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Environmental Impact to the Chemical Signature Emanating from Buried Unexploded Ordnance - Final Report, Project CU-1094

J. M. Phelan, S. W. Webb, P. J. Rodacy, and J. L. Barnett

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14. ABSTRACT

Detecting the presence of buried unexploded ordnance (UXO) using chemical vapors derived from the main charge explosive has been considered possible with advances in sensitivity and selectivity of emerging chemical sensing technologies. Understanding the environmental impacts to this chemical signature is critical, as environmental factors have a dramatic effect on the source release, transport, phase transfers and degradation in soil systems. This project established several tasks to evaluate the environmental impact to the chemical signature from buried UXO. These tasks included simulation model development and utilization to evaluate the interdependent physico-chemical transport phenomena in near surface soils, fundamental property measurement for those parameters needed in the simulation model that had insufficient or poor quality data, and laboratory-scale experiments that produced data for comparison to simulation model results. This project also sponsored work to produce data on the chemical release characteristics of a small subset of ordnance and UXO, and to determine the chemical residues in the field adjacent to actual UXO. This work has resulted in the development of a simulation model, T2TNT, which incorporates the soil chemodynamic processes most important to near surface soil transport of chemical residues from buried UXO. Measurements were made of the temperature dependent water solubility of TNT and DNT, soilliquid partition coefficient for DNT, and the soil-vapor partitioning coefficient as a function of soil moisture content for TNT and DNT. Comparison ofT2TNT simulation results to laboratory-scale vapor flux experiments simulating a buried source release were excellent. UXO source release tests showed_ that prior to firing, ordnance contained a sufficient chemical reservoir for release into the soil. However, after firing and recovery (now as an UXO), the ordnance chemical flux was insufficient to overcome biochemical degradation rates. Data from field characterization of soil residues adjacent to UXO showed that chemical residues were present in arid weather conditions and absent in a site that supports biochemical degradation. These results indicate that source release rates may be insufficient to overcome biochemical degradation, limiting the opportunity for chemical sensing as a method to discriminate buried uxo.

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Abstract

Detecting the presence of buried unexploded ordnance (UXO) using chemical vapors derived from the main charge explosive has been considered possible with advances in sensitivity and selectivity of emerging chemical sensing technologies. Understanding the environmental impacts to this chemical signature is critical, as environmental factors have a dramatic effect on the source release, transport, phase transfers and degradation in soil systems.

This project established several tasks to evaluate the environmental impact to the chemical signature from buried UXO. These tasks included simulation model development and utilization to evaluate the interdependent physico-chemical transport phenomena in near surface soils, fundamental property measurement for those parameters needed in the simulation model that had insufficient or poor quality data, and laboratory-scale experiments that produced data for comparison to simulation model results. This project also sponsored work to produce data on the chemical release characteristics of a small subset of ordnance and UXO, and to determine the chemical residues in the field adjacent to actual UXO.

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Acknowledgements

This work was sponsored by the Strategic Environmental Research and Development Program as project CU-1094, under the direction of Dr. Jeff Marqusee for application to unexploded ordnance. This project was cofunded by the DARPA Dog's Nose Program for application to landmines. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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1.0 Introduction

This is the final project report for the Strategic Environmental Research and Development Program (SERDP) project titled *Environmental Impacts to the Chemical Signature Emanating from Buried Unexploded Ordnance (CU-1094).* The objective of this effort was to evaluate the dynamic physical, chemical and biological impacts to the chemical signature emanating from buried unexploded ordnance (UXO). For this project, unexploded ordnance is defined as military ordnance that has been launched with traditional means, and that for whatever reason, did not initiate the explosive main charge as intended. These items include grenades, mortars, artillery, rockets and bombs; but do not include landmines. The concept of detecting live UXO from inert or practice munitions is desired because traditional range clearance operations using electromagnetic sensing technologies are unable to discriminate explosive containing objects. As such, large numbers of anomalies must be investigated as true UXO, with all the necessary safety precautions, causing slow and costly operations.

Chemical sensing of the explosive in UXO is a complex process that requires leakage from the main charge reservoir, transport through soils to the ground surface, sample collection, and presentation to a detector with sufficient sensitivity and selectivity. Individual elements of this process are shown as a schematic in Figure 1.

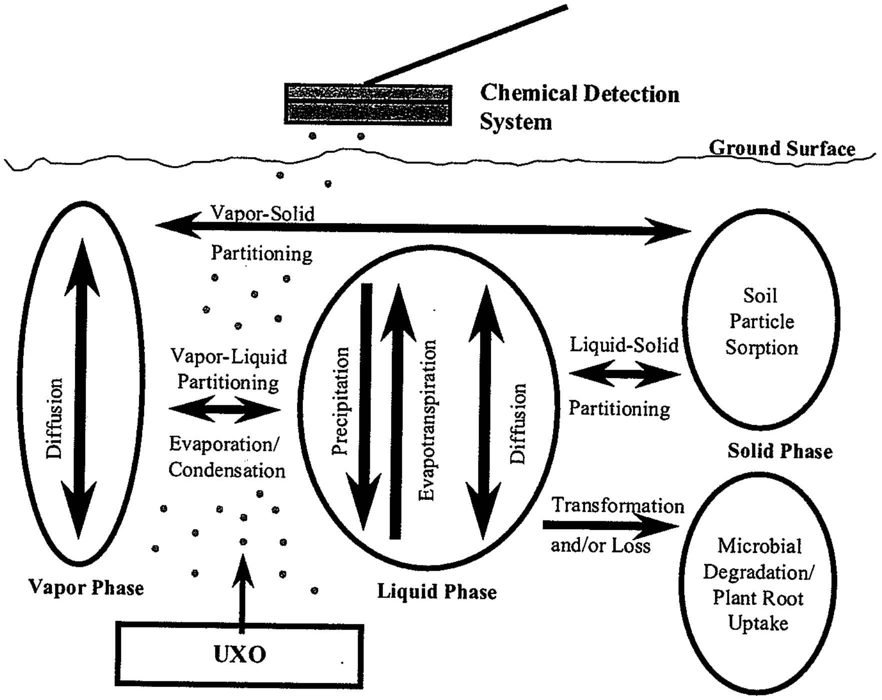


Figure 1. Fundamental Processes for Chemical Sensing of Buried UXO

To fully evaluate this system, this project was divided into six technical tasks and a reporting task as follows:

Task A – Model Development/Utilization – Development and use of simulation models to estimate vapor flux from buried UXO.

Task B – Fundamental Property Measurement – Measurement of critical soil transport parameters that are needed in the simulation models.

Task C – Laboratory Scale Experiments – Development and use of a soil chemodynamic test apparatus to be used to validate simulation model estimates of chemical transport.

Task D – Operational Strategy – Development of a strategy for operational use of chemical sensing to detect buried UXO.

Task E – UXO Chemical Source Release – Determination of the nature and extent of chemical release from new intact ordnance and impact damaged UXO.

Task F – Field Characterization of UXO Chemical Residues – Determination of the explosive signature soil residues from UXO in the field.

Task G – Annual and Final Technical Reports.

A master list of project milestones and report deliverables are shown in Table 1. This report serves as the final project report and will include the highlights of the methods and results from each task. Detailed information on the methods, materials, results and discussion can be found in the individual task reports as noted in Table 1.

Table 1. Master List of Tasks, Milestones and Deliverables

Task Name	Milestone	Date	Status	Deliverable
A - Model Development/ Utilization	Complete analytical model analysis to show critical properties	6/98	Completed	Phelan, J.M. and Webb, S.W., 1998a, "Chemical Detection of Buried Landmines," Proceedings of the 3rd International Symposium on Technology and the Mine Problem, April 6-9, 1998. Mine Warfare Association. Phelan, J.M. and Webb, S.W., 1998b, "Simulation of the Environmental Fate and Transport of Chemical Signatures from Buried Landmines," Proceedings of SPIE Conference on Detection and Remediation Technologies for Mines and Minelike Targets III, Orlando, FL, April 13-17, 1998. Jury, W.A. and L. Guo, 1998. One Dimensional Transport of Vapor From A Buried Landmine. Project report. University of California, Riverside. July 20, 1998. Webb, S.W., S.A. Finsterle, K. Pruess, and J.M. Phelan, 1998. Prediction of the TNT Signature from Buried Landmines. Proceedings of the TOUGH '98 Workshop. Berkeley, CA.
	Complete modifications to TOUGH2 to make T2TNT	9/98	Completed	Webb, S.W., K. Pruess, J. M. Phelan and S. Finsterle, 1999. Development of a Mechanistic Model for the Movement of Chemical Signatures from Buried Landmines/UXO. Proceedings of SPIE Conference on Detection and Remediation Technologies for Mines and

				Minelike Targets IV. Orlando, FL. April 5-9, 1999. A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds. Webb, S.W., 2000, "A simple extension of two-phase characteristic curves to include the dry region," *Water Resources Research,* 36(6), 1425-1430.
	Complete footprint analysis with 2-D model	3/99	Completed	Jury, W.A. and L. Guo, 1998. Two Dimensional Transport of Vapor From A Buried Landmine. Draft project report. University of California, Riverside. September 1, 1998.
	Compare T2TNT to 1-D model	2/99	Completed	Phelan, J. M. and S. W. Webb, 1999. Chemical Soil Physics Phenomena for Chemical Sensing of Buried UXO. Proceedings of UXO Forum 1999, May 25-27, 1999. Atlanta, GA.
	Complete T2TNT soil-plant-air interface	4/99	Cancelled	
B – Fundamental Properties	Complete vapor-solid partitioning data collection	10/98	Completed	Phelan, J.M. and J.L. Barnett. 2001. Phase Partitioning of TNT and DNT in Soils. Sandia National Laboratories Report SAND2001-0310, Albuquerque, New Mexico. February 2001. Phelan, J.M. and J.L. Barnett. 2001. Solubility of 2,4-Dinotrotoluene and 2,4,6-Trinitrotoluene in Water. J. Chem. Eng. Data, Mar/Apr 2001.
	Complete liquid solid partitioning data collection	10/98	Completed	Phelan, J.M. and J.L. Barnett. 2001. Phase Partitioning of TNT and DNT in Soils. Sandia National Laboratories Report SAND2001-0310, Albuquerque, New Mexico. February 2001.
C – Laboratory Experimental Studies	Complete lab-scale experimental design	12/98	Completed	Phelan, J.M., M. Gozdor, S.W. Webb, M. Cal, 2000. Laboratory Data and Model Comparisons of the Transport of

				Chemical Signatures From Buried Landmines/UXO. Proceedings of SPIE Conference on Detection and Remediation Technologies for Mines and Minelike Targets V. Orlando, FL. April 24-28, 2000. A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.
	Complete initial lab-scale experiments	8/99	Completed	Phelan, J.M., M. Gozdor, S.W. Webb, M. Cal, 2000. Laboratory Data and Model Comparisons of the Transport of Chemical Signatures From Buried Landmines/UXO. Proceedings of SPIE Conference on Detection and Remediation Technologies for Mines and Minelike Targets V. Orlando, FL. April 24-28, 2000. A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.
	Complete final lab-scale experiments	6/00	Completed	Phelan, J.M., S.W. Webb, M. Gozdor, M. Cal and J.L. Barnett, 2001. Effect of Wetting and Drying on DNT Vapor Flux – Laboratory Data and T2TNT Model Comparisons. Proceedings of SPIE Conference on Detection and Remediation Technologies for Mines and Minelike Targets VI. Orlando, FL. April 16-20, 2001. A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan, eds.
D –Operational Strategy	Develop operational strategy for chemical sensing	9/00	Completed	This Report.
E –Ordnance Source Term	Complete pre-shot ordnance source term	3/99	Completed	Phelan, J.M. P. Rodacy, T. Jenkins and J. Brannon, 1999. UXO Chemical Source Term - Impact on Range Contamination and UXO/Clutter Discrimination. Presented at 15th Annual International Conference on Contaminated Soils and Water, University of Massachusetts at Amhurst, October 18-21, 1999.
	Complete post-shot ordnance source term	6/99	Completed	Phelan, J.M., P.J. Rodacy and J.L. Barnett,

				2001. Explosive Chemical Signatures from Military Ordnance, Sandia National Laboratories Report SAND2001-0755, Albuquerque, New Mexico. April 2001.
F – UXO Field Site Characterization	Complete UXO Field Site Characterization #1	1/00	Completed	Phelan, J.M., P.J. Rodacy and J.L. Barnett, 2001. Explosive Chemical Signatures from Military Ordnance, Sandia National Laboratories Report SAND2001-0755, Albuquerque, New Mexico. April 2001.
	Complete UXO Field Site Characterization #2	6/00	Completed	Phelan, J.M., P.J. Rodacy and J.L. Barnett, 2001. Explosive Chemical Signatures from Military Ordnance, Sandia National Laboratories Report SAND2001-0755, Albuquerque, New Mexico. April 2001.
G – Annual and Final Technical Reports		12/98;	Completed	Phelan, J.M. , S.W. Webb, D.C. Leggett and W.A. Jury, 1998. FY 98 Interim Technical Report, SERDP Project 1094, Environmental Impacts to the Chemical Signature Emanating from Buried UXO. December 1998.
		12/99;	Completed	Phelan, J.M., S.W. Webb, K. Pruess, S. Finsterle, M. Ca., M. Gozdor, 1999. FY 99 Interim Technical Report, SERDP Project 1094, Environmental Impacts to the Chemical Signature Emanating from Buried UXO. December 22, 1999.
		12/00	Completed	This Report

2.0 Task A – Model Development and Utilization

Analytical Model Analysis to Show Critical Properties

Simulation models were employed to better understand the many parameters that are involved in chemical transport of explosive residues in soil. The first model used was the Behavior Assessment Model for Trace Organics in Soil (Jury et al., 1983, 1984a, 1984b, 1984c, and 1991). Application of the phase partitioning components of this model showed that the mass fractions of TNT and DNT in soils were predominantly sorbed to the soil particles (90+%), the majority of the remaining mass is dissolved in the soil pore water (10+%), and only a trace is found in the soil gas (~ 10^{-6}%). These chemicals are principally transported through soils in the aqueous phase, with a significant influence from soil moisture content and precipitation/evaporation.

The Behavior Assessment Model was modified for the case of buried chemicals (Jury et al., 1990) resulting in the Buried Chemical Model. This one-dimensional model was very useful in categorizing the relative mobility, volatility and persistence of TNT, DNT and DNB chemicals in relation to other well characterized agricultural chemicals. This initial analysis only required a simple set of input parameters: soil-water partitioning coefficient (K_d), soil-air partitioning coefficient (Henry's constant, K_H), diffusion coefficient in air (D_G), and the bio-chemical half-life ($T_{1/2}$).

The Buried Chemical Model was used to evaluate the effect of differing soil properties, water flux conditions and sequences on the behavior of TNT, DNT and DNB. The surface vapor flux was evaluated as this was considered to be the principal method for sampling and analysis of buried UXO. This sensitivity analysis was presented in three conference proceedings (Phelan and Webb, 1998a; Phelan and Webb, 1998b; Webb et al., 1998) and in a project report from Dr. Jury (Jury and Guo, 1998). Table 2 shows the parameters evaluated and a summary of the impacts.

Table 2. Sensitivity Analysis Summary

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

Dr. Bill Jury performed a 2-dimensional analysis (Jury and Guo, 1998) to evaluate the surface soil spatial variation in vapor flux. This showed that the surface vapor flux was greatest directly above a source with a small halo up to twice the length of the buried source. However, the flux drops off exponentially with lateral distance.

While the Buried Chemical Model was valuable for an initial assessment, the one-dimensional assumption demands that the buried UXO itself is permeable, and the assumption of constant liquid content, both spatially and temporally, is obviously a great simplification. In order to address these and other issues, a multidimensional mechanistic code was modified for application to this problem. This code, which is based on the TOUGH code from Lawrence Berkeley Laboratory (Pruess, 1987, 1991), considers air, water vapor, and explosive chemical mass and heat flow in a porous media and is able to address many of these questions. This code has been named T2TNT.

Modifications to TOUGH2 to produce T2TNT:

1. Chemical Components – UXO/landmines typically emit TNT, DNT, and DNB vapors. The behavior of each of these chemicals is different (vapor pressure, vapor/liquid, liquid/solid, and vapor/solid partitioning), so each component is modeled separately with unique properties specified for each chemical.
2. Gas Diffusion – Gas diffusion can be a dominant transport mode for explosive vapors in the subsurface, especially for low moisture content conditions. In order to mechanistically model gas diffusion in a porous medium, the Dusty Gas Model (Webb, 1998) has been implemented.
3. Liquid Diffusion – Liquid diffusion can be a dominant transport mode for explosive vapors in the subsurface, especially for moderate and high moisture content conditions. Liquid diffusion was not present in the original version of TOUGH2. Liquid diffusion using Fick's Law has been included because of the significant chemical concentration in the liquid phase.
4. Liquid-Solid Sorption – The solid-liquid partition coefficient was determined to be a fairly sensitive parameter for soil partitioning and transport (Phelan et al., 1999). Laboratory determined values showed that the sorption isotherm was not linear and followed more of a Freundlich relationship (Phelan and Barnett, 2001). In addition, liquid-solid sorption may not be constant over all soil moisture contents (EPA, 1999). Thus, in T2TNT the liquid-solid sorption coefficient has been incorporated as a Freundlich sorption isotherm that is a linear function of liquid saturation.
5. Vapor-Solid Sorption - Vapor-solid sorption is significant for explosive vapors at low soil moisture contents. The experimental data is well described by the Petersen et al. (1995) function, which was originally developed for volatile organic compounds. The Petersen et al. (1995) expression has been incorporated into T2TNT with TNT and DNT specific parameters.
6. Biodegradation – A simple half-life approach has been implemented to model biodegradation of the explosive vapors.
7. Surface Boundary Conditions – Due to the shallow burial depth of many UXO/landmines, the fluid conditions surrounding the UXO/landmine are strongly influenced by the surface conditions. The parameters necessary to adequately model the surface boundary conditions are numerous, including solar and long-wave radiation, the surface boundary layer that is a function of wind speed and other parameters, precipitation and evaporation at the surface, plants and their root systems, and the diurnal and seasonal variation of these parameters. The models used for these boundary conditions are discussed in more detail below.
8. Capillary Pressure Curve - The typical representation of the capillary pressure curve breaks down at low liquid saturations. The curve considers a liquid residual saturation where the capillary pressure goes to minus infinity. Below this residual saturation, the capillary pressure is undefined. In order to alleviate this situation, a methodology has been developed to extend the capillary pressure curve to include the dry region down to zero liquid saturation. This technique results in a finite value of the capillary pressure below liquid residual saturation, which agrees with the available data (Webb, 2000).
9. Numerical Solution - T2TNT has been developed from the TOUGH2 code. In the initial development, the explosive vapors were added as separate components, and a fully coupled solution was performed for the air, water, and explosive compounds TNT, DNT, and DNB. In order to improve the numerical performance of the code, the trace gas nature of the explosive compounds has been exploited to separate the solution of the air and water components from the explosive compounds. This separation allows for the solution of smaller matrices and results in faster execution times.

Surface Boundary Conditions

The surface boundary conditions discussed above are complex in their own right. Numerous models have been developed to analyze the soil-air-plant system. In order to expedite the inclusion of the important surface conditions into T2TNT, a number of existing models have been evaluated. As a result, the SiSPAT model developed by Braud et al. (1995, 1996) has been selected for inclusion into T2TNT with the kind permission of M. Vauchlin of LTHE in Grenoble, France. Subroutines from SiSPAT have been included directly into T2TNT as necessary.

SiSPAT has been applied to a number of field studies as documented by Braud et al. (1995, 1996), and Boulet et al. (1997), and more are in progress. Therefore, SiSPAT provides a well-documented and tested approach for modeling the soil-plant-atmosphere interface in the T2TNT code.

At the present time, the surface boundary conditions for a bare soil have been implemented, including the surface boundary layer, solar and long-wave radiation, precipitation, and other conditions including the diurnal and seasonal variation of the parameters. Incorporation of the plant portion of the SiSPAT model into T2TNT was postponed due to limited project resources.

T2TNT Comparison to Buried Chemical Model

As part of the verification process for T2TNT, comparison to results of the one-dimensional screening model presented by Phelan and Webb (1997) have been performed. The precipitation/evaporation cycles were not included in this simulation in order to provide comparison with the buried chemical analytical solution of Jury et al. (1990). Note that some of the assumptions made in the analytical model can only be approximated in the numerical code, such as uniform moisture content. In addition, there are differences in the gas diffusion model, which could lead to slightly different answers. However, in general, the analytical and numerical problems were essentially equivalent (Phelan and Webb, 1999).

3.0 Task B - Fundamental Properties

This task involved the measurement of specific transport parameters not currently available in the literature for TNT and DNT. These include temperature dependent water solubility, liquid-solid sorption, vapor-solid sorption as a function of soil moisture content, and rates of biochemical degradation.

Water Solubility Tests

Water solubility data for TNT was prevalent and appeared to be of good quality. Water solubility data for DNT was sparse with only one set of temperature dependent data found tabulated in a military handbook (U.S. Army, 1971). Therefore, temperature dependent DNT water solubility tests were completed. TNT data were collected to validate our techniques.

Results of the water solubility measurements showed that our method produced comparable data for TNT to other reported data and the DNT results were very different from the Military handbook (Phelan and Barnett, 2001a). Figure 2 shows the DNT results and Figure 3 shows the TNT results.

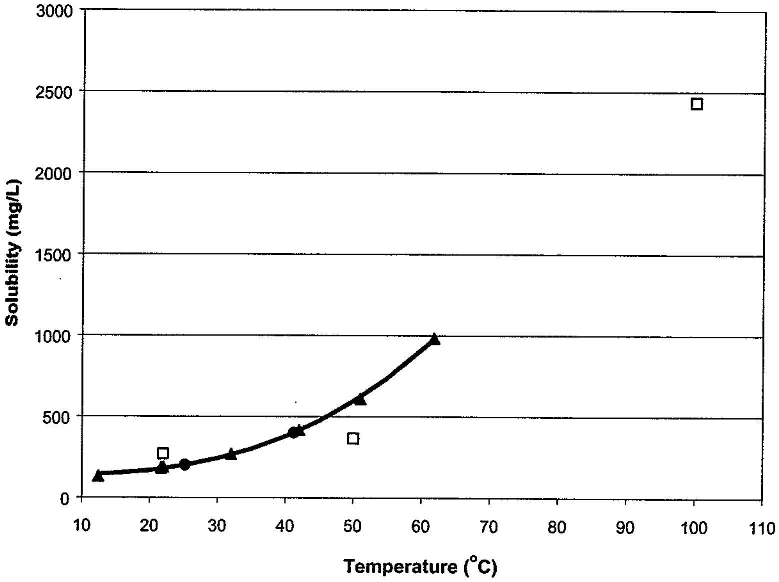


Figure 2. DNT Solubility: (□)Army Materiel Command (1971); (▲)This study, rising to temperature; (●) This study, falling to temperature; (-----) This study curve fit.

An empirical relationship of water solubility was developed for use with T2TNT. A simple power function was determined by curve fitting (Table Curve 2D, Ver. 4, SPSS Inc.) with the results shown in Table 3.

Table 3. Aqueous Solubility Empirical Correlation [$y = a + b(T/°C)^c$]

	a	b	c
DNT	135.59	0.0064382	2.8569
TNT	86.045	0.0034874	2.9131

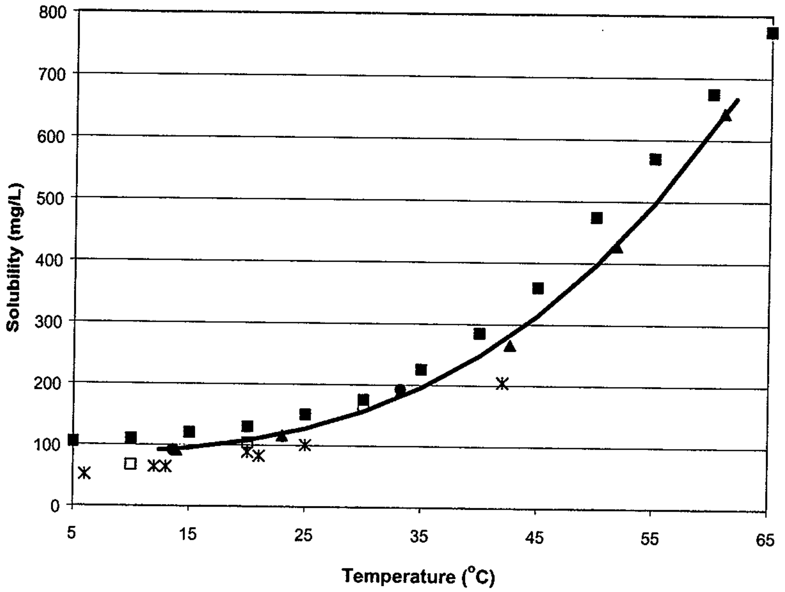


Figure 3. TNT solubility: (■)Taylor and Rinkenbach (1923), interpolated data; (▲)This study, rising to temperature; (●) This study, falling to temperature; (*) Ro et al., 1996; (□) Spanggord, 1983; (-----) This study curve fit.

Soil-Water Partitioning Tests

Measurement of the soil water partitioning parameter has been extensively studied for many organic compounds. To provide comparable values for explosive constituents, we followed the protocol established by Pennington and Patrick (1990). We selected surface soil located adjacent to the Sandia National Laboratories minefield test site as these soils were used for the soil column tests described in Task C. Details of the methods, materials and results are reported in Phelan and Barnett, 2001b.

Two tests were completed. The first was for low solution concentrations of 2,4-DNT and the second was for high concentrations that were planned for injection into the soil column described in Task C.

For the low concentration solutions, the linear soil water partitioning coefficient (K_d) value was 1.7 mL/g. For the higher solution concentrations, the linear K_d value drops to 0.61. This indicates that a Landmuir or Freundlich model probably better represents the sorption isotherm than a linear one. When fitted to a Freundlich, the DNT data indicate a $K_f = 2.1$ and $n = 1.3$ ($R^2 = 0.993$).

Measurement of the soil water partitioning coefficient for 2,4-DNT was also evaluated by Pennington et. al. (1999) for soils found at the DARPA test minefield site at Fort Leonard Wood, MO. For the FLW soils, the mean (std. dev.) K_d for 2,4-DNT was 2.9 (1.4) mL/g. The value obtained for the Sandia soil was slightly less, but within the range found for the FLW soils.

Soil-Vapor Partitioning Tests

Soil vapor partitioning has been explored in relation to pesticide volatilization with several reports greater volatilization with wet soils than with dry soils (Spencer and Cliath, 1973). Computational and experimental work demonstrating moisture content dependent vapor phase sorption has been conducted for the industrial pollutant trichloroethylene (Petersen, et al., 1996; Ong and Lion, 1991a and b; Culver et al., 1991; Ong et al., 1992). Since UXO is present in the near surface soils, which may experience extreme variation in soil moisture content, we believed that measurement of the soil vapor partitioning parameters was critical to the understanding of static soil to soil vapor correlation and the dynamic transport of chemical residues from buried UXO.

The impact of soil moisture on the soil-vapor partitioning coefficient ($K_{d'}$) was evaluated using a sensitivity analysis of the input parameters (Phelan and Webb, 1999). Since no data existed for TNT or DNT, and a sensitivity analysis showed how critical $K_{d'}$ was in depressing vapor levels in dry soils, a laboratory test was devised to measure the soil vapor partitioning parameters as a function of soil moisture content. Phelan and Barnett, 2001a contains the details of the materials, methods and results. Figure 4 illustrates the impact of soil moisture content on the soil-vapor partitioning coefficient ($K_{d'}$) for TNT and DNT on soils. This shows that for a soil containing a fixed total concentration of TNT or DNT, the headspace vapor concentrations can vary over about 10^5 as the moisture content changes from 1 to 11% (wt/wt). The model proposed by Petersen et al., 1995 correlates very well with this data set (R^2=0.98). We have incorporated the numerics of Petersen et al., 1995 into T2TNT with the TNT and DNT specific coefficients.

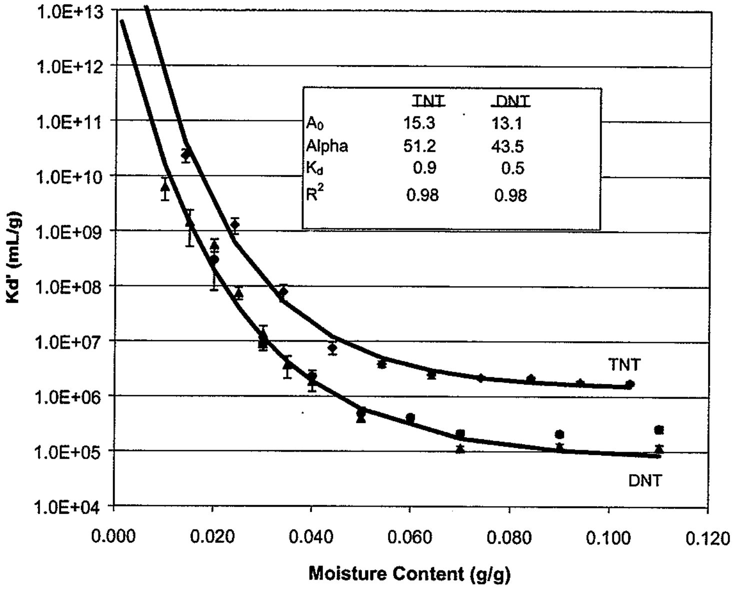


Figure 4. DNT and TNT Data and Model Comparisons

Biochemical degradation

This project recognized at the outset, that the utility of chemical sensing for buried UXO depended on the rates of release of chemicals from the UXO item, transport through soils, and loss through biochemical degradation. This project planned to focus on source release and transport phenomena, and evaluate biodegradation rates as reported in the literature rather than through detailed experimental work.

Loss of explosive residues in soils occurs through combined natural biological and abiotic processes is a very complex phenomenon. To support development of a time dependent simulation assessment for chemical sensing, rates of biochemical degradation are needed. Degradation processes are typically modeled as a simple first order or psuedo-first order process (Sawyer et al., 1994). This simplifies the model input as a degradation rate constant, or half-life, that is independent of the chemical concentration or environmental factors. However, this simplification may lead to significant over or under estimates of the degradation rates due to variations in temperature, moisture content and soil type.

Biochemical reactions take place principally in the aqueous phase, making sufficient soil moisture a necessary component to promote degradation. Increases in temperature increases rates of both biological and abiotic chemical reactions. Population densities of biological communities in soils vary dramatically in time as favorable growth conditions fluctuate.

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

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

For the purposes of maximum holding times, Grant et al., 1993 did not report degradation rate constants. However, these data were re-evaluated in George et al., 2000 along with new data using soil from the Fort Leonard Wood minefield test site. The data did not show true psuedo or actual first order decay rates. In fact, there was an initial fast decline followed by a more moderate decline. Using the initial fast decline, an estimate of the half-life in the loam soils was estimated for TNT to be on the order of 1-3 days at 22°C and for DNT to be about 20 to 60 days. For the clay soil, these values were < 1 day at 22°C. At -4°C, these half-lives increased to 20 to 80 days for TNT, and 90 to 230 days for DNT in the loam soils.

In an evaluation of degradation rates of post-blast residue from detonated landmines, Phelan et al., 2001 (in prep.) varied the soil moisture content with synthetic soil prepared by solid phase enrichment methods. Results from this work showed that at soil moisture contents of 1%(w/w), there was virtually no loss of TNT or DNT over 80 days. However, with soil moisture at 5% and 10%(w/w), the degradation proceeded very quickly. The degradation kinetics were not first order, with a fast initial phase followed by a much slower long term decline, similar to that found by Grant et al., 1993.

These results confirm that degradation rates are quite variable, dependent on soil type, temperature and soil moisture content; and, simple first order degradation kinetics do not properly describe the loss process. Developing quantitative values for use in simulation models will take much more work than is available in this project. As a compromise and to complete the objectives of this project a simple, constant half-life of 30 days was selected for preliminary analysis using simulation models.

4.0 Task C - Laboratory-Scale Experiments

This task involved a laboratory validation study that compared the most critical parameters included in the simulation model through soil column transport experiments. Laboratory-scale soil column experiments were designed after Petersen et al. (1996) and Spencer and Cliath (1973). Both methods used headspace measurements to estimate flux of organic chemical from the soil surface. We used the soil suction control apparatus of Spencer and the soil moisture measurement approach of Petersen et al. (1996). Figure 4 shows a picture of the soil column test apparatus. Details of the experimental methods, parameter estimation and model formulation are described in Phelan et al, 2000.

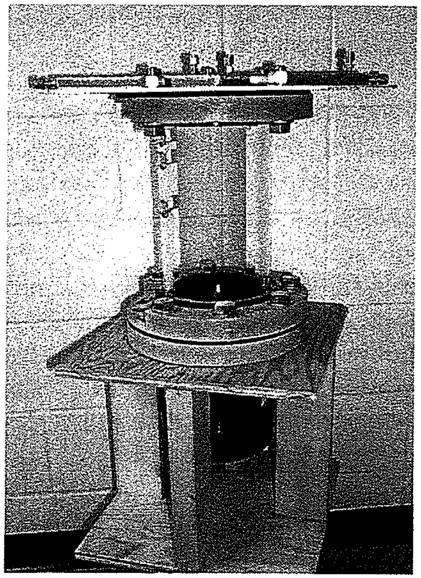


Figure 5. Laboratory Soil Column Test Apparatus.

In the design of this test, soil moisture of about 0.25 cm^3/cm^3 was desired to maintain the soil pore space at about 50% saturation. Data from the water content reflectometers showed that the soil moisture distribution remained relatively constant over the test duration and showed an expected gradient with higher moisture contents at the bottom of the soil column.

The surface flux of DNT was measured in the experiment using Solid Phase Micro Extraction (SPME) fibers. The flux of DNT in the plenum increased by about 10^4 over the duration of the test (Figure 6). The experiment was sacrificed on day 29 and samples were collected for soil moisture and DNT residues. Simulation results from T2TNT were compared to the data and are also shown in Figure 6. Based on the soil-water partitioning coefficient data the low range liquid-solid sorption coefficient, K_d, of 1.5 mL/g was selected for the initial simulations to compare to the data. As shown in Figure 6, while the surface flux as a function of time has the right shape, the values are an order of magnitude or more below the experimental data.

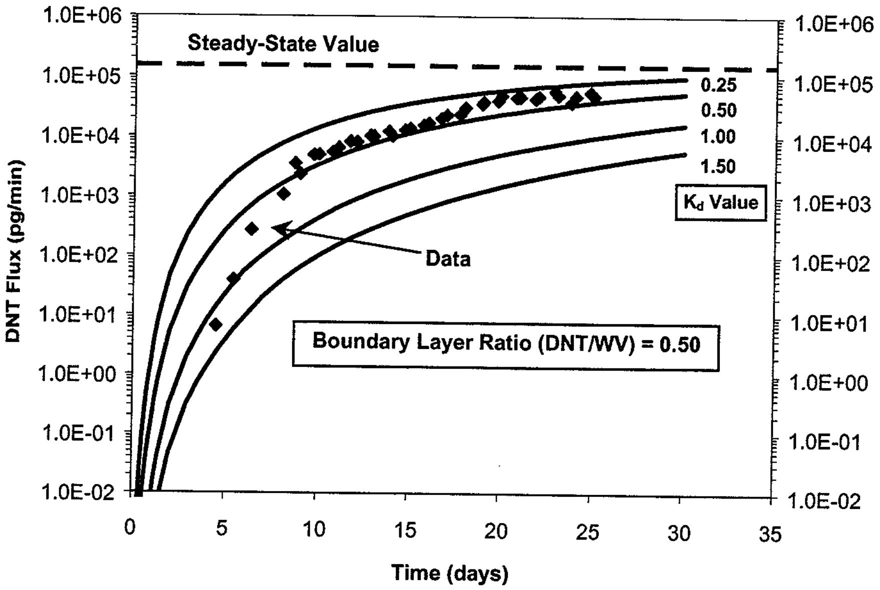


Figure 6. Data Model Comparisons - Effect of K_d Value

The sensitivity of the K_d factor is readily apparent in Figure 6. At this stage of the project, the Fruendlich soil-water partitioning isotherm had not been incorporated into T2TNT. Another factor causing the discrepancy in values obtained from measured K_d versus data-model comparisons is in how the measured K_d is obtained. The low soil:water ratio in the batch equilibration K_d method allows for near complete contact of the soil particle surface to the DNT in the water and allows for migration into secondary porosity of soil minerals. In a soil column test this is not the case. Some proportion of soil surface area is not in contact with the water (and DNT) due to partial saturation and surface-to-surface contact of soil particles. Because of the uncertainty in the value of K_d in the soil column test it was decided to vary the value of K_d until a reasonable match to the data was found as given in Figure 6. The final value of K_d that matches the data reasonably well is ~0.5 mL/g. The results from this initial test indicated that K_d is influenced by partial saturation of the soils and that this must be incorporated into T2TNT. This phenomena has been previously recognized (EPA, 1999); however, there have been mixed results to define the relationship of soil-water partition coefficient to soil saturation.

A second test was performed using the same apparatus and operating conditions. This test was planned to evaluate the effects of wetting and drying phenomena on the vapor flux of DNT. Details of the materials, methods and results are given in Phelan et al., 2001. The data and model comparison for the surface flux of DNT is shown in Figure 7. Unlike the prediction given by Phelan et al. (2000) in Figure 6, no soil-water partitioning parameters were varied to try to improve the data-model comparison. However, T2TNT now includes a Freundlich isotherm for the soil-water partition coefficient, which is also weighted linearly as a function of soil saturation. The simulation results show excellent agreement with the data, especially considering the three order-of-magnitude variations during wetting-drying cycles. The initial surface flux out to 35 days is very close to the data including the transient variation up to that point. Up through Day 35, surface flux results from Test 1 and 2 were very consistent demonstrating good control of fixed experimental parameters. In Test 2, the increase in the surface flux due to the change in the inlet air relative humidity is seen in the model predictions, although the magnitude of the increase is under predicted. The dramatic change in the surface flux data of about three orders of magnitude caused by the wetting and drying events is also reflected in the model predictions, including the timing. The maximum differences are about a factor of 3, which is excellent considering the 5000-fold change in DNT surface flux.

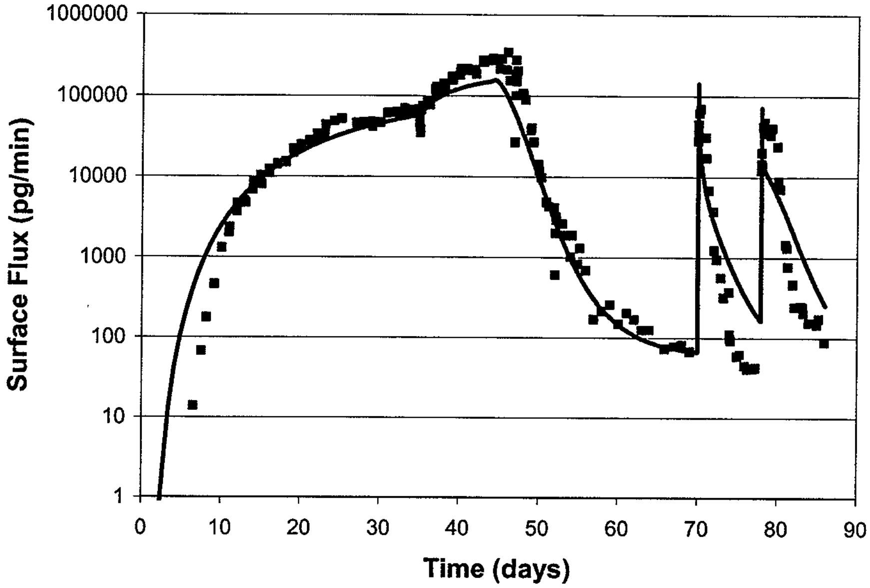


Figure 7. T2TNT Data Model Comparisons

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

The results from this test have shown how important soil-vapor partitioning is to the vapor released by surface soils as indicated by the dramatic rise in the surface flux after wetting. In addition, the soil-water partition coefficient must be modeled with a Freundlich isotherm rather than a linear one, and the soil-water partition coefficient must be weighted for soil saturation.

5.0 Task D - Operational Strategy

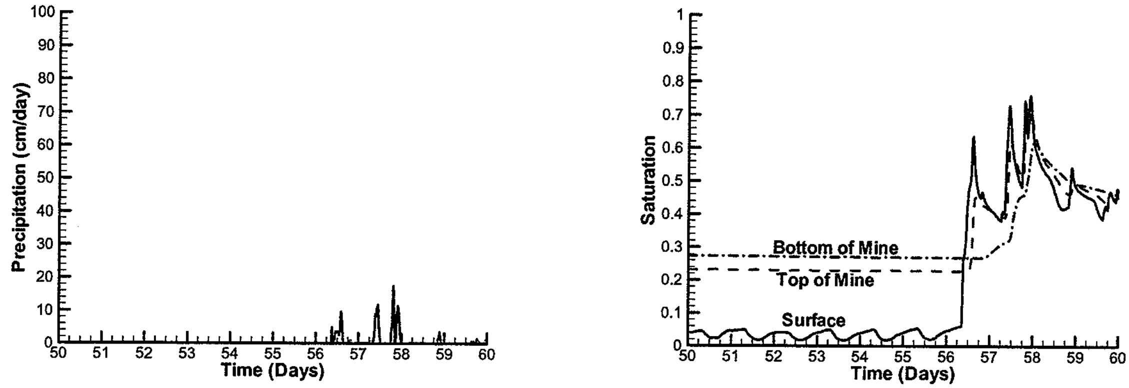
This task was established to use the simulation tools to assess the impacts of environmental conditions on the transport of chemical signature molecules from shallow UXO and to support end-user queries on the utility of chemical sensor platforms for the classification stage in the identification of true unexploded ordnance. The simulation model T2TNT has matured to become an effective tool for such an assessment.

Demonstration calculations were completed with a constant source flux, constant biodegradation rate and variable weather conditions that showed how the vapor concentration in the boundary layer above soils varied over the long-term (1 year) and the short-term (daily). Details on the input data requirements and simulation results can be found in Webb et al., 2000. These calculations used weather data from a standard weather station containing: atmospheric pressure, air temperature, relative humidity, solar radiation, precipitation, wind speed and wind direction at four elevations. In addition to these parameters, the long-wave radiation, which is from the atmosphere, must be included. Because it was not measured, it was estimated from measured weather parameters.

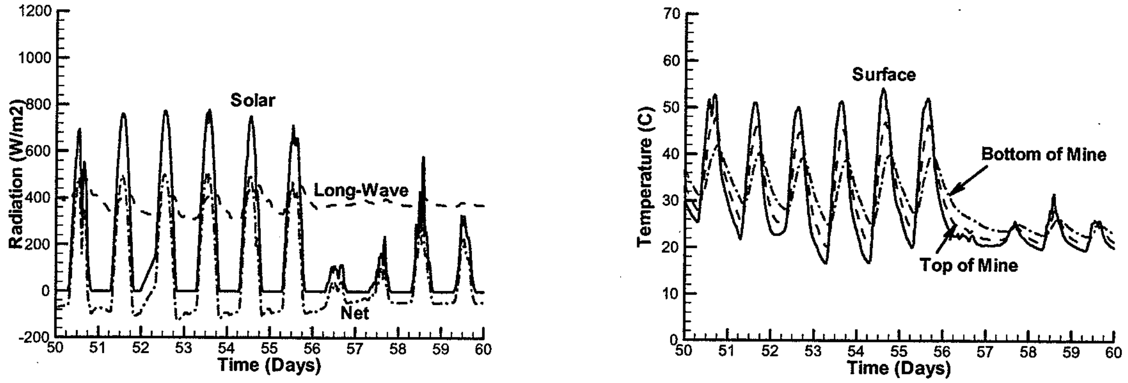
Figures 8 (a) through (h) show the diurnal variation in T2TNT simulation results showing key factors of precipitation and resulting soil saturation, surface radiation balance and resulting soil temperatures at several depths, and chemical concentrations of TNT, DNT and DNB expressed as total concentrations and as separate solid, liquid and gas phase concentrations. Of note is the dramatic increase in surface gas-phase concentrations of all three chemicals following a rainfall event. Figures 9 (a) through (f) show the seasonal variation in T2TNT simulation results showing the surface soil liquid and gas phase concentrations of TNT, DNT and DNB. The seasonal variations in the liquid phase are impacted by changes in soil moisture due to precipitation and the gas phase variations are impacted by changes in the liquid phase concentrations and temperature effects on the vapor-liquid partitioning coefficient (Henry's Law Constant). Of note is the near uniformity of the maximum and minimum values indicated in Figure 9 (a) through (f). This is likely due to the fact that the source release rate and the degradation rate for each chemical are held constant over time, which is a significant simplification.

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

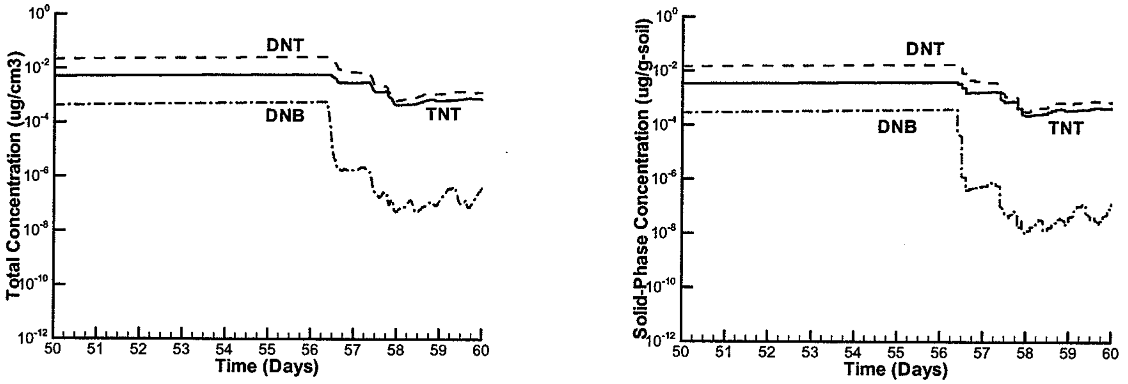
Although T2TNT has shown to be a tremendous asset in the evaluation of chemical sensing for buried UXO, the results from Task E and F have shown a very limited source release of chemicals from UXO. As a result, development of an operational strategy for UXO discrimination was not possible. Nevertheless, for the landmine problem (as this project was co-sponsored by the DARPA Dog's Nose Program), there is value in using T2TNT to develop an operational strategy, and progress is being made in this area in support of humanitarian demining programs.



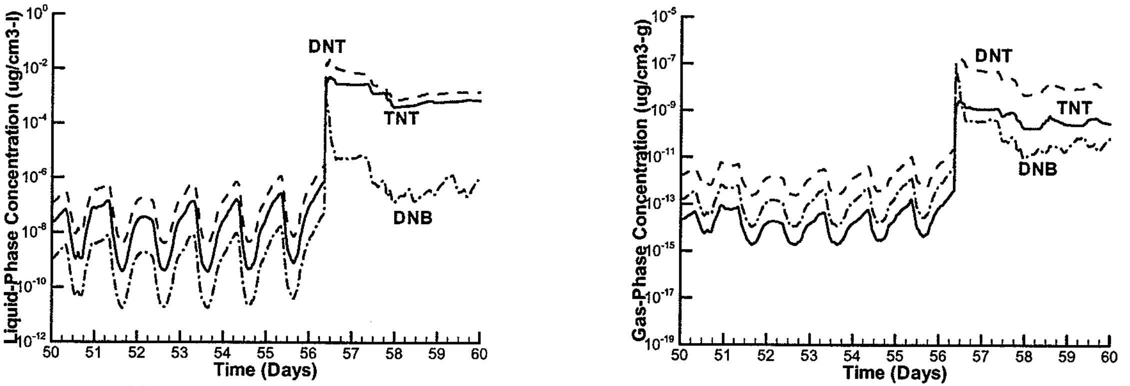
(a) Precipitation (b) Saturations



(c) Surface Radiation Balance (d) Temperatures

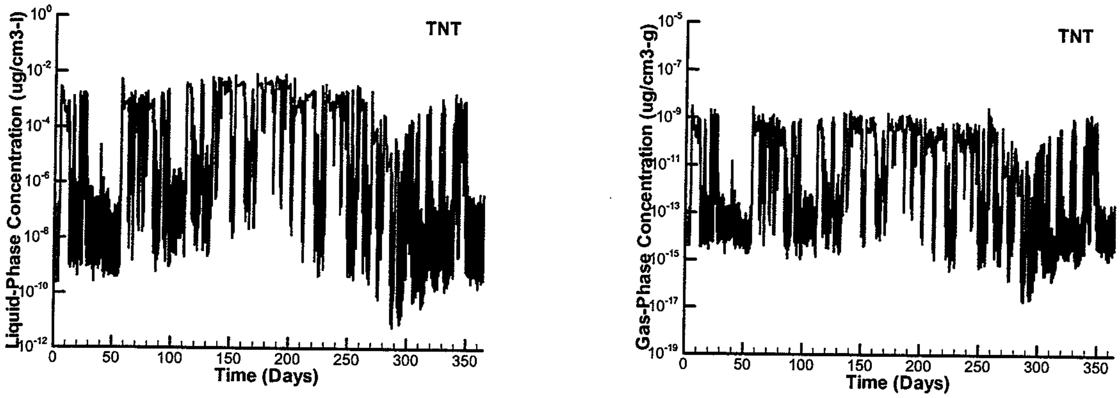


(e) Surface Total Concentration (f) Surface Solid-Phase Concentration



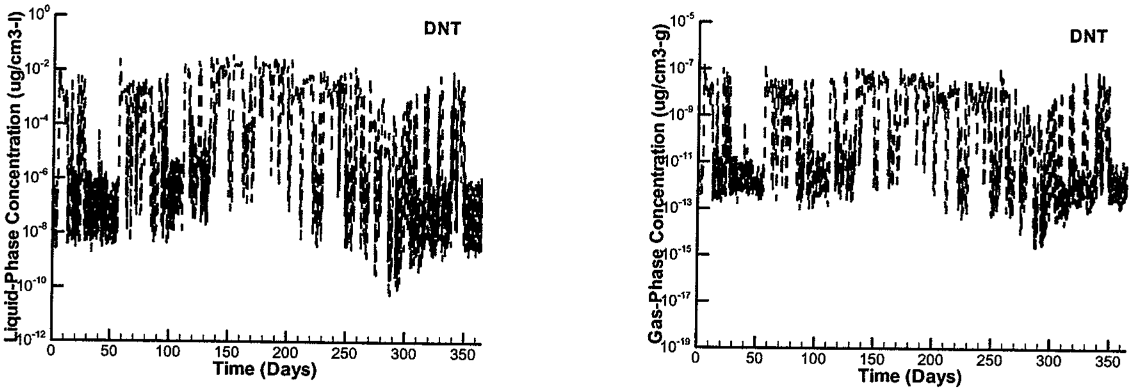
(g) Surface Liquid-Phase Concentration (h) Surface Gas-Phase Concentration

Figure 8. Diurnal Variation of Various Parameters for the Period 50-60 Days



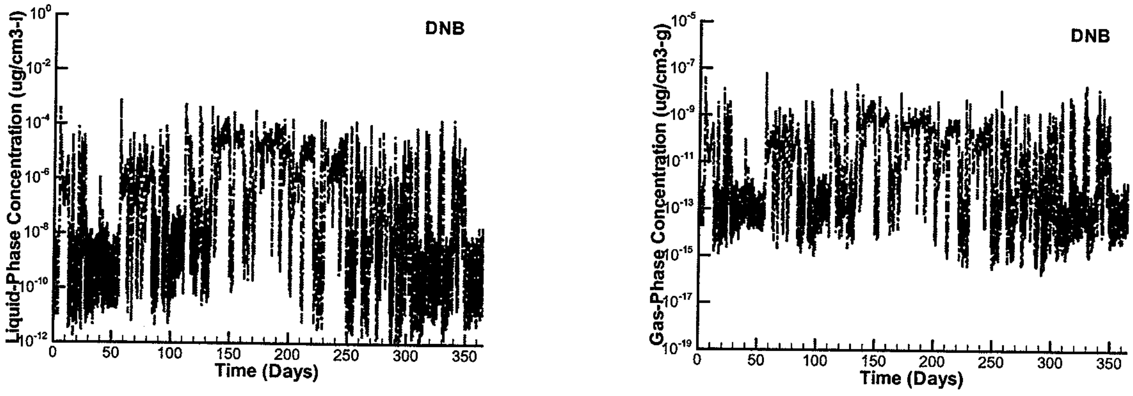
(a) Surface Liquid-Phase Concentration of TNT

(b) Surface Gas-Phase Concentration of TNT



(c) Surface Liquid-Phase Concentration of DNT

(d) Surface Gas-Phase Concentration of DNT



(e) Surface Liquid-Phase Concentration of DNB

(f) Surface Gas-Phase Concentration of DNB

Figure 9. Seasonal Variation of Surface Liquid- and Gas-Phase Concentrations

6.0 Task E - Ordnance Source Term

Use of the T2TNT simulation model to evaluate chemical sensing requires a source term that describes the release of TNT and DNT from the buried UXO. Handling actual field recovered UXO for this purpose is considered unsafe because the ordnance still contains a live firing train, which under the correct circumstances could initiate. To mitigate this safety concern, a plan was devised to create UXO that could be handled safely. Depot-stored ordnance was acquired that contained main charge explosives with either TNT or Composition B (60%RDX/40%TNT). The fuses were disarmed by removing the initiator and booster elements or by using inert fuses. The ordnance was fired with traditional means, located and recovered after impact into the soil. Surface residues were measured with methanol swipe samples. Source release was measured by immersion of the ordnance into water. Full details of the materials, methods, results and discussion can be found in Phelan et al., 2001.

Work scope was organized into the following sequence:

- Ordnance Acquisition
- Pre-Shot Surface Residue
- Pre-Shot Immersion Tests
- Ordnance Firing
- Post-Shot Surface Residue
- Post-Shot Immersion Tests

Ordnance Acquisition

Ordnance acquisition through Rock Island Arsenal began in Fall 1998. While Sandia National Laboratories had previously acquired ordnance from this source, new protocols required execution of a revised interagency transfer agreement between the U.S. Department of Energy and the U.S. Department of Defense. This was completed in late CY 1998. Early in CY1999 the Kosovo conflict placed our acquisition on lower priority. These events caused delayed delivery and initiation of this effort until we received the ordnance in July 1999. Table 4 shows the type and quantity of the units received.

Table 4. Ordnance Received

Ordnance Type	Quantity
60 mm mortar – Target Practice with black powder spotting charge	12
60 mm mortar – HE M49A4 with PD fuze for M2 and M19 mortar. Comp B. Loaded 7-75.	12
81 mm mortar – Target Practice with black powder spotting charge	12
81 mm mortar – HE M43A1 with PD fuze. TNT. Loaded 7-53.	12
105 mm artillery – Target Practice	12
105 mm artillery – M760 Dualgram w/ supplemental charge for howitzer M119 only. TNT. Load date unknown.	12

Pre-Shot Surface Residue

The amount of chemical residue on the exterior surface of the ordnance items will directly influence the initial release of chemical into the environment. Collection of the surface residues was performed using two methods.

- Surface residues were transferred to filter paper soaked with methanol (swipe samples), and
- Paint was scraped from ordnance items.

Chemical leakage over long time periods would be derived from the main charge, passing through assembly seams or damaged locations on UXO. Long-term leakage was measured with aqueous immersion tests, using repetitive time sequenced samples.

Figure 10 shows a comparison of the HE filled rounds versus the TP rounds for each ordnance type. The sample values were scaled up to estimate the total mass per ordnance unit. The error bars represent one standard deviation.

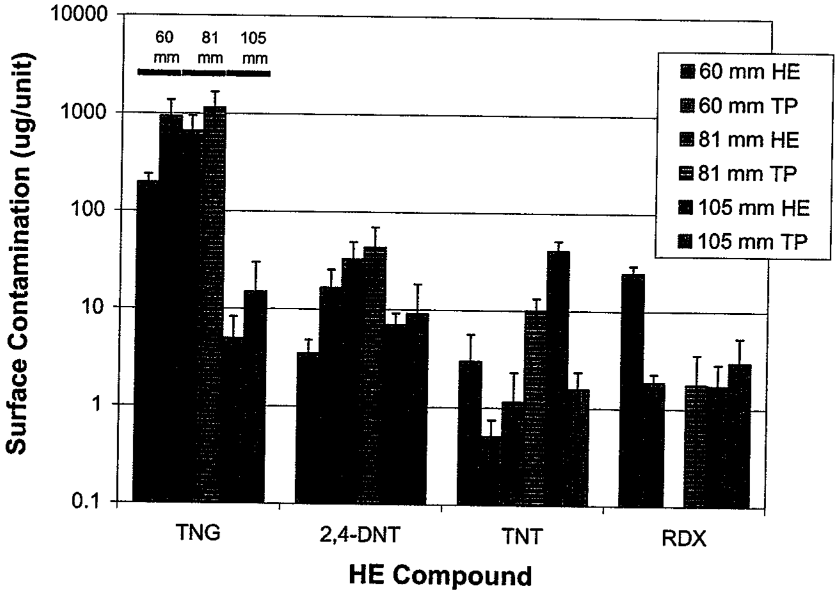


Figure 10. Methanol Removable Surface Contamination for HE and TP Ordnance

The results shown in Figure 10 show an inconsistent trend of HE versus TP surface residues. The mortars contained very high levels of trinitroglycerine (TNG) as this material is used in the propelling charge clipped to the fins on both the HE and TP rounds. During storage in the cardboard tubes, vapors emanating from the propelling charge may deposit on the surface of the ordnance. Since the 105 mm artillery is not exposed to the TNG propelling charge in storage, these levels are significantly less. The presence of TNG on the 105 mm artillery may be due to contamination introduced during manufacturing, handling or storage.

For DNT, the 60 mm mortars show significantly higher levels on the TP rounds. For the 81 mm mortar and 105 mm artillery, the TP ordnance contains slightly higher, but statistically insignificant, amounts of DNT compared to the HE ordnance. For TNT, the 60 mm mortars show greater surface residues on the HE rounds (but not statistically significant). The 81 mm mortars show slightly higher amounts of TNT on the TP rounds. The 105 mm artillery shows significantly less TNT on the TP rounds.

The 60 mm mortars contained Comp B (which contains contains 60% RDX/40% TNT) as the main charge explosive. Detection of RDX on the 60 mm mortars is expected, however, detection of RDX on the 81 mm mortar and 105 mm artillery was unexpected and may also be a result of manufacturing, handling or storage. The lower limit of detection for this method for all compounds is 0.1 to 0.3 µg/mortar or artillery. The average surface contamination was well above the detection limit for each of the compounds shown in Figure 10.

Figure 11 shows the results of the paint scrape tests on the HE containing ordnance.

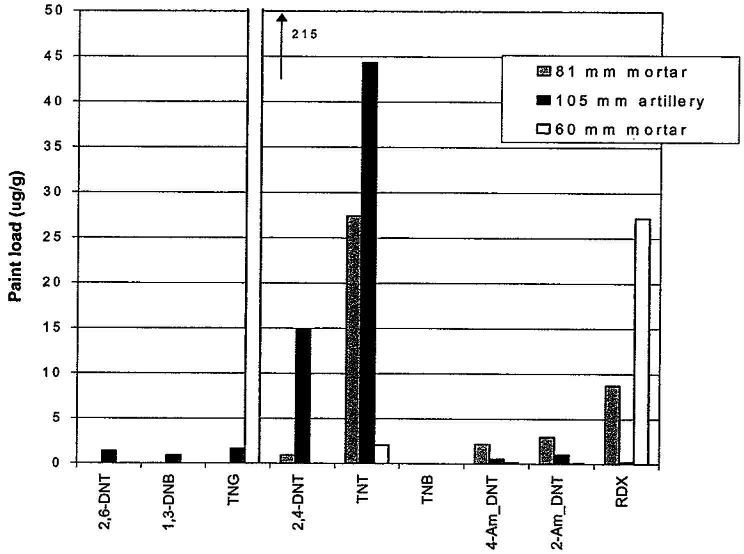


Figure 11. Paint Extract from One Sample Each of an 81 and 60 mm Mortar and one 105 mm Artillery

For the 81 mm mortar, TNG was inadvertently not quantified. There is some consistency with the surface swipe data showing

- the 105 mm HE has significant TNT in both paint and swipe data,
- the 60 mm HE mortar has high TNG and RDX in both the paint and swipe data, and
- and the 105 mm artillery HE has low TNG in the paint and swipe data.

From this limited set of surface residue testing, the results indicate that discrimination of HE from TP rounds would be difficult. For some chemical constituents the TP rounds had similar or greater surface residues, and on others the situation was reversed.

Pre-Shot Immersion Tests

An immersion test apparatus was constructed of stainless steel pipe welded to a flat base plate with a flat plate removable cover. A perforated plate with aircraft cable loop was used to lift the ordnance out of the immersion tube and provide a mixing mechanism. Figure 12 shows a picture of the immersion test apparatus for a 60 mm mortar.

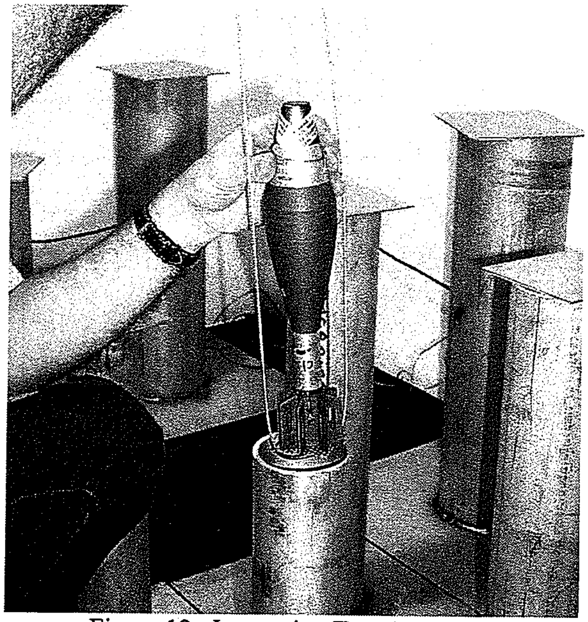


Figure 12. Immersion Test Apparatus

Two ordnance items of each type were selected for the pre-shot immersion flux tests. For the mortars, the propelling charge and initiator train was removed. The fuses and safety wires remained in place. For the 105 mm artillery, the supplemental charge was removed and the plastic cap replaced to limit water filling the supplemental charge well. No fuse was present. The ordnance was placed in the tube and filled with deionized water – over the top of the fuse on the mortars and up to the top of the 105 mm artillery, but not allowing water to pass into the supplemental charge well. A negative control (only deionized water) and a positive control containing all analytes at 10 µg/L were prepared, complete with the ordnance lifting/mixing cable and plate.

Figure 13 shows the data for the positive controls. Of note are the steep to moderate declines of TNT, DNB and DNT which are compounds believed to be important to chemical sensing of buried UXO and landmines (Murrmann et al., 1971). The loss of these compounds in the water solutions introduces challenges when interpreting the flux data from the ordnance items. Charts describing the ordnance are shown as collected and not corrected for loss over time in the positive control solutions. There were no significant explosive constituents found in the negative control solutions.

Figure 14 and 15 shows the results for the long-term flux tests on the 105 mm artillery over time. This chart indicates that the principal compound of interest, DNT, continued to be emitted from the surface over a 65-day period. The estimated flux value at the end of the measurement period is about 1.25 µg/day (based on artillery 105-11). There is no explanation for the sharp decline in TNT and DNT concentrations at about 42 days.

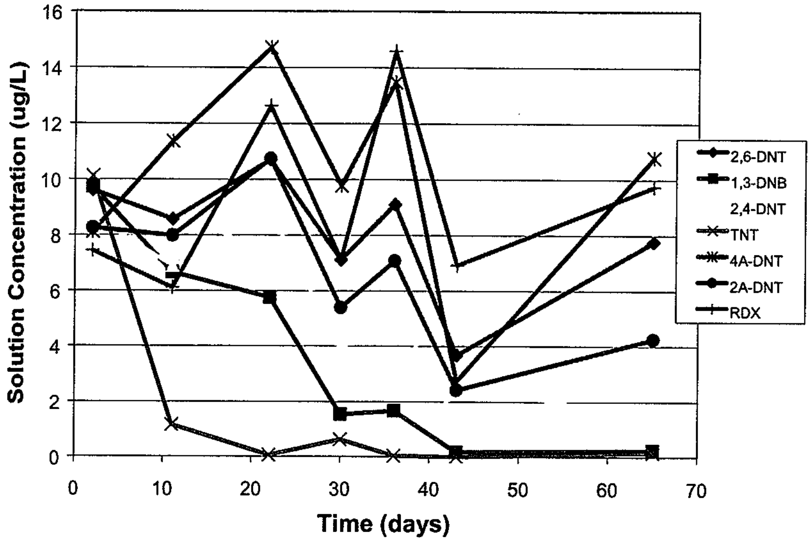


Figure 13. Positive Control (full list)

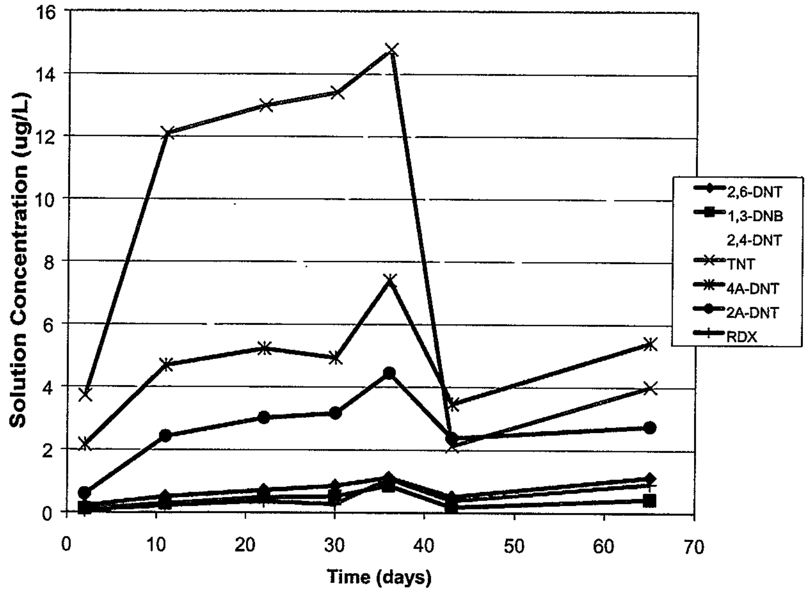


Figure 14. Long-Term Flux Test -105 mm Artillery (number 1)

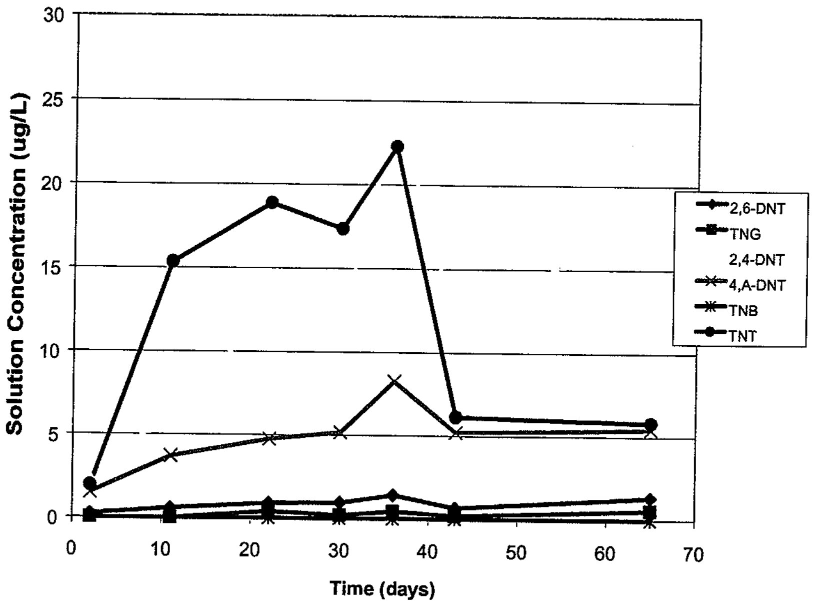


Figure 15. Long-Term Flux Test - 105 mm Artillery (number 11)

For the 81 mm mortars there was no significant flux for any of the compounds except for TNG, which is consistent with the high TNG surface residue data. For the 60 mm mortars there was no measurable flux for any of the compounds except for RDX, which declined quickly. The 60 mm mortars are filled with Comp B, which contains RDX. It is unknown why there was not a similar trend for TNG as with the 81 mm mortars.

The long-term tests with both the 60 and 81 mm mortars were terminated early, as a significant amount of iron oxide (e.g. rust) was observed in suspension in the water. The mortar fuse safety wires appeared to be the source of most of the rust and concern over safety led to removal of the mortars from the immersion tubes. It is possible that the suspension of rust could have sorbed or acted as a catalyst for degradation of the explosive constituents.

The pattern of chemical release into water in these pre-shot tests was inconsistent among the ordnance tested. The 105 mm artillery showed a general increase in chemical concentration for all analytes over the test period. However, for the mortars there were fewer analytes and all were at or near the analytical method detection limit. This was most likely due to the accelerated degradation of the analytes in the immersion test solution from the suspension of iron oxides derived from the safety pin wires. Degradation of these analytes in soils is a complicated process; however, the degradation rates observed here are not inconsistent with the moderate to fast degradation rates observed by others (Grant et. al, 1993 and 1995; Maskarinec et al., 1991).

Ordnance Firing

The mortars were fired at Sandia National Laboratories by the Marine Corps Programs Department, Fallbrook, California during the week of April 3, 2000. Explosive Ordnance Disposal technicians removed the primary explosives from all twelve of the 60 and 81 mm mortar fuses using specialized equipment.

The mortars were transported to Technical Area III and fired to the South. Figures 16 and 17 show the firing position and target location, respectively. To improve the chances of locating mortars downrange, only one propelling charge was used on each mortar. Target distance was set for about 400 to 800 meters. Figure 18 shows the impact depth of an 81 mm mortar. The 60 mm mortars were similar, or with slightly more penetration. The impact area soil is a sandy loam with few stones.

Figures 19 and 20 show the impact damage to the mortars. The paint was slightly burned and the fuse cap was slightly dented on each mortar. The immersion tests were initiated the following day.

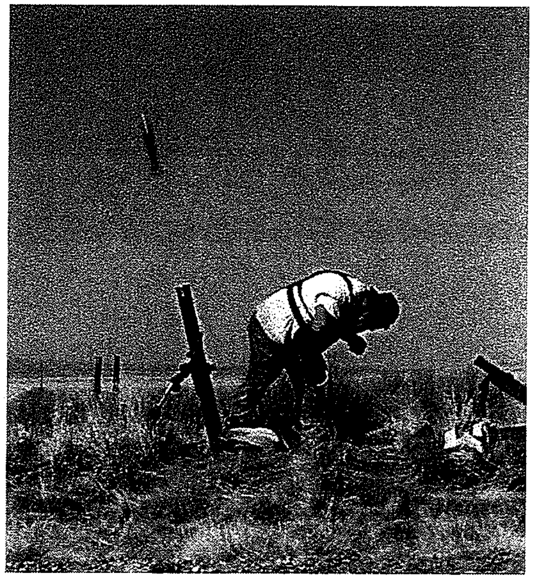


Figure 16. Mortar Firing Position

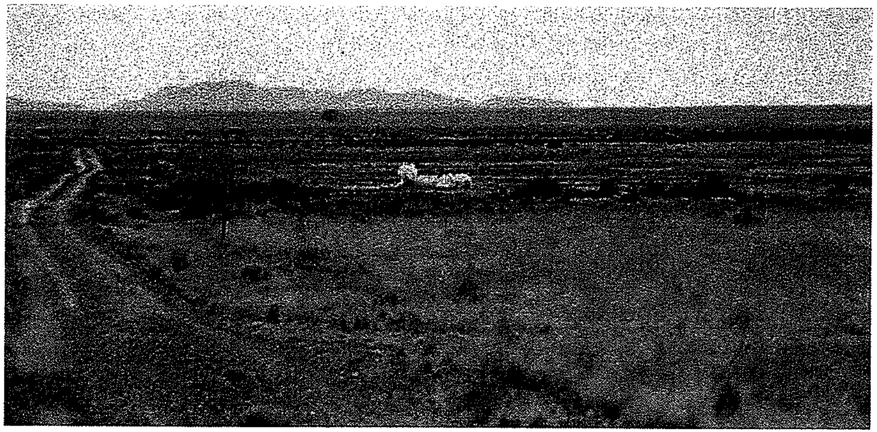


Figure 17. Mortar Target Location

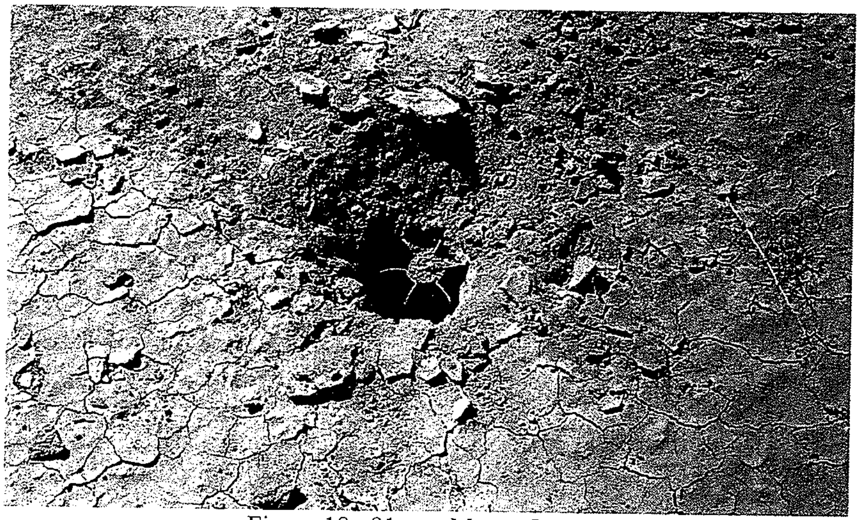


Figure 18. 81 mm Mortar Impact


Figure 19. Recovered 81 mm Mortars

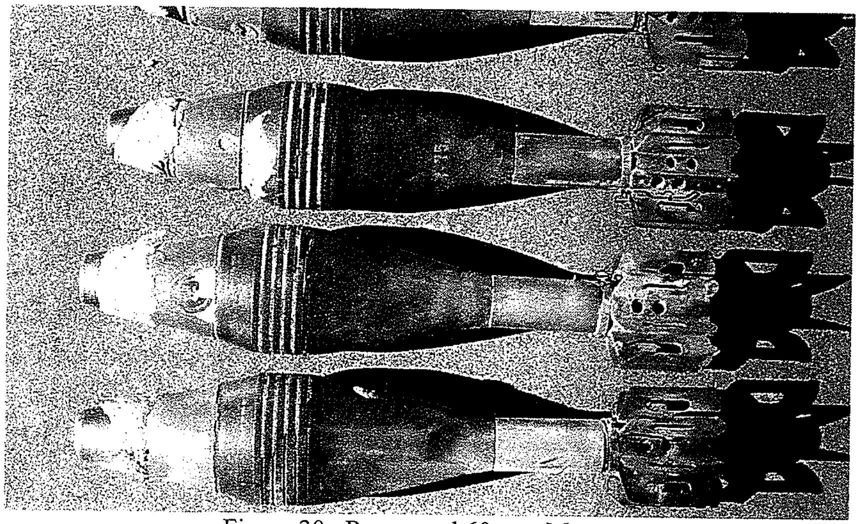


Figure 20. Recovered 60 mm Mortars

A Sandia National Laboratories owned mobile howitzer was used for the 105 mm artillery shots. To make retrieval practical, a 15-degree slope ramp was cut into the soil exposing a vertical face about 8 feet high. The mobile howitzer was placed on the ramp about 18 feet from the face of the excavation (Figure 21).

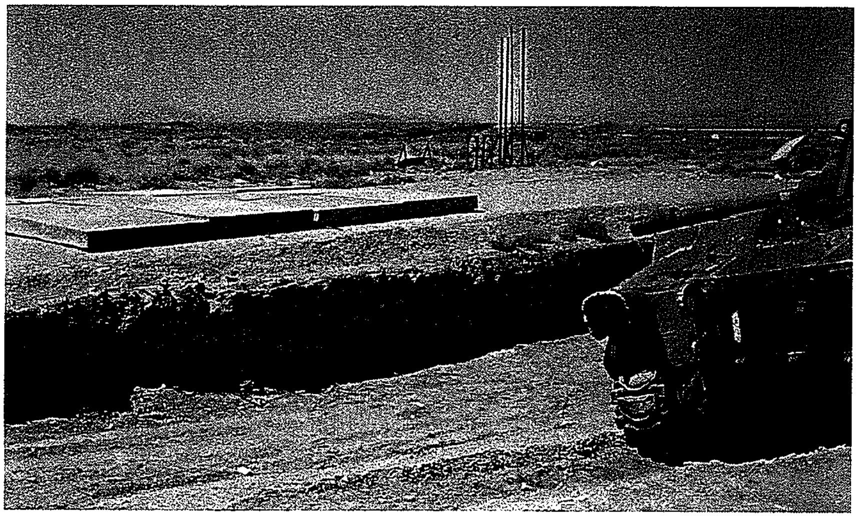


Figure 21. Mobile Howitzer and Target Location for 105 mm Artillery

Soil penetration tables (U.S. Army, 1965) were used to estimate the path length of the 105 artillery shell in this configuration. These tables indicated a trajectory length of about 10 to 20 feet. However, the trajectory path is noted to be straight for two-thirds of the length and then curve near the end. Large concrete slabs were placed on the surface about 8 feet back from the face of the excavation as a safety precaution in case the artillery trajectory turned to the surface.

Figure 22 shows the ejected soil from a target practice round shot on April 7, 2000.

Figure 22. Target Practice Round Shot

Figure 23 shows the impact crater from the first shot. Two target practice rounds were fired before recovery action began.

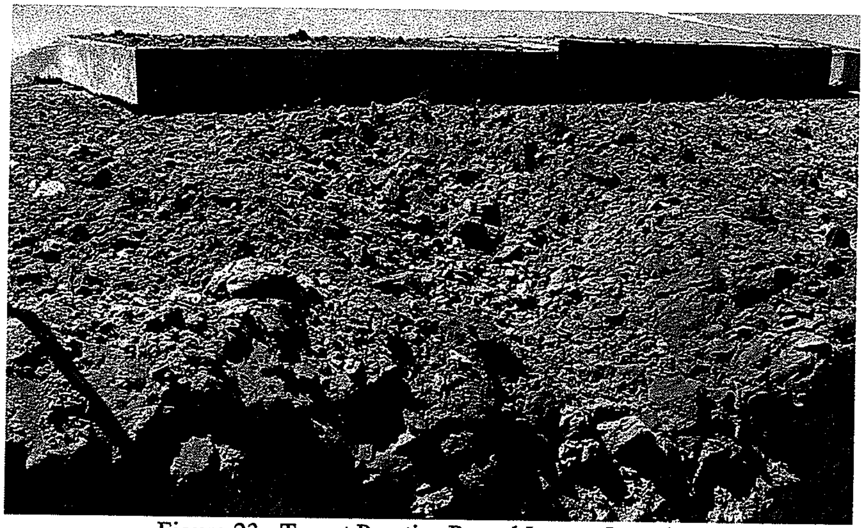


Figure 23. Target Practice Round Impact Location

Figure 24 shows the recovered target practice rounds. The nose cones broke free from the body on both of the rounds. Both items were located about 7-8 feet in from the face of the excavation and about 4 feet below the surface. These are less than the soil penetration table estimates. This is likely due to nose cone damage making penetration more like a blunt nose shape.

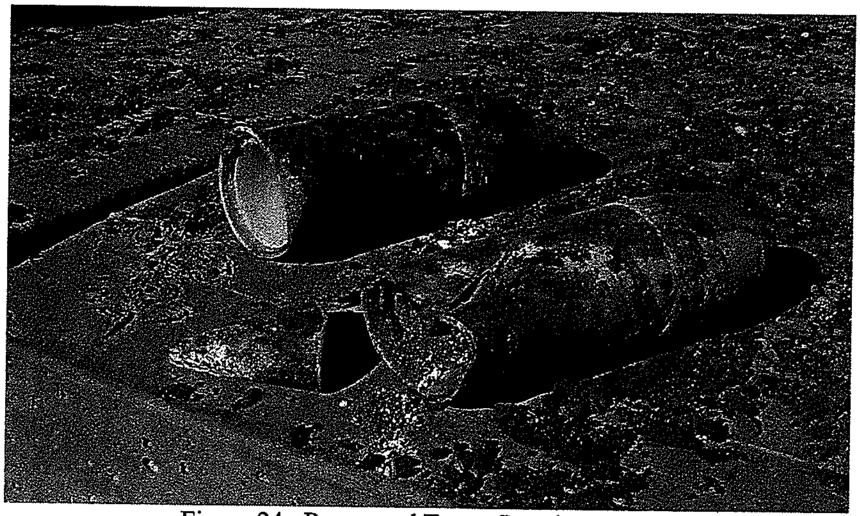


Figure 24. Recovered Target Practice Rounds

On April 8, 2000, the 105 mm artillery HE rounds were fired. An inert fuse was attached to each round and fired with a full bag of propellant. Figure 25 shows a picture of the debris cloud from this shot. The soil ejected from this shot was much greater than for the target practice round. Two rounds were fired prior to recovery actions. Recovery action found that both of these shots resulted in low order detonation of the artillery. Figure 26 shows evidence of neat HE main charge remaining on the interior of a piece of fragment. Figure 27 shows the number of pieces recovered from both low order detonations. There was a large number of soil aggregates containing black soot residue (Figure 28). This black residue was scraped from the soil surface, extracted 5:1 with acetonitrile and analyzed by GC/ECD for explosive constituents. Table 5 shows the results, which indicate very high levels of explosive residues. The analytes shown in Table 5 also give a good indication of the distribution of reaction products formed by the detonation. These are good candidates for evaluation at military firing ranges.

Table 5. Explosive Residues from Soot on Soil (Figure 28) ng/g

2,6-DNT	2,4-DNT	DNB	TNT
420	4,040	300	1,382,500
TNB	4A-DNT	2A-DNT	RDX
3,600	970	1,670	not detected

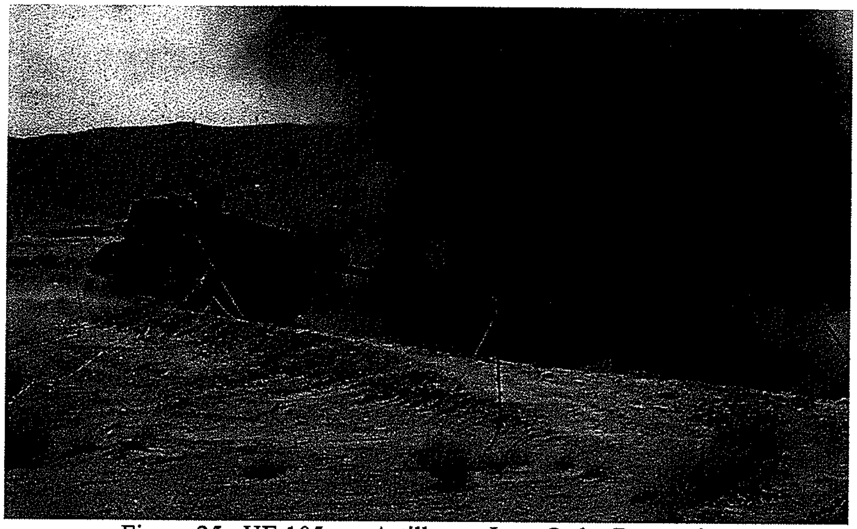


Figure 25. HE 105mm Artillery – Low Order Detonation

Figure 26. HE Residue on Frag from Low Order Detonation

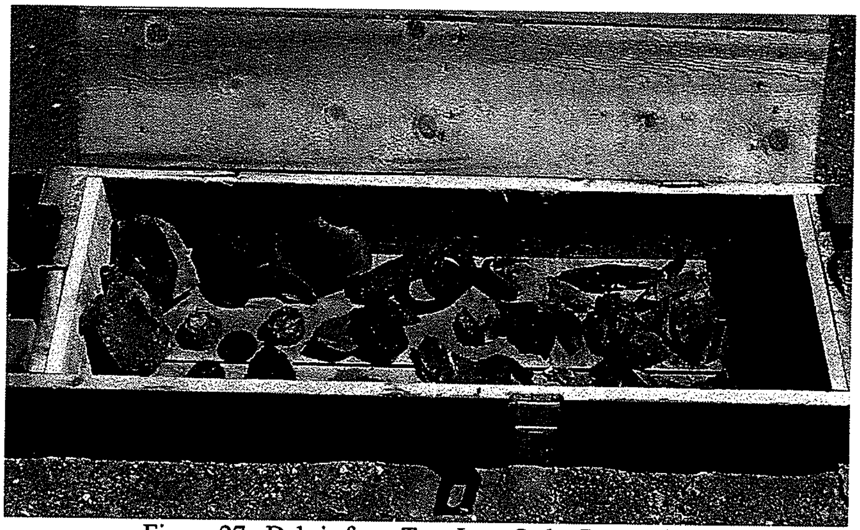


Figure 27. Debris from Two Low Order Detonations

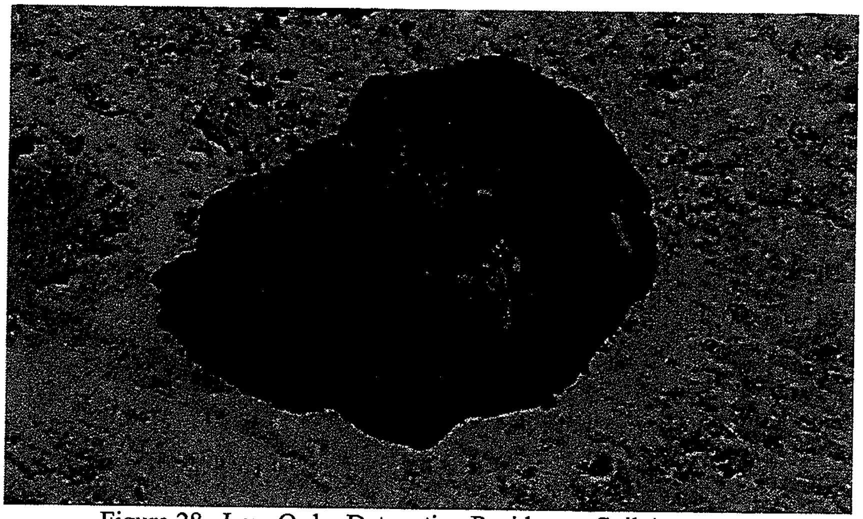


Figure 28. Low Order Detonation Residue on Soil Aggregate

A low order detonation was not desired for these shots. Analysis of the events indicated that the muzzle velocity of the artillery needed to be significantly reduced. These first shots used a full single bag of propellant as provided. An alternative propellant bag one-third the size was used in the next test on May 20, 2000. Figure 29 shows yet another low order detonation. Figure 30 shows a fragment containing a large amount of undetonated TNT. There were two such large pieces; the second was the entire bottom quarter of the round.

Figure 29. Low Order Detonation (1/3 bag propellant)

Figure 30. Low Order Detonation Debris (1/3 bag propellant)

To reduce the muzzle velocity even further, a one-third bag of propellant was separated in half producing a one-sixth bag. Figure 31 shows that this muzzle velocity was sufficiently low to prevent a low order detonation.

Figure 31. Successful Impacts (2) without Detonation (1/6 bag propellant)

Three each 105 mm HE artillery rounds were fired before recovery action proceeded. The approximate depth and angle of penetration was identified by placing a PVC pipe into the penetration hole. Excavation was performed with a backhoe. A metal detector was used to search in the excavation to locate the round. Final excavation was completed by hand. The trajectory was straight for about 8 feet followed by either a curving down (2 each) and a curving up (1 each). Estimated total distance that each artillery round traveled was about 12 feet. Figure 32 shows one of the curve down rounds in place prior to recovery. Figure 33 shows a visual inspection of each round. One of the fuses broke from the round during the trajectory.

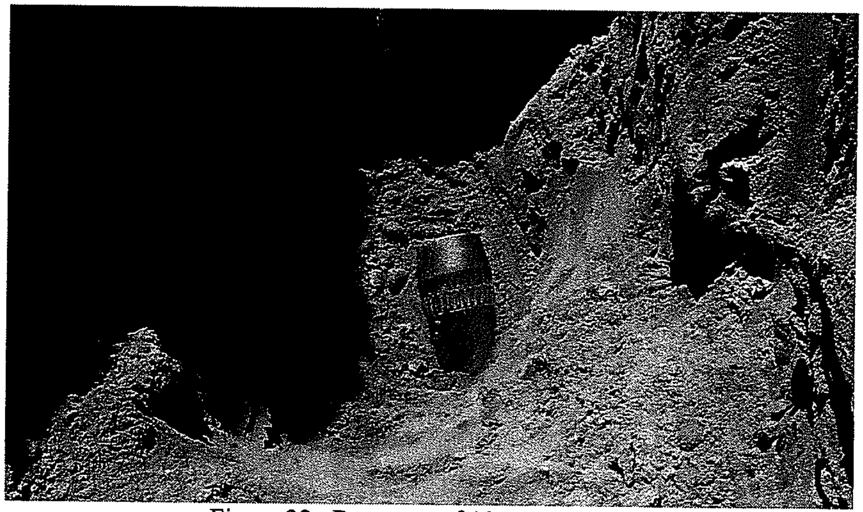


Figure 32. Recovery of 105mm Artillery

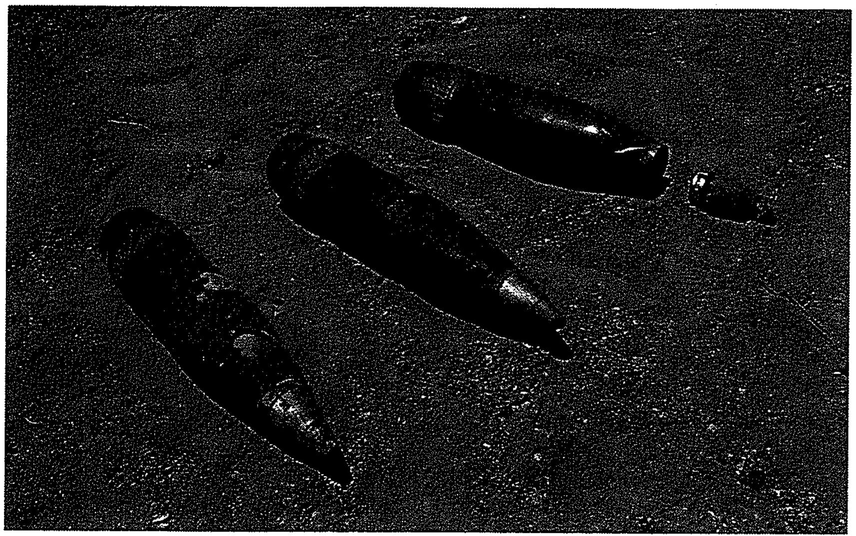


Figure 33. Visual of Each 105mm after Recovery

After recovery, each round was placed back into the cardboard shipping container for transportation to the immersion test facility.

Post-Shot Surface Residues

The surface swipe tests were completed about 24 hours after recovery of the mortars. Figure 34 shows a comparison of the detectable surface residues before the shots and after recovery. The TNG and the 2,4-DNT levels declined significantly for both mortar types. The TNT and RDX both seemed about the same at levels about ten times the detection limit.

For the 105 mm artillery shells, there was a delay of four months before the surface swipe tests were performed. During this time, the recovered 105 mm artillery remained in the original shipping tube located in a storage magazine. It is uncertain what affect this might have had on the surface residue; however, the change from pre-shot conditions appeared minimal.

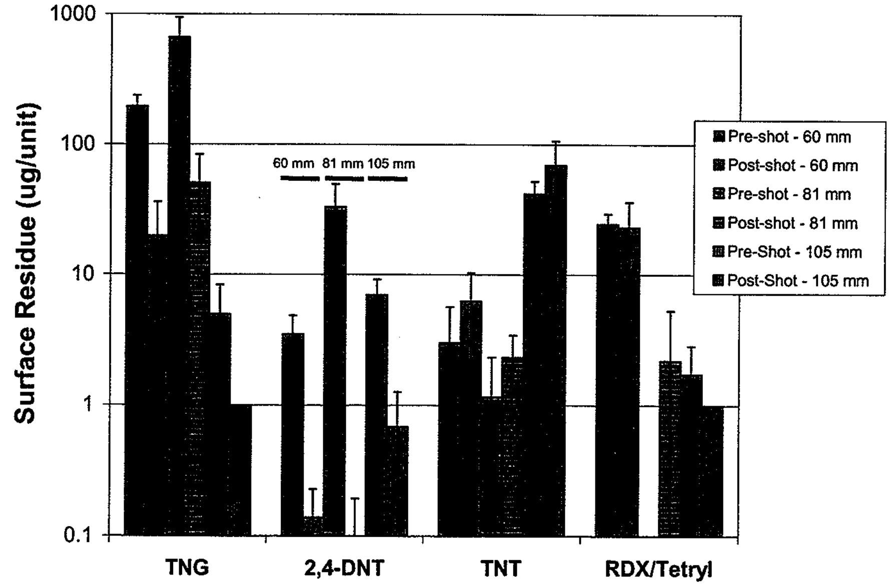


Figure 34. Comparison of pre- and post-shot swipe tests

Post-Shot Immersion Flux Tests

The immersion tests were started after completion of the surface swipe tests. Figure 35 shows the positive control changes over time. As with the pre-test case, loss of all analytes occurred, indicating some biochemical degradation or volatilization. The RDX and Tetryl co-eluted in the chromatography and hence start at twice the value of the other compounds.

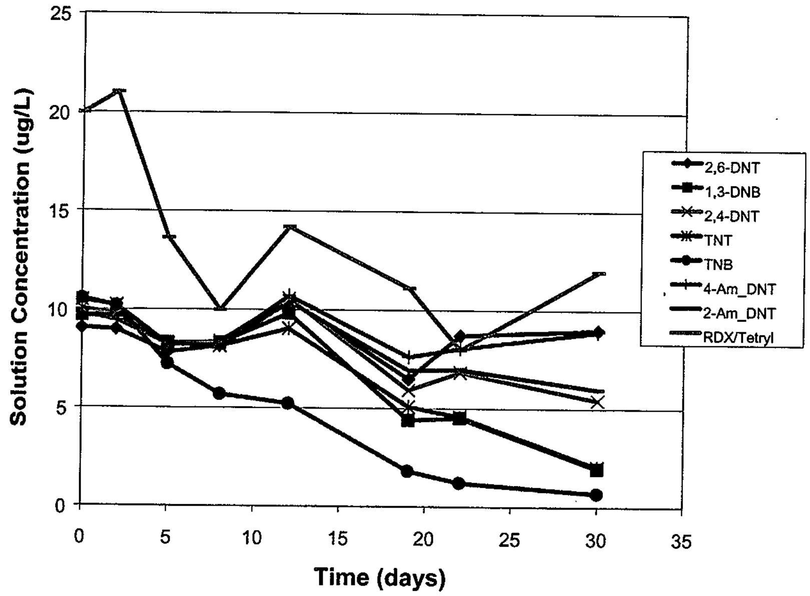


Figure 35. Positive Controls for Mortar Tests

For both the 60 and 81 mm mortars, the average solution concentration declined over the duration of the immersion test (Figures 36 and 37). These both follow the same trend as the positive controls, indicating that any leaching from the ordnance must be less than the biochemical degradation occurring in the test apparatus. Detection limit for this sampling and analysis system is about 0.25 μg/L.

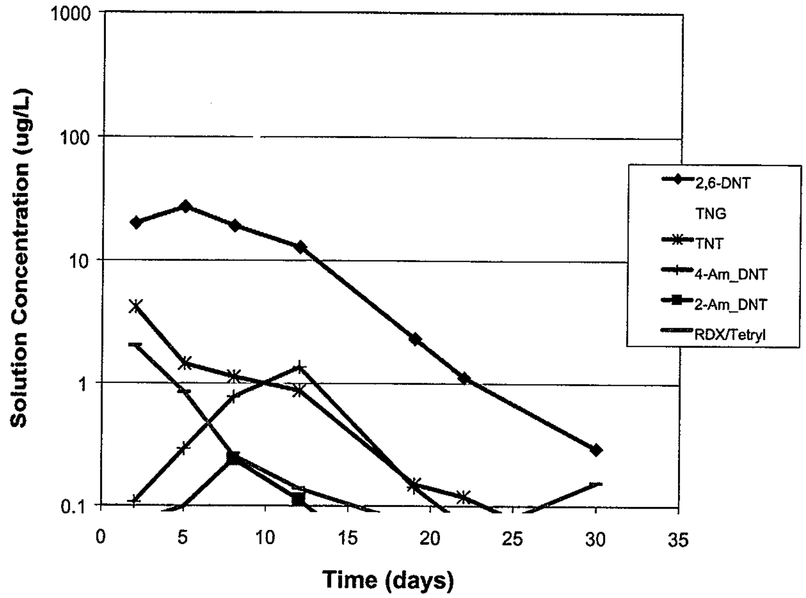


Figure 36. 81 mm Post Shot Immersion Test Results

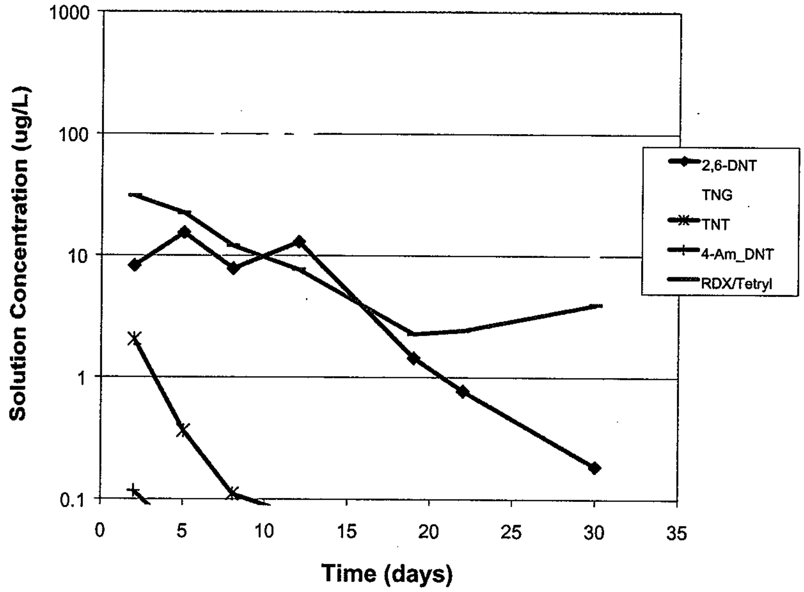


Figure 37. 60 mm Mortar Post-Shot Immersion Test Results

For the 105 mm artillery, the post-firing immersion tests were begun after the surface swipe tests were completed. For two of the three rounds, the fuses were still intact and remained as recovered. One fuse broke off on impact (see Figure 33). The immersion test for this item was completed with the water level high enough to fill the supplemental charge well located below the fuse. Figure 38 shows the positive control (established at 5 µg/L) with similar variability and decline as for the mortar post-shot positive controls.

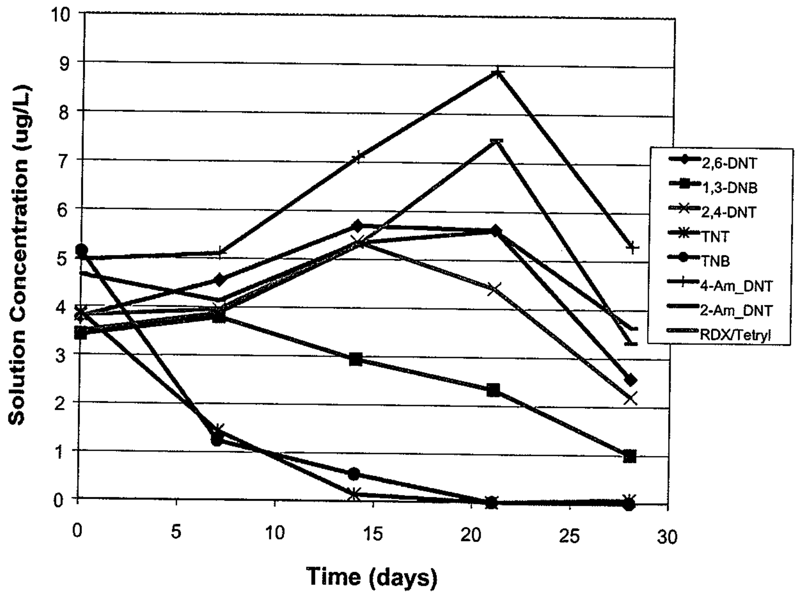


Figure 38. 105 mm Artillery Post-Shot Positive Controls

Figure 39 shows the post-shot 105 mm artillery immersion test results. These have similar patterns of loss over time as the mortars. The three post shot 105 mm artillery shells contained very different initial concentrations of TNT. One started at 1200 µg/L, one at 250 µg/L and one was below the detection limit. The highest one was also the unit without the fuse. Expected concentrations based on the surface swipe data would be around 15 µg/L (similar to the pre-shot immersion test values, Figures 14 and 15). One potential explanation for the high case is a result of transfer of surface contamination from the interior surface of the supplemental charge well.

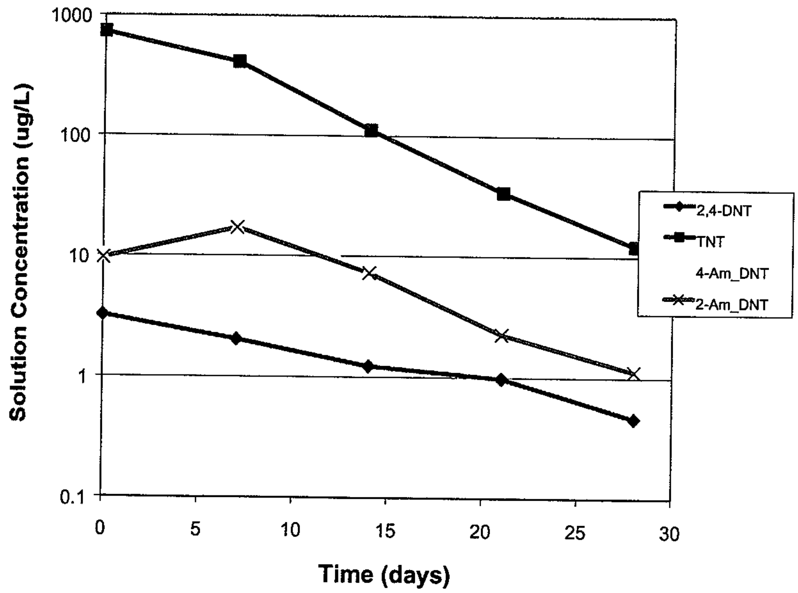


Figure 39. 105 mm Artillery Post-Shot Immersion Test Results

The pattern of post-shot immersion test data is indicative of an initial transfer to the test solution followed by degradation and loss over time. This is very different compared to the 105 mm artillery pre-shot immersion tests that showed a net positive flux to the test solution over time. No direct comparison can be made with the pre-shot mortar data as that test was compromised by the formation of an iron suspension that induced analyte degradation. From the post-shot immersion test data, one can interpret that mass transfer of chemical constituents from the UXO is significantly less than the degradation rate in the test apparatus. One may then conclude from this limited data set that chemical sensing of UXO may be unsuccessful due to the low chemical leakage rate and the high degradation rate.

7.0 Task F – Field Characterization of UXO Chemical Residues

Southwest Proving Ground

Through the Army Corps of Engineers, Huntsville, contacts were made available to coordinate the collection of soil samples from the Formerly Used Defense Site (FUDS) located at Southwest Proving Ground (SWPG) in Hope, AR. The purpose of this effort was to quantify the explosive chemical residue adjacent to shallow buried UXO that had been in place for a long period of time. Soil residues would document the combined effect of UXO leakage and environmental distribution and degradation.

This site was last used in 1946 at the end of WWII. Classification (live vs. inert) of the UXO was completed upon detonation, which occurred subsequent to collection of the soil samples. We traveled to SWPG in early November 1999 and collected an initial set of samples. American Technologies, Inc collected additional samples from November 1999 through February 2000.

The operations at the site were pre-planned for comparison of mag/flag and electromagnetic induction. Anomalies were located using mag/flag and visual means. Intrusive identification of the magnetic anomaly was performed by hand with shovels. When ordnance was located, soil samples were collected adjacent to the item. A plastic hand trowel was used to completely fill a four (4) ounce wide mouth clear glass jar at each sample location. Five (5) individual soil samples were collected, equidistant, in a line from the tip to the tail. Samples were as close as possible and beneath the UXO item. Figure 40 shows the large number of magnetic anomalies (flags) and the magnetic anomaly detector (Shonstad) at the site.

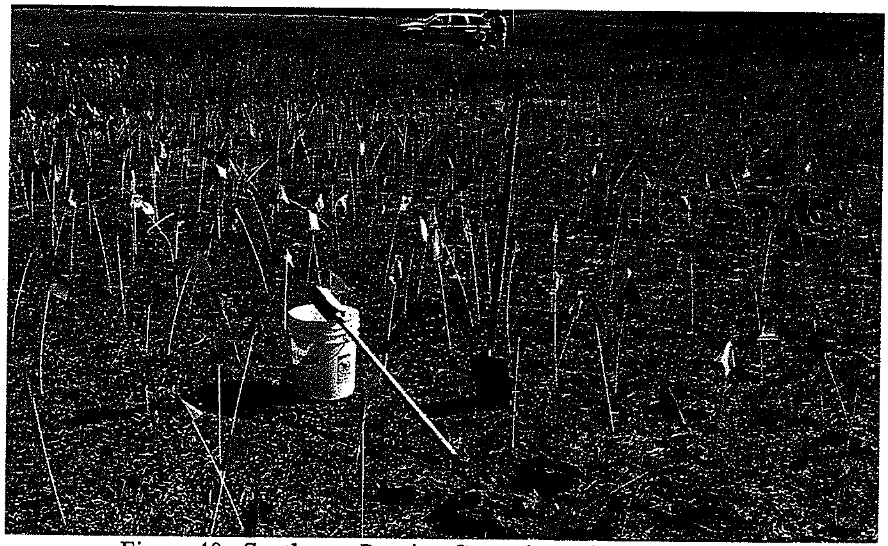


Figure 40. Southwest Proving Ground Mag/Flag Anomalies

Table 6 shows the number of HE and TP items sampled. Figure 41 shows an example of one of the 155 unfused artillery lying just below the ground surface.

Table 6. Summary of UXO Sampled at SWPG

	HE		TP	
	Fused	Unfused	Fused	Unfused
155 mm	1		6	1
105 mm	5		1	
81 mm	7	1		
75 mm	4		1	1
60 mm				1
Background - 5 locations				

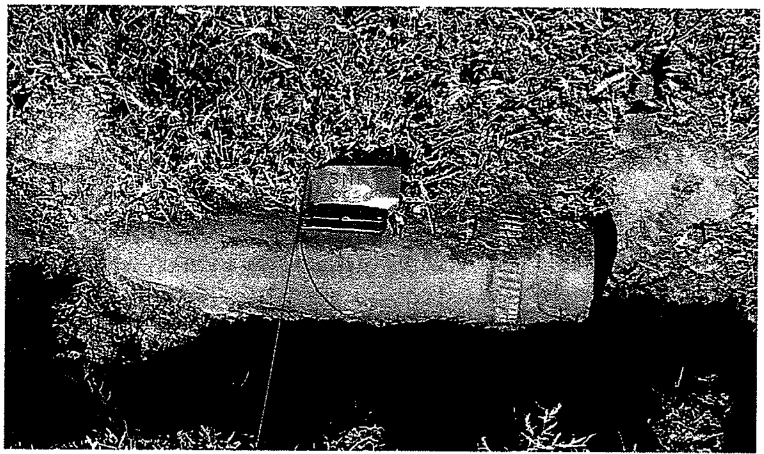


Figure 41. 155 mm Unfused Artillery at Southwest Proving Ground

The analytical results from each of the samples collected at SWPG did not show a discernable pattern that would allow discrimination of HE versus TP items. The 95% confidence interval method detection limit is about 5 – 10 ng/g for all the analytes and the majority of the detectable results were in this range. With values at the method detection limit, there is much more uncertainty that these values are actually greater then zero. There are several factors that may have contributed to the limited residues found in these samples. The length of time since the last shot was fired was about 56 years ago. The data from the swipe and immersion tests shown above indicate that ordnance items that are fairly intact have little to no chemical release after the initial surface deposits are released. Weather cycles at SWPG include very warm and wet periods that will enhance the biodegradation of these compounds.

Kaho'olawe Island

The Kaho'olawe Island site was chosen for sampling as it represented a location having a climate that would preserve chemical residues that leaked from UXO. The limited rainfall and persistent dry soil condition will preserve soil residues for an extended time period. Biodegradation needs both warm and wet conditions to prevail. On August 30 and 31, 2000 seven UXO items were sampled at Kaho'olawe in a similar fashion as for Southwest Proving Ground. These items were mostly found on the ground surface during previous visual inspections of the site. Figures 42 through 48 shows pictures and tabulated results for each item. Figures 43, 44 and 46 show very high soil residues adjacent to UXO items with severe case corrosion. Figures 42, 45, and 48 have mostly low values under ten times the method detection limit (95% confidence interval). The UXO item in Figure 47 was a unit that contained ammonium picrate as the main charge explosive. This material is extremely soluble in water and its presence on the ground surface provides a historical record of the arid conditions at Kaho'olawe.

Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		3	13			
2			5			
3			6			
4 (tail)			7			

Figure 42. BIP 9205, 155 mm Projectile and Sample Results (ng/g)

Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		9910	894051	21565	23707	
2			4	24	12	
3		24		162	67	
4 (tail)		230	769	645	266	

Figure 43. BIP 14093, 250 lb. Bomb and Sample Results (ng/g)

Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		351	691	14		
2		84	80	27	31	
3		631	877	127	176	
4 (tail)		36	20			

Figure 44. BIP 8753, 100 lb. Bomb and Sample Results (ng/g)

Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)			11			
2			5			
3			6			
4 (tail)			32			

Figure 45. BIP 14149, 5 inch Projectile and Sample Results (ng/g)

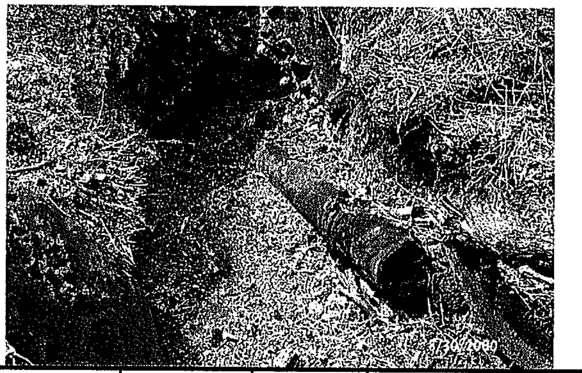
Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		9	42			
2		12	20			
3		21	27			
4 (tail)		297	586	36	49	

Figure 46. BIP 8754, 5 inch Projectile and Sample Results (ng/g)

Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)						
2						
3						
4 (tail)						

* Yellow material confirmed as ammonium picrate

Figure 47. BIP 14070, 5 inch Projectile and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)			68			
2			12			
3			9			
4 (tail)			10			

Figure 48. BIP 9143, 5 inch Rocket and Sample Results (ng/g)

8.0 Summary and Conclusions

Unexploded ordnance is recognized as a significant legacy related to military testing and training activities. Cleanup of active and former range sites has been challenged with the difficulty of discriminating unexploded ordnance from target practice rounds, ordnance fragments and other range scrap. The main charge energetics that remain in unexploded ordnance is a unique feature that could be exploited to distinguish these items. Trace chemical sensing of the residue emitted from unexploded ordnance has been considered as a technology that could be exploited to discriminate the explosive containing charge in UXO. To assess the utility of chemical sensing for buried UXO, six tasks were established to evaluate various aspects of chemical transport in soils, simulation analysis, and chemical leakage from UXO. A summary of the main conclusions from each task is as follows:

Task A – Model Development/Utilization

The TOUGH2 simulation model was modified to incorporate the most important processes that affect chemical transport in near surface soils. This model, T2TNT, has been used to evaluate the phase partitioning phenomena of the principal chemical components found in military TNT: TNT, DNT and DNB. These compounds are partially sorbed to soil particles providing for a chemical reservoir that can be released to the soil water for upward and downward transport. Soil-vapor partitioning was found to dramatically increase the sorption of these chemicals to soil particles at low soil moisture contents as the competitive sorption of water on the soil particles diminished.

The near surface soil environment is influenced strongly by time dependent weather conditions, which affect the soil moisture status, upward or downward transport of these chemicals in the soil water, and volatilization of the chemical vapor from the ground surface. The effect of transient weather conditions that change the surface soil moisture status such as dew formation or short-term rainfall events is demonstrated with simulation results from T2TNT. The T2TNT simulation model is now fully capable for evaluations of near surface soil chemical leakage to evaluate the potential for discrimination of buried UXO (and landmines).

Task B – Fundamental Property Measurement

The principal chemical components of military TNT include TNT, DNT and DNB. Fundamental properties for temperature dependent water solubility, liquid-solid sorption, vapor-solid sorption and biodegradation found in the literature were of varied quality. Data for TNT was more prevalent with large uncertainties for DNT and DNB. We focused on TNT and DNT, as these compounds were found to be more prevalent and persistent in soil residues than DNB. Temperature dependent water solubility for DNT was measured and provided a significant improvement in the quality of the existing data. Data for TNT was collected to verify the method, and showed a good correlation with past reported data.

Moisture content dependent vapor-solid sorption was believed to be a critical process but no data was available for TNT or DNT. Analogies to data for agricultural chemical and industrial pollutants indicated that this phenomenon was critical to vapor sensing of surface soils. A new method for headspace sampling using Solid Phase Micro Extraction (SPME) fibers was used to measure the vapor-solid sorption coefficient as a function of soil moisture content. This method provided excellent data that could be used to estimate parameters for a function that describes this non-linear vapor-solid sorption process. Excellent correlation results were obtained for TNT and DNT and the process mathematics were incorporated into T2TNT.

Biodegradation of trace chemical signatures was not a major focus of this project. However, past research on analytical holding times for field soil samples has shown that degradation can occur quickly at warm temperatures. This implies that the leakage rate for buried UXO must occur faster than the degradation rate for sufficient chemical signature to be transported to the soil surface.

Task C – Laboratory Scale Experiments

Simulation models have tremendous value in analysis of interdependent multi-phenomena processes such as time dependent weather impacted soil chemodynamic transport needed in the evaluation of buried UXO. However, the value of simulation model results for prediction is debated because of the uncertainty that the model contains all of the necessary physico-chemical processes. One method to improve the confidence in simulation results is to compare simulation results to data from experiments that combine several processes under partially controlled boundary conditions.

A soil column experiment was designed that mimicked a buried chemical release with surface soil vapor sampling and analysis. A small scale soil column was used containing a constant soil chemical release, induced upward soil moisture movement and vapor sampling in a plenum that covered the soil surface. Two experiments were run that lasted 30 and 90 days. The first test showed excellent correlation with the T2TNT model with adjustment of the linear of the liquid-solid sorption coefficient. The second test also showed excellent correlation, but with no modification of the liquid-solid sorption coefficient because it had been encoded as a Freundlich isotherm scaled to soil moisture content. Also in this second test, the soil was cycled through wet and dry periods to test the vapor-solid sorption aspect of the model. Again, T2TNT simulation results showed an excellent comparison to the data through vapor flux variations that spanned about one thousand. This excellent correlation of T2TNT simulation model results with the laboratory-scale test data provides increased confidence that the T2TNT model could be used confidently in an assessment of the chemical transport processes embodied in detection of buried UXO.

Task D – Operational Strategy

The development of an operational strategy for chemical sensing of buried UXO was proposed as a project task because of the potential variation in vapor flux caused by time dependent weather conditions. However, the chemical source release from UXO was found to be insufficient to support chemical sensing (see Task E and F). For buried landmines there is sufficient leakage from certain mine varieties that an operational strategy will be needed that is based on mine leakage rates, time dependent weather cycles and soil physico-chemical properties. Demonstration calculations using T2TNT have shown that this simulation model can incorporate the many input parameters and produce output of the many interdependent properties of chemical transport in soils. This project was co funded with the DARPA Dog's Nose Program for application to buried landmines and the work completed in this project will certainly support the improved detection of buried landmines through chemical sensing.

Task E – UXO Chemical Source Release

Key to the assessment of chemical sensing of buried UXO is a determination of the chemical leakage from UXO. The main charge explosive must leak through seams, seals or damaged areas of ordnance that has been fired with traditional means and impacted the soil without detonation. Measurement of the leakage from actual field recovered UXO was not possible due to the unsafe nature of the UXO. Therefore, we generated UXO that could be handled safely by using inert fuses or removing the primary explosive train in real fuses followed by traditional firing and field recovery.

A small subset of ordnance items (60 and 81 mm mortars, 105 mm artillery) was selected to be representative of the type of unexploded ordnance typically found on military ranges. The chemical signature of this ordnance was evaluated by sampling the surface residue and measurement of the leakage into water during periods of immersion.

The explosive residue found on the surface of new unfired ordnance was not uniquely different from that found on target practice rounds. This may be an effect of storage and handling where cross contamination cannot be avoided. Samples of paint from the ordnance showed a sizeable concentration of explosive signature residues. This provides a reservoir of explosive residues that can be released into the soils. Pre-shot immersion test results showed a net positive flux for the 105 mm artillery; however, the mortar fuse safety wires produced a suspension of iron oxides that are believed to have caused sorption or degradation of chemical constituents in the mortar immersion tests.

Fuse primary explosives were removed and ordnance was fired with conventional means. Post-shot surface residues showed a decline in some chemical constituents and no change in others. This is consistent with the firing process as the ordnance paint was discolored from the high temperatures that occur in the mortar or gun tube when fired. Impact into the soil abrades the ordnance paint removing a principal source of the chemical residue.

Post-shot immersion tests showed a gradual decline in chemical constituents, much different from the net positive flux during the pre-shot immersion tests. These results indicate that the emitted flux from this small set of ordnance items was less than the degradation rate in the test solutions. This implies that chemical leakage through the seams, seals and impact damage was not sufficient to be a continuing long-term source of value to chemical sensing of buried UXO.

Task F – Field Characterization of UXO Chemical Residues

Another method to assess the potential for chemical sensing of buried UXO is to examine the soil residue adjacent to buried UXO in the field. This data would represent the net leakage, transport and degradation processes since the ordnance impact occurred. If a significant residue was found, this would indicate adequate leakage and transport, and insufficient degradation in support of chemical sensing buried UXO.

Sampling soil adjacent to unexploded ordnance items in the field was performed at two locations: Southwest Proving Ground (SWPG) near Hope, AR and Kaho'olawe Island, HI. The results from SWPG showed small soil residue values, most near the method detection limit that failed to show any distinguishing character from target practice rounds. Several of the units sampled at Kaho'olawe showed very high soil residues adjacent to severely corroded unexploded ordnance bombs. The unique arid climate at Kaho'olawe supports preservation of any emitted chemical signature, since moisture is necessary for biotic and abiotic chemical reactions.

The results of the work in Task E and F indicate that the chemical signature emitted from simulated unexploded ordnance is insufficient as a distinguishing character for use in discrimination of live explosive containing items. The rate of biochemical degradation processes for these chemical constituents appears to exceed the flux derived from the main charge explosive. This is supported with field soil residues collected at Southwest Proving Ground. In arid environments where the biochemical degradation processes are limited, accumulation of explosive chemical signatures does occur. However, transport of chemical signatures from depth in arid environments would be minimal since evaporating soil moisture conditions are critical to the movement. This would not support discrimination of a buried geophysical anomaly without excavation.

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