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Environmental Research Necessitated by Inventions of and Improvements to Munitions

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SERDP • ESTCP
SYMPOSIUM
2018 | Enhancing DoD's Mission Effectiveness

Historical Examples from the Romans, the 1800s, and Today

Todays Environmental Challenges with Regards to Insensitive Munitions are Examples of a Key Driver for Environmental Research

- Why does a need persist to develop and demonstrate innovative, cost-effective, and sustainable solutions to meet DoD's environmental challenges associated with munitions constituents?
- Because a never-ending search for increased performance, availability, and affordability precludes lasting technological solutions that ensure environmental sustainability.

Environmental Challenges of Improved Munitions

Greek and Roman Sling “Bullets”

Roman “Bullets” 2nd Century AD, Scotland

Ancient Greek lead sling bullets
Left “winged thunderbolt”
Right –ΔΕΞΑΙ– “take that” or “catch”

Roman lead sling bullet-Drilled Projectile and “Terror” Weapon

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Environmental Challenges of Improved Munitions

Lead Dissolution from Antique and Modern Ammunition

Technology Advancement

Single shot Springfield Model 1873

45-70-405 Government caliber

- ✓ **0.445 caliber, 405-grain bullet**
- ✓ **70 grains of black powder**
- ✓ **Muzzle velocity 1,330 ft/sec**

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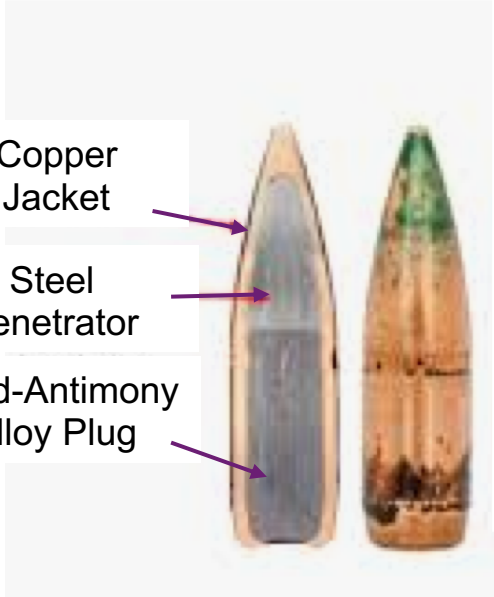
Environmental Challenges of Improved Munitions

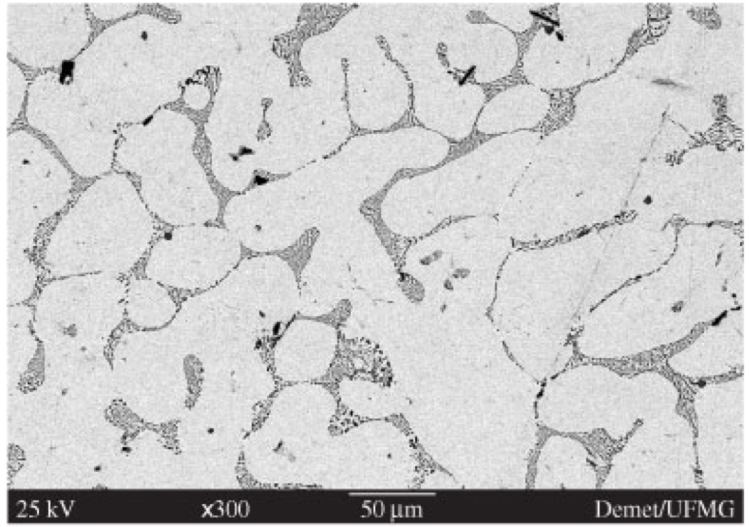
Modern Army Ammunition

5.56 mm M855

61.8 grains mass (app. 4 g)

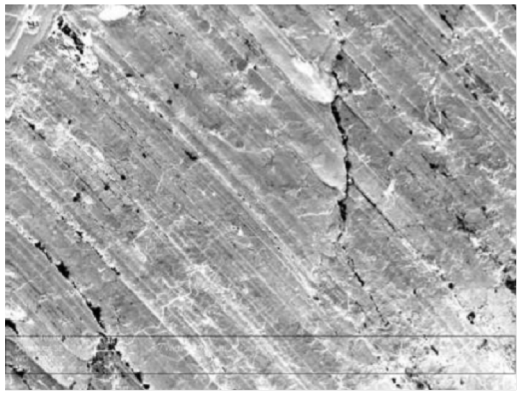
Muzzle velocity approx. (991 m/s)



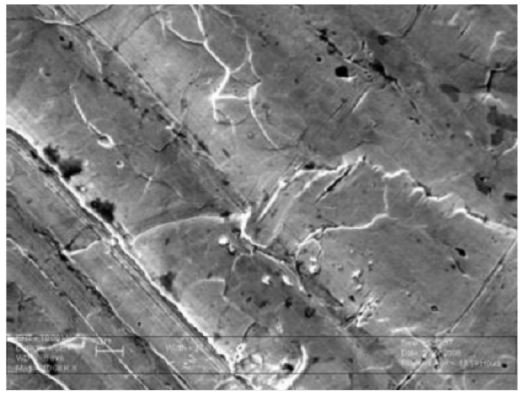


Brinnel Hardness Number:

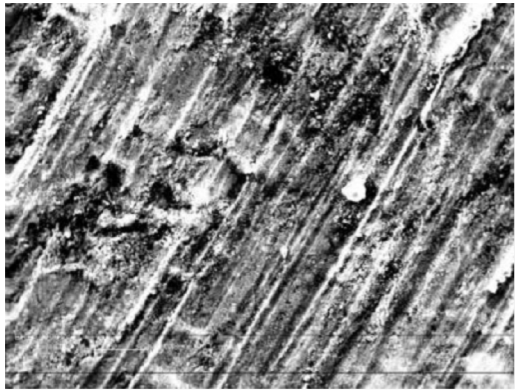
4 (100% Pb) to 10 (1% Sb)



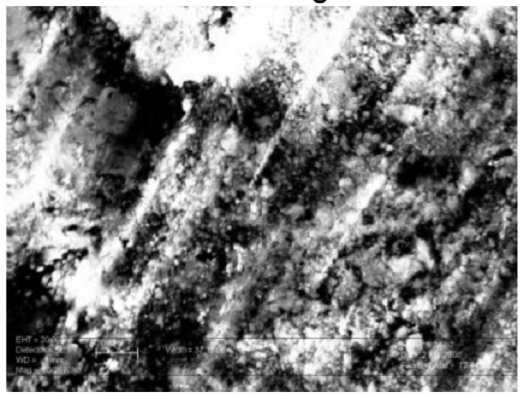
45-70 lead slug 1k x



45-70 lead slug 10k x



Modern lead slug 1k x



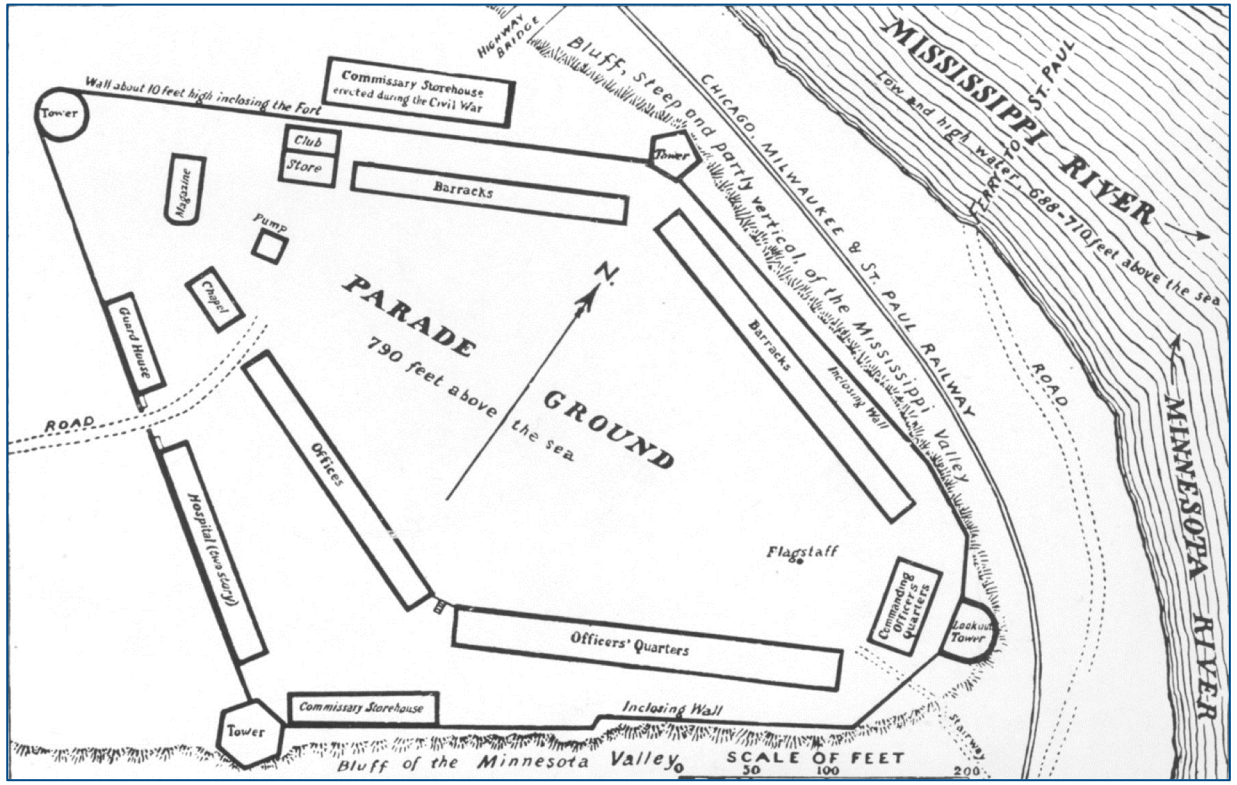
Modern lead slug 10k x

Environmental Challenges of Improved Munitions

Lead Dissolution from Antique and Modern Ammunition

Fort Leavenworth, KS

Buffalo Soldier Monument on Fort Leavenworth, Kansas



New cantonment area expanded beyond the original plans and overlapped many of the outbuildings and training range berms.

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Environmental Challenges of Improved Munitions

The nations prewar production capacity of TNT was only 1 million pounds a month and increased to 16 million pounds a month by the time of the Armistice. Improved methods and quantity production increased output dramatically during the war. *OCH Vol. I, 141-143*

World War I High Explosives Manufacture: The Wild West of Nitration

- Pre-conservation area manufacturing practices at non-government owned chemical plants/works
- No set production quotas-as much as you can
- Shortfalls in chemical precursors

The four largest explosives plants employed around 35,000 laborers total.

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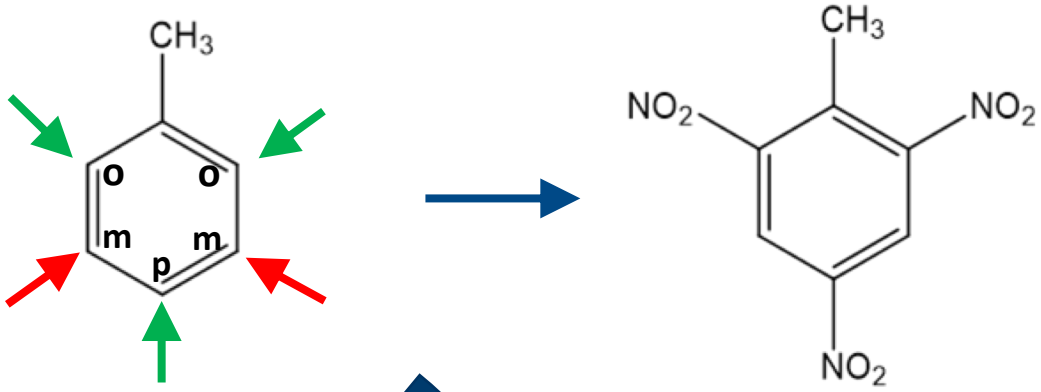
Environmental Challenges of Improved Munitions

Ammunition has historically been manufactured by private chemical companies not through a government industrial base.

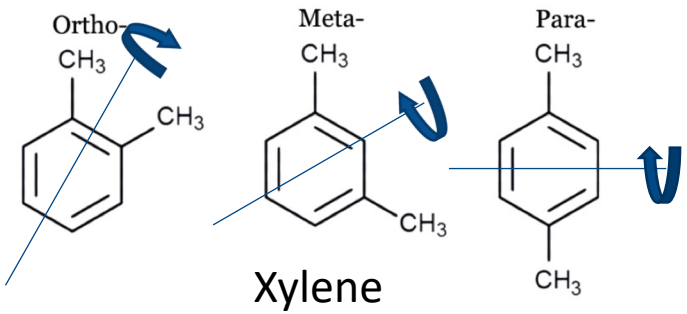
During World War 1, the high demand for TNT created a toluene shortage.

Explosives manufacturers replaced the TNT precursor, toluene, with xylene, creating the explosive compound 2,4,6-TriNitroXylene (TNX) which could be used on its own or mixed with the TNT.



Toluene

2,4,6-Trinitrotoluene (TNT)



Xylene

3 Xylenes, , C2 Sym., 4 Nitration Sites Each = 6 Possible Isomers for Trinitroxylene (TNX)

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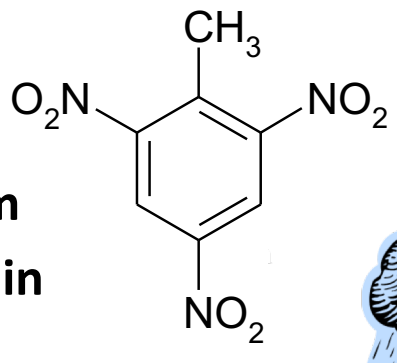
Environmental Challenges of Improved Munitions

Alkaline Hydrolysis

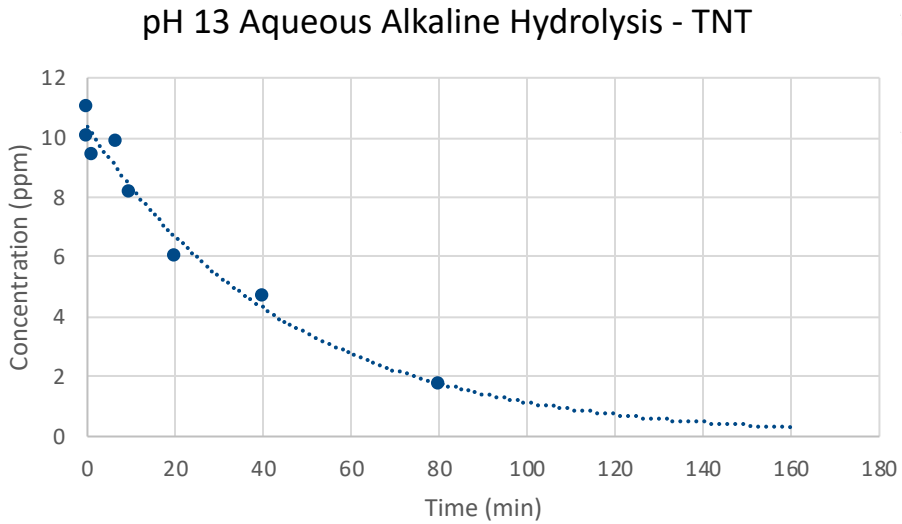
TNT

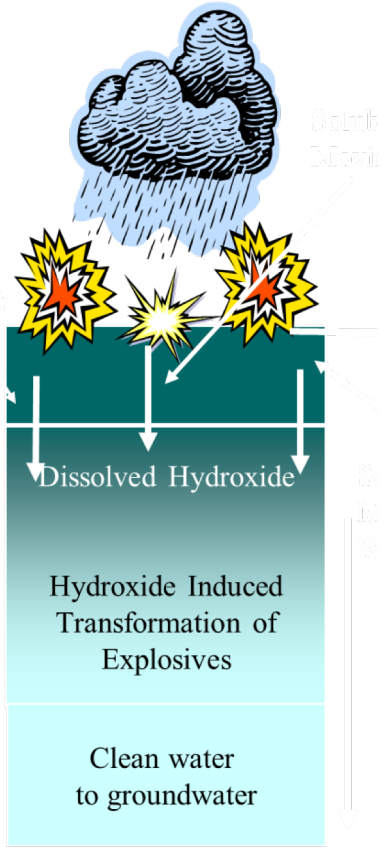
- **Water solubility 145 ppm**
- **pH=13.0, Half Life ~10 min**

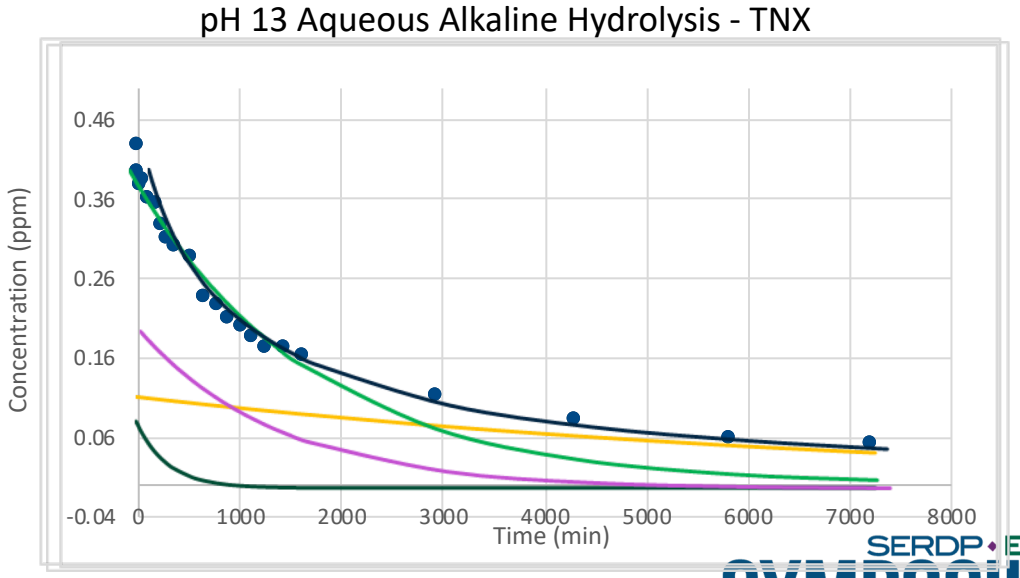


TNX

- **Water solubility 0.7 ppm**
- **pH 13, Half-life Long (3, 10, 120 hours)**







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Environmental Challenges of Improved Munitions

Field Demonstrations Led to Full Scale Treatment of TNT Contaminated Soil

TNX Soil Treatment Techniques Still Under Development

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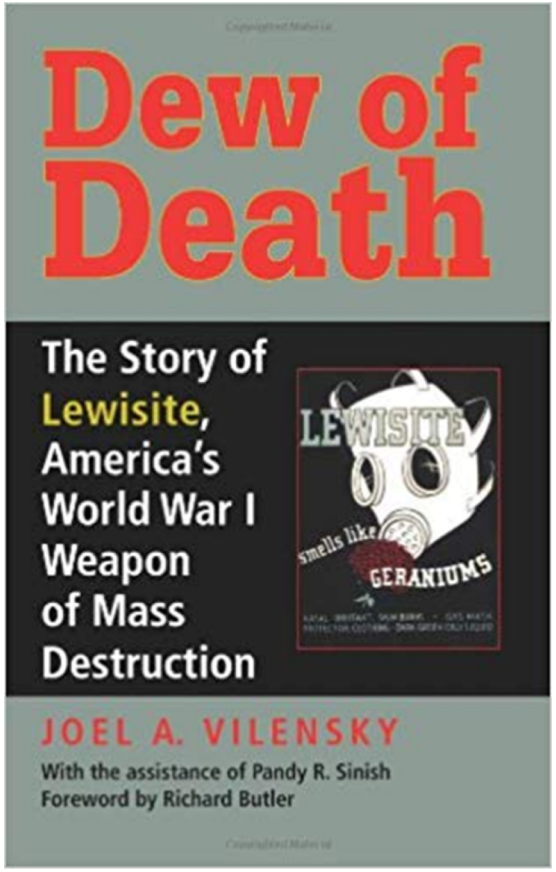
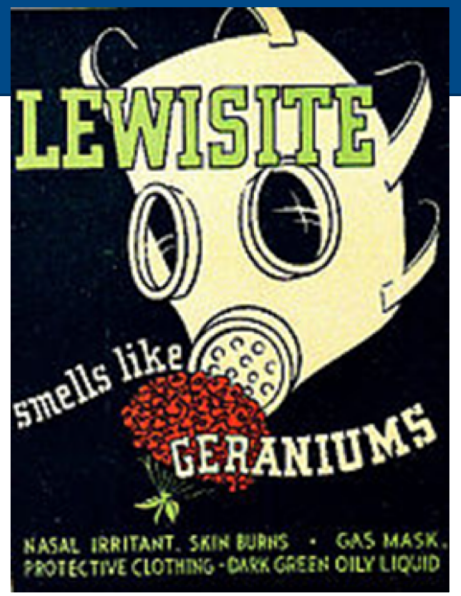
Tracking and Treatment of Legacy and Insensitive Munitions Constituents

Lewisite: Chemical Warfare (Blistering) Agent





Synthesized in 1914 by a Catholic priest, Father Julius Nieuwland, for his Ph.D at Catholic University of America. He was hospitalized for a number of days after exposure.

When Dr. Lewis attempted to purify the compound by distillation, the mixture exploded on heating.

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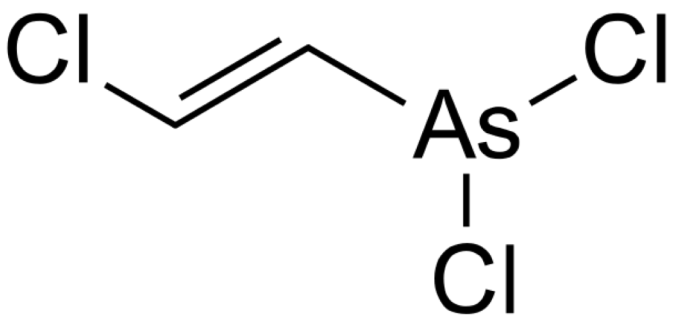
Environmental Challenges of Improved Munitions

Lewisite



Lewisite is an arsenic trichloride, used as a blistering agent.

- Oily, colorless liquid
- Insoluble in water } Makes it difficult to work with
- Odor of geraniums
- High boiling point: 374 °F
- Low freezing point: 0.4 °F

} Useful properties for a chemical warfare agent

Discovery, purification, and production at the Chemical Laboratory of the Catholic University of America in Washington, D.C. (Lewis and Perkins, 1923)

In 2001, lewisite was found in a World War I era site in Washington, D.C. by a man who broke open a glass canister lying on top of the ground. The gas was still active. The man was injured but survived.

Spring Valley, Washington DC – FUDS site

The Corps gave homeowners the option of soil removal or phytoremediation using the brake fern.

Twenty-two homeowners chose these plants. One fern for every square foot of contaminated space was used to extract arsenic over the course of a five month growing season. All homeowners saw arsenic drop to safe levels; 16 properties required a single season, others required multiple plantings.

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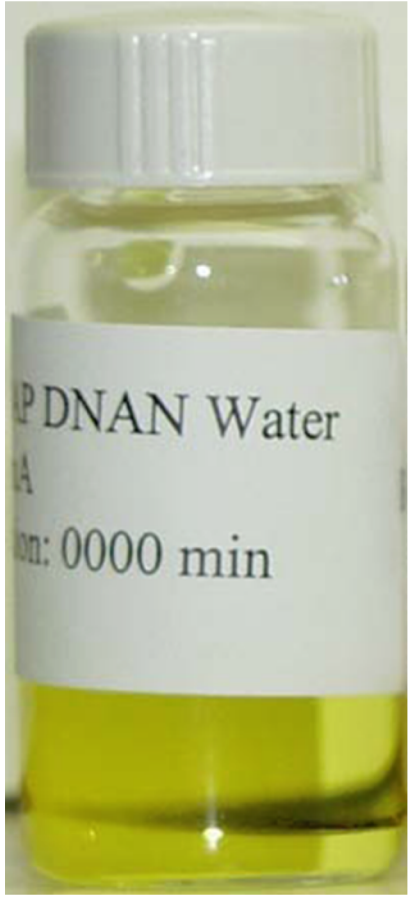
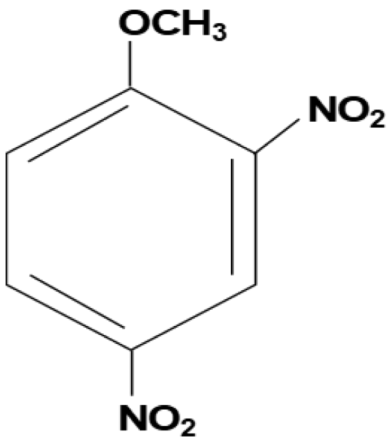
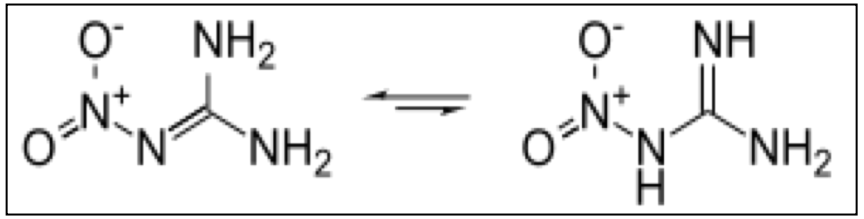
Environmental Challenges of Improved Munitions

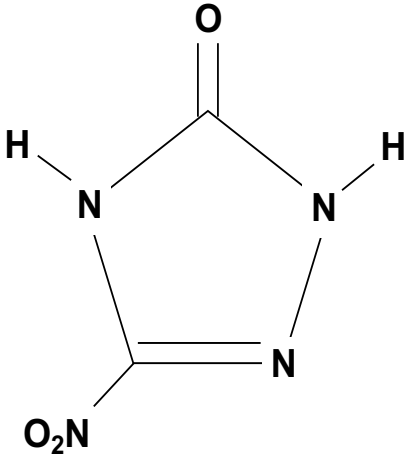




Current Insensitive Munition compounds

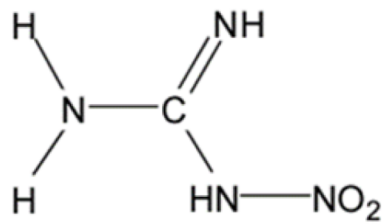


NQ

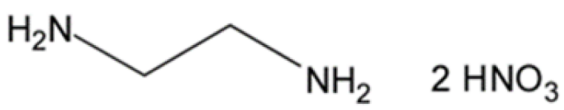


Environmental Challenges of Improved Munitions

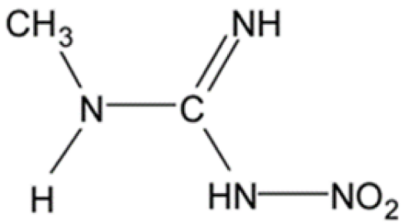
Potential IM



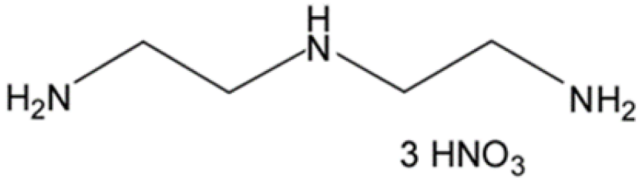
Nitroquanidine



Ethylenediamine Dinitrate

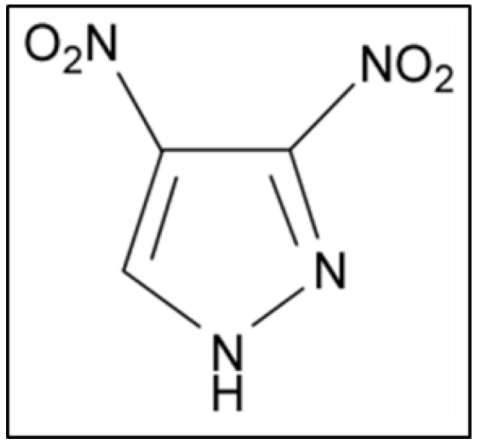


Methyl Nitroquanidine

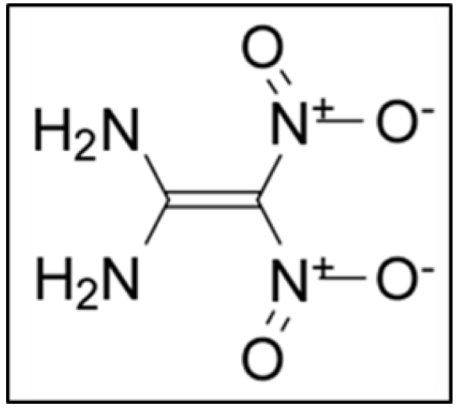


Diethylenetriamine trinitrate

Component compounds of the DEMN formulation



DNP (3,4-dinitropyrazole)



1,1-diamino-2,2-dinitroethene (DADNE or FOX-7)

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Environmental Challenges of Improved Munitions

IM constituent	H-bond donors	H-bond acceptors
DNP	1	4
FOX-7	2	4
DEMN	15	15
RDX	0	3
TNT	0	6

The emerging insensitive munitions (NTO, NQ, MeNQ, DNAN) all exhibit sharing of hydrogen atoms with planar or near planar geometry resulting in a stacked layer form.

Large numbers of hydrogen donors/acceptors affects solubility and solvation.

- High solubility in water
- High mass loading rates in water

Compound	Nomenclature	Solubility (mg/L)
NQ	Nitroguanidine	4,400
MeNQ	N-methyl-N”-nitroguanidine	13,800
EDDN	Ethylenediamine dinitrate	615,000
DETN	Diethylenetriamine trinitrate	772,000
RDX	Hexahydrotrinitrotriazine	43
TNT	Trinitrotoluene	115

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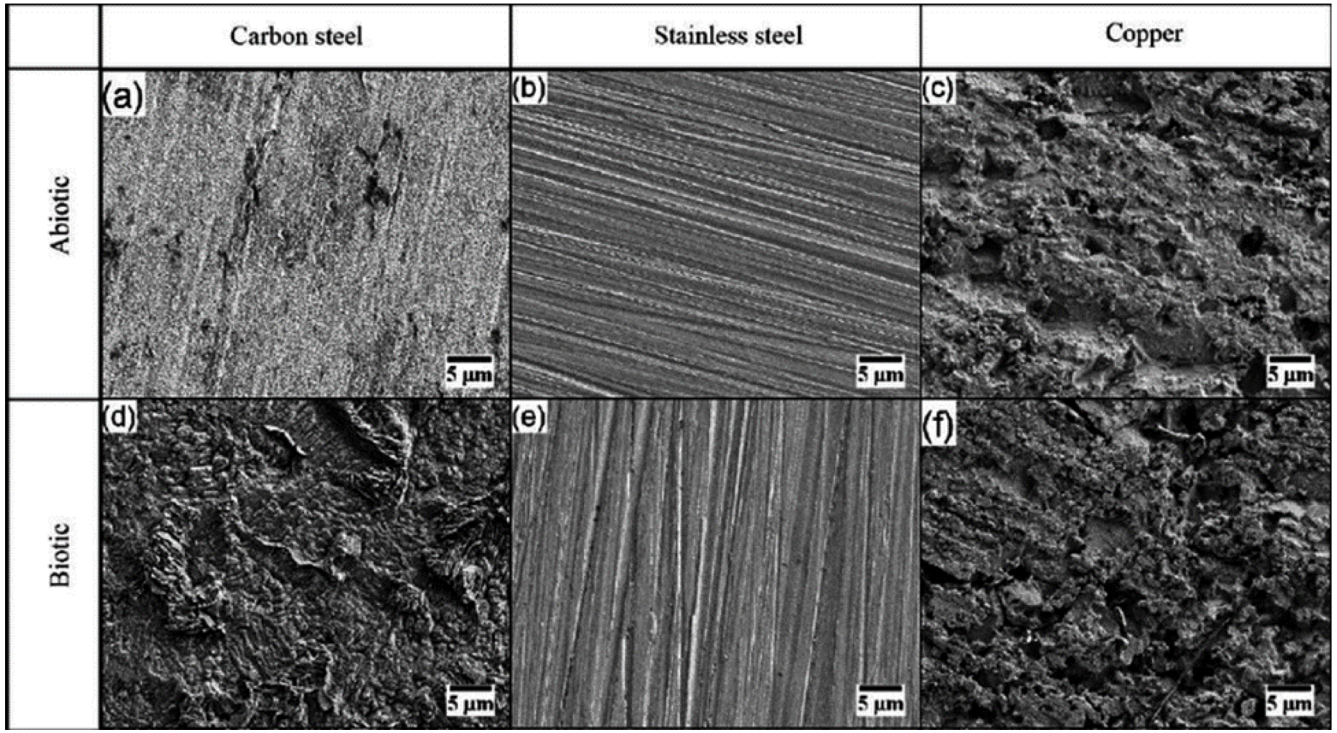
Environmental Challenges of Improved Munitions Materials Science

Low pH + High mass loading

= Corrosion of metal infrastructure
= Spillage and environmental contamination
= Production cost increases



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Environmental Challenges of Improved Munitions Analysis

Water Methods

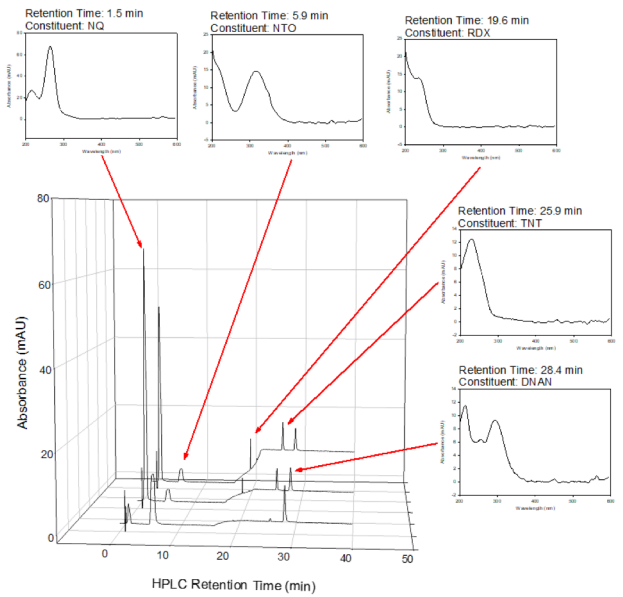
(lower concentrations)

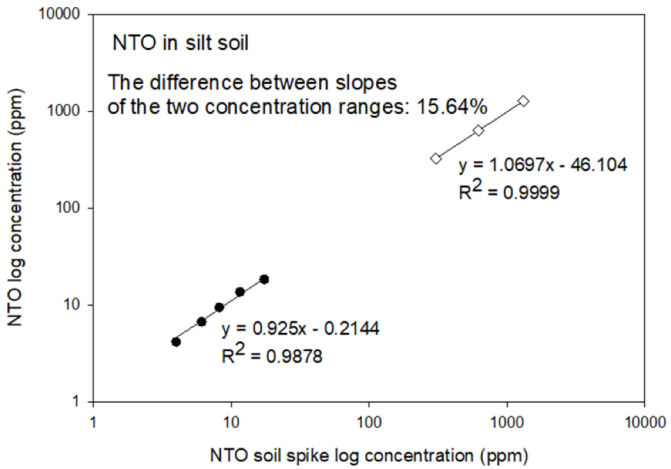
Needed to account for…

- Polar NQ, ionic NTO, hydrophobic constituents
- High water solubility
- Speciation

Method adaptations included…

- Columns (Zr-C, Porous graphite, Synergi PolarRP©)
- Buffering systems, pH control
- Temperature





Soil Methods, and other environmental matrices…

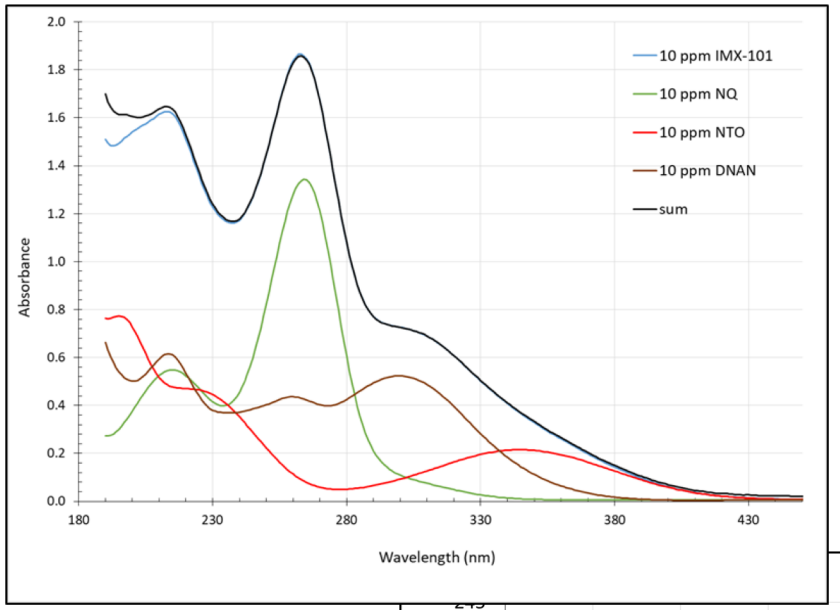
Needed to account for…

- Simultaneous extraction of polar and non-polar constituents
- Disparate dissolution rates
- Influence of soil type, or tissue
- Large range in potential concentration

Environmental Challenges of Improved Munitions Analysis

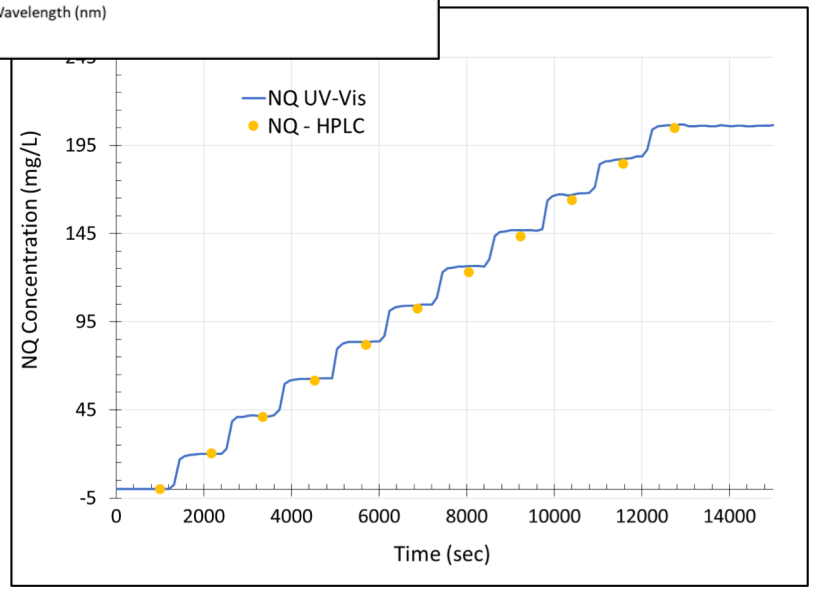
UV/VIS Analysis of IM Wastewater

- High IM compound concentrations
- High solids



Comparison with HPLC process monitoring:

- Real-time monitoring
- Cost-savings from rapid response to treatment conditions
- Allows active or passive decision-making



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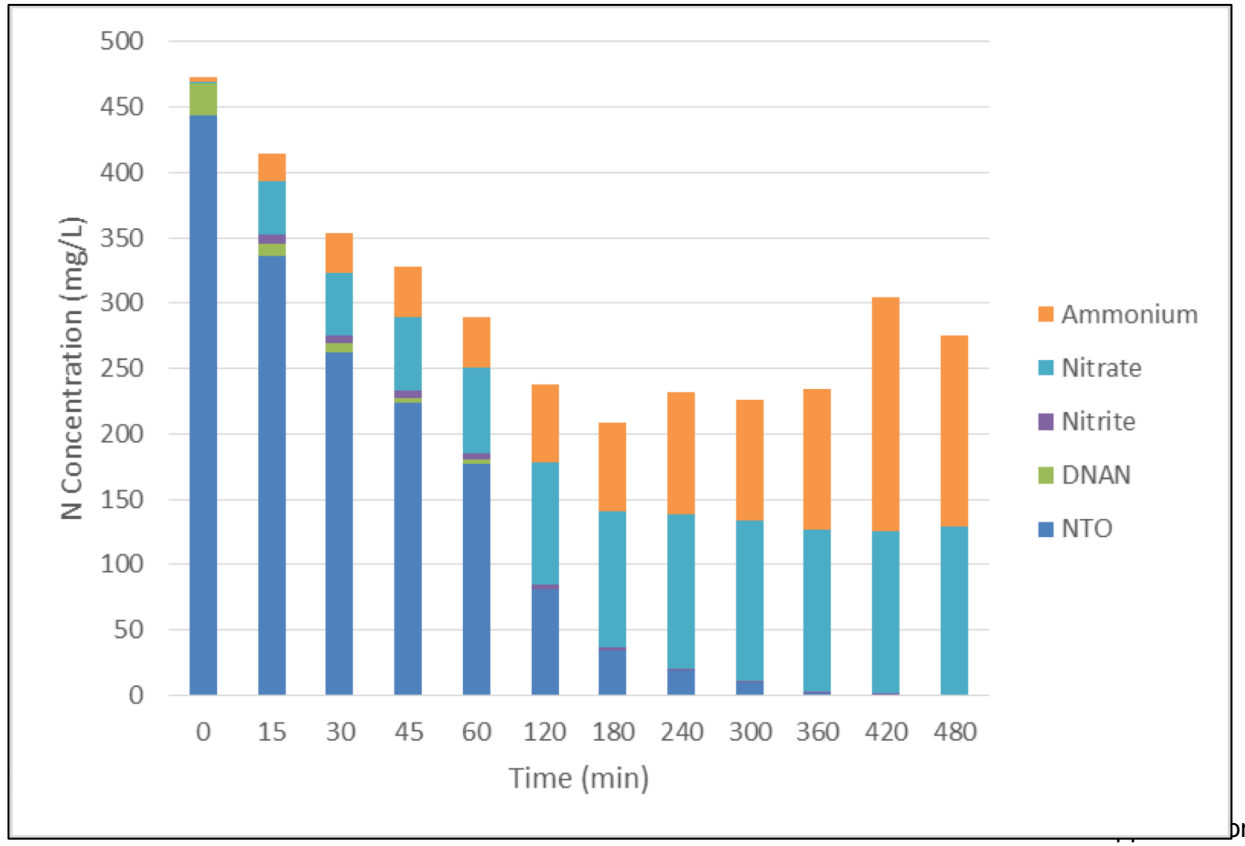
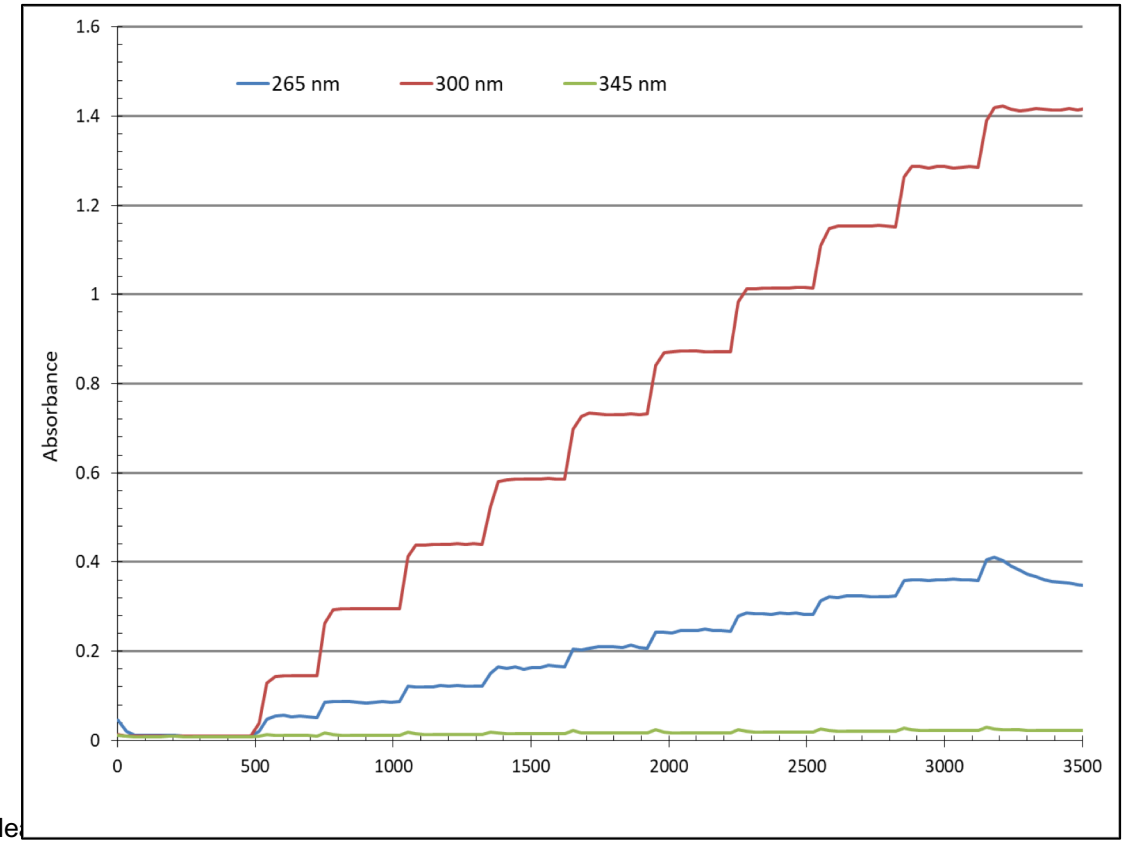
Environmental Challenges of Improved Munitions Increased Nitrogen Generation

Both traditional and insensitive munition compounds generate nitrogen from degradation of the parent compound. The high concentration of IM compounds translates to a high concentration of nitrate.





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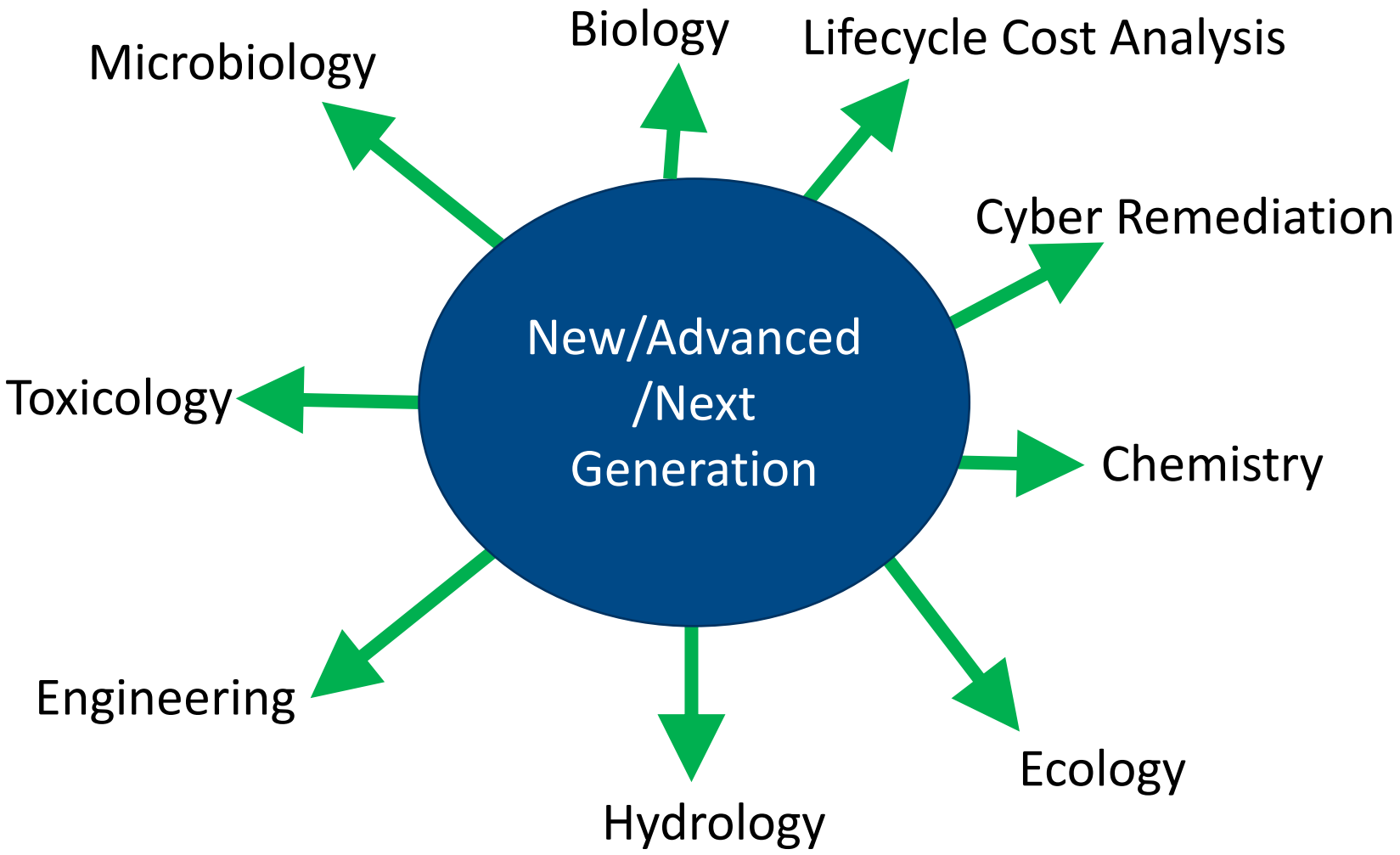
Environmental Challenges of Improved Munitions



Add into the equation the reduced tolerance for environmental disruptions as a result of:

- Societal Affluence
- Education
- Extended Life Expectancies
- Disease Causes
- Disease Identification
- Compromised Immune Systems

- **And on and on**

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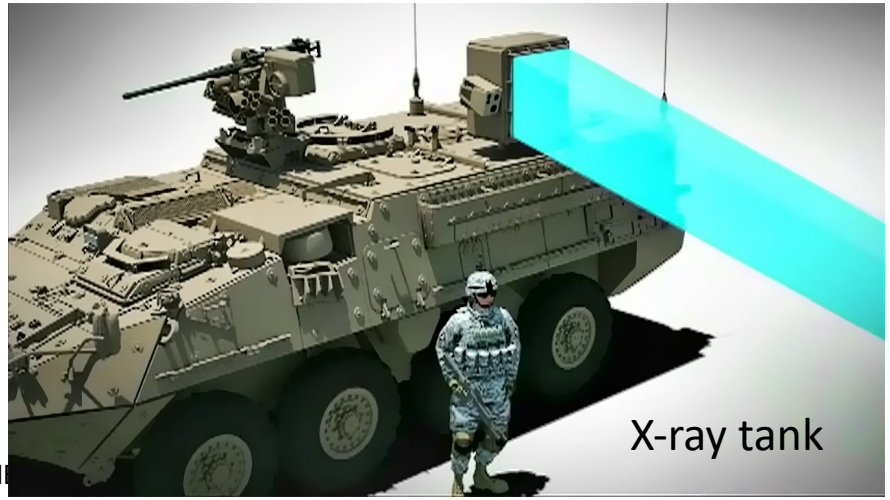
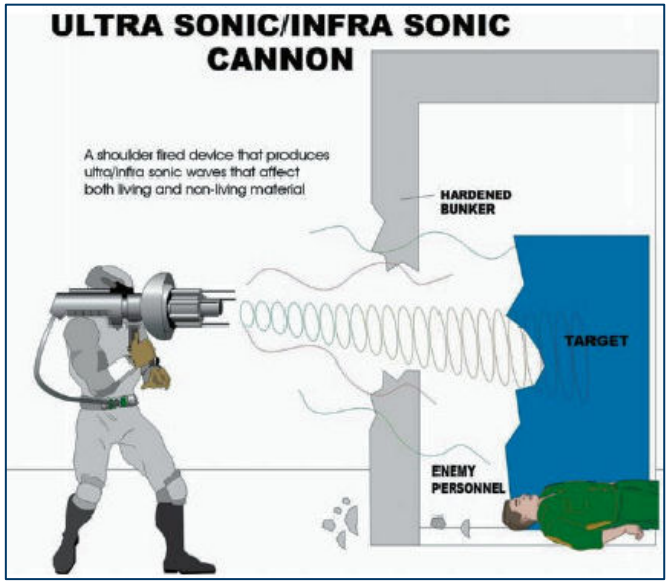
Environmental Challenges of Improved Munitions

- Munitions development through the ages driven by:
  - ✓Lethality
  - ✓Performance
- Later development driven by:
  - ✓ Safety - Military
  - ✓ Safety - Civilian
- Next Gen munitions?

Laser weapons



X-ray tank



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