Predicting Range UXO Source Quantity for Characterizing Associated Health Risk

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ABSTRACT

The 1997 Unexploded Ordinance (UXO) Clearance Report to Congress estimated that millions of square meters throughout the United States, including 1,900 Formerly Used Defense Sites (FUDS) and 130 Base Realignment and Closure (BRAC) installations, potentially contain UXO and explosives contaminants. In addition, testing and training ranges which are essential to maintaining the readiness of the Armed Forces of the United States contain both UXO and munitions residues such as explosives. A key to sustaining training at firing ranges is the ability to determine environmental impacts of range activities and perform the exposure assessment phase of health risk assessments. Tools are required to determine the impacts of present activities and evaluate the potential impacts of future training activities.

A UXO source term model has been developed to estimate the source quantity and fate/transport from the source zone of UXO for use within the Army Risk Assessment Modeling System (ARAMS). ARAMS is based on the widely accepted risk paradigm, where exposure and effects assessments are integrated to characterize health impacts/risk. ARAMS allows the UXO source term model to be readily used as a component in human and/or ecological health risk characterizations for estimating the mass of explosives and fluxes from the source zone that is needed as information to drive media fate/transport models, such as leaching through the vadose model and runoff into surface waters. Calculated media concentrations are then used within ARAMS to compute exposure and assess effects.

The model provides estimates of the source UXO quantity using data from firing range records and other information. Fate/transport from the source zone is handled through an enhancement of the Multimedia Environmental Pollutant Assessment System (MEPAS) Computed Source Term Release Model (CSTRM). The model package includes a munitions database for military explosive formulations.

OBJECTIVE

- To develop a source term model for UXO that can be used to predict the amount of explosives mass available and transported from the source area to other locations and subsequently exposed to human and ecological receptors.

- Evaluate the UXO source term model as a source term module in the Army Risk Assessment Modeling System (ARAMS, http://www.wes.army.mil/el/arams/arams.html, Dortch, M. S., and Gerald, J. A., 2002) for use in evaluating cleanup alternatives and range sustainment management.

INTRODUCTION

The general steps required of the UXO source term model to quantify explosives source material and fluxes from the source zone include the following:

- Estimate residue mass of explosive compounds for source area (i.e., the range impact area or area of concern).
- Estimate surface area to mass ratios of explosives residue required for dissolution.
- Calculate dissolution rates of solid phase explosive residues.
- Estimate soil fate process coefficients, i.e., sorption distribution coefficient and transformation rate, for aqueous phase of explosive residues.
- Compute fate/transport pathway fluxes from the source area and remaining soil concentrations within the source area.

METHODS

- The explosive mass for high-order blast contributions (residual mass after detonation) can be computed using

$$Mass_{BC\_i} = \sum_{j=1}^{j=n}\left[MunMass_{i,j} * N_{fired\_j} * \left(\frac{100 - D_{rate\_j} - LO_{rate\_j}}{100}\right) * \frac{BC_{i,j}}{100}\right] \quad (1)$$

where: $Mass_{BC\_i}$ is mass of explosive i contributed by higher-order blasts; $BC_{i,j}$ is the UXO blast contribution for explosive i from munition type j, in percent; N_{fired_j} is the total number of rounds of munitions of type j fired; $MunMass_{i,j}$ is the mass of explosive i contained in munition type j; D_{rate_j} is the dud rate in percent for munition type j; and LO_{rate_j} is the low order rate in percent for munition type j.

The explosive mass for low-order detonations is computed using

$$Mass_{LowOrder\_i} = \sum_{j=1}^{j=n}\left[MunMass_{i,j} * UXO_{LowOrder\_j} * \left(\frac{100 - Yield_j}{100}\right)\right] \quad (2)$$

where $Mass_{LowOrder\_i}$ is the mass of explosive i contributed to low-order detonations, $UXO_{LowOrder\_j}$ is the number of UXO contributed to low order detonations for munitions type j, and $Yield_j$ is the percent yield for low-order detonations for munitions type j. Again, if the mass density is desired then the above equation could be used along with the signature spread of the munition to determine this. The characterization model user interface is shown in Figure 1.

- Surface area to mass estimates were developed based on existing information. Lynch, Brannon, and Delfino (2002a) measured the surface area to mass ratio for military grade TNT, RDX, HMX, and the military formulation LX-14. This information is shown in Table 1. The surface area to mass ratio multiplied by the mass of explosive gives the surface area of the explosive.

Table1. Surface area to mass ratios ($cm^2 \cdot g^{-1}$) based on average size of particles (0.087 g) reported by Radtke, Gianotto, and Roberto (2002) at a historical explosives testing area and surface area to mass ratios determined on military explosives by Lynch, Brannon, and Delfino (2002a).

Explosive	$Cm^2 \cdot g^{-1}$
TNT	2.02
RDX	8.73
HMX	52.06
Octol HMX	HMX Powder = 36.4 HMX Pellet = 1.42
Octol TNT	TNT Powder = 15.6 TNT Pellet = 0.6
Comp B RDX	RDX Powder = 5.2 RDX Pellet = 1.2
Comp B TNT	TNT Powder = 3.5 TNT Pellet = 0.8
LX-14 HMX	LX-14 pellets = 0.9

- Aqueous dissolution of explosives residues is affected by solid residue surface area, ambient water temperature, water mixing rate, and pH. Studies (Lynch et al. 2001 and Lynch, Brannon, and Delfino 2002a) showed that mixing rate and pH had much less effect on dissolution than surface area and temperature. Thus, the dissolution rate can be expressed (Lynch, Brannon, and Delfino 2002b) as follows for explosives compounds.

$$\frac{dm}{dt} = a\left(\beta e^{\theta T}\right) \quad (3)$$

where: dm/dt is the explosive mass dissolution rate, mg/sec; a is the solid mass surface area, cm^2; T is the water temperature, deg C; and β, θ are empirical coefficients for temperature effects. Values for the coefficients β and θ for different explosives are shown in Table 2.

Table 2. Coefficients for explosive residue dissolution rate equation

Explosive	β	θ
	Pure compound	
TNT	$7x10^{-5}$	0.0755
RDX	$1x10^{-5}$	0.0762
HMX	$5x10^{-5}$	0.0635
	Formulation compounds	
Octol – TNT	$3x10^{-5}$	0.0769
Octol - HMX	$1x10^{-6}$	0.0728
Comp B – TNT	$3x10^{-5}$	0.0690
Comp B – RDX	$7x10^{-6}$	0.0574
LX-14 - HMX	$2x10^{-6}$	0.0903

- Examination of the sorption data summarized in Brannon and Pennington (2002), Ravikrishna et al. (2002), and Brannon (unpublished data) showed that simplification of the coefficient selection process for TNT, RDX, and HMX could be accomplished by dividing the K_d values into classes on the basis of high, medium, and low ranges of the following soil parameters: % clay, cation exchange capacity (CEC), and total organic carbon (TOC). Ranges of values and the mean (±standard error) of K_d associated with ranges of soil characteristics are provided in Table 3.

Table 3. Ranges and mean values of soil partitioning coefficients (K_d in L/Kg) for TNT, RDX, and HMX in relation to soil percent clay, cation exchange capacity (CEC), and total organic carbon (TOC)

% Clay	CEC, mmol · $100g^{-1}$	TOC, %	Range of K_d values, $l \cdot kg^{-1}$	Mean K_d (standard error)	Number of observations
TNT					
0 – 20	0 - 10	0 -1	1.04 – 3.64	0.88 (0.31)	11
20 – 50	11-30	1 – 3	2.3 – 6.16	3.39 (0.32)	14
>50	>30	>3	2.23 - 11	5.54 (0.77)	12
RDX					
0 - 20	0 - 10	0 -1	0.07 – 1.57	0.53 (0.14)	11
20 - 50	11-30	1 –3	0.06 – 1.65	0.85 (0.15)	13
>50	>30	>3	0.31 – 8.4	2.31 (0.63)	15
HMX					
0 - 20	0 - 10	0 -1	0.2 – 5.02	1.68 (0.79)	7
20 - 50	11-30	1 –3	0.12 – 17.7	4.99 (2.33)	7
>50	>30	>3	1.6 – 12.1	5.65 (3.26)	3

- Examination of transformation rate coefficients for TNT, RDX, and HMX and their transformation products tabulated in Brannon and Pennington (2002) showed that redox condition (aerobic or anaerobic) and total organic carbon (TOC) content were the main determinants of transformation rates. Ranges and means of transformation rate constants for TNT, RDX, and HMX are provided in Table 4. Half-lives are used in the model, therefore transformation rates can be converted to half-lives using the formula

$$t_{1/2} = \frac{0.693}{K} \quad (4)$$

Table 4. Ranges and mean values of soil transformation rate coefficients (K in h^{-1}) for TNT, RDX, and HMX in relation to soil total organic carbon (TOC) and aeration status (anaerobic or aerobic)

TOC, %	Range of Transformation Rates, h^{-1}	Mean (SE) of Transformation rates, h^{-1}	Number of observations
	TNT (Aerobic)		
0 – 1	0 –0.144	0.03 (0.023)	6
> 1	0.013 – 0.162	0.064 (0.049)	3
	TNT (Anaerobic)		
0 – 1	0.0003 –0.0014	0.0009 (0.0002)	6
> 1	0.014 – 0.062	*	2
	RDX (Aerobic)		
0 – 1	0 – 0.008	0.0047 (0.0024)	3
> 1	0.008 – 0.0163	0.011 (0.0028)	3
	RDX (Anaerobic)		
0 – 1	0 – 0.0003	0.0001 (0.0001)	4
> 1	0.062 – 0.24	0.141 (0.053)	3
	HMX (Aerobic)		
0 – 1	0 – 0.004	*	2
> 1	0 – 0.0163	*	2
	HMX (Anaerobic)		
0 – 1	0 – 0.00044	0.0001 (0.0001)	4
> 1	0.05 – 0.062	*	2

* Mean and standard error are not provided when only two observations are available.

- Degradation, leaching, wind suspension, water erosion, overland flow, and volatilization loss pathways (Equation 5), can all occur within the source fate/transport model (MEPAS CSTRM), however, volatilization is negligible for UXO compounds, which have a very low Henry's Law Constant. The system of first order, ordinary, differential equations for mass fluxes are numerically solved with a fourth-order Runge-Kutta method using an annual time step. The user-interface for the fate and transport portion is shown in Figure 2.

$$\frac{dM_i}{dt} = \left[\frac{dM_i}{dt}\right]decay + \left[\frac{dM_i}{dt}\right]leach + \left[\frac{dM_i}{dt}\right]susp + \left[\frac{dM_i}{dt}\right]eros + \left[\frac{dM_i}{dt}\right]over + \left[\frac{dM_i}{dt}\right]vol \quad (5)$$

In Equation 5, M_i is the mass of compound i, and t is time (yr) since initiation of the simulation.

In the model, munitions are selected using the "Munition Selection" button. Explosives are selected using the "Explosives of Interest" button. Information from range firing records can be entered using the "Range Firing Records" button. The area of the range or source zone can be entered using the "Source Area" button. Signature spread and blast contribution can be entered using the "Signature Spread and Blast Contribution" button. The user interface for the fate and transport model (MEPAS CSTRM) can be launched by pressing the "Fate and Transport" button. To run the model, press the "Run Model" button.

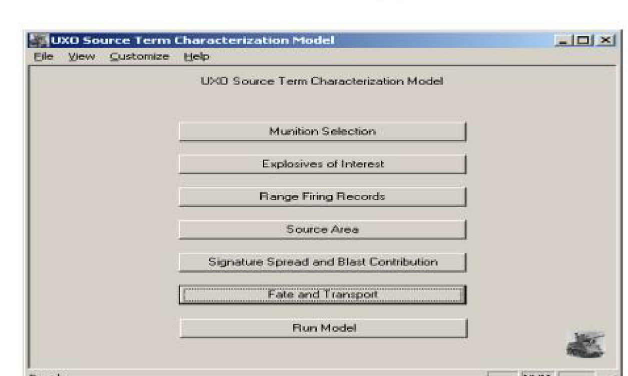

Figure 1. UXO Source Term Model – Characterization

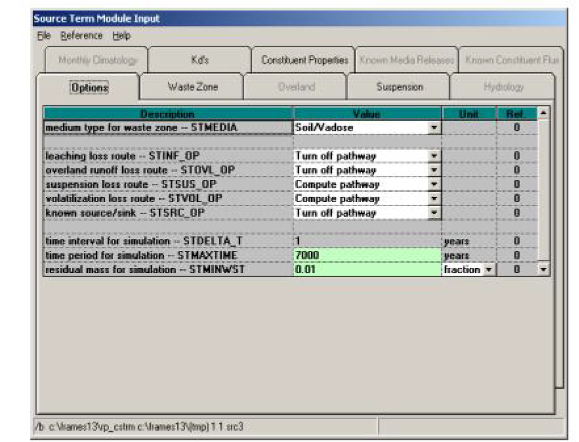

Figure 2. UXO Source Term Model – Fate and Transport

DEMONSTRATION APPLICATION

This application is an example for range sustainment management.

1. Scenario "A" has twice as many rounds fired per year as Scenario "B". The range will be used for 50 years. We would like to know the health risks associated with these 2 scenarios.
2. The receptor is an individual human who trains at the site for 8 hours a day, 38 days a year, for 30 years.
3. The constituent of concern is TNT.
4. The exposure pathways are soil ingestion, dermal contact with soil, and soil inhalation.

The schematic of this modeling scenario and the ARAMS conceptual site module interface are shown in Figures 3 and 4.

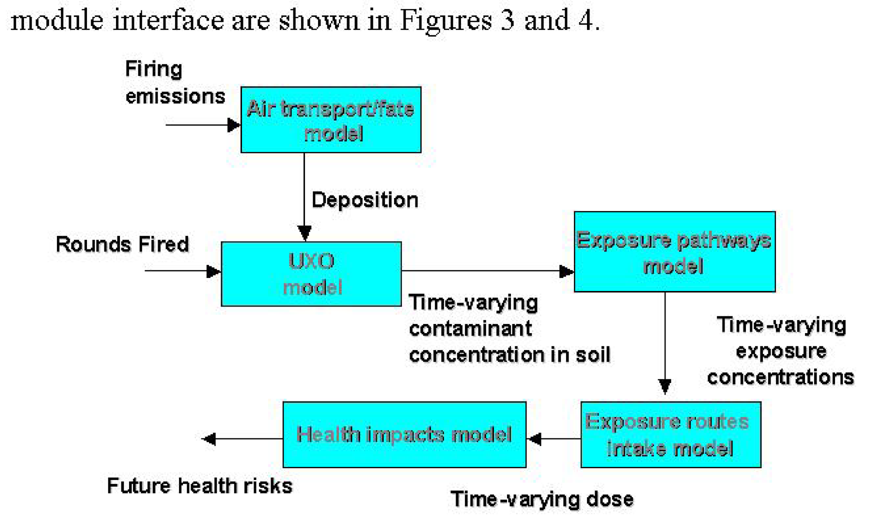

Figure 3. Schematic of range modeling scenario

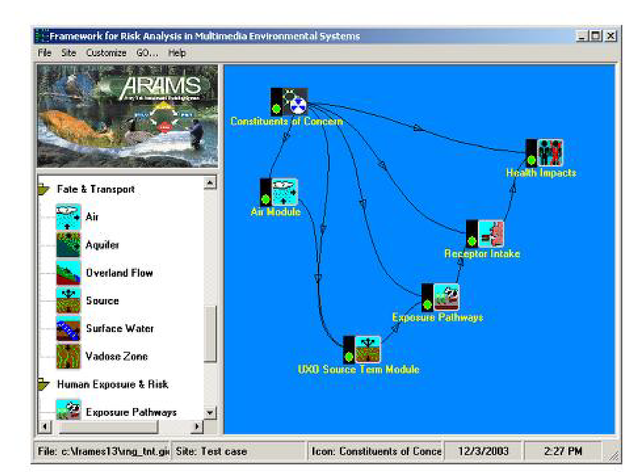

Figure 4. ARAMS conceptual site module interface

The incremental cancer risks are shown in Figure 5 for both scenarios. Note the health risk for scenario A is greater than scenario B.

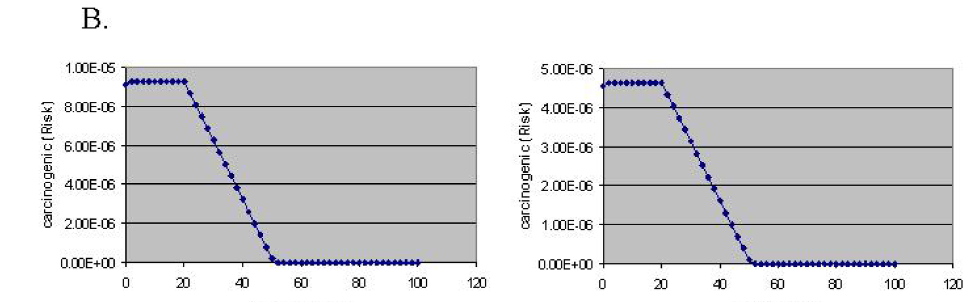

Figure 5. Cancer risk versus time

CONCLUSION

A UXO characterization model was developed which estimates and outputs the mass of the selected explosives of interest. The model also estimates and outputs the mass fluxes versus time for each loss pathway and the mass and concentration remaining in the source zone. The UXO model package has an interactive, user-friendly, interface and associated munitions and explosives database. The software is implemented as a source term component of ARAMS. The software determines the explosive mass from low-order detonations and blast contributions. It also computes the mass of explosive from duds that may be broken or corroded, but does not add this contribution to the mass available for fate and transport at this time because of the lack of data on these sources, the contributions of which are expected to be minor.

Several areas were identified where additional data are needed. These include information on number of broken or cracked munitions, corrosion rates, signature spread, high-order blast contributions, and mass to surface area for low-order explosives residues. Limited availability of such data requires the user to estimate or extrapolate from existing data. Many of these data gaps are currently being addressed and will be included in the next few years. The model does not distinguish between signature spread for high-order and low-order rounds, since no data are available for low-order detonation signature spreads. There are plans to validate the model against lab soil column data in the near future. The model should prove useful for evaluating range sustainment management and range cleanup alternatives.

REFERENCES

Brannon, J. M. and Pennington, J. C. (2002). "Environmental Fate and Transport Process Descriptors for Explosives." ERDC/EL TR-02-10, U. S. Army Engineer Research and Development Center, Vicksburg, MS.

Dortch, M. S., and Gerald, J. A. (2002). "Army risk assessment modeling system for evaluating health impacts associated with exposure to chemicals," *Brownfield Sites: Assessment, Rehabilitation and Development*, edt. by C. A. Brebbia, D. Almorza, and H. Klapperich, WIT Press, Southampton, UK.

Lynch, J. C., Myers, K. F., Brannon, J. M., and Delfino, J.J. (2001). "Effects of pH and temperature on the Aqueous Solubility and Dissolution Rate of 2,4,6 trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)." *Journal of Chemical and Engineering Data,* Vol. 46, 1549-1555.

Lynch, J. C., Brannon, J. M., and Delfino, J.J. (2002a). "Dissolution rates of three high explosive compounds: TNT, RDX, and HMX." *Chemosphere.*, Vol. 47, 725-734.

Lynch, J. C., Brannon, J. M., and Delfino, J.J. (2002b). "Effects of component interactions on the aqueous solubilities and dissolution rates of the explosive formulations octol, composition B, and LX-14." *Journal of Chemical and Engineering Data,* Vol. 47, 542-549.

Ravikrishna, R., Yost, S. L., Price, C. B., Hayes, C. A., Valsaraj, K. T., and Brannon, J. M. (2002). "Vapor-Phase Transport of Explosives Compounds in Soils," ERDC/EL TR-02-26, U. S. Army Engineer Research and Development Center, Vicksburg.

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