

EFFECTS OF ENVIRONMENTAL PARAMETERS ON THE CHEMICAL SIGNATURE OF LANDMINES

by

Vivian Maria Florián Algarín

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Approved by:

Julio G. Briano, Ph.D
President, Graduate Committee

Date

Samuel Hernández, PhD
Member, Graduate Committee

Date

Jaime Benítez, PhD
Member, Graduate Committee

Date

Nelson Cardona, PhD
Chairperson of the Department

Date

Nairmen Mina, PhD
Representative of Graduate Studies

Date

ABSTRACT

The presence of buried landmines is an environmental problem in many parts of the world; strategies to detect and remove landmines are being developed; one of these strategies is the developing of chemical based sensors. Even when most landmines cases are made from plastic, small amounts of explosive may diffuse through the case (or through cracks), enter the soil and migrate to the surface. The spatial and temporal concentration distribution of chemicals released from a landmine at the soil surface is influenced by: the type of soil, environmental factors, water and gaseous phase mobility, molecular and mechanical diffusion, adsorption characteristics, water content, and compaction. In this work we measure the concentration of chemicals at the surface at different ambient conditions. Experiments are carried out using a series of soil tanks with controlled conditions such as: temperature, moisture content, relative humidity and radiation (UV and Visible). Gas Chromatography (GC- μ ECD) with Solid Phase Micro-extraction (SPME) and direct injection were used for the analysis of explosives. The results of the experiments will be used to provide validation for the simulation model describing the spectroscopic signature and its transport through soil. We have obtained the trends on the effect of the ambient conditions on the chemical signature. Of particular interest is the presence of several degradation compounds as time evolves.

Keywords: Landmine Detection, Environmental, Transport, Chemical Sensor.

RESUMEN

La presencia de minas de tierra es uno de los problemas ambientales en muchas partes del mundo, estrategias para detectar y remover minas están siendo estudiadas; una de estas estrategias es el desarrollo de sensores basados en la señal química. Aun cuando la mayoría de las minas tiene cubierta plástica, pequeñas cantidades de explosivos pueden difundir a través de la cubierta (o a través de grietas), entrar en contacto con el suelo y migrar hacia la superficie. La distribución de concentración espacial y temporal de los químicos emitidos desde la mina a la superficie del suelo es influenciada por el tipo de suelo, factores ambientales, movilidad de la fase acuosa y gaseosa, difusión molecular y mecánica, características de adsorción, contenido de agua y compactación. En este trabajo nosotros medimos la concentración de químicos en la superficie para diferentes condiciones ambientales. Los experimentos fueron llevados a cabo usando una serie de tanques de suelo con condiciones controladas tales como: Temperatura, contenido de humedad, humedad relativa y radiación (UV y Visible). Cromatografía de gases (CG- μ ECD) con micro extracción en fase sólida (SPME) e inyección directa son usadas para el análisis de los explosivos. Los resultados de los experimentos fueron usados para proveer validación a los modelos de simulación que describen la señal química y el transporte en el suelo. Hemos obtenido la tendencia de la señal química con los efectos de las condiciones ambientales. Es de particular interés la presencia de muchos compuestos de degradación a medida que el tiempo transcurre.

Palabras Claves: Detección de minas, Ambiente, Transporte, Sensor Químico.

To God, the best of my life,

To my parents, my love and my triumph,

To all those who contributed to the accomplishment of my dreams,

My eternal gratitude.

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1 INTRODUCTION

The detection and removal of antipersonnel and antitank landmines is a great challenge and a worldwide environmental and humanitarian problem. The United Nations estimates that 120 million mines are buried in 70 countries and the rate of installation of new mines far exceeds the rate of removal of old ones. Numerous detection strategies are being developed, including infrared, electrical conductivity, ground-penetrating radar, and chemical sensors. The introduction of land mines using manufactured from plastic and few or no metal parts, has made detecting buried mines using electromagnetic induction (metal detection) very time consuming. Other techniques, such as ground penetrating radar, can sometimes detect buried mines, but discriminating between mines and other buried objects is difficult resulting in false positive rates that are unacceptable for countermining operations, particularly for anti-personnel land mines¹.

The most common charge explosive used is TNT, it has been estimated that in excess of 80% of landmines emplaced worldwide contain some fraction of TNT as their main explosive charge². Other important components of the landmines are 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (TNB), geometric isomers of DNT and DNB, and 2,4,6-trinitrotoluene (2,4,6-TNT).

The present work has been developed as part of the DoD-MURI Program, for the establishment of a Center for Chemical Sensors Development at the University of Puerto Rico – Mayagüez Campus. The final objective of the program is aimed to construct a sensor able to detect traces of explosives from conventional landmines. The detector will be tuned to explosive molecules transported by advection and diffusion to the soil surface from a buried landmine. To achieve this objective, the program considered the formation and establishment of a multidisciplinary team, able to contribute in the research of the fundamental aspects of the sensors applied to the detection of chemical signatures from landmines, some of the analytical methods being studied in our group for detection of explosives and degradation products are (GC), mass spectrometry (MS), high performance liquid chromatography (HPLC), and gas chromatography (GC) with mass spectrometry (GC/MS), this experiments are being accompany with numerical simulation.

This work presents the experiments carried out for about one year for the detection of the chemical signature of explosives buried in soils and its degradation products. These experiments are being implemented using a series of soil tanks with controlled environmental conditions such as: temperature, soil moisture content, relative humidity and radiation (UV and Visible). Gas Chromatography (GC- μ ECD) was used for the analysis of explosives. Finally, the data will be used to provide validation of parametric models that describe the chemical signature and its transport in soil.

1.1 Motivation

Of all the buried landmine identification technologies currently available, sensing the chemical signature from the explosive components released from landmines is the only technique that can discriminate non-explosive objects from the real threat³. The development of chemical sensors must be accompanied for a fundamental understanding of the variables affecting the fate and transport of the chemicals released from a landmine. The chemical signature is affected by multiple environmental phenomena that can enhance or reduce its presence at the soil surface and can affect the distribution of the chemical signature in the environment. The explosives can be present in the vapor, aqueous, and solid phases, the distribution of the chemical among in each phase is important in the designing of appropriate detectors.

The goal for this work is to determine the effect of environmental parameters like temperature, water content, relative humidity and light radiation on the fate and transport of the signature compounds.

1.2 Literature Review

The group at Sandia National Laboratories lead by Professor Phelan has reported several works in the area. In 2000, Phelan et al,⁴ collected data on TNT concentration at the surface and head space in a soil column for comparison to simulation results. A point source of 2, 4-Dinitrotoluene (DNT) in water was injected continuously at a specified

depth at the center of the column, and samples were collected daily from the headspace of the plenum by solid phase micro-extraction (SPME). At the end of the experiment (29 days), the soil column was dismantled and soil samples were used to measure water content and DNT concentration. Figure 1 displays a comparison of experimental and computational data on DNT flux in pg/min.

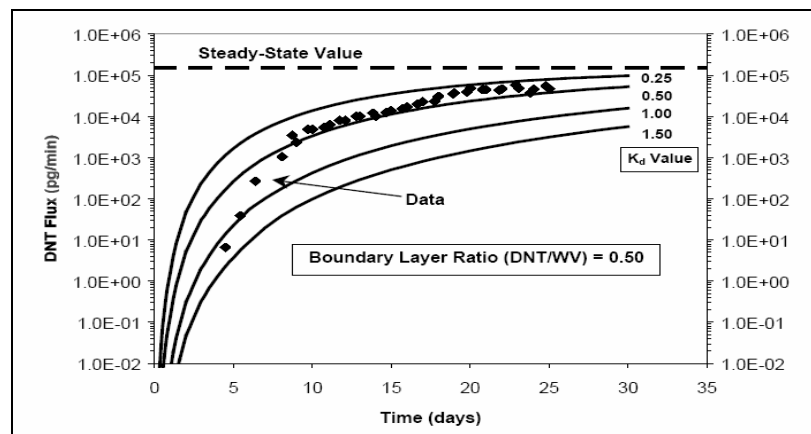


Figure 1. DNT Flux

Figure 2 shows that the maximum concentration was found at the center of the tank, coinciding with the location of the source.

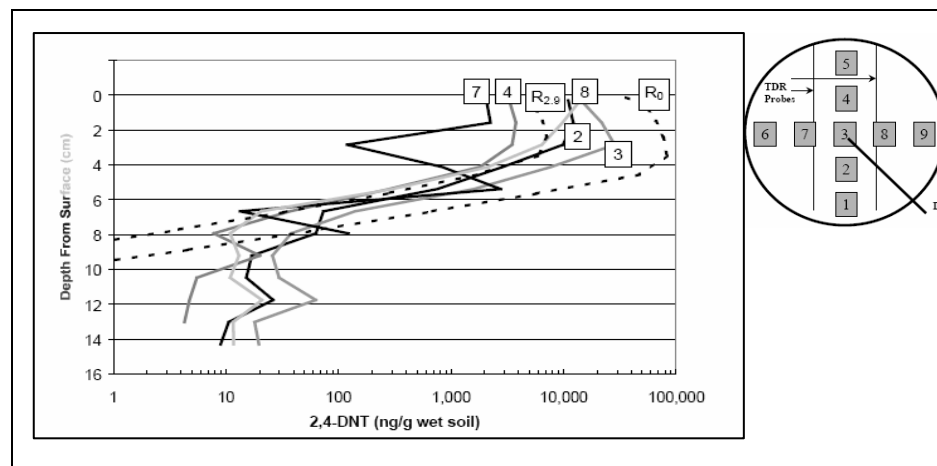


Figure 2. Sub-surface DNT concentration profiles

Phelan et al⁵, 2001 developed a code named T2TNT to simulate buried landmine chemical transport and for comparison to the experimental data. DNT was injected to 3.5 cm in a column soil and after 86 days soil samples were taken at different points and depths. The experimental data showed that centerline soil residues (point 3) were generally higher than adjacent points.

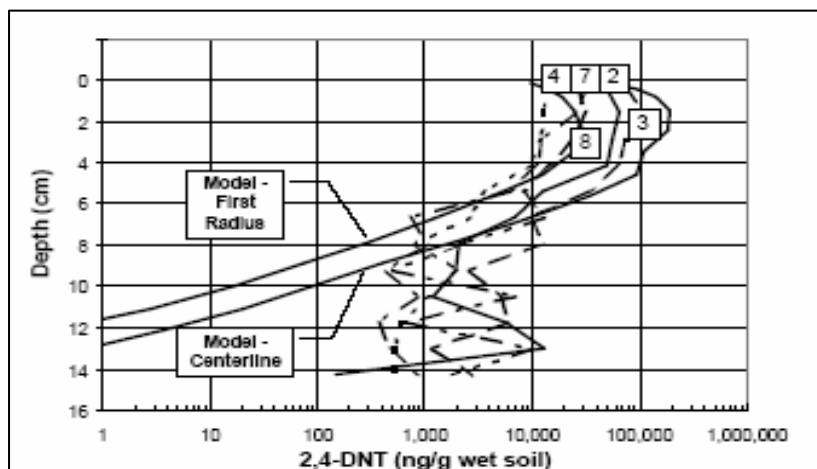


Figure 3. Soil profile DNT after 86 days

A relevant work conducted currently in our research group was: ***Transport of explosives: TNT in soil and its equilibrium vapor***⁶. Small scale experiments with mixtures of TNT-Ottawa sand were used to study the effects of aging, temperature and moisture, the experiments were realized in both head space and immersion mode. A GC- μ ECD was used for analysis of TNT in sand. In the headspace experiments it was possible to detect appreciable amounts of TNT vapor as early as 1 hour after preparation of the samples, at room temperature. The strongest signal was found for 2,4-DNT, as shown in figure 4. After 12 hours the mass of 2, 4-DNT was approximately three time

that of the first detection. The concentration of DNT increases several orders of magnitude in 24 hours as a consequence of its relatively high vapor pressure.

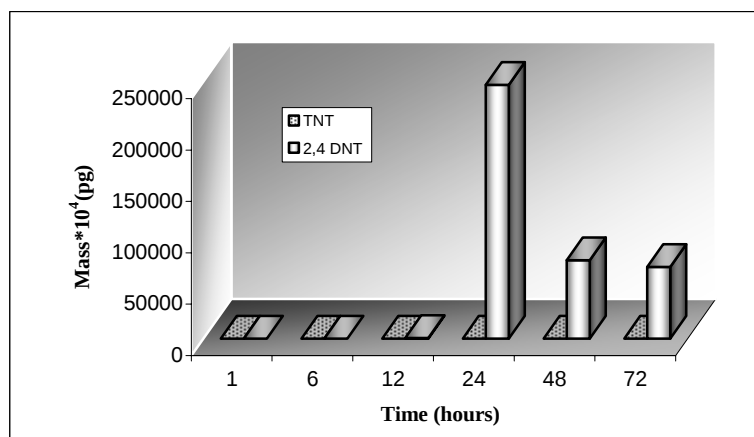


Figure 4. TNT and DNT vapor from TNT buried in sand vs. time

In the immersion experiments, (sample consisting of few milligrams of contaminated sand) I-SPME technique allowed for the detection of concentrations as low as 0.010 mg of explosive per kilogram of soil. The results obtained (at room temperature) by using I-SPME demonstrated an increase in the amount of TNT (see figure 5). The detection of 2,4-DNT was very low compared to TNT.

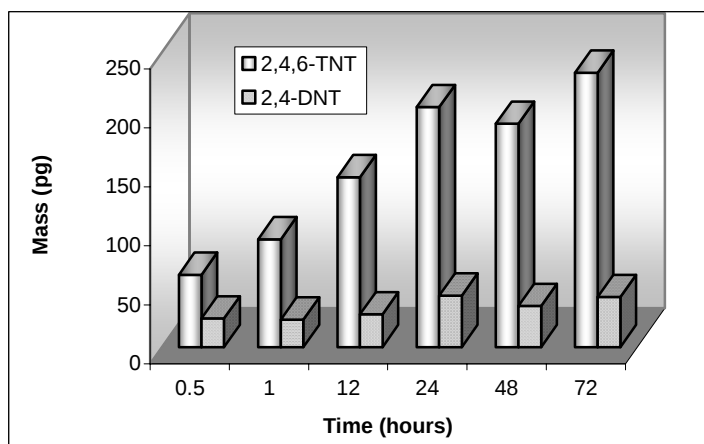


Figure 5. Extraction efficiencies of TNT and DNT by SPME vs. Time

2. THEORETICAL BACKGROUND

1.3 Chemical signature of landmine

1.3.1 *Composition of landmines*

A landmine is a type of self-contained explosive device which is placed onto or into the ground, exploding when triggered by the pressure exerted by a vehicle or person.⁷ Two types of landmines are showed in figure 6, the PMA-2 is a small, circular, plastic caged, designed to wound or kill by blast effect, the PMA-2 contains 70g of TNT and Tetryl booster pellet and the TMA-5 is a square with plastic bodied designed to damage or destroy vehicles by blast effect, this have a total charge explosive of 5.55kg.⁸



Figure 6. Landmines: PMA2 and TMA5

TNT (2, 4, 6-Trinitrotoluene) represents the main charge explosive in the majority of landmines in the world, the mass of TNT contained in these mines ranges from as little as 7 grams in an antipersonnel mine to as much as 13 kilograms in an anti tank mine.⁹ Table 1 shows the composition for the principal types of landmine.

Table 1. Specification of some landmines (Jenkins, 2000)¹

Type	Main charge	Booster	Size (L × W × H) (mm)
TMA-5	TNT (5.5 kg)	RDX (200 g)	(312 × 275 × 113)
TMM-1	TNT (5.6 kg)	None	(326 diam. × 90)
PMA-1A	TNT (200 g)	None	(140 × 68 × 31)
PMA-2	TNT (100 g)	Hexogen*(14.5 g)	(68 diam. × 30)
Type 72	TNT/RDX (5.4 kg)	PETN	(270 diam. × 100)
VS2.2	TNT/RDX (1.93 kg)	None	(240 diam. × 117.6)
TS50	TNT/RDX (50 g)	None	(90 diam. × 45)
VS50	RDX (43 g)	None	(90 diam. × 45)

2, 4, 6-Trinitrotoluene is a nitroaromatic compound, which has a pale yellow color when in crystalline form. TNT is manufactured by nitration of toluene with a nitric acid solution. It has a number of advantages which have made it widely used in military explosives before World War I and up to the present time. These include low manufacturing costs and cheap raw materials, safety of handling, a low sensitivity to impact and friction, and a fairly high explosive power.⁹ The structural formula for TNT is presented in Figure 7.

Table 2. Characteristics of TNT (Gibbs, 1980)⁹

Characteristics	TNT
Molecular weight	227.1
Melting temperature/°C	80.8
Thermal ignition temperature/°C	300
Energy of formation/KjKg ⁻¹	-184.8
Enthalpy of formation/KjKg ⁻¹	-261.5
Crystal density at 20°C/gcm ⁻³	1.654

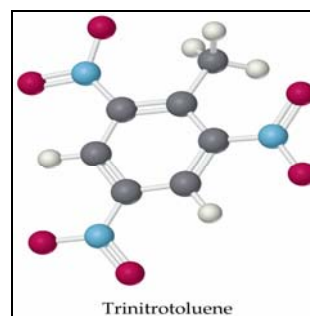


Figure 7. Trinitrotoluene

The synthesis process favors the production of 2, 4, 6-trinitrotoluene, but other isomers (chemicals with same molecular formula, but with different structures) can be formed in smaller quantities and they may remain in the TNT as contaminants at up to several percent by mass. Some of these explosive-related compounds are significant contributors to the chemical fingerprint.⁹ Table 3 shows the impurities present before and after purification of TNT with anhydrous sodium sulfite.

Table 3. Impurities present in TNT (Phelan, 2002)¹⁰

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

1.3.2 Chemical Emission of Landmines

The overall emission rate from a landmine depends on the specific type of construction and material. Chemicals from the explosive charge within the landmine are released into the surrounding soil by diffusion through the mine or by leakage through cracks, seams, and holes in the mine. Examples of landmines with plastic and metal cases are showed in figure 8.



Figure 8. Examples of landmines PMA 2 and PMA 1¹⁰

Chemical compounds escaping from a mine are quickly adsorbed on the soil or dissolve in soil water. For a typical soil, approximately 95% of the total mass of the explosive is adsorbed onto soil, followed by approximately 5% into soil water, with a trace (approximately 1×10^{-6} %) partitioning into the vapor phase.¹⁰ Diffusion and convection are the main mechanisms contributing to the chemical transport in soils. Migration or flow of water underground is responsible for the transport of solutes to the surface.

1.3.3 Chemical degradation in soils

Degradation of explosive residues in soils is a very complex phenomenon occurring through combined natural biological and abiotic processes. Both biological and abiotic chemical reactions produce similar degradation by-products due to the nature of the oxidation and reduction reactions.¹⁰

It has been suggested (Gibbs, 1980)⁹ that the reduction of nitro groups to amino groups proceeds through the nitroso and hydroxylamino compounds according to the following mechanisms:

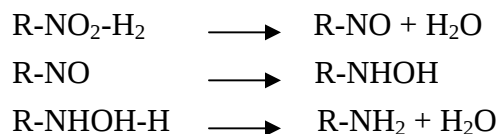


Figure 9, shows the schema of degradation of TNT

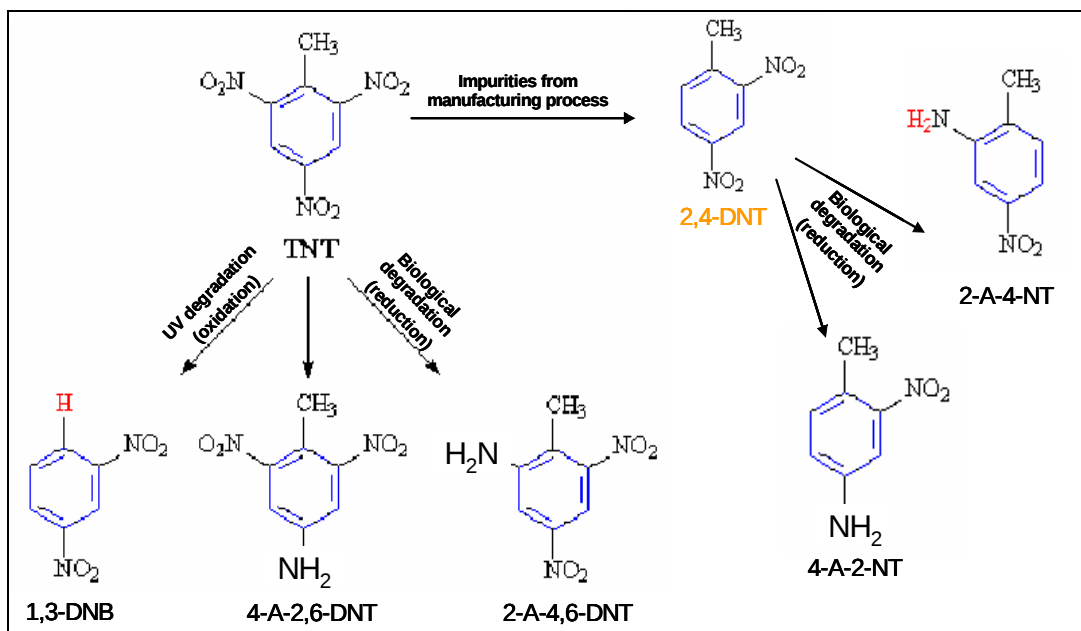


Figure 9. Degradation Mechanism of TNT

Table 4 indicates the principal degradation by-products for TNT, DNT and DNB.

Table 4. Parent and degradation by-products of TNT, DNT and DNB (Phelan, 2002)¹⁰

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

Exposure of TNT, both as a solid and in solution, to strong sunlight or ultra-violet radiation, results in the formation of decomposition products, as a result of photodecomposition, aqueous solutions of TNT first turn pink, then change into a rusty-orange colored solution. It was reported (Gibbs, 1980)⁹ that after light decomposition of solid TNT the by-products were 1,3,5-trinitrobenzene (TNB), 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehyde, and 2,4,6-trinitrobenzonitrile. The compounds found after irradiation of an aqueous solution of TNT with UV light included: 1, 3, 5-trinitrobenzene, 4, 6-dinitroisoanthranil, and 3, 5-dinitrophenol among others.⁹

2.14 Environmental parameters affecting the chemical signature

The effect of environmental variables on the chemical signature of landmines at the soil surface is dynamic and complex. The chemical signature is affected by multiple environmental conditions that can enhance or reduce its presence and transport behavior. A fundamental understanding of the variables affecting the detection of the chemical signature of TNT and their degradation products, is needed to minimize the presence of a false negative, when using a chemical-based-sensor and to ensure a good level of detection.¹¹

The fate and transport of chemicals emanating from buried landmines is strongly influenced by physical-chemical properties of the soil and by environmental conditions. The environmental conditions affecting the transport, and therefore the spectroscopic signature are: pressure, soil characteristics, solar radiation (UV and visible), relative humidity,

temperature, precipitation (rainfall), and vegetation. In addition, soil parameters like porosity, compaction, etc; also affect the fate and transport of the chemicals.

Figure 10 pictures all the variables affecting the fate and transport of chemicals released from a buried unexploded object (i.e. landmine).

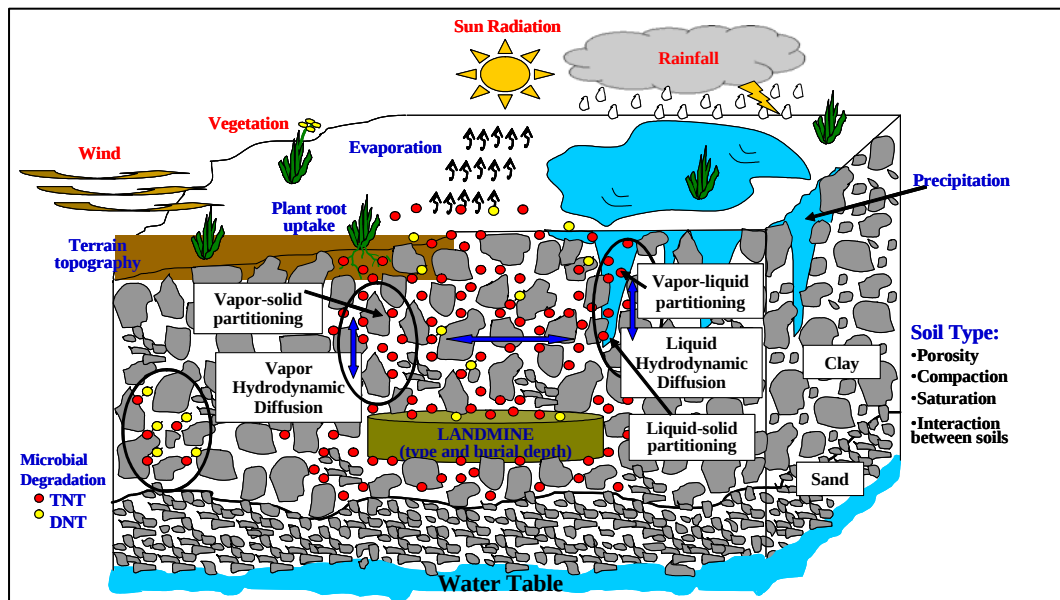


Figure 10. Parameters affecting the fate and transport of chemicals from landmines

3. EXPERIMENTAL SECTION

3.1 Chemicals

Explosives in solid form and in solution were used in this work. The solid explosives were seeded into the reaction tanks to study the changes in the spectroscopic signature, and the solutions were used to construct the calibration curves. The explosives in solution were: 2,4,6 TNT, 2,4-DNT and a mix (called Mix A) containing: 2-amino-diinitrotoluene (2-ADNT); 4-amino-2,6-dinitrotoluene (4-ADNT); 1,3-dinitrobenzene (1,3-DNB); 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); 1,3,5-trinitro-1,3,5-triazine (RDX); 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX); tetryl; 1,3,5-trinitrobenzene (TNB); and 2,4,6-trinitrotoluene (TNT); each at a concentration of 1 mg/ml. The solvent used was acetonitrile HPLC (High Purity Liquid Chromatography) grade and Water HPLC grade obtained from Fisher Scientific and Aldrich Chemical Co respectively.

3.2 Materials

3.2.1 *Materials for extraction*

Amber vials, magnetic stirrings bars, 0.45um filters, syringes and needles were purchased from Fisher Scientific. Materials for SPME analysis such as SPME fiber (Polidimethyl siloxene/ Divinilbenzene) and holders were acquired from SUPELCO Co.

3.2.2 Environmental Chamber

The building of the environmental chamber required of several equipment and materials such as: visible and ultra violet lighting (*Spectrolite*), temperature controllers, standard probes penetration, thermometer 24 channels with probes, data logger kit and heating tape, radiometer, moisture meter and water control reflectometer acquired from Campbell Scientific Company. The tanks were designed in our group and constructed by Mr. Efrain Gregory a technician from the Chemistry Engineering Department.

3.3 Equipment: Gas Chromatography with μ -ECD

The analyses were carried out using an Agilent Technologies, Inc. Palo Alto, CA model 6890N, Network GC system equipped with a micro cell, ^{63}Ni Electron Capture Detector (μ -ECD) (Figure 11). A capillary column was used for separation, RTX-5 (cross bonded 5% diphenil-95% dimethyl polysiloxane) 15 m x 0.25 mm ID x 0.25 μm df, acquired from Restek Corporation.



Figure 11. Gas Chromatograph

3.4 Methodology

The work schedule is presented in figure 12, the initial steps consisting on literature review and experimental design. The last stage includes a numerical simulation of the transport problem and its comparison to experiments.

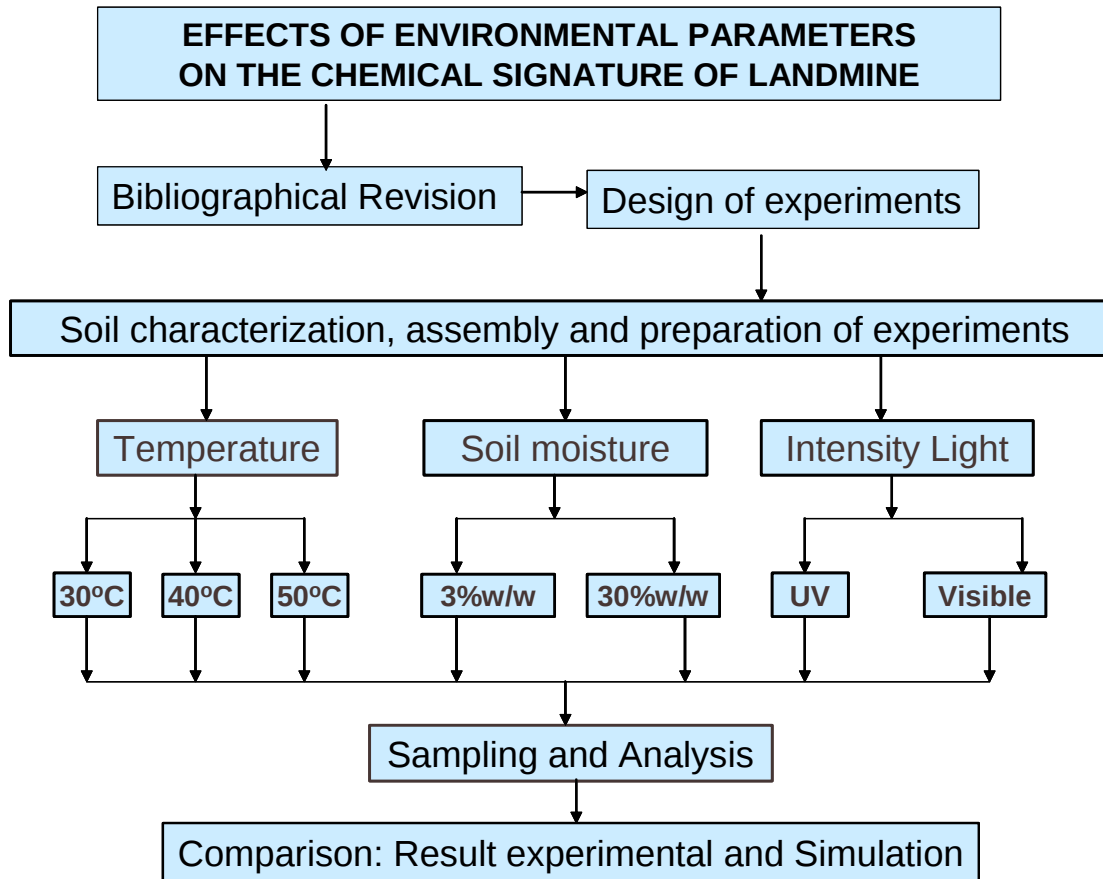


Figure 12. Task Schedule

3.4.1 Soil Properties

The soil employed for these experiments was taken from Jobos beach in west of Puerto Rico and belong to Cataño soil series that consists of deep, excessively drained, nearly sea level soils that are calcareous and rapidly permeable. The dominant texture for this type of soil is sand. The soil was sieved to retain the less than 1-mm in diameter fraction, and mixed for homogeneity. Soil analysis showed that the soil was a sandy-loam with low organic carbon, a moderate electrical conductivity, and a substantial specific surface area (Table 5). The organic matter analysis, measurements of electrical conductivity, particle size distribution, and mineralogical analysis were carried out at the Department of Agriculture Science at UPRM. The particle size distribution, which measures the texture of soil, is presented in table 6.

Table 5. Soil Properties

Soil Property	Value
Classification	Sand
Organic Matter	2.1%
Electrical Conductivity	325($\mu\text{mhos.cm}^{-1}$)
pH	8.64
Density (g/cm^3)	2.5587

Table 6. Percentage passing sieve

# Mesh	4 (4.75mm)	10 (2.0mm)	20 (0.85mm)	140 (0.106 mm)
% Sand	100	100	95.4	4.62

The microscopic characterization of the sand was performed using a Scanning Electron Microscope (JSM-6460LV), with the elemental analysis by Energy Dispersive X-ray fluorescence microscopy (EDAX). Figure 13 shows the elemental composition and the intensity for each element. X-ray diffraction was employed for the mineralogical characterization of the sand main minerals; the results are shown in table 7.

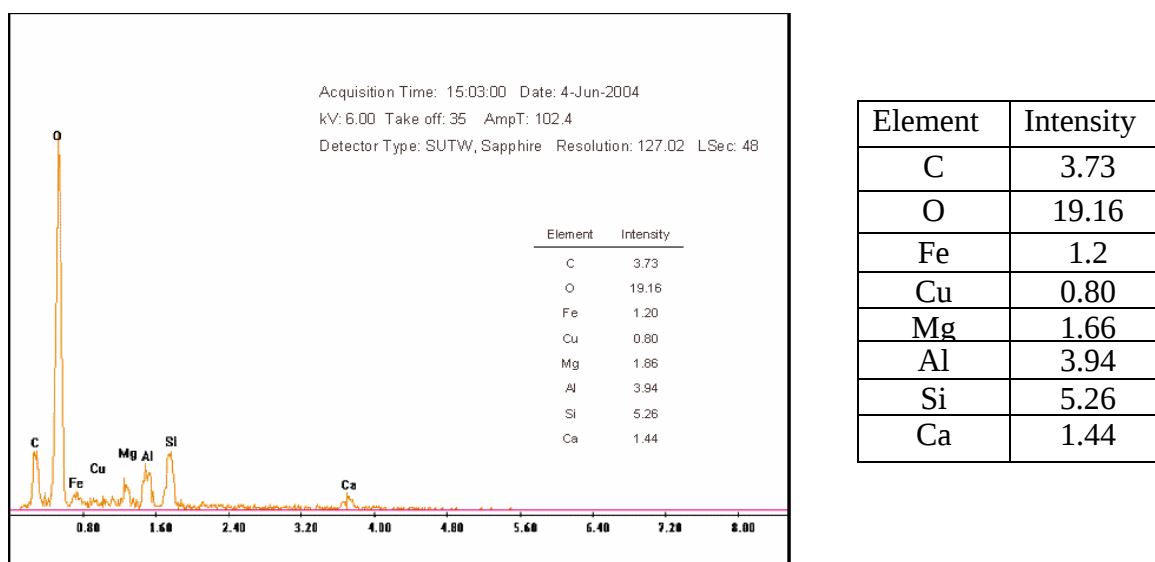


Figure 13. Elemental Composition of soil

Table 7. Mineralogical Composition

Compound	Formula
Quartz	SiO ₂
Calcite Magnesian	(Mg.064Ca.936)(CO ₃)
Calcium Carbonate	CaCO ₃
Aragonite	Ca(CO ₃)

3.4.2 Assembly of Tanks

The experiments were conducted in tanks of 14 cm i.d and 55cm tall, the height of the soil column was 33cm. A mesh was used as a porous plate to warranty saturation humidity at the bottom of the soil, and to support the soil column. The column was connected by flexible tubing to a graduated cylinder providing a hanging water column to control the soil moisture content as showed in figure 14. 7,500 gr of sand was located in each tank, and the initial and final compaction was 1.35 gr./cm^3 and 1.42 gr./cm^3 .

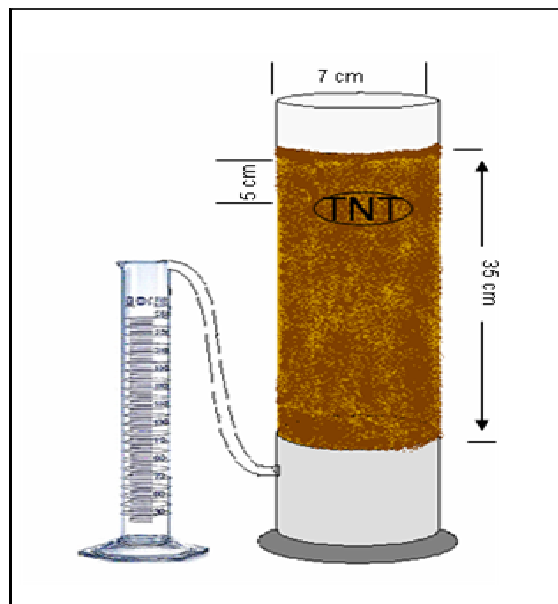


Figure 14. Schematic of a soil column with moisture control

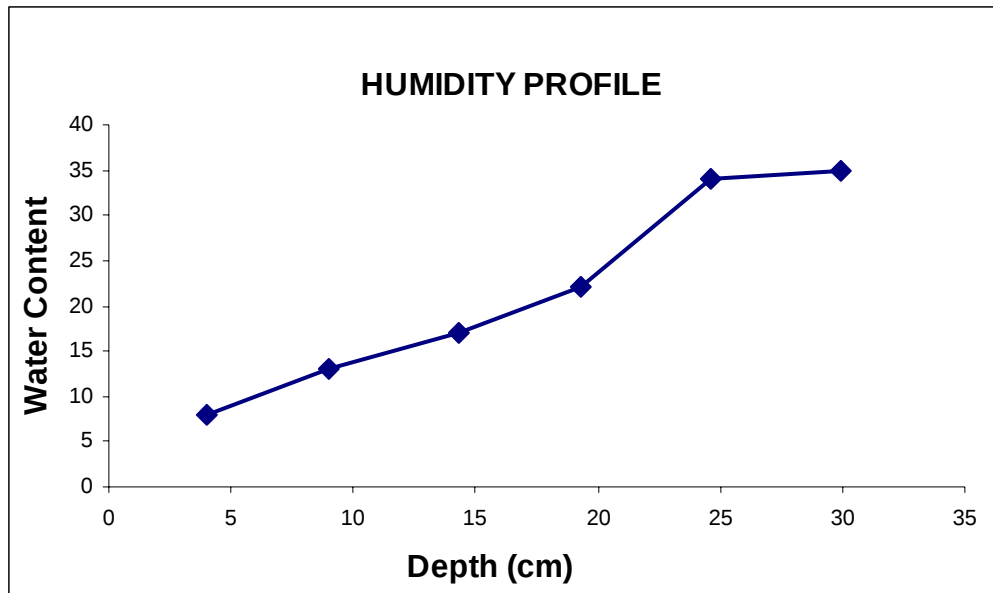


Figure 15. Humidity Profile

To monitoring the soil moisture content at different depths, six Campbell Scientific model CS620, water content reflectometers (WCR) were installed horizontally into the column at depths 4, 9, 14.3, 19.3, 24.6 y 29.9 cm from the surface of the soil. To obtain a moisture profile, from saturation at the bottom, an initial volume of water of 1000 cm^3 in the cylinder graduated was fixed; the results obtained are showed in figure 15.

3.4.3 Ambient Conditions

- **Temperature:** Experiments were performed in tanks at controlled temperatures of 30°C, 40°C and 50°C to simulate extreme environmental conditions.



Figure 16. Temperature Controlled

- **Radiation UV:** UV radiation was expected to have a strong impact on the chemical photo-degradation, UV light of 254nm was used for two reason:
 1. At this wavelength the largest bactericide activity is detected.
 2. This wavelength has been used by EPA in the method 8330 for analysis of explosives.

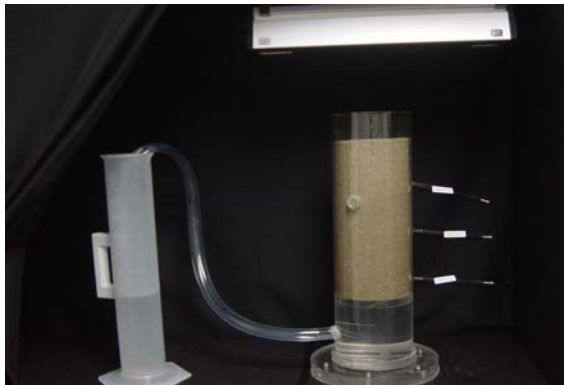


Figure 17. UV radiation

- **Radiation Visible:** For this study, the daylight was produced by special lamps with sun equivalent of 6500K.



Figure 18. Visible Light

- **Water Content:** Tanks with water content of 3% (dry tank) and 30% (humid tank), were used. The dry tank was used as blank.



Figure 19. Water content 3% and water content 30 %

3.4.4 Sampling Method

For these experiments, 500mg of 2, 4, 6 TNT 98% purity in crystal form were located at 5.0 cm from the surface in each of the soil columns. Three soil samples were collected at the surface using a manual stainless-steel hand auger in specific direction every week. In each case, 0.100g of sand sample was removed from the surface and extracted with acetonitrile for direct injection to the GC.



Figure 20. Sampling procedure

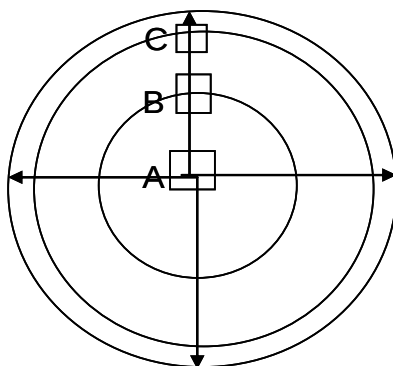


Figure 21. Radial Sampling

3.4.5 Extraction methodology

Two methodologies were used for the sampling of explosives from soil: SPME-Immersion Analysis (Solid Phase Micro Extraction) and Direct Injection.

➤ SPME- Immersion analysis

1.00 g of sand was placed in an 5ml amber vials and 1.5 ml acetonitrile (HPLC grade) was added for extraction. After 18 hours of stirring, the supernatant was removed and placed in a new vial and 2 ml of water were added, the analyte was extracted by the immersion of a fiber into the solution. After 30 min, the fiber was retracted into the SPME holder and transferred to the injection port of the GC. The SPME fiber was exposed for 5 min into the GC- μ ECD; SPME was performed using a fiber of polydimethylsiloxane divinilbencene (PDMSDVB).

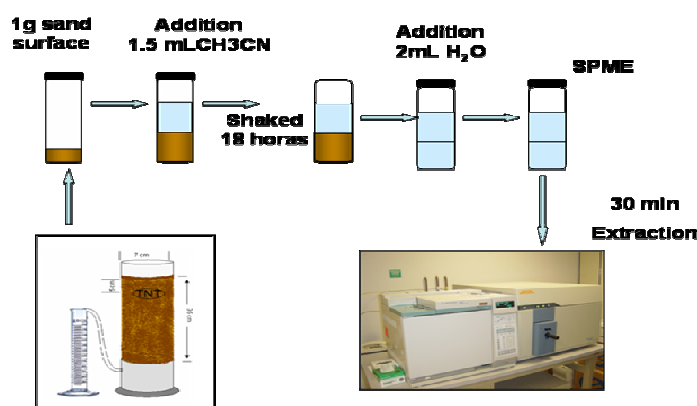


Figure 22. Scheme of the SPME method

➤ **Direct Injection**

After sampling, the sand was put into the 2mL vials and extracted with 0.5 ml of acetonitrile. After 18 hours of stirring, the extracts were injected to the GC- μ ECD.

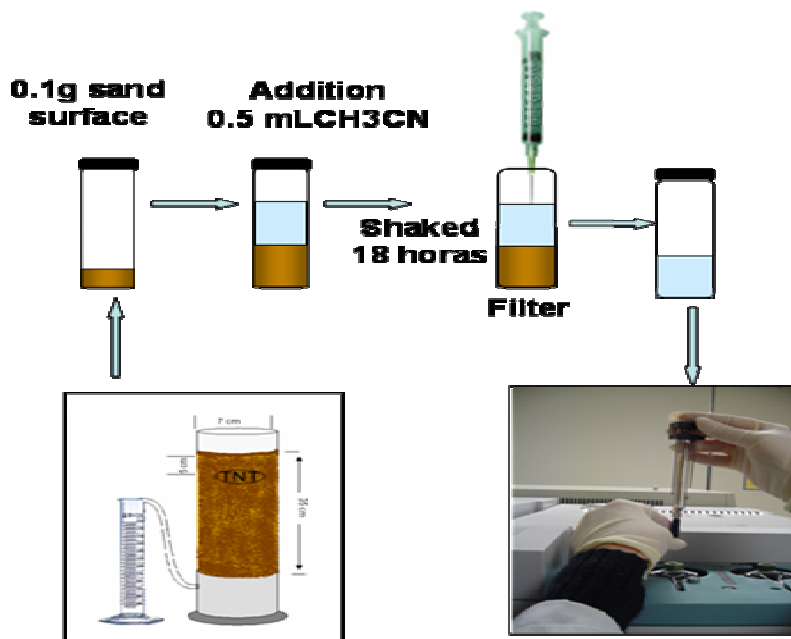


Figure 23. Scheme for Direct Injection Method

3.4.6 Gas chromatography analysis

The analyses were performed with 1 μ L injection into the Gas Chromatograph, model 6890N, equipped with a micro cell, 63Ni Electron Capture Detector (μ -ECD), The splitless injector was programmed for a 250 °C inlet temperature, starting column temperature of 100°C for 1 min, ramped to 180°C at 10°C /min after to 275°C at 30°C /min then held for 5 min.

3.5 Numerical Simulation.

The software codes used for the simulation were: LaGriT and FEHM Code.

3.5.1 *LaGriT Code:*

It is a library of user callable tools that provide mesh generation, mesh optimization and dynamic mesh maintenance in three dimensions for a variety of applications. Geometric regions within arbitrarily complicated geometries are defined as combinations of bounding surfaces, where the surfaces are described analytically or as collections of points in space. Figure 24, shows an example of a grid obtained with this program.

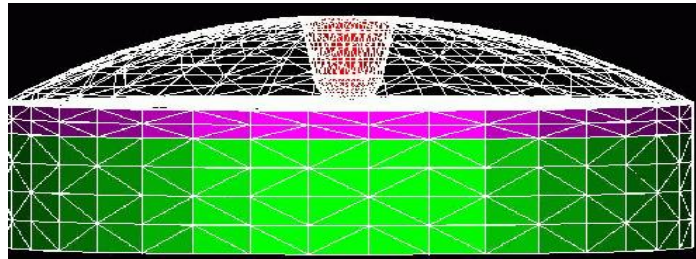


Figure 24. Mesh for scanning microscopy simulation

Mesh generation uses a Delaunay tetrahedralization algorithm that respects material interfaces and assures that there are no negative coupling coefficients. The data structures created to implement this algorithm are compact and powerful and expandable to include hybrid meshes as well as tetrahedral meshes. Mesh refinement and smoothing are available to modify the mesh to provide more resolution in areas of interest.¹²

3.5.2 Finite Element Heat and Mass Transfer Code: (FEHM)

FEHM is a numerical simulation code for subsurface transport processes. It models: 3-D, time-dependent, multiphase, multicomponent, non-isothermal, reactive flow through porous and fractured media. It can accurately represent complex 3-D geologic media and structures and their effects on subsurface flow and transport.¹³ Its main capabilities are:

- 3-D
- Multiple chemically reactive and sorbing tracers
- Particle tracking transport
- Finite element/finite volume formulation
- Saturated and unsaturated media
- Complex geometries with unstructured grids

4. RESULTS

4.1 Calibration Curves

The effect of the environmental parameters on the chemical signature at the surface is dynamic and complex. A fundamental understanding of the variables that affect the detection of the chemical signature of TNT and its degradation products is needed to ensure a good level of detection in the subsequent stages. This section presents the results of all experiments described in the previous chapter. The first experiment was the identification of the peak position for the chemical explosives in mix A (figure 25).

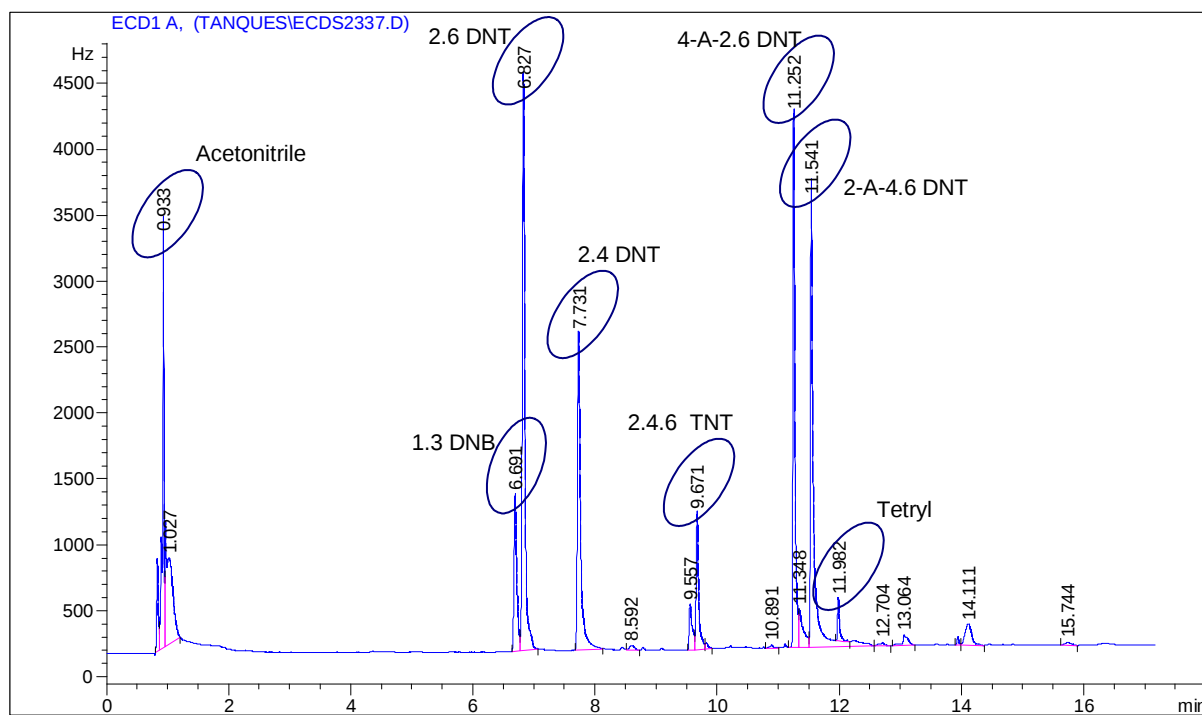


Figure 25. Chromatogram Mix A

A calibration curve for TNT was constructed using direct injection. The relation Mass versus Chromatographic Area is given by equations 1 and 2 (TNT and DNT in acetonitrile, respectively).

$$2.4.6 \text{ TNT} \quad y = 36.272x \quad R^2 = 0.9891 \quad (1)$$

$$2.4 \text{ DNT} \quad y = 85.347x \quad R^2 = 0.9934 \quad (2)$$

Figure 26 shows the chromatogram for the blank (clean sand) which is used for the characterization of sand and for comparison of the experiments.

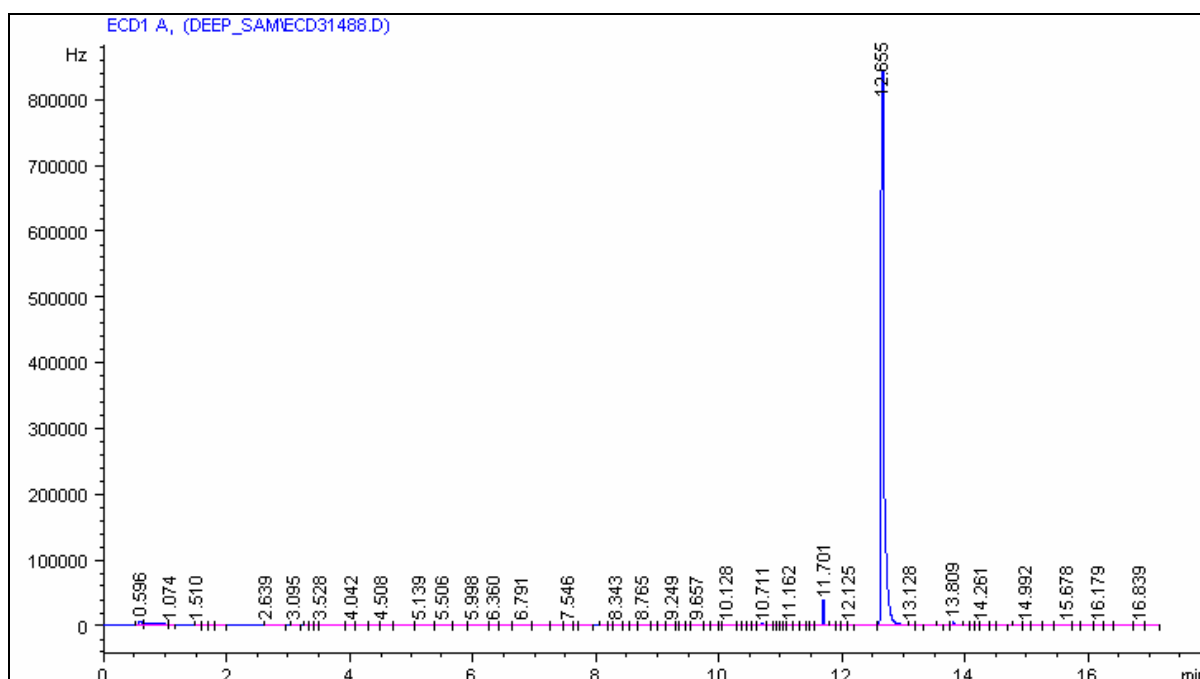


Figure 26. Sand Blank

The sand sample was extracted with 0.5 mL of acetonitrile, followed by 18 hours of stirring, then the sample was allowed to settle for 1 hour. The extract was removed, filtered and injected to the GC-uECD.

4.2 Sampling Characteristics

Six tanks with different conditions were studied; the tanks were sampled each week during a minimum period of 14 weeks. The sampling method explained in section 3.4.4 was radial. Tank characteristics were:

- Tank 1: Dry (water content ~3%) and room temperature.
- Tank 2: Water content~30% and temperature 50°C
- Tank 3: Water content~30% and temperature 30°C
- Tank 4: Water content~30% and temperature 40°C
- Tank 5: Water content~30% and room temperature
- Tank 6 and tank 7: Water content~30%, visible and UV light, and room temperature.

4.2.1 Tank 1: Dry and room temperature:

This tank was studied for 36 weeks, in this, the presence of TNT remain small at the surface, after six months the concentration of TNT detected was less than 1 µg/g soil, the amount of DNT was higher than TNT in the experiment. Presence of degradation products was not observed; both biologic and abiotic reactions require water for degradation reactions to proceed.⁹

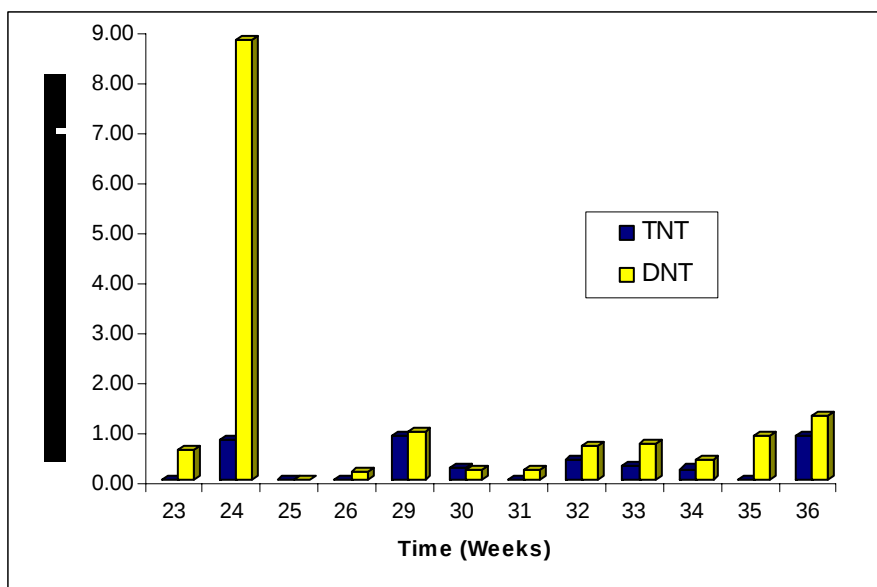


Figure 27. Concentration of TNT and DNT vs. time for the Dry Tank

The larger presence of DNT respect to TNT at the top surface is explained by it considerably higher vapor pressure. DNT is a natural contaminant in the process of making TNT and also it may be produced by chemical degradation of TNT. The maximum water content for this soil was 35%, in this tank the water content was 3% equivalent to 8.6% saturation. Figure 28 shows a dramatic decline in the effective diffusivity below 15% saturation, this mean that for dry soil, transport of chemicals is essentially halted.

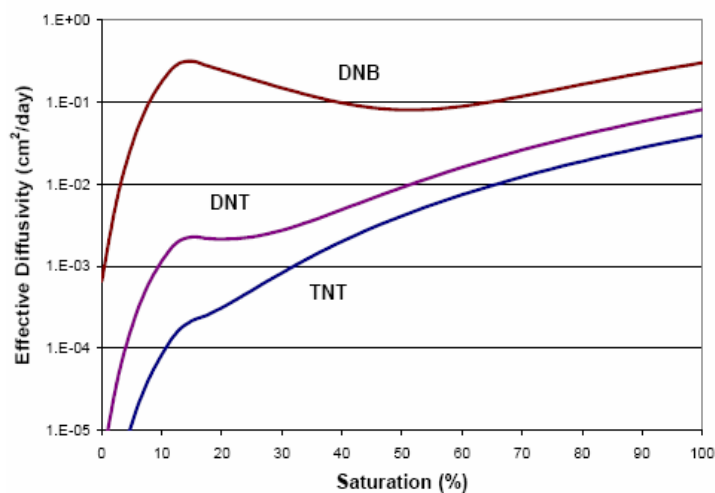


Figure 28. Effective Diffusivity for TNT, DNT and DNB¹⁰

4.2.2 Tank 2: Water content~30% and temperature 50°C

In this tank, TNT and 2,4-DNT were detected at the second day after burying the explosive, and degradation products such as 2-amino 4, 6-DNT and 4-amino 2, 6-DNT were detected after two weeks.

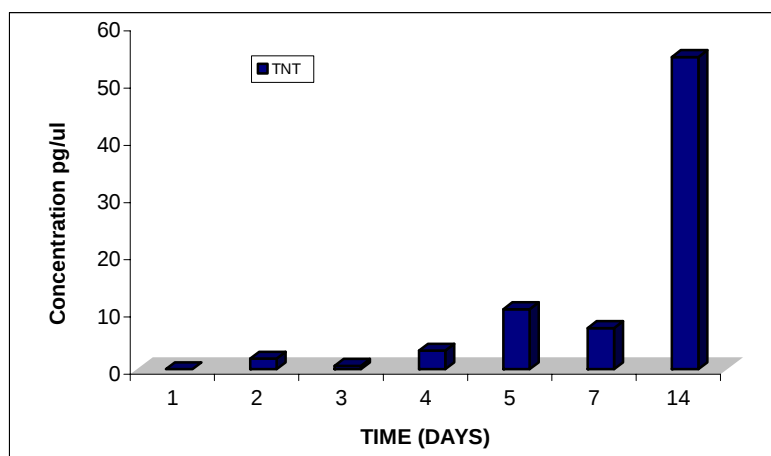


Figure 29. Concentration of TNT detected during first 15 days using SPME

Six months later SPME sampling was carried out with the intention of identifying degradation products. The presence of degradation products was revealed by a change of color at the surface of the soil in the center of the tank as showed in figure 30.



Figure 30. Evidence of TNT-Degradation

The amount of TNT was consistently higher than that of 2,4 DNT and a continuous growth is observed as time evolves (see figure 31).

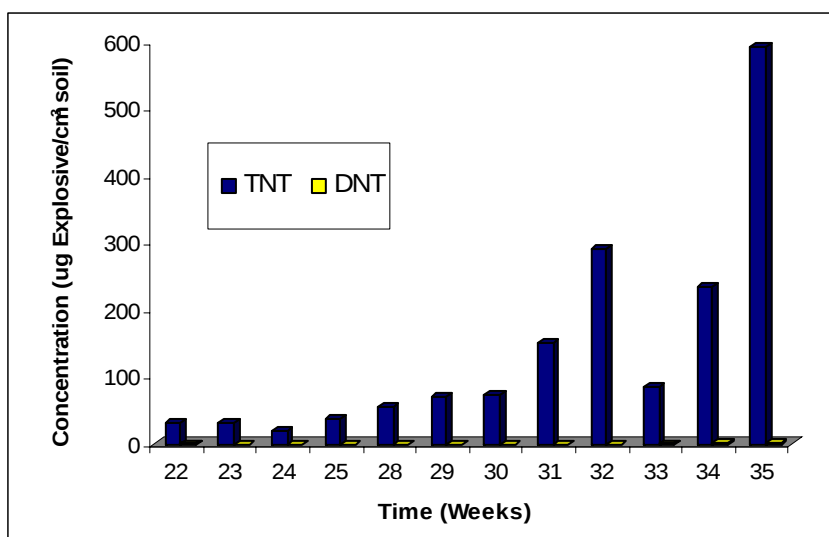


Figure 31. Comparison TNT and 2,4-DNT detected in tank 2

2,6-DNT was also found at the surface in a much smaller amount. In addition the presence of degradation products 4A-2,6DNT and 2A-4,6DNT was observed in about the same order of magnitude than DNT.

Figure 32 shows that solute diffusivity in the liquid phase dominates vapor diffusivity at soil saturation; this is valid for soil saturation values greater than about 15% under this value soil-vapor sorption becomes significantly greater. In the present experiment where saturation is close to 85% in average, the transport of TNT occurs mainly by diffusion through the soil pore water.

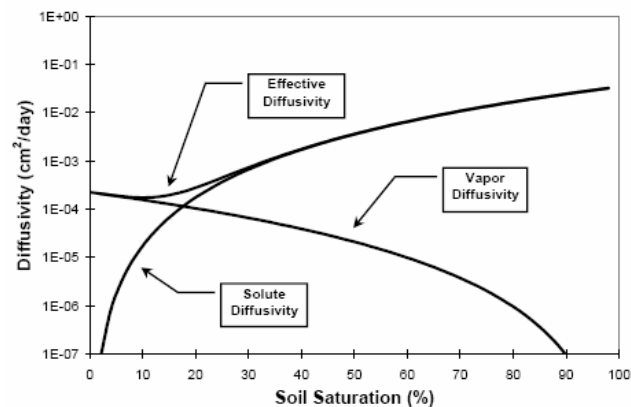


Figure 32. Effective Diffusivity for TNT (Phelan and Webb, 1997)¹⁰

Sampling of this tank was performed at several points, in a radial array. The results are shown in figure 33, where (as found by previous researchers) significantly higher concentrations were detected at the center of the top surface.

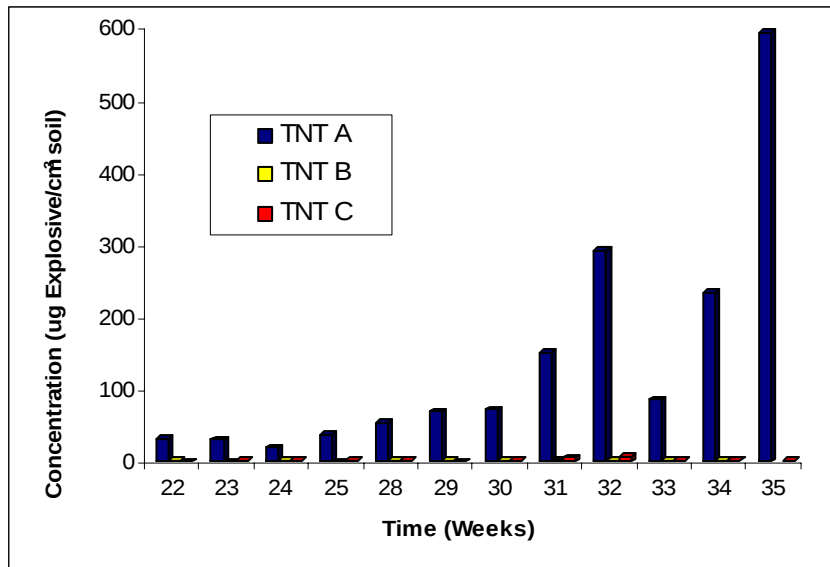


Figure 33. Radial behavior on tank 2

Comparison between Tank 1 and Tank 2

The dry tank (tank 1) is a great point for comparing the results from tank 2. Both tanks were assembled at the same time, but maintained at different temperatures (ambient temperature and 50°C). In addition tank 2 has a imposed humidity profile and tank 1 is a dry one. Figure 34 shows the concentration of TNT detected in both tank 1 and tank 2. The data confirms what was expected, experiments with tanks at higher temperature results in a larger concentration of TNT at the surface. Increasing temperature accelerate all transport mechanics.

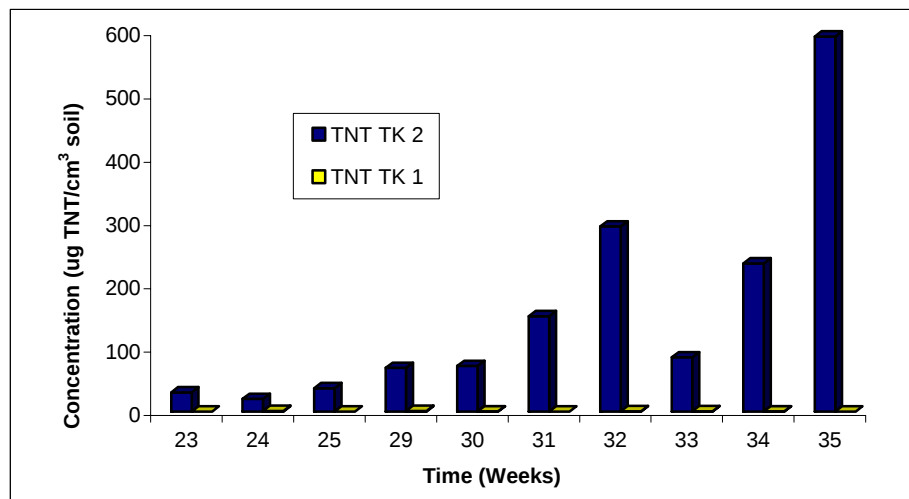


Figure 34. Comparison of Tank 1 and 2 for TNT

On the other hand 2,4-DNT is consistently found at higher concentrations in tank 1 (Figure 35). The high vapor pressure of 2, 4-DNT is responsible for its high presence at the surface. Tables 8 and 9 show the properties for both TNT and DNT.

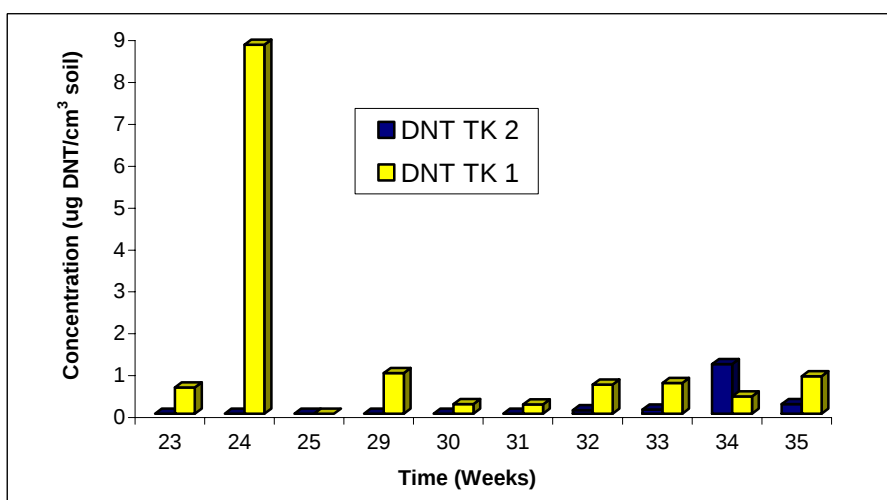


Figure 35. Comparison of Tank 1 and 2 for 2,4 DNT

Under typical soil temperatures, the predicted 2,4 DNT vapor pressure is about 10 to 30 times larger than that of 2,4,6 TNT even though it may be a minor constituent (about 0.1 mole %) in the solid phase¹⁰

Table 8. Vapor Pressure versus temperature relationship (Phelan, 1977)¹⁴

Chemical Vapor Pressure Equations
TNT $\log_{10}(p/\text{Torr}) = (12.31 \pm 0.34) - (5175 \pm 105) \text{ K/T}$
DNT $\log_{10}(p/\text{Torr}) = (13.08 \pm 0.19) - (4992 \pm 59) \text{ K/T}$

Table 9. Properties of TNT and DNT at 20°C (Phelan, 1997)¹⁵

Compound	Temp	Vapor Pressure	Density	Water Solubility	Henry's Law Constant
	°C	atm	μg/m ³	Mg/L	atm-m ³ /mol
TNT	20	4.61E-09	43.5	130	8.05E-09
DNT	20	1.61E-08	121.8	270	1.35E-08

4.2.3 Tank 3: Water content~30% and temperature 30°C

As expected, a considerable higher concentration of TNT with respect to 2,4DNT was consistently detected in this tank. Again, degradation compounds identified as 4-amino-2,6-dinitrotoluene (4ADNT) and 2-amino-4,6-dinitrotoluene (2ADNT) were observed very early in the process. This fact tells the needs for considering these two compounds as essential part in the chemical signature of landmines.

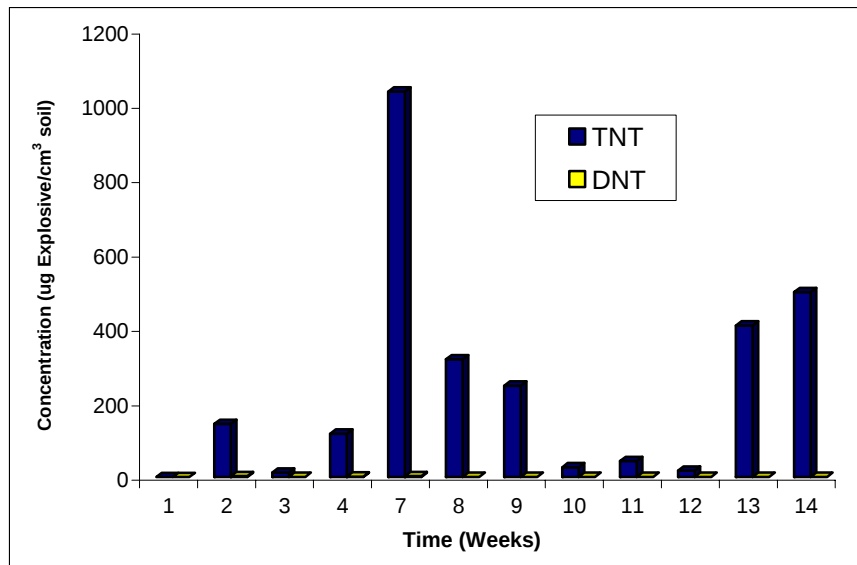


Figure 36. Comparison TNT and 2, 4 DNT concentration in tank 3

Similar results to those for tank 2, were found when sampling in a radial fashion as displayed by figure 37.

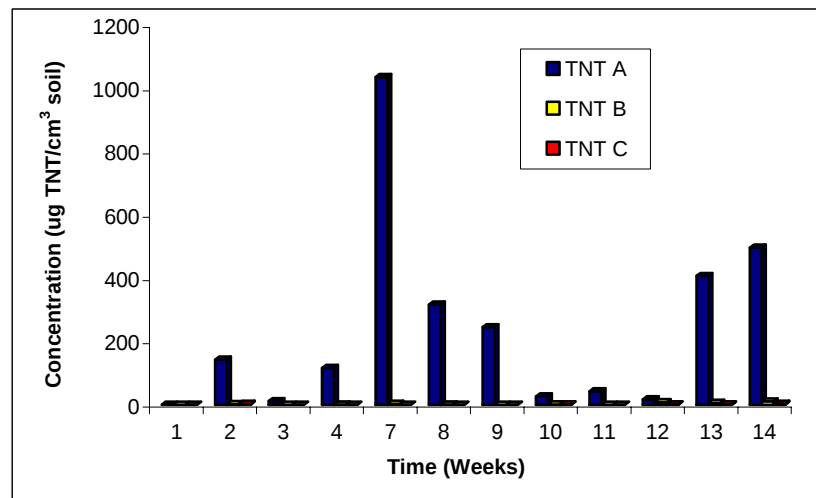


Figure 37. TNT concentration detected in radial sampling

4.2.4 Tank 4: Water content~30% and temperature 40°C.

In this case, TNT was detected at the surface from day 1. Degradation products (2,4DNT, 4Amino and 2-Amino) were appreciated after the 12th week.

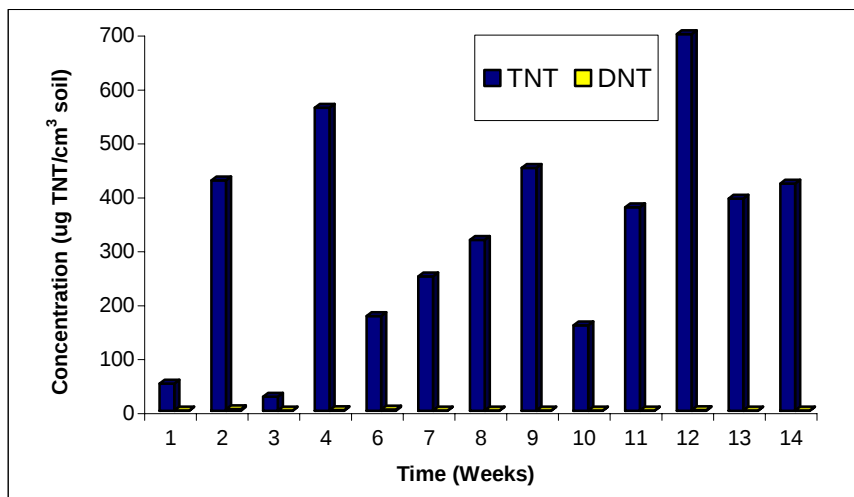


Figure 38. Comparison TNT and DNT concentration in the tank 4

A similar conclusion is obtained this time when sampling at different locations

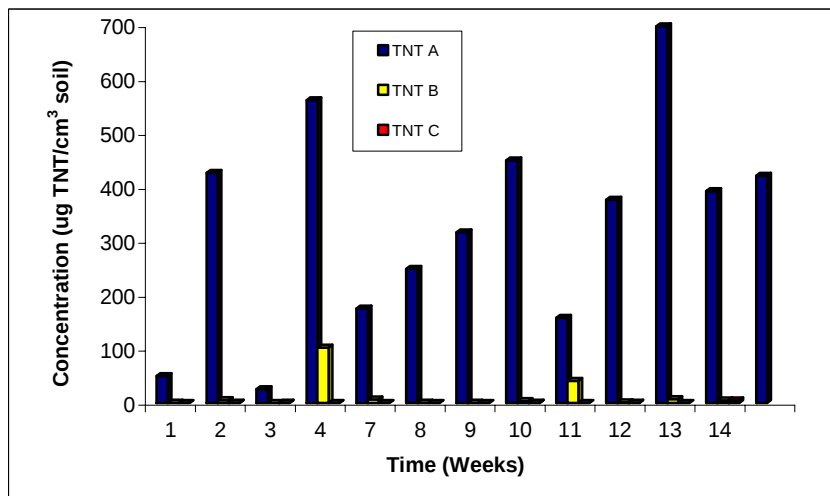


Figure 39. TNT Concentration detected from radial sampling

Differences between tanks 3 and 4 are no necessarily conclusive. In general, we obtained higher concentration for the tank at higher temperature and we noticed a faster formation of degradation products.

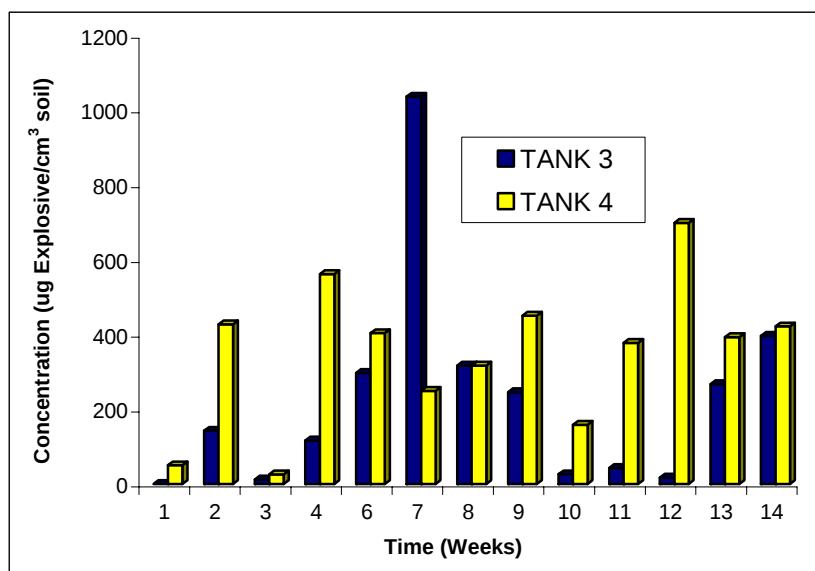


Figure 40. Comparison of TNT concentration for tanks 3 and 4

Temperature was expected to play an important role in these experiments, theoretically an increase in temperature should raise the vapor-liquid partitioning coefficient (Henry's constant). In addition, increase vaporization at the surface must lead to a sharp increase in the advection mechanism which drives solutes upward. Also, degradation reactions should be enhanced by increasing temperature.

4.2.5 Tank 5: Water content~30% and temperature 20°C:

As in the previous cases, water content determines the dominant transport mechanism. Again, detected concentrations of TNT at the surface are orders of magnitude higher than DNT concentrations. Also, we observe a fast formation of degradation compounds.

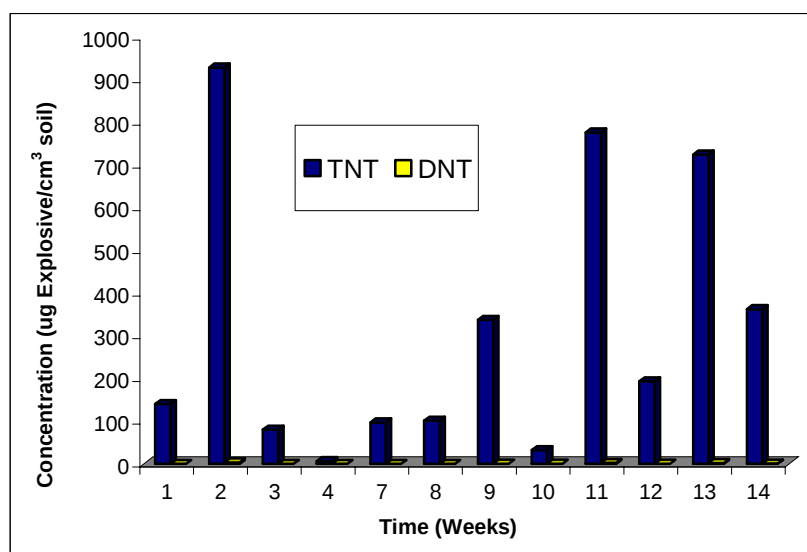


Figure 41. . Comparison of TNT and 2, 4DNT concentrations in tank 5

Again, sampling at different points of the surface gave the same conclusions than in the previous cases.

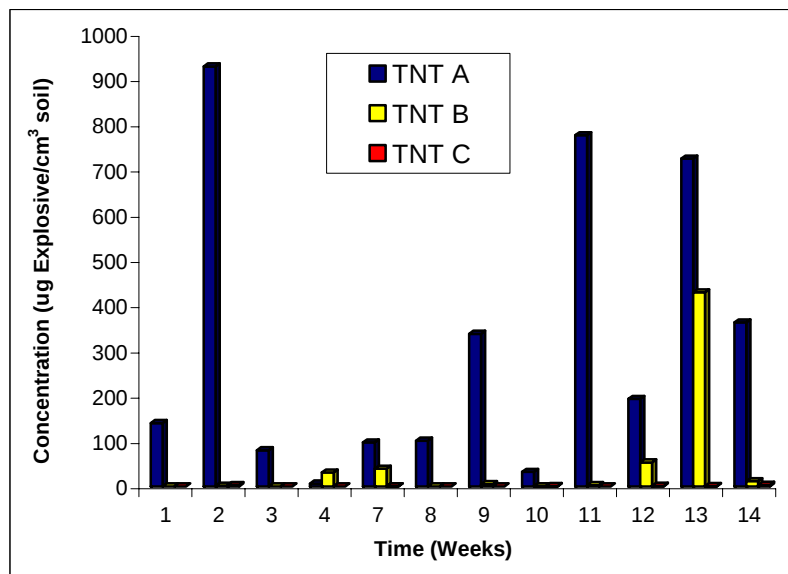


Figure 42. TNT Concentration from radial sampling

4.2.6 Tank 6 and 7: Visible and UV light

Exposure of TNT as a solid or in solution to strong sunlight or ultraviolet radiation, results in the formation of decomposition products. As a result of photodecomposition, aqueous solutions of TNT first turn pink, then gradually after a period of 4-h, change into a rusty-orange colored solution, known as ‘pink water’, caused by the following photodecomposition products: 1,3,5-trinitrobenzene (TNB), 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehyde and 2,4,6-trinitrobenzonitrile.¹⁶ The presence of TNT 6 and 7 was lower respect to the previous cases, figures 43 and 45 show TNT and DNT concentrations for both tanks.

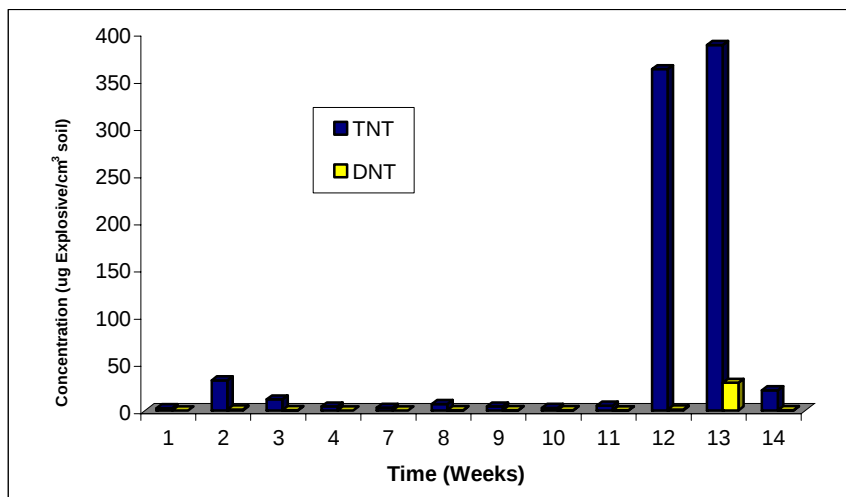


Figure 43. Visible light

In the tank 6 the maximum concentration detected was 400ug/cm³ soil approximately, in this tank we did not observe the presence of fungi, and additional degradation products were not detected.

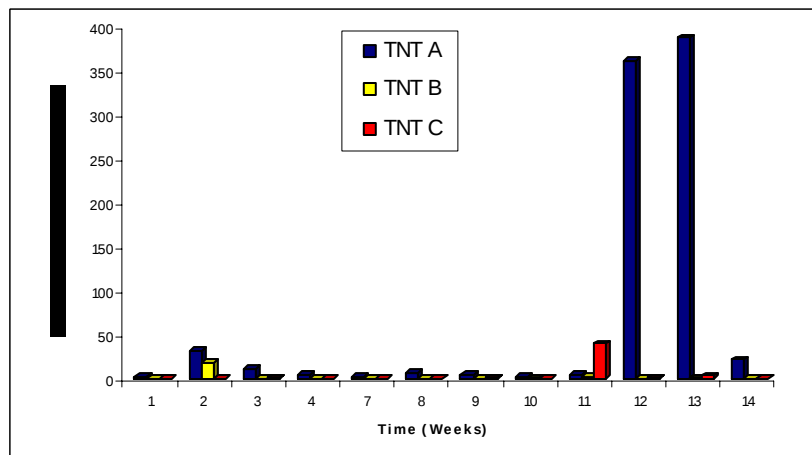


Figure 44. TNT Concentration from radial sampling

In both tanks we performed radial sampling. As usual, point A showed the highest concentrations.

In the tank 7 the maximum concentration detected was 60ug/cm³ soil approximately, in this tank we did not observe the presence of fungi, and additional degradation products were not detected.

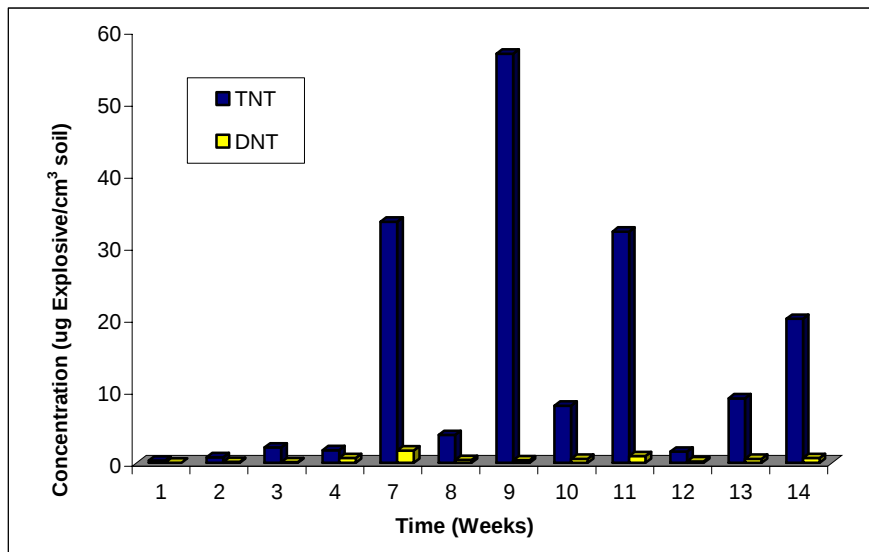


Figure 45. Comparison TNT and DNT, Tank UV Light

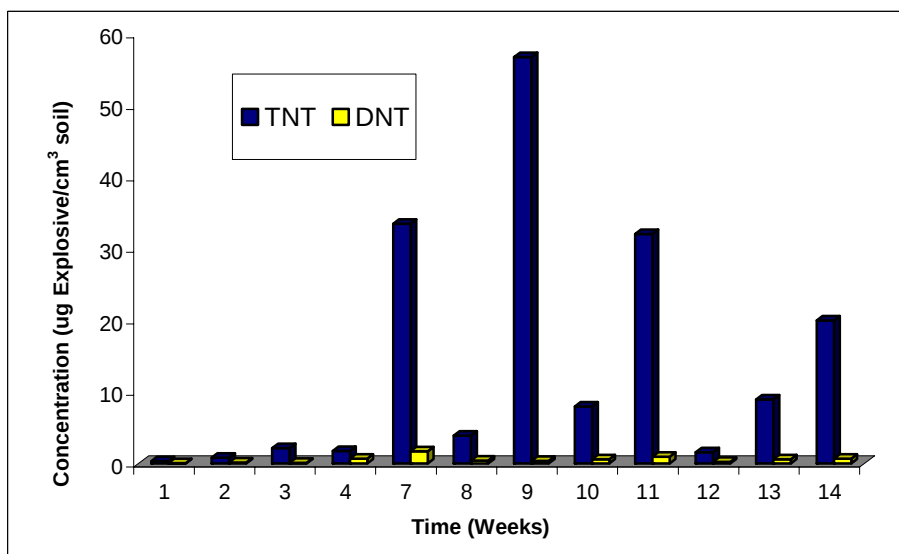


Figure 46. Sampling Radial, tank UV light

4.3 Depth Sampling

Tank No. 2 was dismantled after 1 year, figure 47 shows the coloration at the surface due to the formation of degradation compounds.



Figure 47. Tank 2 after 1 year

Sampling in depth was realized at points A, B and C, with the objective to obtain a concentration profile.



Figure 48. Depth sampling for tank 2

Table 10 shows the results for this experiment, the higher concentrations was located at 3 cm depth, and presence of TNT as far as 8 cm below the point where the solid was seeded. As expected, the highest concentrations of TNT were found at point A (center of the tank). Very small quantities of TNT were detected at positions B and C.

Table 10. Depth Sampling

	A	B	C
Depth	ug/cm3 soil	ug/cm3 soil	ug/cm3 soil
12 cm	2	3.4	4.4
11 cm	0	18.4	24.1
9.5 cm	2	4.7	1.0
8 cm	9	0.2	0.2
6.5 cm	52	0.5	3.5
5 cm	1463	0.0	15.0
3.5 cm	3341	0.3	0.3
3 cm	107847	0.1	0.5
2.5 cm	58002	0.2	4.0
2 cm	496	0.3	0.3
1.5 cm	25	0.2	2.3
1 cm	53	1.6	1.64

We did an approximate mass balance to account for the TNT seeded a year ago. The results are presented in tabular form (table 11).

Table 11. Mass balance of TNT

TNT Point A	TNT Point B	TNT Point C	TNT Point (A+B+C)
Mass (pg)	Mass (pg)	Mass (pg)	Total Mass (pg)
8.E+06	3.E+07	1.E+07	3.E+07
5.E+05	1.E+08	6.E+07	1.E+08
6.E+06	2.E+07	4.E+06	2.E+07
4.E+07	4.E+07	5.E+05	4.E+07
2.E+08	2.E+08	1.E+07	2.E+08
5.E+09	5.E+09	5.E+07	5.E+09
1.E+10	1.E+10	9.E+05	1.E+10
2.E+11	2.E+11	1.E+06	2.E+11
1.E+11	1.E+11	1.E+07	1.E+11
1.E+09	1.E+09	1.E+06	1.E+09
7.E+07	8.E+07	7.E+06	8.E+07
3.96.E+08	4.E+08	6.66.E+06	4.E+08
Total mass (pg)			3.8E+11
Total mass (g)			0.38
Total mass (mg)			380

The mass for degradation products and 2,4 DNT were neglected when compared to that of TNT. The initial mass located of TNT was 500 mg at 5 cm of depth.

$$TNT = (500 - 380)mg = 120mg$$

4.4 Simulation

In order to solve the transport equations in this cylindrical system, we used, the finite volume technique. Grids and geometries were generated using the LaGriT® Code. In order to maximize the resolution in the system, memory resources, and computational time, a cylindrical system was created with three different zones: air boundary layer 5 cm thickness, a high resolution zone of 0.5 cm mesh (in which the explosive was seeded), and zone with a resolution of 1.0 cm.

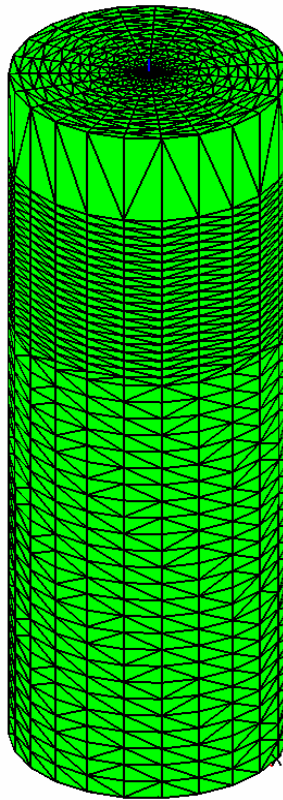


Figure 49. Grid for tank 2

The numerical solution of the transport equations was obtained by using the FEHM® code. This may solve the transport of contaminants and water profiles underground. Simulations were performed in two stages: the first one a stabilization stage which was run for two weeks. Results from these calculations include the steady state humidity profiles in the column as shown in figure 50.

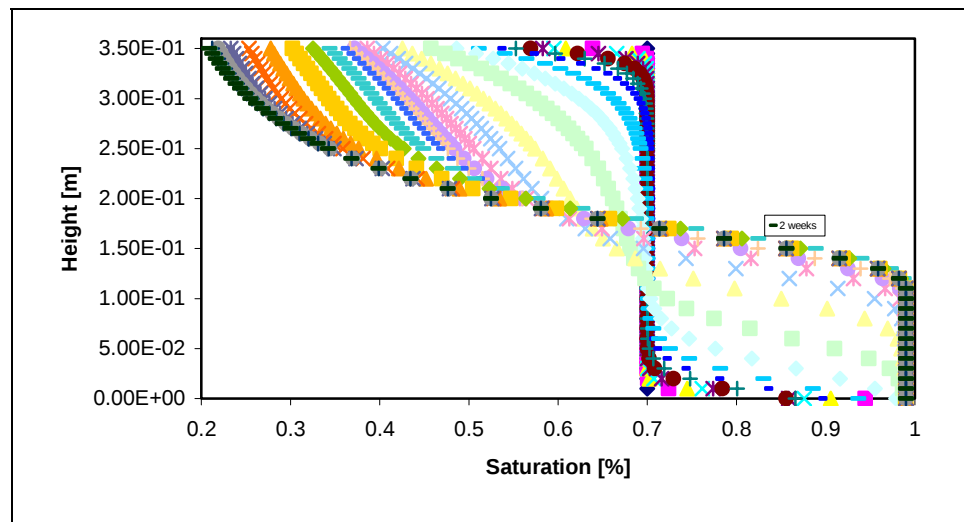


Figure 50. Stabilization Humidity Profile

The figure 51 shows the relation between depth and percentage of saturation for the soil column. This figure shows and compares the experimental humidity and the final profile obtained with the simulation. Saturation was observed below 10 cm.

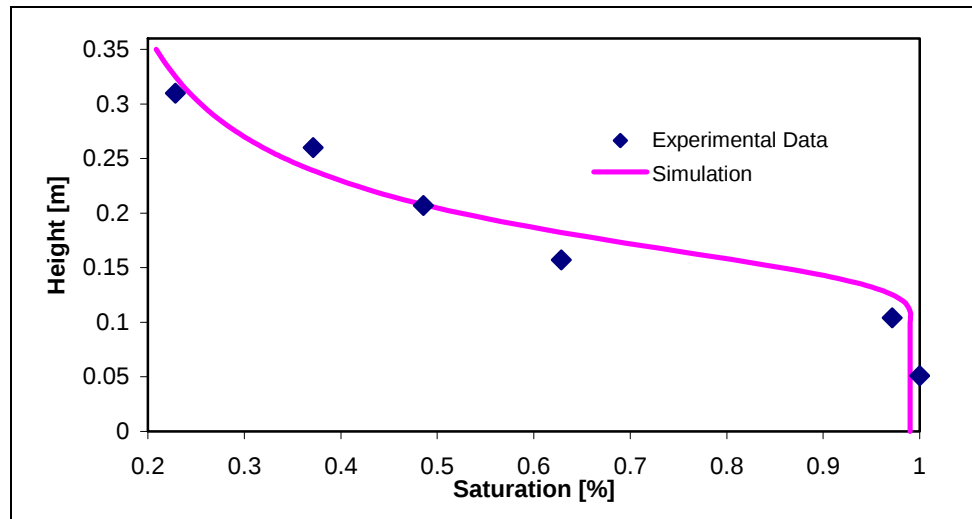


Figure 51. Final Humidity Profile Comparison

Second stage of the simulation was evaporation. In this part the spatial and temporal distribution of concentration of TNT were obtained. This step was run for a simulated time of 1 year to coincide with the experiments. The results are showed in the figure 52.

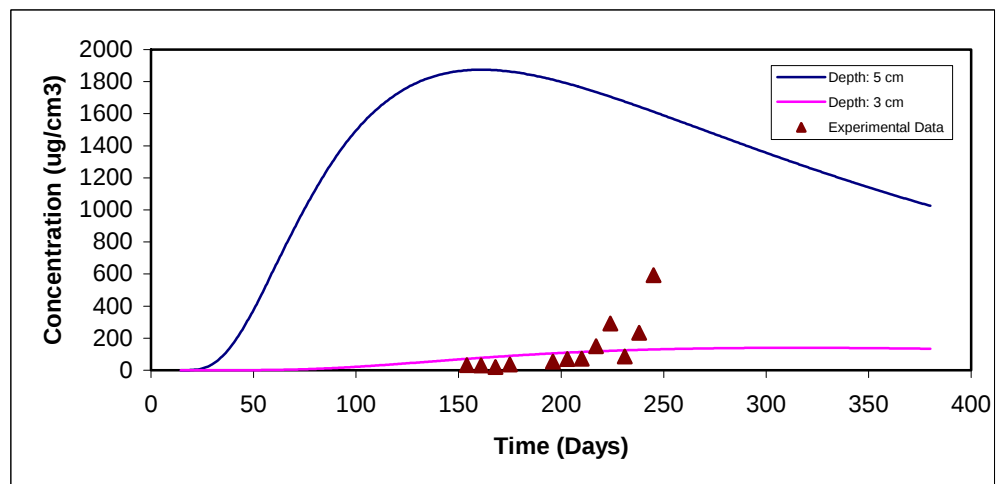


Figure 52. Temporal distribution of TNT

In this picture it is possible appreciate a same order of magnitude in both experimental and simulation data. Figure 53 shows depth vs concentration of TNT and 2,4-DNT, at the final time of the second stage. The highest concentration was obtained near three centimeter from surface, and it is in the order of $1e5 \text{ ug/cm}^3$.

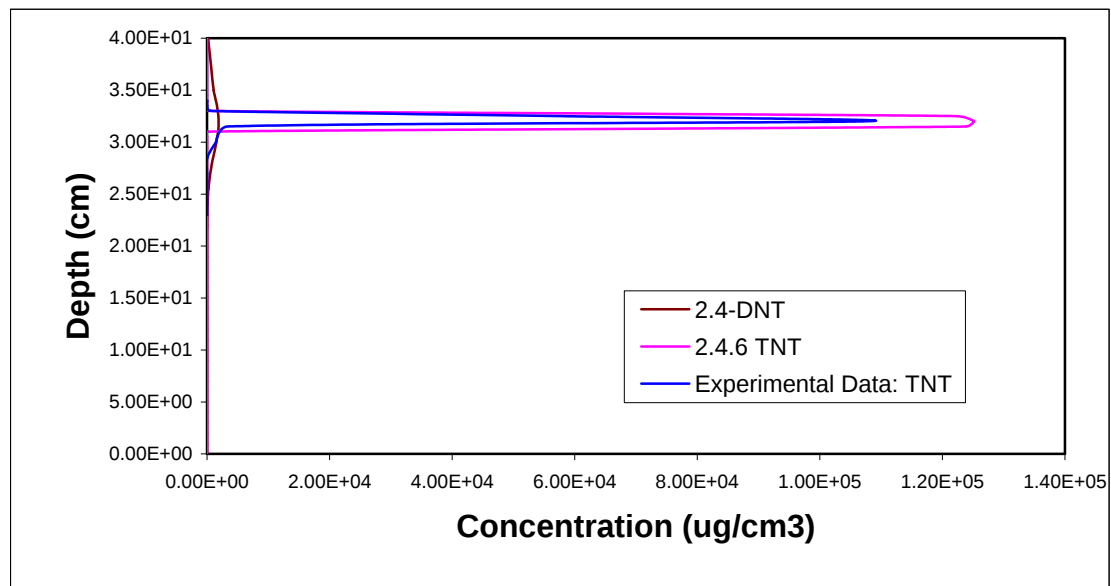


Figure 53. Comparison simulation and experimental data: Depth Sampling

5. CONCLUSIONS

The results obtained in with GC- μ ECD established that the chemical signature released from source of TNT to surface strongly depends on the environmental conditions: soil temperature, soil water content and radiation.

The most important variables in the TNT degradation process was the water content and temperature. Higher concentrations of TNT and its degradation products were detected when the water content increased. The degradation products observed were: 2,4-DNT, 4-amino-2,6-DNT, 2-amino-4,6-DNT and 2,6-DNT. Due to its high vapor pressure, only 2,4-DNT was detected in a tank with low water content (dry tank).

For the radial study, systematically higher concentrations were found at the center of the tanks. In the depth sampling the highest concentration was detected at 3 cm depth. Numerical simulations were in good agreement to the experimental findings. The experimental data may be used to validate numerical model.

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