



Assessment of Environmental Health Impacts in Munitions Research, Development, Testing and Evaluation: A Phased Approach



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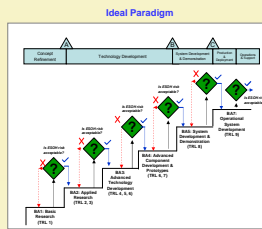
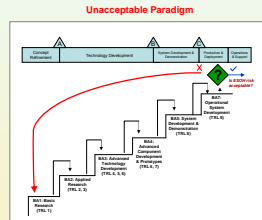
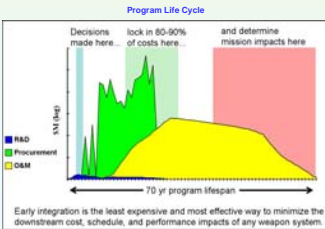
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Abstract

Environmental consequences of using specific compounds in military applications have led to undesirable outcomes. Examples include expensive clean up operations, off-site groundwater migrations, and closing of operational ranges. Additionally, the use of specific systems containing compounds with few toxicity data may lead to adverse health consequences to soldiers and civilians. The Army Environmental Quality Technology Ordnance Environmental Program (EQT-OEP) is currently exploring replacement substances for compounds identified as hazardous to health from an environmental and/or occupational perspective. To evaluate the environmental and occupational health consequences of new compounds, a tiered approach has been developed and used within the program. Early in the research stage models are primarily relied upon (e.g. QSAR approaches) and as the technology progresses, a greater reliance is placed on experimental data, beginning with *in vitro* techniques. As greater investment decisions are made in systems development, more reliable *in vivo* data are collected to reduce uncertainty. Together, these data and weighted lines of evidence are used to help guide life cycle decisions in the development of new systems.

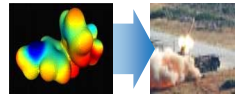
Introduction

Sustaining range operations while maintaining force health is vital to our national security. Current research is focused on discovering munition constituents that have a negligible environmental health impact. Determining the potential for adverse environmental health effects requires an interdisciplinary approach that must be phased coincident with munition design. They must be applied in a logical, tiered way consistent with the research, development, and engineering level of effort. The U.S. Army EQT-OEP has developed a protocol and an ASTM guide (E2552-08) to address assessment of environmental health risks during the research and development of new energetic materials. This protocol establishes environmental properties as being critical performance parameters equivalent to traditional performance parameters required in new energetic development. This process will enable researchers to determine and evaluate environmental health properties throughout development—from modeling and simulation in the early stages to testing in the later stages. Researchers will use this knowledge to identify and address potential environmental health risks at each stage of development. This knowledge will also help in preparing other required documents that evaluate environmental health impacts, including the Programmatic Environment, Safety and Occupational Health Evaluation (PESHE) and the Environmental Assessment (EA).



RDT&E Technical Research Levels

- **Conception** - computer simulation only
- **Synthesis** - benchtop operation, small quantities
- **Demonstration/Validation** - refinement of synthesis, stabilization of mixtures, use of COTS
- **Testing** - System evaluation



Methods

Experimental data for the parameters described in Tables 1-3 are preferred in estimating the potential for an adverse environmental outcome. Initial investments are low, therefore the use of molecular structure to predict chemical and toxicological properties are suggested. Quantitative Structure-Property Relationship (QSPRs) or Quantitative Structure-Activity Relationship (QSARs) models can be used to gather chemical and toxicological information, respectively. It must be understood that the reliability of these predictions is only as good as the variability and robustness of the data within the models, and is subject to a high degree of uncertainty relative to experimental data. Most modeling results do provide estimates regarding the reliability of the predicted values.

In later stages of development, more comprehensive experimental data are required in order to make the necessary ESOH decisions.

Final substance rankings depend upon the relative importance of the toxicological endpoints. For example, cancer classification may be more important than acute toxicity if concentrations in the environment are expected to be low. Additionally, substances that have a high vapor pressure could have a relatively high potential for inhalation exposures, particularly in occupational scenarios that would greatly increase exposure, particularly for a carcinogen. Developers should seek assistance from experienced environmental and occupational health professionals in the interpretation of the results.

Table 1. Chemical property information useful in predicting environmental fate.

Property	Units	Utility	Comments
Vapor pressure	kPa ^a	Determining persistence an exposure via inhalation.	Values > 1 are of occupational concern.
Water solubility	mg/L ^b	Estimating likelihood for ground water migration from soil.	Values exceeding 1 suggest great potential for groundwater infiltration.
Lipid solubility	logKow (unitless)	Octanol/water partition coefficient. Useful in estimating bioaccumulation potential.	Log Kow values > 3.5 suggest bioaccumulation potential.
Henry's Law constant	atm·m ³ /mol	Air-water partition coefficient. Useful in determining % life in water.	Can be calculated from vapor pressure, molecular weight, and water solubility.
Affinity to organic carbon	Koc	Organic carbon normalized soil sorption coefficient. Used to determine likelihood of reaching ground water.	Koc values <1000 suggest potential for ground water contamination. Can be calculated from logKow values.

^a Determined at given temperature (20-25°C) and at 1 atm.

Cost/Time Relationship for data requirements

Stage	Data Requirement	Means	Estimated cost (\$1000) (k=1000)	Timeline
Conception	MW, water solubility, Henry's law, vapor pressure, Koc, Kow, boiling point, mammalian toxicity	QSAR approaches	\$5k	Two weeks
Synthesis	Water solubility, Koc, Kow, vapor pressure, boiling point	Experimentally determined	\$15k	3 months
Testing	Sorption Dissolution rate Acute, subacute, subchronic toxicity testing	Experimentally determined	\$15 - \$150k	1-3 months 5 months
DemVal	Environmental % leach (soil, water, sediment, aerobic/anaerobic conditions) Feasibility	Experimentally determined	\$15-30k	3 months
	Cancer <i>in-vitro</i> screening assays	Experimentally determined	\$7-30k	3 months
	Ecotoxicology information (96 hr minnow, invertebrate assays (soil, water), Avian bioassay (acute, subchronic))	Experimentally determined	\$0.7k - \$150k	Two weeks Two months 4 months
Totals			>\$600k	> 3 yrs

Table 2. Toxicology information useful in determining relative degree of risk for human extrapolation.

Parameter	Utility	Ratings (oral: mg/kg)
Acute	LD ₅₀ /LC ₅₀ and slope useful to compare toxicity between compounds from single exposures.	Extremely toxic ≤ 1 Highly toxic = 1 - 50 Moderately toxic = 50 - 500 Slightly toxic = 500 - 5000 Practically nontoxic = 5000 - 15000 Relatively harmless > 15g
Sub-acute (mg/kg-d)	Repetitive exposures up to 14-days.	Used to determine range of lethal and sub-lethal effects. No ratings available.
Sub-chronic (mg/kg-d)	Repetitive exposures up to 10% life span.	Used to develop safe exposure values; focus on No Observable Adverse Effect Levels (NOAELs).
Carcinogenic	Potential for developing cancer as a result of exposure.	Based on rodent model, predicted from QSARs or experimental data.
Mutagenic	Describes potential mechanism for cancer - <i>in vitro</i> screen.	Depends on agreement between tests; positive or negative ratings.

Table 3. Acute toxicity ratings relevant for ecological receptors.

Relative toxicity	Aquatic (LC50 mg/L)	Airway (LC50 mg/kg food)	Mammalian (LD50 mg/kg bw)
Super toxic	< 0.01	-	-
Extremely toxic	0.010-0.01	< 40	< 5
Highly toxic	0.1 - 1.0	40 - 200	50 - 500
Moderately toxic	1 - 10	200 - 1000	500 - 5000
Slightly toxic	10 - 100	1000 - 5000	5000 - 15000
Practically nontoxic	100 - 1000	> 5000	> 15g
Relatively harmless	> 1000	-	-

Criteria for determining relative ESOH importance

	LOW	MODERATE	HIGH
PERSISTENCE	Readily biodegrades (<6h)	Degradation % life: water <40 d soil <120 d	Degradation % life: water <48 d soil > 120 d
TRANSPORT	Water sol. < 10 mg/L Log Kow > 2.0	Water sol. 10-1000 mg/L Log Kow 2.0-1.0	Water sol. > 1000 mg/L Log Kow < 1.0
BIOACCUMULATION	log Kow < 0.8	log Kow 3.0-4.5	log Kow > 4.5
TOXICITY	No evidence of carcinogenicity/mutagenicity; Subchronic LOAEL > 200 mg/kg-d	Mixed evidence for carcinogenicity/mutagenicity (BL 2); Subchronic LOAEL 5-500 mg/kg-d	Positive corroborative evidence for carcinogenicity/mutagenicity; LOAEL < 5 mg/kg-d
ECOTOXICITY	Acute LC ₅₀ > 1 mg/L or 100 mg/kg; Subchronic EC ₅₀ > 100 µg/L or LOAEL > 10-100 mg/kg-d	Acute LC ₅₀ > 14.1 mg/L or 100-10 mg/kg; Subchronic EC ₅₀ 10-10 µg/L or LOAEL > 10-100 mg/kg-d	Acute LC ₅₀ < 100 µg/L or < 50 mg/kg; Subchronic LOAEL < 10 mg/kg-d

Example assessment of formulation for M274 training warhead

M274/Smoke Mix	Persistence	Transport	Bioaccumulation	Human Health	Ecologic Health	Data Gaps
Aluminum	Green	Green	Green	Green	Green	Green
Calc-D-Bit	Green	Green	Green	Green	Green	Green
Sulfuric Acid	Green	Green	Green	Green	Green	Green
Strontium Nitrate	Green	Green	Green	Green	Green	Green
Potassium Nitrate	Green	Green	Green	Green	Green	Green
Sulfur	Green	Green	Green	Green	Green	Green
Magnesium (Mg ₂ Al ₂)	Green	Green	Green	Green	Green	Green

Legend: Green = Good, Yellow = Fair, Orange = Poor, Red = Very Poor

Implementation of tiered approach for RDT&E of new energetics

Stage	Action	Data req.	Risk
Conception	Computer modeling (QSAR)	Chem/phys. properties Human toxicity estimates	CONFIDENTIAL
Synthesis	Develop empirical chem. prop. data	Chem/phys. properties (estimate fate, transport, bioaccumulation)	
Testing	Conduct toxicity testing Tier I	Toxicity data, acute <i>In vitro</i> cancer screen	
DemVal	Conduct toxicity testing Tier II, Tier I Ecotox screening	Toxicity data, subchronic	
Production	Tier II Ecotox toxicity testing	Toxicity data, cancer	
Storage & Use	Monitoring	Media samples	
Demil	Monitoring	Media samples	

Conclusions

The protocol and ASTM guideline (E2552-08) have been used successfully within the Ordnance Environmental Program for 14 work units. The published product is an Environmental Health Assessment which serves as a technical foundation to address ESOH concerns (e.g. PESHEs, Environmental Assessments, Health Hazard Assessments, and Toxicity Clearances) for the Program Manager/Program Executive Officer.