest increasing retardation. This is attributed to dissolution in the water phase and potential adsorption at the air-water interface (if interfacial areas are increasing in the pellicular or pendular water regimes).
- Variations in water contents induce variation in vapor concentrations and transport characteristics. Results show that a decrease in water contents caused by evaporation produced a rapid reduction of vapor DNT concentrations.

- The ratio of concentrations at 35°C and 22°C is greater at distances further away • from the source than closer. Closer to the source the ratio is similar to the ratio of vapor pressures at 35°C and 22°C. This indicates that higher vapor concentration at high temperatures is due to the higher vapor pressures of the explosives source at distances closer to the source. It is postulated that at farther distances from the source, vapor concentrations are controlled to a greater extent by diffusive transport, than mass-transfer processes from the source. Higher temperatures also seem to influence the rate of vapor transport with distance. For instance, vapor concentration at Port 1 was 7.8 times higher than that at Port 3 after 40 days of transport at 22°C, but was only 3.8 higher at 35°C. The higher vapor concentration near the source than away, at lower temperatures, suggests that diffusive and mass transfer limitations influence vapor concentrations away from the source to a lesser extent at 35°C than 22°C. Faster rate of increase in DNT vapor concentrations with temperature indicates faster diffusive transport at higher temperatures.
- Measured TNT and DNT vapor concentrations near the source (≈ 3-cm) represent a very low fraction (<3.5%) of their vapor pressure at a given temperature. Lower than vapor pressure concentrations, are generally expected away from the source in a diffusive system. The low vapor concentrations near the source relative to the transport pressure and the inability to reach equilibrium after a long period of time (>40 days) suggest rate-limited mass transfer processes affecting the transport of TNT and DNT vapor in low water content soils. Mass transfer limitations from the source occur by slow rates of vaporization (solid to gas), dissolution (solid to water), volatilization (water to gas), and sorption and desorption processes.
- Spatial measurements of DNT vapor concentrations at different conditions indicate that vapor transport is slow, taking more than 80 days to reach equilibrium.

- Vapor phase concentrations control the retention of DNT and TNT in wet soils, except at very dry conditions. Consequently, TNT retained concentrations for wet soils were lower than those measured for DNT. Similarly, TNT and DNT retained concentrations in the wet soil as function of water content and space tend to follow similar behavior as the vapor phase concentration: decrease initially as water content increases from very dry conditions, then increases reaching a maximum value, and decreases with further increase in water content.
- Retarded (slower) increment with distance suggests that sorption is higher further away from the source and/or that retention processes are rate-limited and have not reached equilibrium.
- The relationship between TNT and DNT vapor concentrations and retained concentration tends to be linear at higher temperatures (35°C), but not linear at the lower ones (22°C). This suggests decreasing sorptive capacities with concentrations at the lower temperature. This retention capacity is generally higher for low water content soils.
- Linear sorption coefficients were slightly higher for TNT than DNT, but follow similar trends as function of water contents. Generally, K_d " values initially decrease, and then increase or remain constant as water content increases. Gassoil partition constants are nearly a steady value when water contents are larger than the equivalent of 17 layers of waters. This behavior is attributed to the higher sorptive capacities by direct sorption to solid surface at lower water contents and decreasing capacity with increasing water contents due to increasing competition with water at the surface. These results support previously reported research on the effect of water content on sorption of VOCs and ERCs.
- Higher linear air-soil distribution coefficients at distances further away from the source at lower temperatures (22°C) suggest non-equilibrium. At higher temperatures, *K_d*" values were generally lower at greater distance from the source.

- Estimated source vapor fluxes for DNT and TNT suggest vaporization mass transfer limitations from the source. Temporal flux data indicate transient source characteristics. Furthermore, analytical flux modeling indicates lower equivalent vapor pressure at the source than given by the compound's vapor pressure. This indicates that the vaporization rate is slower than the vapor transport rate, suggesting mass transfer limitation of the source. Lower fluxes for TNT than DNT result from lower concentration gradients and, potentially, lower mass transfer rates from its source.
- Measured DNT and TNT vapor fluxes in soils follow a similar behavior than those from the source, but they are slower and lower in concentration. Temporal variations of vapor fluxes are much slower and maximum fluxes are much lower than these in air. This behavior indicates that diffusive vapor transport in soils is influenced by, not only air porosity, but also by retention and mass transfer mechanisms.
- Measured DNT and TNT fluxes show similar behavior to vapor-phase concentrations as a function of water contents: generally, they increase from initially dry soils, reaches a maximum value, and then decrease with increasing water content. Earlier measured fluxes and higher fluxes indicate lower retardation in wetter soils.
- Measured vapor fluxes in the columns with soil were in the range of 10^{-5} to 10^{-6} µg/cm²-day for DNT, and from 10^{-7} to 10^{-8} µg/cm²-day for TNT. Meanwhile, vapor fluxes in the columns without soil ranged from 10^{-3} to 10^{-5} µg/cm²-day for DNT, and 10^{-6} to 10^{-7} µg/cm²-day for TNT. Therefore, the presence of soil reduces the vapor flux 2 to 3 orders of magnitude when compared with the fluxes in the empty columns. This reduction is due the distribution of the ERCs through the different soil phases and by the restrictions of free air space within the soil.

• Higher fluxes in the presence of water indicate that greater mass transfer limitations exist when the explosive is transferred from solid to vapor phase than form the liquid to vapor phase.

SPME sampling required exposing the fiber to soil-air in a stainless steel sampling tube fitted with a 100-µm porous cup to maximize vapor sampling mass, protect the fiber from damage, and ensure sampling consistency. Although previous research [Padilla et al., 2006] have shown high sampling efficiencies of the porous sampling for aqueous DNT and TNT, this study shows that the efficiency was reduced for vapor sampling. Evaluation of passive porous samplers for vapor diffusion measurements indicates limited efficiencies caused by vapor diffusion and retention across the porous stainless steel material. Active liquid sampling techniques reported by others [Padilla et al., 2006] do not show sampling efficiencies and suggest that, like in soils and landmine materials, vapors are more retained than solutes. It is recommended that better characterization of the sampler sorptive and efficiency characteristics be conducted.

Preliminary vapor transport modeling using HYDRUS-1D supports the experimental work, but indicates that vapor transport of TNT and DNT in soils must consider heterogeneous transport characteristics in space. Accurate representation of spatial vapor breakthrough required individual modeling of each breakthrough in space; resulting in different transport parameters in space. It is postulated that differences in water contents in space affects sorption, diffusion, and mass transfer characteristics. Consequently, the assumptions of homogeneous transport characteristics and linear partitions are limited. The use of a homogeneous model is, therefore, limited for comparative studies and is not intended as a predictive tool. For accurate development of predictive models, it is recommended that future modeling work considers the use of heterogeneous transport properties.

Comparative modeling results of vapor transport processes provide an excellent tool for evaluating the effect of environmental conditions on diffusive DNT and TNT transport in unsaturated soils. These results provide the following observations and conclusions:

- DNT and TNT must be simulated at lower concentrations at the source than those given by their respective vapor pressures. It is postulated that the source are transient in nature and must be modeled using a kinetic model.
- A large portion of retention sites are not at equilibrium, thus DNT and TNT vapor transport must take into account kinetic retention. The fraction of equilibrium sorption sites follow similar behavior to measured vapor-phase concentrations as a function of water content, but showed no major influences between temperatures and sampling distances.
- Diffusive transport is influenced by mass transfer and retention processes. Assuming that the Millington and Quirk model applies soil-water diffusive coefficients decreases with increasing water content. These values must, however, be modified with retention and mass transfer parameters.
- DNT vapor concentrations are highly influenced by source concentrations, and equilibrium and non-equilibrium retention parameters; but less influenced by the Henry's Law Constant, the first order mass transfer coefficient, and the effective soil-air diffusion coefficients.
- It is concluded from this study that the most important factors on the vapor transport is soil-water content and temperature. Water content determines the availability of the pore space for gas diffusion and is related directly with the magnitude of the vapor sorption. Meanwhile, the principal effect of temperature was on the ratio of volatilization of the explosive source.

The best environmental and soil conditions for the detection of ERCs vapors in the vadose zone are the following: moist soil with a water contents of about 8%, and high temperatures, soil with small specific surface areas, and soil with low organic matter contents. Suitable moments for the better detection on the soil surface are: during events of pressure reduction above the soil surface, during increments of temperatures, and during increments of soil water content. It is at these conditions that vapor concentrations produce higher concentrations for detection of vapor into and above the unsaturated soils.

CHAPTER 7: RECOMMENDATIONS

After the conclusion of this research and the achievement of the experimental objectives, some recommendations can be made as the results of the experimental experience. These suggestions should be used to reduce the experimental time and extend the analysis to more complex systems.

- Monitor temporal water contents and characterize water evaporation flux.
- Evaluate the effect of water evaporation on the overall DNT and TNT transport.
- Determine and quantify the porous cups efficiencies at the same distance from the source and use those that have similar efficiencies.
- Utilize a GC with mass spectrometer to identify those compounds resulting from degradation or contamination.
- Use a non-sorptive compound (non-reactive tracer) in combination with TNT and DNT.
- Modify the physical model to use a vapor phase explosive source instead of a solid source to avoid the uncertainties of the phase transition.
- Characterize the lower boundary condition concentrations so that it can be used in the model simulations.
- Use heterogeneous properties to model the experimental results using HYDRUS.
- Expand the scope of the research to work with other types of soils, temperatures, and higher water contents (above the soil field capacity).
- Apply to the physical model other important environmental factors like water flow, changes in atmospheric pressure, and variations in light intensity.

CHAPTER 8: REFERENCES

- Abriola, L.M., and G.F. Pinder (1985). "A Multiphase Approach to the Modeling of Porous Media Contamination by Organic Compounds, 2 - Numerical Simulations". *Water Resour. Res.*, 21(1): 19-26.
- Anaya, A., I. Padilla, and S. Hwang (2007). "Influence of Environmental Conditions on the Fate and Transport of ERCs in a Physical 3D Model: Spatial and Temporal Assessment Effects in a Sandy Soil". Proceedings of SPIE on Detection and Remediation Technologies for Mines and Minelike Targets, XII SPIE Defense and Security Symposium, Orlando, FL, vol. 6553.
- ATSDR (Agency for Toxic Substances and Disease Registry) (1995). "Toxicological Profile for 2,4,6-Trinitrotoluene". http://www.atsdr.cdc.gov/toxprofiles/tp81.html. Last accessed on June, 2008.
- ATSDR (Agency for Toxic Substances and Disease Registry) (1998). "Toxicological Profile for 2,4- and 2,6-Dinitrotoluene". http://www.atsdr.cdc.gov/toxprofiles/tp109.pdf. Last accessed on June, 2008.
- Ayres, K.W., R.G. Button, and E. Dejong (1972). "Soil Morphology and Soil Physical Properties, 1. Soil Aeration". *Can. J. Soil Sci.*, 52:311-321.
- Baehr, A.L. (1987). "Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor Phase Partitioning". *Water Resour. Res.*, 23(10): 1926-1938.
- Bakker, J.W., and A.P. Hidding (1970). "The Influence of Soil Structure and Air Content on Gas Diffusion in Soils". *Neth. J. Agric. Sci.*, 18:37-48.
- Bartelt-Hunt, S. L., and Smith, J. A. (2002). "Measurement of Effective Air Diffusion Coefficients for Trichloroethylene in Heterogeneous Soil". J. Cont. Hydr., 56:193-208.
- Batterman, S., I. Padmanabham, and P. Milne (1996). "Effective Gas-Phase Diffusion Coefficients in Soils at Varying Water Content Measured Using a One-Flow Sorbent-Based Technique". *Environ. Sci. Technol.*, vol. 30, no.3.
- Blake, G.R., and J.B. Page (1948). "Direct Measurements of Gaseous Diffusion in Soils". Soil Science Soc. Am. Proc. 13, 37-41.
- Brannon, M.J., P. Deliman, C. Ruiz, C. Price, M. Qasim, J.A. Gerald, C. Hayes, and S. Yost (1999). "Conceptual Model and Process Descriptor Formulations for Fate and Transport of UXO". US Army Corps of Engineers Waterways Experimental Station, IRRP-99-1.
- Brown, T.L., H.E. LeMay, and B.E. Bursten (2000). "Chemistry the Central Science". 8th ed., *Prentice Hall*, NJ.
- Bruant, R. G. and M. H. Conklin (1998). "Adsorption of hydrophobic organic contaminants at the air/water interface". United States/Mexico Conference on Hazardous Waste Management and Technologies.

- Bruschini, C. (2001). "Commercial Systems for the Direct Detection of Explosives (for Explosive Ordnance Disposal Tasks)"., *ExploStudy*, http://diwww.epfl.ch/lami/detec/explostudy.html. Last accessed on June, 2008.
- Brusseau, M.L. (1991). "Transport of Organic Chemicals by Gas Advection in Structured or Heterogeneous Porous Media: Development of a Model and Application to Column Experiments". *Water Resour. Res.*, Vol. 27, No. 12, pp. 3189–3199.
- Buckingham, E. (1904). "Contributions to Our Knowledge of the Aeration of Soils". U.S. Bureau of Soils Bulletin, 38.
- Call, F. (1957). "The Mechanisms of Sorption of Ethylene Dibromide on Moist Soils". J. Sci. Food Agric., 8:630-639.
- Casey, F.X.M., and J. Šimůnek (2001). "Inverse Analyses of Transport of Chlorinated Hydrocarbons Subject to Sequential Transformation Reactions". J. Environ. Qual., 30:1354-1360.
- Charbeneau, R.J. (2000). "Groundwater Hydraulics and Pollutant Transport". Waveland Press, Inc., IL.
- Chatwin, P. (1998). "Diffusion in Natural Porous Media". *Kluwer Academic Publishers*. Norwell, MA.
- Choi, J.W, F.D. Tillman, and J.A. Smith (2002). "Relative Importance of Air-Phase Diffusive and Advective Trichloroethylene Fluxes in the Unsaturated Zone Under Natural Conditions". *Environ. Sci. Technol.*, 36 (14), 3157 -3164.
- Comfort, S.D., P.J. Shea, and L.S. Hundal (1995). "TNT Transport and Fate in Contaminated Soil". J. Environ. Qual., vol.24, pp.1174-82.
- Corapcioglu, M.Y. and A.L. Baehr (1987). "A Compositional Multiphase Model for Groundwater Contamination by Petroleum Products, 1, Theoretical Considerations". *Water Resour. Res.*, 23(1), 191-200.
- Costanza, M.S., and M.L. Brusseau (2000). "Contaminant Vapor Adsorption at the Gas-Water Interface in Soils". *Environ. Sci. Technol.*, vol. 34 (1).
- Costanza, M.S., and M.L. Brusseau (2002). "Gas Phase Advection and Dispersion in Unsaturated Porous Media". *Water Resour. Res.*, vol. 38, No.4.
- Cragin, J.H., and D.C. Leggett (2003). "Diffusion and Flux of Explosive-Related Compounds in Plastic Mine Surrogates". *Cold Regions Research and Engineering Laboratory*, ERDC/CRREL TR-03-12.
- 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(9): 2259-2270.
- Currie, J.A. (1960). "Gaseous Diffusion in Porous Media Part 1: A Non-Steady State Method". *Rothamsted Experimental Station, Harpenden Herts.*

- Currie, J.A. (1961). "Gaseous Diffusion in Porous Media". Part 3. Brit. J. Appl. Phys., 12:275-281.
- Cussler, E.L. (1997). "Diffusion Mass Transfer in Fluid Systems". 2nd Edition. *Cambridge* University Press, NY, pp.31.
- Dean, J.A. (1999). "Lange's Handbook of Chemistry". 15th Edition. McGraw-Hill, New York.
- Dionne, B.C., D.P. Rounbehler, E.K. Achter, J.R. Hobbs, and D.H. Fine (1986). "Vapor Pressure of Explosives". J. Ener. Mat., vol. 4, 447-472.
- Dye, R.F., and J.M. Dallavalle (1958). "Diffusion of Gases in Porous Media". Ind. Eng. Chem., 50:1195-1200.
- Edwards, G.T. (1950). "The vapour pressure of 2,4,6-Trinitrotoluene" *Trans. Faraday Soc.*, 46, 423.
- Eriksson, J., and U. Skyllberg (2001). "Binding of 2,4,6-Trinitrotoluene and its Degradation Products in a Soil Organic Matter Two-Phase System". *J. Environ. Qual.*, 30:2053-2061.
- Fetter, C.W (1999). "Contaminant Hydrogeology". 2nd ed., Prentice Hall, NJ.
- Fetter, C.W. (2001). "Applied Hydrogeology". 4th ed., Prentice Hall, NJ.
- Fuentes, H.R., W.L. Polzer, J.L. Smith (1991). "Laboratory Measurements of Diffusion Coefficients for Trichloroethylene and Orthoxylene in Undisturbed Tuff". J. Environmental Quality, 20, 215.
- 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". *Proceedings of the SPIE 13th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls*, Orlando, FL, Vol. 3710, pp. 258-269.
- Gierke, J.S., N.J. Hutzler, and J.C. Crittenden (1990). "Modeling the Movement of Volatile Organic Chemicals in Columns of Unsaturated Soil". *Water Resour. Res.*, 26(7), 1529-1547.
- Gierke, J.S., N.J.Hutzler, and D.B. Mckenzie (1992). "Vapor Transport in Unsaturated Soil Columns: Implications for Vapor Extraction". *Water Resour. Res.* 28(2), 323-335.
- Gordon L., and W.R. Hartley (1989). "Health Advisory on 2,4,6-Trinitrotolune". Office of Drinking Water, US EPA, Washington, D.C.
- Gradwell, M.W. (1961). "A Laboratory Study of the Diffusion of Oxygen through Pasture Topsoils". N.Z J. Sci. 4:250-270.
- Hale, V.Q., T.B. Stanford, and L.G. Taft (1979). "Evaluation of the Environmental Fate of Munition Compounds in Soils". U.S. Army Medical Research and Development Command, Final Report AD-A082874.

- Hernández, M.D., I. Santiago, and I.Y. Padilla (2006). "Macro-Sorption of 2,4-Dinitrotoluene onto Sandy and Clay Soils". Proceedings of SPIE on Detection and Remediation Technologies for Mines and Minelike Targets, XI SPIE Defense and Security Symposium, Orlando, FL, vol. 6217.
- Hoff, J.T., R.W. Gillham, D. Mackay, and W.Y. Shiu (1993). "Sorption of organic Vapors in a Sand Aquifer Material". *Environ. Sci. Tech.*, Vol. 27. No. 13, pp. 2789-2794.
- Hutchinson, G.L., and G.P. Livingston (2002). "Soil Atmosphere Gas Exchange". Methods of Soil Analysis. Part 4. SSSA Book Ser. 5. p.1159-1182. Madison, WI.
- Hutzler, N.J., J.S. Gierke, and L.C. Krause (1989). "Movement of Organic Chemicals in Soils, in Reactions and Movement of Organic Chemicals in Soils"., edited by B.L. Sawhney and K. Brown, Soil Sci. of Am. and Am. Soc. of Agron, Spec. Publ. 22, chap 15, pp. 373-403.
- IPCS (International Programme on Chemical Safety) (2000). "2,4,6-Trinitrotoluene". ICSC: 0967. http://www.inchem.org/documents/icsc/icsc/eics0967.htm. Last accessed on June, 2008.
- Jenkins, T.F., D.C. Leggett, and T.A. Ranney (1999). "Vapor Signature from Military Explosives: Part 1. Vapor Transport from Buried Military-Grade TNT". U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report, 99-21.
- Jenkins, T.F., M.E. Walsh, P.H. Miyares, J.A. Kopczynski, T.A. Ranney, V. George, J.C. Pennington, and T.E. Berry Jr. (2000). "Analysis of Explosives-Related Chemical Signatures in Soil Samples Collected Near Buried Land Mines". U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Technical Report ERDC TR-00-5.
- Jin, Y., and W.A. Jury (1996). "Characterizing the Dependency of Gas Diffusion Coefficient on Soil Properties". Soil. Sci. Soc. Am. J., 60:66-71.
- Jury, W.A., W.F. Spencer, and W.J. Farmer (1983). "Behavior Assessment Model for Trace Organics in Soil, 1, Model description". J. Environ. Qual., 12(4): 558-564.
- Jury W.A., W.J. Farmer, and W. F. Spencer (1984). "Behavior Assessment Model for Trace Organics in Soil, II, Chemical Classification and Parameter Sensitivity". J. Environ. Qual., 13(4), 567-572.
- Jury, W.A., and R. Horton (2004). "Soil Physics". 6th ed., John Wiley and Sons, Inc., NY.
- Karimi, A.A., W.J. Farmer, and M.M. Cliath (1987). "Vapor-Phase Diffusion of Benzene in Soil". J. Environ. Qual., 16:38-43.
- Karimi-Lotfabad, S., M.A Pickard, and M.R. Gray (1996). "Reactions of Polynuclear Aromatic Hydrocarbons on Soil". *Environ. Sci. Technol.*, vol. 30, no.4.
- Leggett, D.C., J.H. Cragin, T.F. Jenkins, and T.A. Ranney (2001). "Release of Explosive-related Vapors from Landmines". U.S. Army Engineer Research and Development Center, ERDC/CRREL Technical Report TR-01-6.

- 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 Cold Regions Research and Engineering Laboratory, Special Report 77-16.
- Lenchitz, C., and R.W. Velicky (1970). "Vapor Pressure and Heat of Sublimation of Three Nitrotoluenes". J. Chem. Eng. Data, 15(3); 401-403.
- Livingston, H.F. (1949). "The cross-sectional areas of molecules adsorbed on solid surfaces". J. Collod Sci., 4:447-458.
- Luning, D.J., and D.W. O'Sullivan (2006). "Solubility of 2,4-Dinitrotoluene and 2,4,6-Trinitrotoluene in Seawater". J. Chem. Eng. Data, 51:448-450.
- Lynch, J.C., K.F. Myers, J.M. Brannon, and J.J. Delfino (2001). "Effects of pH and Temperature on the Aqueous Solubility and Dissolution Rate of 2,4,6-Trinitrotoluene (TNT), Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)". J. Chem. Eng. Data, 46:1549-1555.
- MacDonald, J., J. R. Lockwood, J. McFee, T. Altshuler, T. Broach, L. Carin, C. Rappaport, W.R. Scott, and R. Weaver (2003). "Alternatives for Landmine Detection, Alternatives for Landmine Detection". *RAND*, Santa Monica, CA, p.336.
- Marshall, T.J. (1959). "The Diffusion of Gas trough Porous Media". J. Soil Sci., 10: 79-80.
- Mayfield, H.T., E. Burr, and M. Cantrell (2006). "Analysis of Explosives in Soil Using Solid Phase Microextraction and Gas Chromatography". *Analytical Letters*, 39:1463-1474.
- McGrath, C.J. (1995). "Review of Formulations for Process Affecting the Subsurface Transport of Explosives". U.S. Army Engineer Waterways Experiment Station, Technical Report IRRP-95-2.
- Metcalfe, D.E., and G.J. Farquhar (1987). "Modeling Gas Migration Through Unsaturated Soils from Waste Disposal Sites". *Water, Air Soil Pollut.*, 32:247-259.
- 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 Landmines". U.S. Army Engineer Research and Development Center, ERDC/CRREL TR-00-17.
- Molard, L. (1958). Mem. Poudres, 40, 13.
- Moldrup, P., T. Olesen, D.E. Rolston, and T. Yamaguchi (1997). "Modeling Diffusion and Reactions in Soils: VII, Predicting Gas and Ion Diffusivity in Unsaturated and Sieved Soils". *Soil Sci.*, 162(9), 632.
- Moldrup, P., T. Olesen, J. Gamst, P. Schjonning, T. Yamaguchi, and D.E. Rolston (2000). "Predicting the Gas Diffusion Coefficient in Repacked Soil: Water-Induced Linear Reduction Model". Soil Sci. Soc. Am. J., 64:1588-1594.

- Mohsen, M.F., G.J. Farquhar, and N. Kouwen (1980). "Gas Migration and Vent Design at Landfill Site". *Water, Air Soil Pollut.*, 13: 79-97.
- Molina, G.M., I. Padilla, M. Pando, and D. Pérez (2006). "Field Lysimeters for the Study of Fate and Transport of Explosive Chemical in Soils under Variable Environmental Conditions". *Proceedings of SPIE*, vol. 6217-137.
- Ong, S.K, and L.W. Lion (1991). "Mechanism for Trichloroethylene Vapor Sorption onto Soil Minerals". J. Environ. Qual., 20:180-188.
- 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". J. Contam. Hydrol., 11:273-290.
- Owen Compliance Services (2006). "Material Safety Data Sheet (MSDS-TNT)". http://www.ocsresponds.com/ref/msds/msds-tnt.pdf. Last accessed on June, 2008.
- Padilla, A.C., I.Y. Padilla, and I. Santiago (2006). "Multiphase extraction sampling of explosives in unsaturated soils". *Proceedings of SPIE on Detection and Remediation Technologies for Mines and Minelike Targets, XI SPIE Defense and Security Symposium*, Orlando, FL, vol. 6217.
- Padilla, I.Y. (1998). "Transport of Nonreactive and Volatile Solutes in Unsaturated Porous Media under Wetting and Draining Conditions". *Dissertation Thesis of the University of Arizona*, AZ.
- Pella, P.A. (1977). "Measurement of the Vapors Pressures of TNT, 2,4-DNT, 2,6-DNT, and EGDN". J. Chem. Thermodynamics, 9:301-305.
- Penman, H.L. (1940). "Gas and Vapors Movements in the Soil: I. The Diffusion of Vapors Through Porous Solids". J. Agric. Sci., 30:437-462.
- Pennington, J.C., and W.H. Patrick (1990). "Adsorption and Desorption of 2,4,6-Trinitrotoluene by soils". J. Environ. Qual., 19: 559-567.
- Petersen, L.W., D.E. Rolston, P. Moldrup, and T. Yamaguchi (1994). "Volatile Organic Vapor Diffusion and Adsorption in Soils". J. Environ. Qual., 23:799-805.
- 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.
- 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.
- 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.*, 22(5):571-578.

- Phelan, J.M., and J.L. Barnett (2001a). "Solubility of 2,4-Dinitrotoluene and 2,4,6-Trinitrotoluene in Water". J. Chem. Eng. Data, 46:375-376.
- Phelan, J.M., and J.L. Barnett (2001b). "Phase Partitioning of TNT and DNT in Soils". Sandia National Laboratories, Sandia Report SAND2001-0310.
- 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.
- Phelan, J.M., and S.W. Webb (1998). "Chemical Detection of Buried Landmines". *Proceedings* of the 3rd International Symposium on Technology and the Minelike Problem, Mine Warfare Association.
- Phelan, J.M., and S.W. Webb (1999). "Chemical Soil Physics Phenomena for Chemical Sensing of Buried UXO". Proceedings of UXO Forum, Department of Defense Explosive Safety Board and U.S. Army Environmental Center.
- Phelan, J.M., S.W. Webb, M. Gozdor, and M. Cal (2000). "Laboratory Data and Model Comparison of the Transport of Chemical Signatures from Buried Landmines". Proceeding of the SPIE 14th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mine and Minelike Targets V, Orlando, FL., vol.4038.
- Phelan, J.M., S.W. Webb, P.J. Rodacy, and J.L. Barnett (2001). "Environmental Impact to the Chemical Signature Emanating from Buried Ordance, Final Report, Project CU-1094". Sandia National Laboratories, SAND2001-2902.
- Phelan, J.M., and S.W. Webb (2002). "Chemical Sensing for Buried Landmines Fundamental Processes Influencing Trace Chemical Detection". Sandia National Laboratories. SAND2002-0909.
- Pinder, G.F. and L.M. Abriola (1986). "On the Simulation of Non-Aqueous Phase Organic Compounds in the Subsurface". *Water Resour. Res.*, 22(9), 109S-119S.
- Price, A.R., C.J. Pennington, L.S. Larson, D. Neumann, and A.H. Charolett (2002). "Uptake of RDX and TNT by Agronomy Plants". *Soil and Sediment Contamination*, 11(3):307-326.
- Pruess, K. (1991). "TOUGH2- A General –Purpose Numerical Simulator for Multiphase Fluid and Heat Flow". *Lawrence Berkeley Laboratory*, LBL-29400.
- Ravikrishna, R., S.L. Yost, C.B. Price, K.T. Valsaraj, J.M. Brannon, and P.H. Miyares (2002). "Vapor Phase Transport of Unexploded Ordnance Compounds through Soils". *Environ. Tox. Chem.*, Vol. 21, No. 10, pp. 2020-2026.
- Rhue, R.D., P.S.C. Rao, and R.E. Smith (1988). "Vapor Phase Adsorption of Alkylbenzenes and Water on Soils and Clays". *Chemosphere*, 17:727-741.
- Ritchie, J.T. (1964). "Soil Aeration Characterization Using Gas Chromatography". Ph.D. Dissertation, Iowa State University, Ames, IA, 149.

- Rittfeldt, L. (2001). "Determination of Vapor Pressure of Low-Volatility Compounds using a Method to Obtain Saturated Vapor with Coated Capillary Columns". Anal. Chem., vol. 73, no. 11, pp. 2505-2411.
- Ro, K.S., A. Venugopal, D. Dean, D. Constant, K. Qaisi, K.T. Valsaraj, L.J. Thibodeaux, and D. Roy (1996). "Solubility of 2,4,6-Trinitrotoluene (TNT) in Water". J. Chem. Eng. Data, 41:758-761.
- Rodríguez, S., I. Padilla, and I. Santiago (2006). "Development of a Multiscale Packing Methodology for Evaluating Fate and Transport Processes of Explosive-Related Chemicals in Soil Physical Models". *Proceedings of SPIE*, vol. 6217.
- Runkles, J.R. (1956). "Diffusion, Sorption and Depth Distribution of Oxygen in Soils". Ph.D. Dissertation. Library, Iowa State University, Ames, IA, pp. 156.
- Rust, R.H., A. Klute, and J.E. Gieseking (1957). "Diffusion-Porosity Measurements using Non-Steady State System". Soil Sci. 84:453-463.
- Sallam, A. W.A. Jury, and J. Letey (1983). "Measurement of Gas Diffusion Coefficient under Relatively Low Air-Filled Porosity". *Division S-1-Soil Physics*.
- Sallam, A., W.A. Jury, and J. Letey (1984). "Measurement of Gas Diffusion Coefficient under Relatively Low Air-Filled Porosity". J. Soil Sci. Soc. Am., 48:3-6.
- Scanlon, B. (2004). "Review of HYDRUS-1D". Soutwest Hydrology, 37.
- Schaefer, C.E., R. Arands, H.A. Van der Sloot, and D.S. Dosson (1997). "Modeling of the Gaseous Coefficient through Unsaturated Soil Systems". J. Contam. Hydrol., 29, 1-21.
- Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden (2003). "Environmental Organic Chemistry". 2nd Edition. *John Wiley and Sons, Inc.* Hoboken, NJ.
- Shoemaker, C.A., T.B. Culver, L.W. Lion, and M.G. Peterson (1990). "Analytical Models of the Impact of Two Phase Sorption on Subsurface Transport of Volatile Chemicals". *Water Resour. Res.*, 26:745-758.
- Šimůnek, J., M.T. van Genuchten, and M. Šejna (1995). "The HYDRUS-1D Software Package for Simulating the One-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media". Department of Environmental Engineering Science, University of California Riverside, Riverside, CA.
- Sleep, B.E., and J.F. Sykes (1989). "Modeling the Transport of Volatile Organics in Variably Saturated Media". *Water Resour. Res.*, 25(1), 81-92.
- Spanggord, R.J., T. Mill, T. Chou, W.R. Mabey, J.H. Smith, and L. Shonh (1980). "Environmental Fate Studies on Certain Munition Wastewater Constituents - Final Report, Phase II - Laboratory studies," *Defense Technical Information Center*, Technical Report Project No. LSU 7934.
- Spangler, G.E. (1975). "Measurements on the Availability of TNT Vapor from Antitank Mines". U.S. Army Mobility Equipment Research and Development Center, MERADCOM-R-2159.

- Spectrum Laboratories (2003). "Spectrum Chemical Fact Sheet". Cas #118967 http://www.speclab.com/compound/c118967.htm. Last accessed on June, 2008.
- Springer, E.P. (1986). "Modeling of Organic Vapor Movement at Area L Disposal Site". Los Alamos Natl. Lab., Los Alamos, NM, Tech. Rep. LA-UR-864359, pp.94.
- Stephanatos, B.N. (1985). "Groundwater Pollution by Gas-Phase Transport of Contaminants through the Vadose Zone". *M.S. Thesis, Univ. of Illinois*, Urbana, IL.
- Stephen, H., and T. Stephen (1963). "Solubilities of Inorganic and Organics Compounds". Vol. 1, Binary Systems, Part 1. *The Macmillan Company*, NY.
- Taylor, S.A. (1949). "Oxygen Diffusion in Porous Media as a Measure of Soil Aeration". Soil Sci. Soc. Proc.
- Tillman, F.D., J.W. Choi, and J.A. Smith (2002). "Design and Testing of a Chamber Device to Measure Organic Vapor Fluxes from the Unsaturated Zone under Natural Conditions". *CSCE/EWRI of ASCE Environmental Engineering Conference*, Niagara.
- Torres, A., I. Padilla, and S. Hwang (2007). "Physical Modeling of 2,4-DNT Gaseous Diffusion Through Unsaturated Soil". Proceedings of SPIE on Detection and Remediation Technologies for Mines and Minelike Targets, XII SPIE Defense and Security Symposium, Orlando, FL, vol. 6553.
- Troeh, F.R., J.D. Jabro, and D. Kirkham (1982). "Gaseous Diffusion Equations for Porous Materials". *Geoderma*, 27:239-253.
- U.S. Army Materiel Command (1971). "Engineering Design Handbook: Explosives Series, Properties of Explosives of Military Interest". Washington, D.C.
- USGS (U.S. Geological Survey) (2006). "General Facts and Concepts about Ground Waters". http://pubs.usgs.gov/circ/circ1186/html/gen facts.html. Last accessed on June, 2008.
- Van Bavel, C.H.M. (1952). "Gaseous Diffusion and Porosity in Porous Media". Soil Sci., 73:91-104.
- Verschueren, K. (1983). "Handbook of Environmental Data on Organic Chemicals". 2nd ed., *Van Nostrand Reinhold*, NY.
- Walsh, M.E., T.F. Jenkins, and P.G. Thorne (1995). "Laboratory and Analytical Methods for Explosives Residues in Soil". J. Energ. Mat., Vol. 13, 357-383.
- Webb, S.W., K. Pruess, J.M. Phelan, S.A. Finsterle (1999). "Development of a Mechanistic Model for the Movement of Chemical Signatures from Buried Landmines/UXO". *Proceedings of SPIE on Detection and Remediation Technologies for Mines and Minelike Targets IV*, vol. 3710, pp. 270-282.
- Webb, S.W., and J.M. Phelan (2000). "Effect of Diurnal and Seasonal Weather Variations on the Chemical Signatures from Buried Landmines/UXO". Proceedings of SPIE Conference on Detection and Remediation Technologies for Mines and Minelike Targets.

- 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 Workshop '98, *Lawrence Berkeley National Laboratories*, Report LBNL-41995.
- Weeks, E.P., D.E. Earp, G.M. Thompson (1982). "Use of Atmospheric Fluorocarbons F-11 and F-12 to determine the diffusion Parameters of the Unsaturated Zone in the Southern High Plains of Texas". *Water Resour. Res.*, 18(5): 1365-1378.
- Werner, D., and P. Höhener (2003). "In Situ Method to Measure Effective and Sorption-Affected Gas-Phase Diffusion Coefficients in Soils". *Environ. Sci. Technol.*, 37, 2502-2510.
- Wesseling, J.H. (1962). "Some Solutions of the Steady-State Diffusion of Carbon-Dioxide Through soils". *Neth. J. Agric. Sci.*, 10: 109-117.
- Wesseling, J.H., and W.R. Van Wijk (1957). "Land Drainage in Relation to Soil and Crops. 1. Soil Physical Conditions in Relation to Drain Depth". Drainage of Agricultural Land. Agron. Monogr. 7. ASA, CSSA, and SSSA, Madison, WI. pp. 461-504.
APPENDICES

Appendix A: Materials and Equipments



Figure 66. Experimental system



Figure 67. Data collection system and power supply



Figure 68. Air humidifying system, flow meter and mass flow controller



Figure 69. Pressure transducer



Figure 70. System monitoring



Figure 71. SPME calibration



Figure 72. Sand moistening



Figure 73. Solid explosive on the column bottom



Figure 74. Ultrasonic bath used for soil extractions



Figure 75. Soil extraction with acetonitrile



Figure 76. SRI 8610C GC



Figure 77. Perkin Elmer S200 HPLC

Appendix B: Gas Concentrations



B-1 Gas concentrations of DNT measured in the sampling ports located at different distances from the explosive source.



























B-2 Gas concentrations of DNT measured in the same sampling port and temperature at different soil water contents.















C-1 Vapor Fluxes of DNT measured in the sampling ports located at different distances from the explosive source.

























C-2 Vapor Fluxes of TNT measured in the sampling Port 1 at different soil-water contents and temperatures.



Appendix D: HYDRUS Modeling

D-1 Vapor concentrations of 2,4-DNT corrected by the sampling ports efficiencies.

		^		2,4-DNT	Concentratio	ons (µg/L)			
Day	Column #1 Column #2 O Port #1 Port #2 Port #3 Port #1 Port #2 Port #1 O						Column #3		
	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
3	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000
4	0.000	0.000	0.000	0.011	0.000	0.000	0.002	0.000	0.000
5	0.000	0.000	0.000	0.019	0.000	0.000	0.007	0.000	0.000
6	0.003	0.000	0.000	0.028	0.000	0.000	0.010	0.000	0.000
8	0.005	0.000	0.000	0.043	0.000	0.000	0.019	0.000	0.000
10	0.011	0.000	0.000	0.074	0.000	0.000	0.036	0.000	0.000
12	0.024	0.000	0.000	0.108	0.000	0.000	0.051	0.000	0.000
14	0.032	0.000	0.000	0.125	0.003	0.002	0.060	0.004	0.002
16	0.048	0.000	0.000	0.144	0.004	0.003	0.082	0.005	0.007
20	0.067	0.002	0.002	0.163	0.006	0.003	0.101	0.009	0.009
23	0.078	0.003	0.002	0.180	0.010	0.006	0.114	0.016	0.016
27	0.106	0.005	0.004	0.199	0.018	0.014	0.139	0.026	0.030
30	0.113	0.008	0.006	0.223	0.028	0.020	0.159	0.039	0.041
33	0.110	0.009	0.008	0.208	0.036	0.026	0.166	0.044	0.053
35	0.121	0.011	0.010	0.236	0.044	0.034	0.168	0.056	0.061
38	0.144	0.016	0.018	0.250	0.063	0.053	0.208	0.066	0.074
42	0.134	0.017	0.022	0.250	0.073	0.063	0.207	0.068	0.099
44	0.135	0.019	0.027		0.077	0.067	0.194	0.068	0.082
48	0.127	0.026	0.032	0.253	0.079	0.084	0.242	0.089	0.132
51	0.161	0.030	0.035	0.298	0.110	0.100	0.225	0.105	0.133
57	0.173	0.041	0.052	0.322	0.140	0.123	0.262		0.153
62	0.178	0.047	0.060	0.326	0.160	0.140	0.392	0.142	0.161
64	0.172	0.047	0.071	0.318	0.159	0.134	0.328	0.198	0.163
66	0.172	0.051	0.061	0.327	0.163		0.413		0.175
69	0.191	0.058		0.361	0.182	0.162	0.371	0.162	0.182
71	0.174	0.056	0.078	0.336	0.174		0.268	0.144	0.172
76	0.176	0.060	0.082	0.341	0.160	0.166	0.402		0.188
79	0.181		0.090		0.191	0.179	0.309		0.191

 Table 15.
 Corrected vapor concentration of Set 1

		2,4	-DNT Conce	ntrations (µg	/L)	
Day		Column #2			Column #3	
	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3
0	0.000	0.000	0.000	0.000	0.000	0.000
1	0.000	0.000	0.000	0.000	0.000	0.000
3	0.052	0.000	0.000	0.018	0.000	0.000
5	0.119	0.000	0.000	0.060	0.000	0.000
6	0.166	0.000	0.000	0.067	0.000	0.000
7	0.163	0.000	0.000	0.091	0.003	0.004
9	0.162	0.003	0.011	0.110	0.010	0.020
11	0.172	0.011	0.033	0.142	0.019	0.040
14	0.202	0.030	0.090	0.186	0.055	0.106
16	0.199	0.035	0.112	0.169	0.069	0.179
18	0.186	0.041	0.137	0.169	0.084	0.196
21	0.187	0.051	0.171	0.171	0.107	0.273
23	0.199	0.067	0.206	0.199	0.145	0.324
27	0.325	0.124	0.374	0.331	0.259	0.606
29	0.395	0.182	0.453	0.392	0.322	0.699
31	0.313	0.179	0.468	0.371	0.276	0.543
34	0.367	0.776	0.517	0.410	0.339	0.720
37	0.336	1.282	0.483	0.372	0.350	0.750
40	0.317	1.431	0.529	0.403	0.544	0.650
43	0.311	1.412			0.647	
48	0.530			0.569	0.621	
51	0.467	1.465	0.770	0.563	0.568	0.981

 Table 16.
 Corrected vapor concentration of Set 2

		•		2,4-DNT	Concentratio	ons (µg/L)			
Day		Column #1			Column #2			Column #3	
	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
4	0.001	0.000	0.000	0.004	0.000	0.000	0.002	0.000	0.000
6	0.003	0.000	0.000	0.013	0.000	0.000	0.009	0.000	0.000
7	0.004	0.000	0.000	0.017	0.000	0.000	0.014	0.000	0.000
9	0.013	0.000	0.000	0.023	0.000	0.000	0.024	0.000	0.000
12	0.023	0.000	0.000	0.032	0.000	0.000	0.037	0.001	0.000
14	0.026	0.000	0.000	0.039	0.000	0.000	0.045	0.001	0.000
15	0.038	0.000	0.000	0.048	0.000	0.000	0.056	0.003	0.000
18	0.037	0.000	0.000	0.050	0.000	0.000	0.064	0.004	0.000
20	0.040	0.001	0.000	0.056	0.002	0.000	0.073	0.006	0.000
22	0.066	0.003	0.000	0.080	0.007	0.000	0.122	0.011	0.000
24	0.078	0.003	0.000	0.093	0.008	0.000	0.131	0.017	0.000
27	0.089	0.008	0.000	0.086	0.014	0.000	0.125	0.020	0.000
29	0.096	0.010	0.000	0.115	0.022	0.000	0.175	0.031	0.005
31	0.100	0.011	0.000	0.109	0.021	0.000	0.167	0.033	0.005
34	0.105	0.012	0.000	0.116	0.034	0.000	0.182	0.039	0.008
36	0.106	0.013	0.000	0.120	0.032	0.003	0.208	0.045	0.006
38	0.107	0.014	0.000	0.114	0.034	0.004	0.207	0.042	0.007
41	0.107	0.014	0.000	0.117	0.036	0.006	0.183	0.045	0.009
43	0.132	0.023	0.000	0.136	0.047	0.005	0.222	0.060	0.016
45	0.150	0.020	0.000	0.174	0.057	0.003	0.243	0.063	0.011
50	0.147	0.019		0.183	0.068	0.004		0.077	0.020
52	0.148	0.018	0.000	0.166	0.080	0.004		0.078	0.018
53	0.128	0.016		0.166	0.071	0.006		0.070	0.017
55	0.133	0.018	0.001	0.176	0.095	0.005	0.288	0.086	0.020
58	0.106	0.015		0.160	0.085	0.004	0.250	0.074	0.019
68	0.082	0.010		0.226	0.122	0.012	0.314	0.106	0.036
70	0.067	0.005	0.000		0.102	0.011	0.353	0.094	0.046
71	0.061	0.005		0.188	0.102	0.011	0.320	0.095	0.033
73	0.055	0.004	0.000	0.214	0.110	0.015	0.332	0.095	0.039
79	0.065	0.004		0.263	0.153	0.022	0.398	0.133	0.054
80	0.062	0.003	0.000	0.291	0.149	0.023	0.416	0.136	0.054

 Table 17.
 Corrected vapor concentration of Set 3

		<u> </u>		2,4-DNT	Concentratio	ns (µg/L)			
Day		Column #1			Column #2			Column #3	
	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	0.009	0.000	0.000	0.028	0.002	0.000	0.036	0.000	0.000
4	0.056	0.002	0.000	0.079	0.002	0.000	0.218	0.002	0.000
6	0.091	0.007	0.000	0.122	0.005	0.000	0.464	0.005	0.000
8	0.136	0.018	0.000	0.142	0.010	0.000	0.482	0.041	0.000
11	0.170	0.054	0.000	0.210	0.025	0.000	0.699	0.096	0.000
13	0.210	0.080	0.006	0.214	0.031	0.002	0.723	0.127	0.002
15	0.224	0.089	0.012	0.230	0.043	0.005	0.854	0.147	0.004
19	0.294	0.139	0.031	0.295	0.078	0.013	0.944	0.196	0.016
22	0.307	0.175	0.046	0.304	0.107	0.023	0.972	0.225	0.025
26	0.346	0.201	0.063	0.331	0.124	0.034	0.954	0.249	0.041
29	0.394	0.238	0.093	0.365	0.169	0.058	0.970	0.327	0.069
33	0.409	0.273	0.132	0.376	0.191	0.081	0.967	0.369	0.094
36	0.409	0.292	0.153	0.389	0.203	0.099	0.937	0.405	0.115
40	0.441	0.317	0.190	0.403	0.232	0.138	0.987	0.466	0.147
43	0.469	0.345	0.225	0.423	0.263	0.170	1.000	0.491	0.182

 Table 18.
 Corrected vapor concentration of Set 4

 Table 19.
 Corrected vapor concentration of Set 5

				2,4-DNT	Concentratio	ons (µg/L)			
Day		Column #1			Column #2			Column #3	
	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3	Port #1	Port #2	Port #3
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4	0.005	0.000	0.000	0.017	0.000	0.000	0.002	0.000	0.000
5	0.011	0.000	0.000	0.036	0.000	0.000	0.003	0.000	0.000
7	0.018	0.000	0.000	0.053	0.000	0.000	0.007	0.000	0.000
8	0.025	0.000	0.000	0.064	0.000	0.000	0.012	0.000	0.000
9	0.029	0.003	0.000	0.079	0.000	0.000	0.018	0.000	0.000
12	0.039	0.006	0.000	0.098	0.000	0.000	0.035	0.000	0.000
13	0.041	0.009	0.000	0.095	0.004	0.000	0.039	0.000	0.000
15	0.049	0.012	0.000	0.115	0.006	0.000	0.056	0.000	0.000
18	0.049	0.015	0.000	0.122	0.007	0.000	0.077	0.004	0.000
20	0.060	0.026	0.000	0.137	0.010	0.000	0.079	0.004	0.000
21	0.058	0.031	0.000	0.134	0.012	0.000	0.108	0.006	0.000
24	0.063	0.036	0.005	0.134	0.016	0.000	0.108	0.005	0.000
27	0.056	0.040	0.007	0.163	0.018	0.000	0.108	0.008	0.000
29	0.090	0.054	0.008	0.190	0.032	0.000	0.135	0.013	0.000
30	0.074	0.057	0.011	0.158	0.030	0.000	0.127	0.014	0.000
33	0.082	0.062	0.013	0.216	0.036	0.000	0.129	0.019	0.000
36	0.089	0.063	0.017	0.227	0.042	0.005	0.147	0.021	0.005
40	0.112	0.094	0.024	0.253	0.061	0.012	0.190	0.034	0.007
42	0.117	0.102	0.028	0.300	0.066	0.013	0.216	0.043	0.006
45	0.113	0.103	0.033	0.311	0.069	0.015	0.195	0.038	0.007
47	0.121	0.113	0.036	0.341	0.085	0.019	0.246	0.058	0.008
49	0.121	0.127	0.045	0.358	0.083	0.022	0.249	0.060	0.008
54	0.138	0.144	0.059	0.422	0.116	0.028	0.269	0.078	0.010
56	0.138	0.150	0.063	0.428	0.114	0.034	0.255	0.086	0.013
61	0.167	0.174	0.082	0.485	0.145	0.052	0.330	0.109	0.018
63	0.181	0.184	0.093	0.549	0.149	0.059	0.328	0.120	0.019

D-2 Iterations made during the modeling of the experimental conditions.

Iteration	Tortuosity	р *	л *	<i>K</i> *	<i>K</i> *	Fraction	Alnha	Unner BC	Lower BC	\mathbf{P}^2	Fitting Ports
1	Vag	5 461	0 606	A <i>d</i>	124 822	0.142	2 662E 02	Mangurad	Mongurad	0.075	1.2
2	1 cs	5,401	0.000	20,739	124,022	0.142	2.002E-02	Maasurad	Maasured	0.973	1,2
2	Vec	5,401	0.000	20,739	0	0.108	2.863E-02	Measured	Measured	0.975	1,2
3	Vec	5,401	0.000	20,897	124 822	1.000	0.000E+00	Measured	Measured	0.831	1,2
4	I es	2,401	0.000	19,903	124,022	0.142	0.000E+00	Measured	Measured	0.075	1,2
5	No	2,702	0.030	20,739	124,022	0.142	2.002E-02	Maggured	Magurad	0.975	1,2
7	No	2,793	0.000	20,739	124,022	0.142	2.002E-02	Niedsuieu	Magurad	0.973	1,2
/ 0	N0 Vor	5,795	0.000	20,739	124,822	0.144	2.392E-02	0	Measured	0.941	1,2
0	Vas	5.461	0.000	20,739	124,022	0.143	2.481E-02	0		0.941	1,2
10	Vec	5.461	0.000	30,739	0	0.142	2.002E-02	Massurad	1.00	0.902	1,2
10	Ves	5 461	0.000	12 739	0	1.000	0.000E+00	Measured	1.01	0.977	1,2
12	Ves	5 461	0.000	30 739	0	0.298	2 760E-02	Measured	1.01	0.900	1,2
13	Ves	5 461	0.000	30,739	124 822	0.298	2.760E-02	Measured	1.01	0.974	1,2
14	Ves	5 461	0.000	30,739	124,022	0.142	2.700E-02	Measured	Measured	0.957	1,2
15	Ves	5 461	0.606	30,739	124,022	0.142	2.568E-02	0	Measured	0.963	1
16	Yes	5 461	0.606	30,739	0	0.140	2.308E-02	0	Measured	0.960	1
17	Yes	5 461	0.606	30,739	0	0.293	4 852E-03	0	0.58	0.984	1
18	Yes	5 461	0.606	30,739	0	0.302	2 666E-02	0	1.01	0.964	1
19	Yes	5 461	0.606	30 739	0	2.41E-04	1 138E-01	0	1.01	0.876	1
20	Yes	5 461	0.606	12,530	0	1 000	0.000E+00	0	0.58	0.951	1
21	Yes	5 461	0.606	30 739	0	1.000	4 430E-02	0	1.01	0.913	1
22	Yes	5.461	0.606	8.460	0	1.000	0.000E+00	0	0.43	0.979	1
23	Yes	5.461	0.606	30,739	0	0.275	0.000E+00	0	0.43	0.979	1
24	Yes	5.461	0.606	30,739	124.822	0.243	0.000E+00	0	0.43	0.979	1
25	Yes	5,461	0.606	30,739	0	0.301	2.668E-02	0	1.01	0.964	1
26	Yes	5.461	0.606	12,739	0	1.000	0.000E+00	0	1.01	0.949	1
27	Yes	5,461	0.606	30,739	0	0.301	2.672E-02	0	1.01	0.964	1
28	Yes	5,461	0.606	10,112	0	1.000	0.000E+00	0	1.45	0.985	2
29	Yes	5,461	0.606	7,925	0	1.000	0.000E+00	0	1.01	0.958	2
30	Yes	5,461	0.606	1	0	0.258	0.000E+00	0	1.01	0.000	2
31	Yes	5,461	0.606	7,931	0	1.000	0.000E+00	0	1.01	0.958	2
32	Yes	5,461	0.606	29,191	0	1.000	0.000E+00	0	1.45	0.805	1
33	Yes	5,461	0.606	21,765	0	1.000	0.000E+00	0	1.00	0.868	1
34	Yes	5,461	0.606	16,621	0	1.000	0.000E+00	0	0.75	0.915	1
35	Yes	5,461	0.606	10,406	0	1.000	0.000E+00	0	0.50	0.967	1
36	Yes	5,461	0.606	7,609	0	1.000	0.000E+00	0	0.40	0.982	1
37	Yes	5,461	0.606	4,905	0	1.000	0.000E+00	0	0.30	0.974	1
38	Yes	5,461	0.606	10,108	0	1.000	0.000E+00	0	1.45	0.985	2
39	Yes	5,461	0.606	7,871	0	1.000	0.000E+00	0	1.00	0.957	2
40	Yes	5,461	0.606	6,343	0	1.000	0.000E+00	0	0.75	0.918	2
41	Yes	5,461	0.606	4,580	0	1.000	0.000E+00	0	0.50	0.839	2
42	Yes	5,461	0.606	3,826	0	1.000	0.000E+00	0	0.40	0.785	2
43	Yes	5,461	0.606	10,108	0	1.000	0.000E+00	0	1.45	0.985	2
44	Yes	5,461	0.606	30,739	0	0.339	7.050E-04	0	0.50	0.970	1
45	Yes	5,461	0.606	30,739	0	0.311	1.130E-02	0	0.75	0.982	1
46	Yes	5,461	0.606	59,627	0	0.139	9.766E-05	0	0.75	0.964	2
47	Yes	5,461	0.606	59,627	0	0.170	1.950E-05	0	1.45	0.985	2

 Table 20.
 Parameters used in HYDRUS for the modeling of the Column 1 (Set 1)

Iteration	Tortuosity	D _{W-M} *	D_{A-M}^{*}	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,461	0.606	28,616	124,822	0.047	1.366E-02	Measured	Measured	0.973	1,2
2	No	524	0.220	28,616	124,822	0.047	1.366E-02	Measured	Measured	0.973	1,2
3	No	3,350	0.000	28,616	124,822	0.047	1.366E-02	Measured	Measured	0.973	1,2
4	Yes	5,461	0.606	28,616	0	0.047	1.366E-02	Measured	Measured	0.909	1,2
5	Yes	5,461	0.606	28,616	0	0.148	1.660E-02	Measured	Measured	0.974	1,2
6	Yes	5,461	0.606	28,616	124,822	0.047	1.366E-02	Measured	Measured	0.973	1,2
7	Yes	5,461	0.606	28,616	124,822	0.047	1.366E-02	0	Measured	0.773	1,2
8	Yes	5,461	0.606	28,616	124,822	0.059	1.260E-02	0	Measured	0.777	1,2
9	Yes	5,461	0.606	28,616	124,822	0.047	1.366E-02	0	1.01	0.677	1,2
10	Yes	5,461	0.606	28,616	124,822	0.302	1.350E-02	Measured	1.01	0.973	1,2
11	Yes	5,461	0.606	28,616	124,822	0.050	1.404E-02	Measured	Measured	0.985	1
12	Yes	5,461	0.606	28,616	124,822	0.056	1.363E-02	0	Measured	0.983	1
13	Yes	5,461	0.606	28,616	0	0.155	1.666E-02	0	Measured	0.987	1
14	Yes	5,461	0.606	28,616	0	0.318	1.040E-02	0	0.95	0.986	1
15	Yes	5,461	0.606	28,616	0	0.242	5.435E-02	0	1.45	0.972	1
16	Yes	5,461	0.606	28,616	0	0.315	1.343E-02	0	1.01	0.988	1
17	Yes	5,461	0.606	28,616	0	0.244	1.330E-07	0	0.58	0.987	1
18	Yes	5,461	0.606	10,000	0	1.000	0.000E+00	0	1.01	0.985	1
19	Yes	5,461	0.606	16,426	0	1.000	0.000E+00	0	1.01	0.953	1
20	Yes	5,461	0.606	6,981	0	1.000	0.000E+00	0	0.58	0.987	1
21	Yes	5,461	0.606	4,069	0	1.000	0.000E+00	0	0.43	0.959	1
22	Yes	5,461	0.606	28,616	0	0.315	1.340E-02	0	1.01	0.988	1
23	Yes	5,461	0.606	28,616	0	0.301	2.960E-08	0	1.01	0.988	1
24	Yes	5,461	0.606	28,616	0	0.098	2.668E-02	0	1.01	0.975	1
25	Yes	5,461	0.606	28,616	0	0.315	0.000E+00	0	1.01	0.987	1
26	Yes	5,461	0.606	28,616	0	0.315	1.342E-02	0	1.01	0.988	1
27	Yes	5,461	0.606	9,878	0	1.000	0.000E+00	0	1.01	0.085	1
28	Yes	5,461	0.606	28,616	0	0.301	1.480E-02	0	1.01	0.123	1
29	Yes	5,461	0.606	4,900	0	1.000	0.000E+00	0	1.01	0.923	2
30	Yes	5,461	0.606	24,948	0	1.000	0.000E+00	0	1.45	0.902	1
31	Yes	5,461	0.606	16,211	0	1.000	0.000E+00	0	1.00	0.955	1
32	Yes	5,461	0.606	10,759	0	1.000	0.000E+00	0	0.75	0.982	1
33	Yes	5,461	0.606	5,319	0	1.000	0.000E+00	0	0.50	0.978	1
34	Yes	5,461	0.606	3,602	0	1.000	0.000E+00	0	0.40	0.946	1
35	Yes	5,461	0.606	7,415	0	1.000	0.000E+00	0	0.60	0.988	1
36	Yes	5,461	0.606	2,689	0	1.000	0.000E+00	0	1.45	0.720	2
37	Yes	5,461	0.606	2,136	0	1.000	0.000E+00	0	1.00	0.623	2
38	Yes	5,461	0.606	1,819	0	1.000	0.000E+00	0	0.75	0.555	2
39	Yes	5,461	0.606	1,487	0	1.000	0.000E+00	0	0.50	0.467	2
40	Yes	5,461	0.606	1,330	0	1.000	0.000E+00	0	0.40	0.432	2
41	Yes	5,461	0.606	2,689	0	1.000	0.000E+00	0	1.45	0.720	2
42	Yes	5,461	0.606	2,136	0	1.000	0.000E+00	0	1.00	0.623	2
43	Yes	5,461	0.606	1,819	0	1.000	0.000E+00	0	0.75	0.555	2
44	Yes	5,461	0.606	1,487	0	1.000	0.000E+00	0	0.50	0.467	2
45	Yes	5,461	0.606	1,330	0	1.000	0.000E+00	0	0.40	0.432	2
46	Yes	5,461	0.606	20,819	0	0.256	3.130E-04	0	0.50	0.977	1
47	Yes	5,461	0.606	20,819	0	0.407	5.880E-03	0	0.75	0.986	1
48	Yes	5,461	0.606	26,436	0	0.169	1.483E-08	0	0.75	0.899	2
49	Yes	5,461	0.606	26,436	0	0.189	4./68E-10	0	1.45	0.927	2

 Table 21. Parameters used in HYDRUS for the modeling of the Column 2 (Set 1)

Iteration	Tortuosity	D _{W-M} *	D_{A-M}^{*}	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,461	0.606	26,967	124,822	6.174E-06	1.483E-03	Measured	Measured	0.921	1,2
2	No	2,890	0.000	26,967	124,822	6.174E-06	1.483E-03	Measured	Measured	0.921	1,2
3	No	2,890	0.000	26,967	124,822	6.174E-06	1.483E-03	Measured	Measured	0.921	1,2
4	Yes	5,461	0.606	1,187	124,822	1.000	0.000E+00	Measured	Measured	0.920	1,2
5	Yes	5,461	0.606	26,967	124,822	6.174E-06	1.483E-03	0	Measured	0.677	1,2
6	Yes	5,461	0.606	26,967	124,822	1.953E-04	1.290E-03	0	Measured	0.754	1,2
7	Yes	5,461	0.606	26,967	124,822	6.174E-06	1.483E-03	0	1.00	0.716	1,2
8	Yes	5,461	0.606	26,967	124,822	4.643E-06	1.370E-03	0	Measured	0.921	1
9	Yes	5,461	0.606	26,967	124,822	2.384E-08	1.820E-09	0	Measured	0.922	1
10	Yes	5,461	0.606	26,967	0	0.212	2.120E-03	0	Measured	0.918	1
11	Yes	5,461	0.606	26,967	0	0.212	2.120E-03	0	0.95	0.902	1
12	Yes	5,461	0.606	26,967	0	0.313	4.880E-03	0	1.45	0.921	1
13	Yes	5,461	0.606	26,967	0	0.273	6.010E-04	0	1.01	0.923	1
14	Yes	5,461	0.606	26,967	0	0.139	1.190E-07	0	0.58	0.877	1
15	Yes	5,461	0.606	7,775	0	1.000	0.000E+00	0	1.01	0.925	1
16	Yes	5,461	0.606	26,967	0	0.288	0.000E+00	0	1.01	0.925	1
17	Yes	5,461	0.606	26,967	0	0.273	6.000E-04	0	1.01	0.923	1
18	Yes	5,461	0.606	26,967	0	0.301	5.880E-08	0	1.01	0.925	1
19	Yes	5,461	0.606	26,967	0	1.104E-04	2.670E-02	0	1.01	0.924	1
20	Yes	5,461	0.606	26,967	0	0.273	0.000E+00	0	1.01	0.924	1
21	Yes	5,461	0.606	26,967	0	0.273	6.005E-04	0	1.01	0.923	1
22	Yes	5,461	0.606	26,967	0	0.261	1.410E-03	Measured	1.01	0.941	1,2
23	Yes	5,461	0.606	7,996	0	1.000	0.000E+00	Measured	1.01	0.941	1,2
24	Yes	5,461	0.606	3,367	0	1.000	0.000E+00	0	1.01	0.865	2
25	Yes	5,461	0.606	11,283	0	1.000	0.000E+00	0	1.45	0.917	1
26	Yes	5,461	0.606	7,686	0	1.000	0.000E+00	0	1.00	0.925	1
27	Yes	5,461	0.606	5,365	0	1.000	0.000E+00	0	0.75	0.912	1
28	Yes	5,461	0.606	3,042	0	1.000	0.000E+00	0	0.50	0.846	1
29	Yes	5,461	0.606	6,784	0	1.000	0.000E+00	0	0.90	0.922	1
30	Yes	5,461	0.606	8,550	0	1.000	0.000E+00	0	1.10	0.925	1
31	Yes	5,461	0.606	9,375	0	1.000	0.000E+00	0	1.20	0.923	1
32	Yes	5,461	0.606	2,529	0	1.000	0.000E+00	0	1.45	0.775	2
33	Yes	5,461	0.606	1,910	0	1.000	0.000E+00	0	1.00	0.669	2
34	Yes	5,461	0.606	1,218	0	1.000	0.000E+00	0	0.50	0.494	2
35	Yes	5,461	0.606	2,185	0	1.000	0.000E+00	0	1.20	0.721	2
36	Yes	5,461	0.606	26,967	0	0.113	9.307E-09	0	0.50	0.846	1
37	Yes	5,461	0.606	26,967	0	0.199	9.766E-05	0	0.75	0.911	1
38	Yes	5,461	0.606	30,154	0	0.130	3.906E-04	0	1.45	0.900	2
39	Yes	5,461	0.606	30,154	0	0.104	3.815E-10	0	0.75	0.846	2

 Table 22.
 Parameters used in HYDRUS for the modeling of the Column 3 (Set 1)

Iteration	Tortuosity	D _{W-M} *	D _{A-M} *	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,889	0.838	24,139	0	1.000	0.000E+00	0	7.19	0.822	1
2	Yes	5,889	0.838	24,139	0	1.000	0.000E+00	0	6.00	0.822	1
3	Yes	5,889	0.838	24,139	0	1.000	0.000E+00	0	4.00	0.822	1
4	Yes	5,889	0.838	18,766	0	1.000	0.000E+00	0	2.00	0.826	1
5	Yes	5,889	0.838	8,392	0	1.000	0.000E+00	0	1.00	0.796	1
6	Yes	5,889	0.838	5,356	0	1.000	0.000E+00	0	0.90	0.767	1
7	Yes	5,889	0.838	4,277	0	1.000	0.000E+00	0	7.19	0.922	2
8	Yes	5,889	0.838	3,881	0	1.000	0.000E+00	0	6.00	0.906	2
9	Yes	5,889	0.838	3,043	0	1.000	0.000E+00	0	4.00	0.855	2
10	Yes	5,889	0.838	1,849	0	1.000	0.000E+00	0	2.00	0.726	2
11	Yes	5,889	0.838	1,104	0	1.000	0.000E+00	0	1.00	0.571	2
12	Yes	5,889	0.838	24,139	0	0.348	1.265E-03	0	1.00	0.792	1
13	Yes	5,889	0.838	24,139	0	0.227	2.740E-02	0	1.50	0.776	1
14	Yes	5,889	0.838	5,701	0	0.750	1.563E-03	0	7.19	0.922	2
15	Yes	5,889	0.838	5,701	0	0.418	1.526E-07	0	1.25	0.782	2

 Table 23. Parameters used in HYDRUS for the modeling of the Column 2 (Set 2)

Table 2-	i, raram	cters us	u III II	DRU		e mouem	ig of the C	Johumn 5			
Iteration	Tortuosity	D _{W-M} *	D _{A-M} *	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	\mathbf{R}^2	Fitting Ports
1	Yes	5,889	0.838	18,618	0	1.000	0.000E+00	0	7.19	0.884	1
2	Yes	5,889	0.838	26,187	0	1.840E-04	8.114E-02	0	7.19	0.952	1
3	Yes	5,889	0.838	16,839	0	1.000	0.000E+00	0	6.00	0.900	1
4	Yes	5,889	0.838	13,104	0	1.000	0.000E+00	0	4.00	0.930	1
5	Yes	5,889	0.838	7,615	0	1.000	0.000E+00	0	2.00	0.948	1
6	Yes	5,889	0.838	3,513	0	1.000	0.000E+00	0	1.00	0.892	1
7	Yes	5,889	0.838	2,905	0	1.000	0.000E+00	0	7.19	0.944	2
8	Yes	5,889	0.838	2,570	0	1.000	0.000E+00	0	6.00	0.924	2
9	Yes	5,889	0.838	1,900	0	1.000	0.000E+00	0	4.00	0.854	2
10	Yes	5,889	0.838	1,130	0	1.000	0.000E+00	0	2.00	0.685	2
11	Yes	5,889	0.838	752	0	1.000	0.000E+00	0	1.00	0.534	2
12	Yes	5,889	0.838	26,187	0	0.134	1.563E-03	0	1.00	0.880	1
13	Yes	5,889	0.838	26,187	0	0.134	3.997E-03	0	1.50	0.839	1
14	Yes	5,889	0.838	16,728	0	0.111	7.813E-09	0	1.25	0.864	2
15	Yes	5,889	0.838	16,728	0	0.172	6.104E-08	0	7.19	0.946	2

 Table 24.
 Parameters used in HYDRUS for the modeling of the Column 3 (Set 2)

Iteration	Tortuosity	D _{W-M} *	\boldsymbol{D}_{A-M}^{*}	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	\mathbf{R}^2	Fitting Ports
1	Yes	5,461	0.606	18,798	0	1.000	0.000E+00	0	1.01	0.932	1,2
2	Yes	5,461	0.606	122,700	0	0.153	0.000E+00	0	1.01	0.932	1,2
3	Yes	5,461	0.606	122,700	0	0.101	3.775E-03	0	1.01	0.978	1,2
4	Yes	5,461	0.606	122,700	0	0.301	3.775E-03	0	1.01	0.809	1,2
5	Yes	5,461	0.606	122,700	0	0.101	0.000E+00	0	1.01	0.971	1,2
6	Yes	5,461	0.606	122,700	0	0.101	3.774E-03	0	1.01	0.976	1
7	Yes	5,461	0.606	18,797	0	1.000	0.000E+00	0	1.01	0.934	1
8	Yes	5,461	0.606	10,778	0	1.000	0.000E+00	0	1.01	0.791	2
9	Yes	5,461	0.606	25,210	0	1.000	0.000E+00	0	1.01	0.254	3
10	Yes	5,461	0.606	12,805	0	1.000	0.000E+00	0	1.01	0.236	3
11	Yes	5,461	0.606	18,801	0	1.000	0.000E+00	0		0.932	1,2
12	Yes	5,461	0.606	122,700	0	0.101	3.775E-03	0	1.01	0.978	1,2
13	Yes	5,461	0.606	122,700	0	0.101	3.775E-03	0	1.01	0.977	1,2
14	Yes	5,461	0.606	10,778	0	1.000	0.000E+00	0	1.01	0.791	2
15	Yes	5,461	0.606	23,145	0	1.000	0.000E+00	0	1.45	0.875	1
16	Yes	5,461	0.606	18,715	0	1.000	0.000E+00	0	1.00	0.914	1
17	Yes	5,461	0.606	15,518	0	1.000	0.000E+00	0	0.75	0.940	1
18	Yes	5,461	0.606	11,435	0	1.000	0.000E+00	0	0.50	0.965	1
19	Yes	5,461	0.606	9,421	0	1.000	0.000E+00	0	0.40	0.970	1
20	Yes	5,461	0.606	7,100	0	1.000	0.000E+00	0	0.30	0.965	1
21	Yes	5,461	0.606	11,962	0	1.000	0.000E+00	0	1.45	0.766	2
22	Yes	5,461	0.606	10,746	0	1.000	0.000E+00	0	1.00	0.792	2
23	Yes	5,461	0.606	9,827	0	1.000	0.000E+00	0	0.75	0.811	2
24	Yes	5,461	0.606	8,568	0	1.000	0.000E+00	0	0.50	0.838	2
25	Yes	5,461	0.606	7,051	0	1.000	0.000E+00	0	0.30	0.868	2
26	Yes	5,461	0.606	26,629	0	1.000	0.000E+00	0	1.45	0.252	3
27	Yes	5,461	0.606	25,183	0	1.000	0.000E+00	0	1.00	0.254	3
28	Yes	5,461	0.606	24,051	0	1.000	0.000E+00	0	0.75	0.254	3
29	Yes	5,461	0.606	22,443	0	1.000	0.000E+00	0	0.50	0.255	3
30	Yes	5,461	0.606	122,700	0	0.093	1.253E-04	0	0.50	0.966	1
31	Yes	5,461	0.606	122,700	0	0.094	2.297E-03	0	0.75	0.974	1
32	Yes	5,461	0.606	884,531	0	0.012	1.459E-04	0	1.45	0.810	2
33	Yes	5,461	0.606	884,531	0	0.010	1.117E-04	0	0.75	0.849	2
34	Yes	5,461	0.606	884,531	0	0.008	3.591E-04	0	1.00	0.927	2
35	Yes	5,461	0.606	74,391	0	0.184	1.333E-03	0	1.45	0.434	3
36	Yes	5,461	0.606	74,391	0	0.174	9.537E-08	0	0.75	0.432	3

Table 25. Parameters used in HYDRUS for the modeling of the Column 1 (Set 3)

Iteration	Tortuosity	D _{W-M} *	D _{A-M} *	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,461	0.606	25,388	0	1.136E-03	1.136E-03	0	1.01	0.955	1
2	Yes	5,461	0.606	25,388	0	1.000	0.000E+00	0	1.01	0.943	1
3	Yes	5,461	0.606	25,388	0	0.004	2.783E-01	0	1.01	0.954	1
4	Yes	5,461	0.606	14,688	0	1.000	0.000E+00	0	1.01	0.947	1
5	Yes	5,461	0.606	9,688	0	1.000	0.000E+00	0	0.43	0.923	2
6	Yes	5,461	0.606	5,804	0	1.000	0.000E+00	0	1.01	0.964	2
7	Yes	5,461	0.606	5,457	0	1.000	0.000E+00	0	1.01	0.899	3
8	Yes	5,461	0.606	13,388	0	1.000	0.000E+00	0	1.01	0.943	1
9	Yes	5,461	0.606	5,586	0	1.000	0.000E+00	0	1.01	0.122	2
10	Yes	5,461	0.606	5,457	0	1.000	0.000E+00	0	1.01	0.899	3
11	Yes	5,461	0.606	25,388	0	1.000	0.000E+00	0	1.45	0.943	1
12	Yes	5,461	0.606	25,388	0	1.000	0.000E+00	0	1.00	0.943	1
13	Yes	5,461	0.606	19,927	0	1.000	0.000E+00	0	0.75	0.950	1
14	Yes	5,461	0.606	12,562	0	1.000	0.000E+00	0	0.50	0.940	1
15	Yes	5,461	0.606	9,276	0	1.000	0.000E+00	0	0.40	0.919	1
16	Yes	5,461	0.606	5,975	0	1.000	0.000E+00	0	1.45	0.727	2
17	Yes	5,461	0.606	4,721	0	1.000	0.000E+00	0	1.00	0.723	2
18	Yes	5,461	0.606	3,827	0	1.000	0.000E+00	0	0.75	0.716	2
19	Yes	5,461	0.606	2,704	0	1.000	0.000E+00	0	0.50	0.700	2
20	Yes	5,461	0.606	5,323	0	1.000	0.000E+00	0	1.20	0.725	2
21	Yes	5,461	0.606	6,076	0	1.000	0.000E+00	0	1.45	0.915	3
22	Yes	5,461	0.606	5,440	0	1.000	0.000E+00	0	1.00	0.899	3
23	Yes	5,461	0.606	4,956	0	1.000	0.000E+00	0	0.75	0.884	3
24	Yes	5,461	0.606	4,287	0	1.000	0.000E+00	0	0.50	0.861	3
25	Yes	5,461	0.606	5,751	0	1.000	0.000E+00	0	1.20	0.907	3
26	Yes	5,461	0.606	20,367	0	0.617	5.377E-07	0	0.50	0.940	1
27	Yes	5,461	0.606	20,367	0	0.428	1.507E-01	0	0.75	0.957	1
28	Yes	5,461	0.606	15,877	0	0.446	4.724E-04	0	1.45	0.958	2
29	Yes	5,461	0.606	15,877	0	0.304	5.472E-06	0	0.75	0.965	2
30	Yes	5,461	0.606	15,877	0	0.363	1.239E-04	0	1.00	0.964	2
31	Yes	5,461	0.606	15,393	0	0.395	2.706E-05	0	1.45	0.915	3
32	Yes	5,461	0.606	15,393	0	0.322	1.953E-04	0	0.75	0.884	3

 Table 26.
 Parameters used in HYDRUS for the modeling of the Column 2 (Set 3)

Iteration	Tortuosity	D _{W-M} *	D _{A-M} *	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	\mathbf{R}^2	Fitting Ports
1	Yes	5,461	0.606	28,562	0	0.163	2.688E-04	0	1.01	0.976	1
2	Yes	5,461	0.606	4,874	0	1.000	0.000E+00	0	1.01	0.977	2
3	Yes	5,461	0.606	3,521	0	1.000	0.000E+00	0	1.01	0.946	2
4	Yes	5,461	0.606	2,692	0	1.000	0.000E+00	0	1.01	0.951	3
5	Yes	5,461	0.606	3,521	0	1.000	0.000E+00	0	1.01	0.946	2
6	Yes	5,461	0.606	4,874	0	1.000	0.000E+00	0	1.01	0.977	1
7	Yes	5,461	0.606	7,009	0	1.000	0.000E+00	0	1.45	0.954	1
8	Yes	5,461	0.606	4,905	0	1.000	0.000E+00	0	1.00	0.980	1
9	Yes	5,461	0.606	3,559	0	1.000	0.000E+00	0	0.75	0.981	1
10	Yes	5,461	0.606	2,075	0	1.000	0.000E+00	0	0.50	0.944	1
11	Yes	5,461	0.606	2,684	0	1.000	0.000E+00	0	0.60	0.966	1
12	Yes	5,461	0.606	3,839	0	1.000	0.000E+00	0	0.80	0.982	1
13	Yes	5,461	0.606	4,383	0	1.000	0.000E+00	0	0.90	0.982	1
14	Yes	5,461	0.606	4,315	0	1.000	0.000E+00	0	1.45	0.924	2
15	Yes	5,461	0.606	3,500	0	1.000	0.000E+00	0	1.00	0.947	2
16	Yes	5,461	0.606	2,916	0	1.000	0.000E+00	0	0.75	0.960	2
17	Yes	5,461	0.606	2,171	0	1.000	0.000E+00	0	0.50	0.968	2
18	Yes	5,461	0.606	1,805	0	1.000	0.000E+00	0	0.40	0.965	2
19	Yes	5,461	0.606	3,106	0	1.000	0.000E+00	0	1.45	0.956	3
20	Yes	5,461	0.606	2,681	0	1.000	0.000E+00	0	1.00	0.950	3
21	Yes	5,461	0.606	2,363	0	1.000	0.000E+00	0	0.75	0.943	3
22	Yes	5,461	0.606	1,934	0	1.000	0.000E+00	0	0.50	0.926	3
23	Yes	5,461	0.606	1,710	0	1.000	0.000E+00	0	0.40	0.913	3
24	Yes	5,461	0.606	16,663	0	0.125	4.883E-05	0	0.50	0.925	1
25	Yes	5,461	0.606	16,663	0	0.206	4.883E-05	0	0.75	0.968	1
26	Yes	5,461	0.606	26,385	0	0.164	2.277E-04	0	1.45	0.926	2
27	Yes	5,461	0.606	26,385	0	0.110	8.059E-05	0	0.75	0.961	2
28	Yes	5,461	0.606	26,385	0	0.102	1.182E-03	0	1.00	0.966	2
29	Yes	5,461	0.606	19,821	0	0.157	5.445E-05	0	1.45	0.955	3
30	Yes	5,461	0.606	19,821	0	0.119	4.883E-05	0	0.75	0.943	3

Table 27. Parameters used in HYDRUS for the modeling of the Column 3 (Set 3)

Iteration	Tortuosity	D _{W-M} *	D _{A-M} *	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,889	0.838	16,745	0	0.119	2.635E-02	0	5.00	0.990	1
2	Yes	5,889	0.838	2,745	0	1.000	0.000E+00	0	5.00	0.974	1
3	Yes	5,889	0.838	23,515	0	0.093	2.289E-02	0	7.19	0.989	1
4	Yes	5,889	0.838	1,690	0	1.000	0.000E+00	0	1.01	0.994	1
5	Yes	5,889	0.838	689	0	1.000	0.000E+00	0	1.01	0.945	2,3
6	Yes	5,889	0.838	2,216	0	1.000	0.000E+00	0	5.00	0.813	2,3
7	Yes	5,889	0.838	9,505	0	0.130	1.153E-02	0	7.19	0.830	2,3
8	Yes	5,889	0.838	23,218	0	0.092	2.342E-02	0	7.19	0.989	1
9	Yes	5,889	0.838	3,218	0	1.000	0.000E+00	0	7.19	0.960	1
10	Yes	5,889	0.838	8,799	0	1.000	0.000E+00	0	6.00	0.791	1
11	Yes	5,889	0.838	6,814	0	1.000	0.000E+00	0	4.00	0.846	1
12	Yes	5,889	0.838	3,848	0	1.000	0.000E+00	0	2.00	0.940	1
13	Yes	5,889	0.838	1,665	0	1.000	0.000E+00	0	1.00	0.994	1
14	Yes	5,889	0.838	1,542	0	1.000	0.000E+00	0	0.95	0.994	1
15	Yes	5,889	0.838	2,669	0	1.000	0.000E+00	0	7.19	0.769	2,3
16	Yes	5,889	0.838	2,441	0	1.000	0.000E+00	0	6.00	0.790	2,3
17	Yes	5,889	0.838	1,953	0	1.000	0.000E+00	0	4.00	0.842	2,3
18	Yes	5,889	0.838	1,232	0	1.000	0.000E+00	0	2.00	0.922	2,3
19	Yes	5,889	0.838	682	0	1.000	0.000E+00	0	1.00	0.944	2,3
20	Yes	5,889	0.838	649	0	1.000	0.000E+00	0	0.95	0.941	2,3
21	Yes	5,889	0.838	2,669	0	1.000	0.000E+00	0	7.19	0.769	2
22	Yes	5,889	0.838	2,441	0	1.000	0.000E+00	0	6.00	0.790	2
23	Yes	5,889	0.838	1,953	0	1.000	0.000E+00	0	4.00	0.842	2
24	Yes	5,889	0.838	1,232	0	1.000	0.000E+00	0	2.00	0.922	2
25	Yes	5,889	0.838	682	0	1.000	0.000E+00	0	1.00	0.944	2
26	Yes	5,889	0.838	649	0	1.000	0.000E+00	0	0.95	0.941	2
27	Yes	5,889	0.838	1,675	0	1.000	0.000E+00	0	7.19	0.988	3
28	Yes	5,889	0.838	1,565	0	1.000	0.000E+00	0	6.00	0.993	3
29	Yes	5,889	0.838	1,324	0	1.000	0.000E+00	0	4.00	0.998	3
30	Yes	5,889	0.838	935	0	1.000	0.000E+00	0	2.00	0.986	3
31	Yes	5,889	0.838	591	0	1.000	0.000E+00	0	1.00	0.930	3
32	Yes	5,889	0.838	1,158	0	1.000	0.000E+00	0	3.00	0.996	3
33	Yes	5,889	0.838	1,456	0	1.000	0.000E+00	0	5.00	0.996	3
34	Yes	5,889	0.838	33,709	0	0.049	1.563E-03	0	1.00	0.988	1
35	Yes	5,889	0.838	33,709	0	0.056	1.456E-03	0	1.50	0.987	1
36	Yes	5,889	0.838	21,695	0	0.053	1.693E-03	0	3.00	0.996	2
37	Yes	5,889	0.838	21,695	0	0.041	1.510E-05	0	1.25	0.998	2
38	Yes	5,889	0.838	21,695	0	0.042	3.566E-04	0	1.50	0.998	2
39	Yes	5,889	0.838	21,695	0	0.047	8.476E-04	0	2.00	0.997	2
40	Yes	5,889	0.838	15,504	0	0.108	1.057E-04	0	7.19	0.989	3
41	Yes	5,889	0.838	15,504	0	0.055	4.883E-09	0	1.25	0.977	3

 Table 28. Parameters used in HYDRUS for the modeling of the Column 1 (Set 4)
Iteration	Tortuosity	D _{W-M} *	\boldsymbol{D}_{A-M}^{*}	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,889	0.838	25,081	42,724	0.099	1.980E-01	0	7.19	0.853	1
2	Yes	5,889	0.838	25,081	0	0.034	4.198E-02	0	7.19	0.947	1
3	Yes	5,889	0.838	25,081	0	1.000	0.000E+00	0	7.19	0.731	1
4	Yes	5,889	0.838	24,358	0	1.000	0.000E+00	0	6.00	0.738	1
5	Yes	5,889	0.838	18,965	0	1.000	0.000E+00	0	4.00	0.794	1
6	Yes	5,889	0.838	10,826	0	1.000	0.000E+00	0	2.00	0.900	1
7	Yes	5,889	0.838	4,696	0	1.000	0.000E+00	0	1.00	0.986	1
8	Yes	5,889	0.838	4,347	0	1.000	0.000E+00	0	0.95	0.989	1
9	Yes	5,889	0.838	2,936	0	1.000	0.000E+00	0	0.75	0.993	1
10	Yes	5,889	0.838	4,425	0	1.000	0.000E+00	0	7.19	0.723	2,3
11	Yes	5,889	0.838	4,102	0	1.000	0.000E+00	0	6.00	0.735	2,3
12	Yes	5,889	0.838	3,393	0	1.000	0.000E+00	0	4.00	0.764	2,3
13	Yes	5,889	0.838	2,271	0	1.000	0.000E+00	0	2.00	0.818	2,3
14	Yes	5,889	0.838	1,351	0	1.000	0.000E+00	0	1.00	0.853	2,3
15	Yes	5,889	0.838	1,293	0	1.000	0.000E+00	0	0.95	0.853	2,3
16	Yes	5,889	0.838	4,466	0	1.000	0.000E+00	0	7.19	0.899	2
17	Yes	5,889	0.838	4,151	0	1.000	0.000E+00	0	6.00	0.913	2
18	Yes	5,889	0.838	3,467	0	1.000	0.000E+00	0	4.00	0.943	2
19	Yes	5,889	0.838	2,387	0	1.000	0.000E+00	0	2.00	0.984	2
20	Yes	5,889	0.838	1,463	0	1.000	0.000E+00	0	1.00	0.994	2
21	Yes	5,889	0.838	1,403	0	1.000	0.000E+00	0	0.95	0.993	2
22	Yes	5,889	0.838	2,114	0	1.000	0.000E+00	0	7.19	0.996	3
23	Yes	5,889	0.838	1,987	0	1.000	0.000E+00	0	6.00	0.997	3
24	Yes	5,889	0.838	1,706	0	1.000	0.000E+00	0	4.00	0.995	3
25	Yes	5,889	0.838	1,248	0	1.000	0.000E+00	0	2.00	0.969	3
26	Yes	5,889	0.838	833	0	1.000	0.000E+00	0	1.00	0.900	3
27	Yes	5,889	0.838	1,860	0	1.000	0.000E+00	0	5.00	0.997	3
28	Yes	5,889	0.838	35,156	0	0.134	6.013E-04	0	1.00	0.988	1
29	Yes	5,889	0.838	35,156	0	0.114	6.264E-03	0	1.50	0.978	1
30	Yes	5,889	0.838	30,113	0	0.071	2.032E-03	0	3.00	0.995	2
31	Yes	5,889	0.838	30,113	0	0.058	1.736E-05	0	1.25	0.996	2
32	Yes	5,889	0.838	30,113	0	0.064	1.043E-03	0	2.00	0.996	2
33	Yes	5,889	0.838	15,206	0	0.139	5.779E-05	0	7.19	0.996	3
34	Yes	5,889	0.838	15,206	0	0.076	7.629E-09	0	1.25	0.953	3

Table 29. Parameters used in HYDRUS for the modeling of the Column 2 (Set 4)

Iteration	Tortuosity	D _{W-M} *	D _{A-M} *	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,889	0.838	20,259	42,724	0.028	1.410E-02	0	7.19	0.960	1
2	Yes	5,889	0.838	20,259	0	0.091	2.083E-02	0	7.19	0.925	1
3	Yes	5,889	0.838	9,545	0	1.000	0.000E+00	0	7.19	0.560	1
4	Yes	5,889	0.838	8,067	0	1.000	0.000E+00	0	6.00	0.605	1
5	Yes	5,889	0.838	5,144	0	1.000	0.000E+00	0	4.00	0.723	1
6	Yes	5,889	0.838	1,704	0	1.000	0.000E+00	0	2.00	0.924	1
7	Yes	5,889	0.838	830	0	1.000	0.000E+00	0	1.45	0.967	1
8	Yes	5,889	0.838	358	0	1.000	0.000E+00	0	1.00	0.966	1
9	Yes	5,889	0.838	4,556	0	1.000	0.000E+00	0	7.19	0.914	2
10	Yes	5,889	0.838	4,153	0	1.000	0.000E+00	0	6.00	0.927	2
11	Yes	5,889	0.838	3,289	0	1.000	0.000E+00	0	4.00	0.954	2
12	Yes	5,889	0.838	1,986	0	1.000	0.000E+00	0	2.00	0.985	2
13	Yes	5,889	0.838	985	0	1.000	0.000E+00	0	1.00	0.962	2
14	Yes	5,889	0.838	928	0	1.000	0.000E+00	0	0.95	0.956	2
15	Yes	5,889	0.838	1,476	0	1.000	0.000E+00	0	1.45	0.985	2
16	Yes	5,889	0.838	3,316	0	1.000	0.000E+00	0	7.19	0.989	3
17	Yes	5,889	0.838	3,119	0	1.000	0.000E+00	0	6.00	0.993	3
18	Yes	5,889	0.838	2,688	0	1.000	0.000E+00	0	4.00	0.997	3
19	Yes	5,889	0.838	1,987	0	1.000	0.000E+00	0	2.00	0.989	3
20	Yes	5,889	0.838	1,350	0	1.000	0.000E+00	0	1.00	0.947	3
21	Yes	5,889	0.838	2,924	0	1.000	0.000E+00	0	5.00	0.995	3
22	Yes	5,889	0.838	2,391	0	1.000	0.000E+00	0	3.00	0.997	3
23	Yes	5,889	0.838	8,727	0	0.041	3.906E-04	0	1.00	0.961	1
24	Yes	5,889	0.838	8,727	0	0.103	1.017E-06	0	1.50	0.965	1
25	Yes	5,889	0.838	8,478	0	0.229	7.285E-03	0	3.00	0.982	2
26	Yes	5,889	0.838	8,478	0	0.149	1.953E-04	0	1.25	0.980	2
27	Yes	5,889	0.838	8,478	0	0.204	2.145E-03	0	2.00	0.985	2
28	Yes	5,889	0.838	12,282	0	0.270	2.203E-04	0	7.19	0.990	3
29	Yes	5,889	0.838	12,282	0	0.152	9.766E-09	0	1.25	0.984	3

 Table 30.
 Parameters used in HYDRUS for the modeling of the Column 3 (Set 4)

Iteration	Tortuosity	D _{W-M} *	D _{A-M} *	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	R ²	Fitting Ports
1	Yes	5,461	0.606	5,146	0	0.005	1.180E+00	0	1.01	0.961	1
2	Yes	5,461	0.606	3,092	0	1.000	0.000E+00	0	1.01	0.911	1
3	Yes	5,461	0.606	1,516	0	1.000	0.000E+00	0	1.01	0.992	2
4	Yes	5,461	0.606	1,193	0	1.000	0.000E+00	0	1.01	0.970	3
5	Yes	5,461	0.606	5,146	0	1.000	0.000E+00	0	1.45	0.956	1
6	Yes	5,461	0.606	5,146	0	1.000	0.000E+00	0	1.00	0.956	1
7	Yes	5,461	0.606	4,901	0	1.000	0.000E+00	0	0.75	0.957	1
8	Yes	5,461	0.606	3,362	0	1.000	0.000E+00	0	0.50	0.956	1
9	Yes	5,461	0.606	2,630	0	1.000	0.000E+00	0	0.40	0.947	1
10	Yes	5,461	0.606	1,821	0	1.000	0.000E+00	0	0.30	0.923	1
11	Yes	5,461	0.606	1,895	0	1.000	0.000E+00	0	1.45	0.991	2
12	Yes	5,461	0.606	1,506	0	1.000	0.000E+00	0	1.00	0.992	2
13	Yes	5,461	0.606	1,231	0	1.000	0.000E+00	0	0.75	0.984	2
14	Yes	5,461	0.606	886	0	1.000	0.000E+00	0	0.50	0.959	2
15	Yes	5,461	0.606	1,693	0	1.000	0.000E+00	0	1.20	0.993	2
16	Yes	5,461	0.606	1,778	0	1.000	0.000E+00	0	1.30	0.992	2
17	Yes	5,461	0.606	1,380	0	1.000	0.000E+00	0	1.45	0.983	3
18	Yes	5,461	0.606	1,188	0	1.000	0.000E+00	0	1.00	0.970	3
19	Yes	5,461	0.606	1,030	0	1.000	0.000E+00	0	0.75	0.954	3
20	Yes	5,461	0.606	820	0	1.000	0.000E+00	0	0.50	0.925	3
21	Yes	5,461	0.606	1,291	0	1.000	0.000E+00	0	1.20	0.977	3
22	Yes	5,461	0.606	1,337	0	1.000	0.000E+00	0	1.30	0.980	3
23	Yes	5,461	0.606	4,516	0	0.744	2.611E-03	0	0.50	0.955	1
24	Yes	5,461	0.606	4,516	0	0.744	2.621E-03	0	0.75	0.955	1
25	Yes	5,461	0.606	3,947	0	0.480	5.574E-04	0	1.45	0.992	2
26	Yes	5,461	0.606	3,947	0	0.312	1.350E-07	0	0.75	0.984	2
27	Yes	5,461	0.606	3,947	0	0.382	2.577E-05	0	1.00	0.992	2
28	Yes	5,461	0.606	3,120	0	0.449	1.261E-07	0	1.45	0.984	3
29	Yes	5,461	0.606	3,120	0	0.370	2.384E-08	0	0.75	0.966	3

 Table 31. Parameters used in HYDRUS for the modeling of the Column 1 (Set 5)

Iteration	Tortuosity	D _{W-M} *	D_{4-M}^{*}	K_d^*	<i>K</i> _{<i>H</i>} [*]	Fraction	Alpha	Upper BC	Lower BC	\mathbf{R}^2	Fitting Ports
1	Yes	5,461	0.606	5,270	0	1.000	0.000E+00	0	1.01	0.830	1
2	Yes	5,461	0.606	3,599	0	1.000	0.000E+00	0	1.01	0.984	2
3	Yes	5,461	0.606	2,369	0	1.000	0.000E+00	0	1.01	0.950	3
4	Yes	5,461	0.606	5,270	0	1.000	0.000E+00	0	1.45	0.830	1
5	Yes	5,461	0.606	5,270	0	1.000	0.000E+00	0	1.00	0.830	1
6	Yes	5,461	0.606	5,270	0	1.000	0.000E+00	0	0.75	0.830	1
7	Yes	5,461	0.606	3,178	0	1.000	0.000E+00	0	0.50	0.773	1
8	Yes	5,461	0.606	2,049	0	1.000	0.000E+00	0	0.40	0.733	1
9	Yes	5,461	0.606	4,361	0	1.000	0.000E+00	0	1.45	0.992	2
10	Yes	5,461	0.606	3,578	0	1.000	0.000E+00	0	1.00	0.983	2
11	Yes	5,461	0.606	3,014	0	1.000	0.000E+00	0	0.75	0.971	2
12	Yes	5,461	0.606	2,290	0	1.000	0.000E+00	0	0.50	0.945	2
13	Yes	5,461	0.606	1,932	0	1.000	0.000E+00	0	0.40	0.927	2
14	Yes	5,461	0.606	2,723	0	1.000	0.000E+00	0	1.45	0.961	3
15	Yes	5,461	0.606	2,360	0	1.000	0.000E+00	0	1.00	0.950	3
16	Yes	5,461	0.606	2,085	0	1.000	0.000E+00	0	0.75	0.940	3
17	Yes	5,461	0.606	1,704	0	1.000	0.000E+00	0	0.50	0.922	3
18	Yes	5,461	0.606	1,496	0	1.000	0.000E+00	0	0.40	0.910	3
19	Yes	5,461	0.606	3,919	0	0.811	6.104E-07	0	0.50	0.769	1
20	Yes	5,461	0.606	3,919	0	0.838	4.883E-07	0	0.75	0.863	1
21	Yes	5,461	0.606	4,868	0	0.896	2.246E-04	0	1.45	0.992	2
22	Yes	5,461	0.606	4,868	0	0.619	3.125E-07	0	0.75	0.971	2
23	Yes	5,461	0.606	4,868	0	0.735	3.815E-07	0	1.00	0.983	2
24	Yes	5,461	0.606	2,857	0	0.988	3.052E-06	0	1.45	0.964	3
25	Yes	5,461	0.606	2,857	0	0.799	6.250E-04	0	0.75	0.947	3

 Table 32.
 Parameters used in HYDRUS for the modeling of the Column 2 (Set 5)

Table 33.	Parameters used in	HYDRUS for the	modeling	g of the Column 3 ([Set 5])
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Iteration	Tortuosity	D _{W-M} *	D_{A-M}^{*}	K_d^*	K_{H}^{*}	Fraction	Alpha	Upper BC	Lower BC	\mathbf{R}^2	Fitting Ports
1	Yes	5,461	0.606	30,511	0	0.328	5.000E-07	0	1.01	0.973	1
2	Yes	5,461	0.606	10,017	0	1.000	0.000E+00	0	1.01	0.973	1
3	Yes	5,461	0.606	6,357	0	1.000	0.000E+00	0	1.01	0.971	2
4	Yes	5,461	0.606	5,715	0	1.000	0.000E+00	0	1.01	0.967	3
5	Yes	5,461	0.606	13,617	0	1.000	0.000E+00	0	1.45	0.972	1
6	Yes	5,461	0.606	9,926	0	1.000	0.000E+00	0	1.00	0.973	1
7	Yes	5,461	0.606	7,452	0	1.000	0.000E+00	0	0.75	0.961	1
8	Yes	5,461	0.606	4,602	0	1.000	0.000E+00	0	0.50	0.923	1
9	Yes	5,461	0.606	5,788	0	1.000	0.000E+00	0	0.60	0.944	1
10	Yes	5,461	0.606	7,976	0	1.000	0.000E+00	0	0.80	0.965	1
11	Yes	5,461	0.606	7,509	0	1.000	0.000E+00	0	1.45	0.983	2
12	Yes	5,461	0.606	6,326	0	1.000	0.000E+00	0	1.00	0.971	2
13	Yes	5,461	0.606	5,462	0	1.000	0.000E+00	0	0.75	0.957	2
14	Yes	5,461	0.606	4,331	0	1.000	0.000E+00	0	0.50	0.933	2
15	Yes	5,461	0.606	6,340	0	1.000	0.000E+00	0	1.45	0.973	3
16	Yes	5,461	0.606	5,698	0	1.000	0.000E+00	0	1.00	0.967	3
17	Yes	5,461	0.606	5,211	0	1.000	0.000E+00	0	0.75	0.961	3
18	Yes	5,461	0.606	4,540	0	1.000	0.000E+00	0	0.50	0.951	3
19	Yes	5,461	0.606	12,424	0	0.370	1.689E-08	0	0.50	0.923	1
20	Yes	5,461	0.606	12,424	0	0.600	1.577E-07	0	0.75	0.961	1
21	Yes	5,461	0.606	28,186	0	0.266	1.192E-08	0	1.45	0.983	2
22	Yes	5,461	0.606	28,186	0	0.194	5.033E-08	0	0.75	0.957	2
23	Yes	5,461	0.606	28,186	0	0.224	7.813E-04	0	1.00	0.968	2
24	Yes	5,461	0.606	44,250	0	0.143	1.563E-03	0	1.45	0.969	3
25	Yes	5,461	0.606	44,250	0	0.098	1.394E-03	0	0.75	0.929	3



D-3 Final HYDRUS modeling results compared with the measured data.

Time (days)

0.05





































































