



# Canadian Programme on the Environmental Impacts of Munitions

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DRDC | RDDC

# ARMED FORCE READINESS DEPENDS ON TRAINING WITH LIVE AMMUNITION

## UNDERSTAND AND MINIMIZE ENVIRONMENTAL IMPACTS OF WEAPONS



# Environmental Impacts of Weapons



Munitions Constituents  
(MC)  
Contamination

Source Terms  
Fate and Transport  
Toxicity

Mitigation,  
Range Design &  
Greener Munitions





# Deposition Studies



Type of detonation:

High-order

Low-order

Close-proximity

Field disposal by blow-in-place



# Explosives



**Close-proximity detonations: Rupture of UXOs**



**Low-order detonations**

# Explosives



**UXO BIP using C4**



**UXO corrosion**

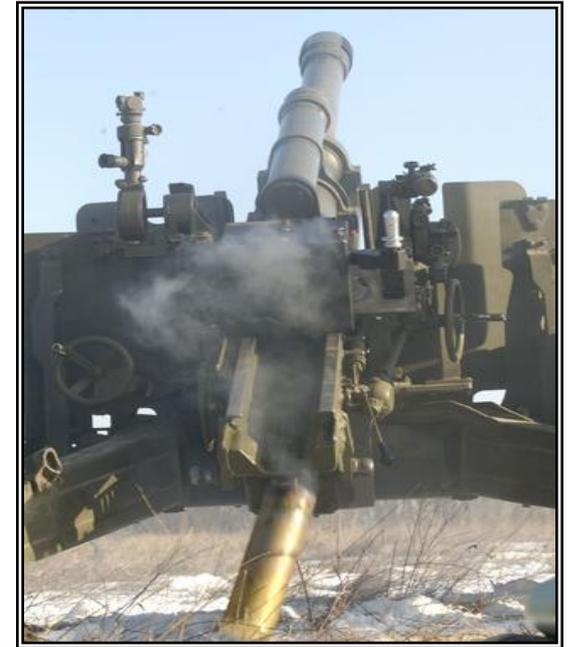


**High-order detonations**

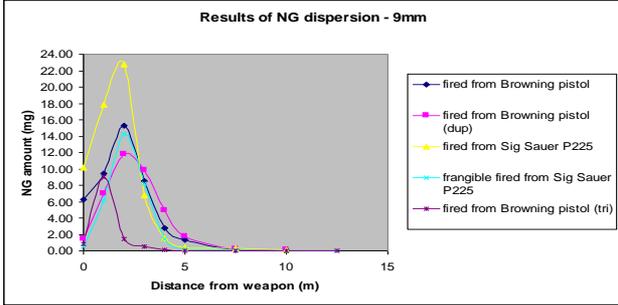
**100 000 high order =  
one low-order detonations**



# Incomplete combustion in guns



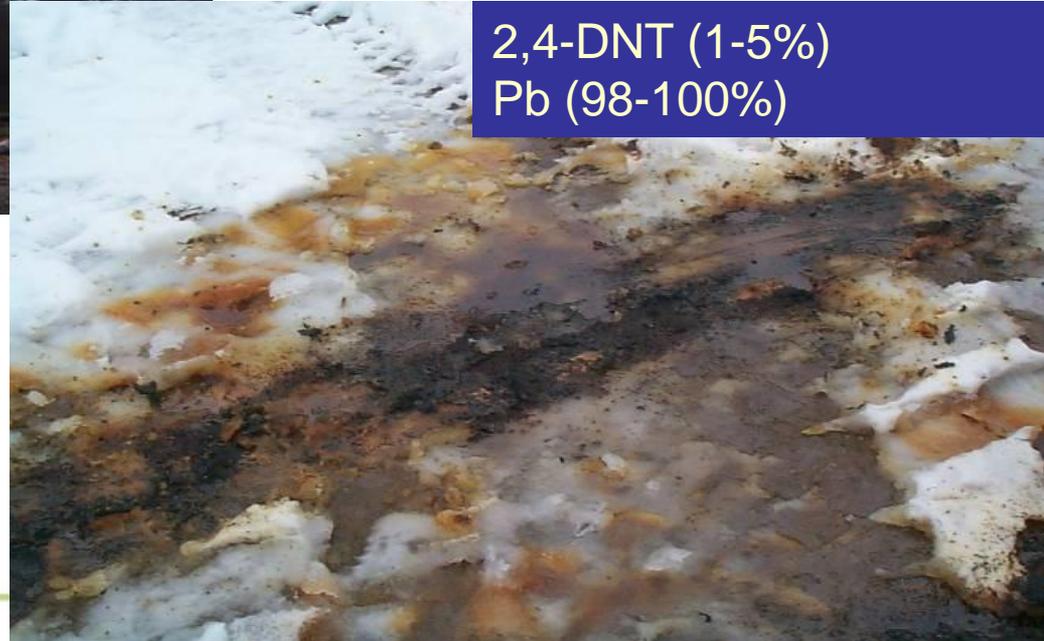
# Deposition Studies



# Results

Weapon	% of unburned EM
5.56-mm MG (NG)	0.7
7.62-mm MG (NG)	1.0
9-mm Pistol (NG)	2.5
12.7-mm MG (NG)	0.7
0.338 Cal Rifle (NG)	0.001
0.5 Cal MG (NG)	0.02
0.5 Cal Rifle (NG)	0.02
20-mm M61 (NG)	$7 \times 10^{-4}$
40-mm Mk281 (NG)	0.6
40-mm M430 (NG)	8.0
60-mm Mortar (NG)	0.007
81-mm Mortar (NG)	3.3
120-mm Mortar (NG)	1.4
84-mm AT4 (NG)	73
84-mm Carl Gustav (NG)	14
66-mm M72 LAW (NG)	0.2
204-mm GMLRS (AP)	nd
203-mm MK-58 AIM-7 (AP)	$3 \times 10^{-7}$
105-mm Howitzer (DNT)	0.05 - 0.3
155-mm British (NQ)	$2 \times 10^{-5}$
155-mm British (NG)	$3 \times 10^{-5}$
105-mm Tank (DNT)	0.003

# Open burning of excess charge bags



2,4-DNT (1-5%)  
Pb (98-100%)

# Metals

Munition casings & hard targets : Pb, Sb, Cu, Zn, Sr, Cd.



# Sampling Objectives in Range and Training Areas

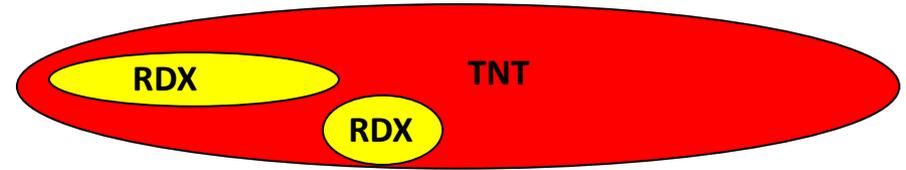
- Measure the surface soil contaminants that may:
  - Pose a threat to the health of users
  - Further be dissolved and brought to water bodies
  - Pose a threat to ecological receptors
  - Combination of all of the above



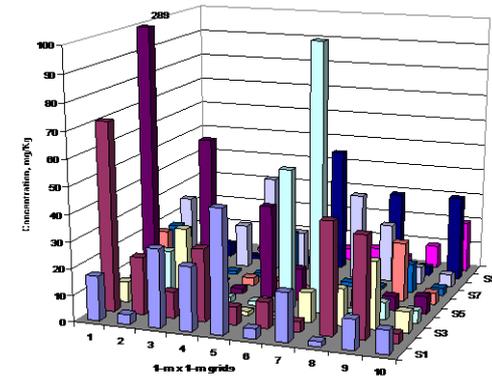


# Dispersion of Munitions Residues

## Compositional Heterogeneity: Fundamental Error (FE)



## Distributional Heterogeneity: Segregation Error (SE)



# Control over Heterogeneity

If the entire population is not well represented

**Under or overestimation by orders of magnitude**



To minimize FE : greater sample mass

To minimize SE : many increments



**Sample treatment is as important as sample collection**

# Decision Units Definition



# DUs for Various Objectives

- Risk-based human health
- Protection of surface or GW
- DU for risk-based ecological receptors



# Results

## Anti-tank Range Contamination

**Energetic**  
HMX, TNT, RDX

**Propellants**  
NG, 2,4 DNT

**Metals**  
Pb

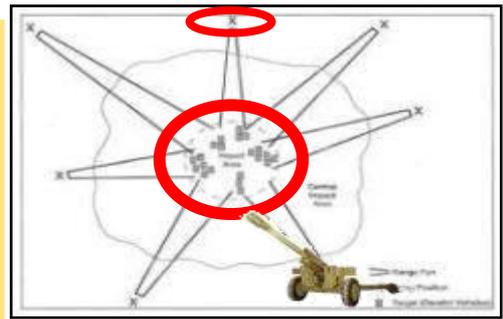


## Artillery Range Contamination

**Energetic**  
RDX, HMX, TNT

**Propellants**  
NG, 2,4 DNT

**Metals**  
Pb, Zn, Cu....



## Small Arms Ranges Contamination

**Metals**  
Pb, Sb

**Propellants**  
NG



## Demolition Range Contamination

All types of ammo

**Energetic** : TNT, RDX  
(low detonation)



## Grenade Range Contamination

**Energetic**  
RDX

**Metals**  
Sb, As





# Aqueous dissolution of formulations

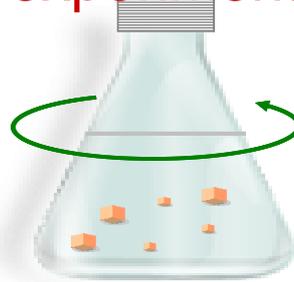


EC

Dissolution

EC in Water

Batch  
experiment



- Formulation (10mg) in 100 mL DW (T = 10, 25, and 30°C)

Dripping  
experiments



- Formulation (10 mg)
- DW (0.5 mL/min) at r.t.

# Sorption on soils

## Batch experiments



- Soil (1.5 g)
- Deionized water (10 ml)
- Energetic chemical (4-50 ppm)
- Static; aerobic; dark; r.t.

⇒  $K_d$  values

## Column experiments

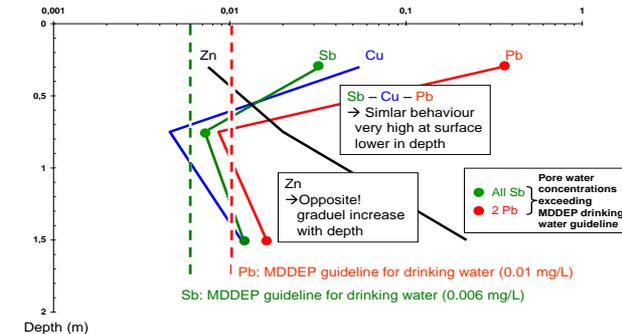


- Soil (90 g)
- Energetic formulation
- Flow rate: 0.4 mL/min, T = 22.5°C

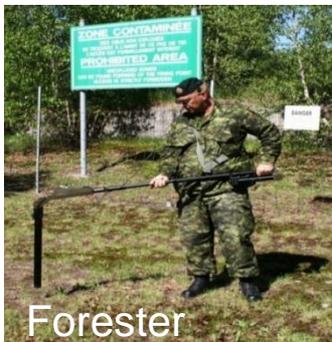
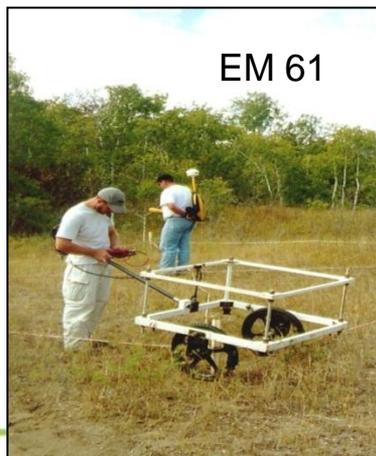
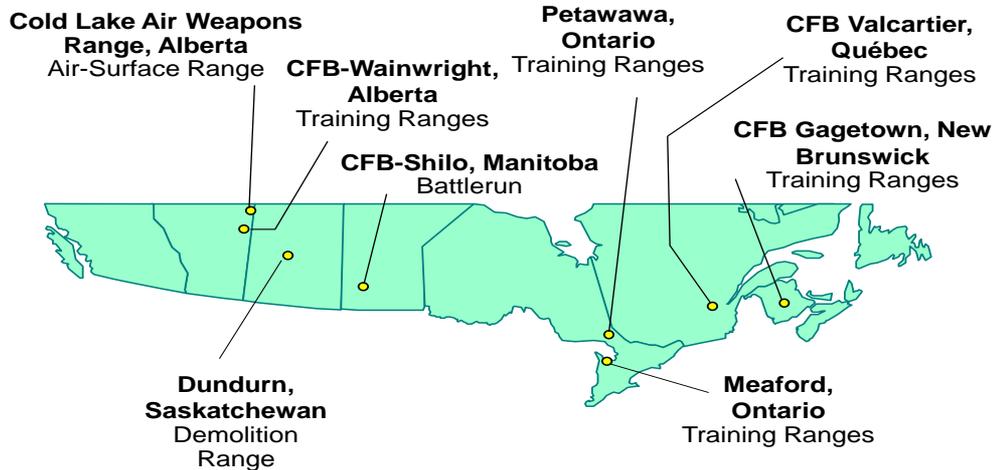
⇒ Breakthrough curves / transport modeling

# Lessons Learned on Fate, Transport and Toxicity

- RDX and AP : Toxic and bioavailable
- HMX : Much less toxic & bioavailable than RDX
- TNT : Toxic & soluble but non-bioavailable (through transformation/sorption)
- NG & 2,4-DNT : Toxic but low bioavailability (NC binding)
- NC : Neither toxic nor bioavailable
- Metals - Sb, Pb, Cd, Sr, toxic and bioavailable

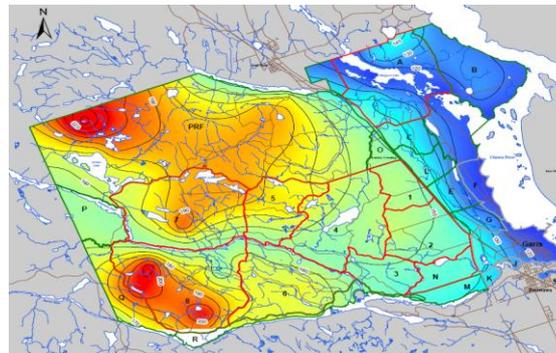
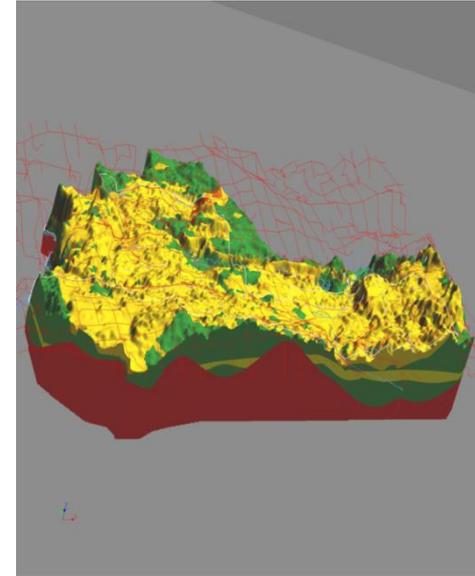
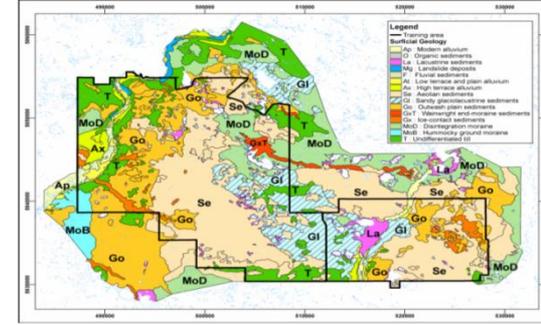


# Large Scale Fate and Transport: Hydrogeological Characterization



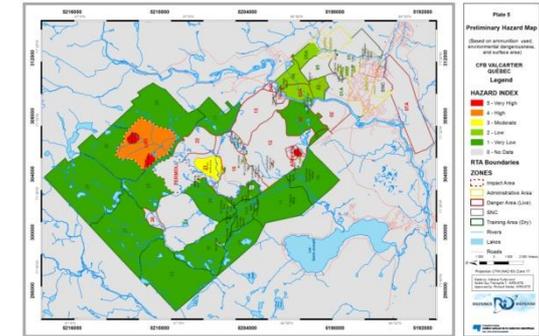
# Hydrogeology

- Surveillance wells in major training areas
- Production of several thematic maps
- Modeling aquifer flow and direction
- Prediction of contaminants transport
- Surveillance programs

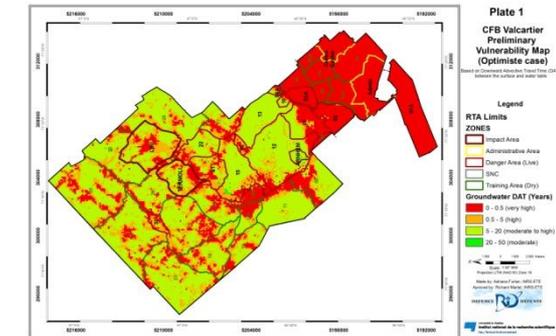


# Hydrogeology / Risk Management Tool

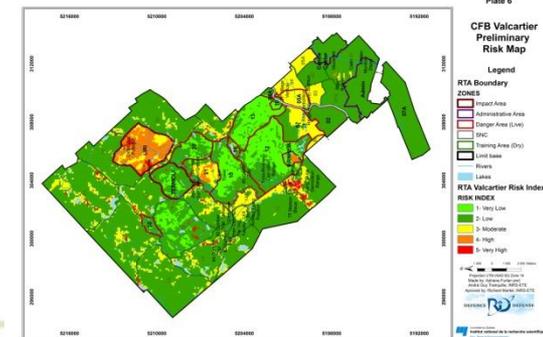
- Munition use logs/Surface sampling/ Deposition studies: Source terms **Hazard maps**



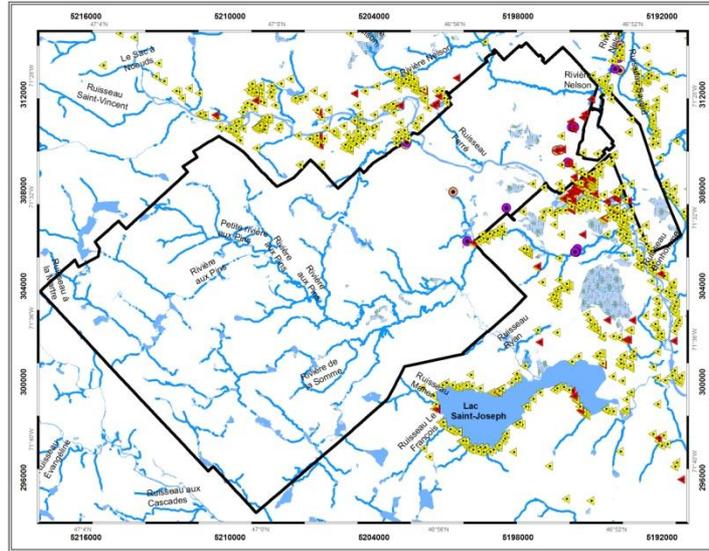
- Hydrogeological studies: Contaminant transport **Vulnerability maps**



- Combination of the vulnerability and hazard maps – **Risk maps**



# Receptors & Surface water vulnerability



**Plate 3**  
**CFB Valcartier Private wells Installation**

**Legend**

**Private well Installation**

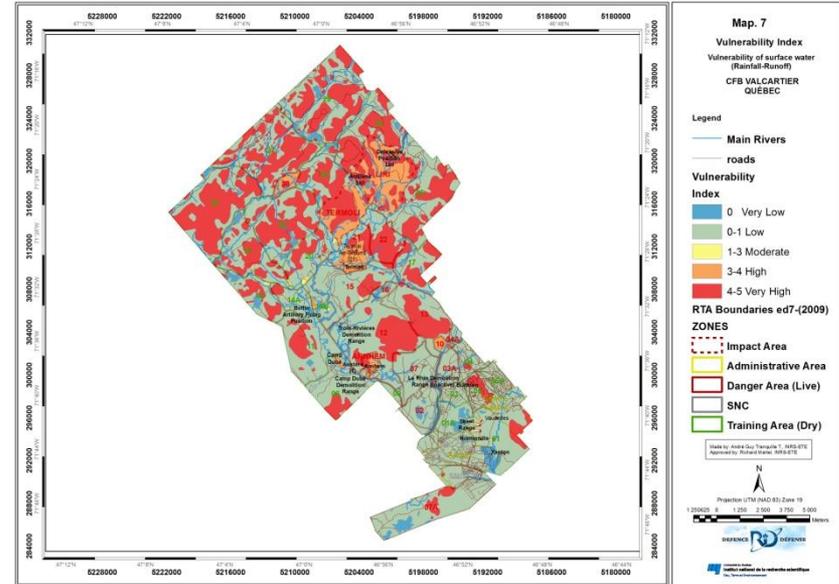
- Alluvial deposits
- Rock
- Limit base
- River
- Lake
- Wetland

**CFB Valcartier water supply**

- actif
- inactif

Scale: 1:61 000  
Projection UTM NAD 83 Zone 19  
Source: MDDEP, 2012

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**Map. 7**  
**Vulnerability Index**  
**Vulnerability of surface water (Potential Runoff)**  
**CFB VALCARTIER QUEBEC**

**Legend**

- Main Rivers
- roads
- Vulnerability Index

**Vulnerability Index**

- 0 Very Low
- 0-1 Low
- 1-3 Moderate
- 3-4 High
- 4-5 Very High

**RTA Boundaries ed7-(2009)**

**ZONES**

- Impact Area
- Administrative Area
- Danger Area (Live)
- SNC
- Training Area (Dry)

Scale: 1:250 000  
Projection UTM NAD 83 Zone 19  
Approved by: Richard Falaris, MDEP-ETS

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# In situ monitoring using RAMAN spectroscopy: Theory

- Raman is a weak optical phenomena: Nanoparticles significantly improves the response (work conducted by Professor Masson, U. Montreal)

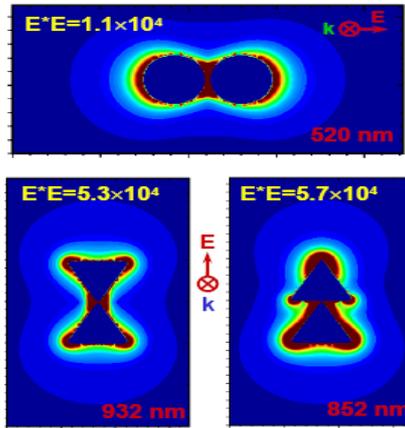


Figure 11. Contours of  $|E|^2$  for dimers of silver particles, including two spheres (separation 2 nm) and two triangular prisms placed head to head and head to tail (edge length 12 nm, width 12 nm, snip 2 nm and separation 2 nm).

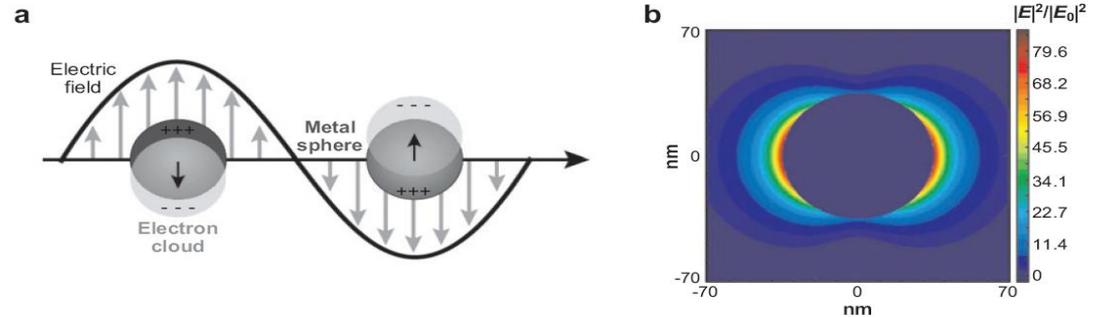


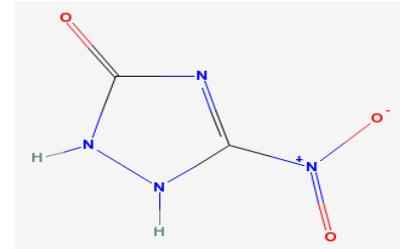
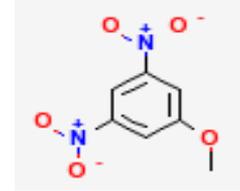
Figure 1  
 (a) Illustration of the localized surface plasmon resonance effect. (b) Extinction efficiency (ratio of cross section to effective area) of a spherical silver nanoparticle of 35-nm radius in vacuum  $|E|^2$  contours for a wavelength corresponding to the plasmon extinction maximum. Peak  $|E|^2 = 85$ .

# Climate change, Arctic deployment & Ecosystemic Values

- Climate changes: strong impact on contaminants fate and transport
- Canadian Army training ranges are located abroad Canada in various meteorological and geological settings
- A study will be initiated to predict potential problems in ranges and training areas related to climate changes
- Canada plans to open new ranges in Northern Arctic environment
- Live fire training must be conducted in a sustainable manner
- Ecosystemic value of our training ranges will be evaluated.

# Future Work: Insensitive Munitions (IM)

- International pressure to develop IM
- New explosives and propellant ingredients:
  - Dinitroanisole (DNAN)
  - 3-nitro-1,2,4-triazole-5-one (NTO)
  - 1,1-Diamino 1,2-dinitroethylene (FOX-7)
  - Guanylurea dinitramide (FOX-12)
  - Ammonium dinitramide (ADN)
- Toxicity and fate ?

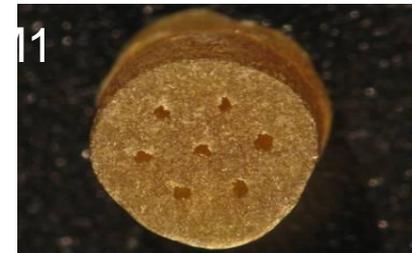


## Formulations already being used:

Octol (HMX/TNT); Comp B (RDX/TNT); PBX (HMX/Polyurethane/DOA/...);  
M1 (NC/2,4-DNT/DPB/...); .....

## New formulations:

GIM (HMX/TNT/ETPE); IMX series (DNAN/NTO/...); PAX series (DNAN/...)  
Helova (HMX/NC/ETPE/TEGDN/....); Green M1 (NC/TEGDN/...);  
Triple Base (NC/TEGDN/NQ/...)



## Aqueous solubility and $K_{ow}$ of traditional and new ECs

	Aqueous Solubility at 25°C (mg/L)	$K_{ow}$ at 22 °C
<b>TNT</b>	137	39.8
<b>RDX</b>	55.5	7.94
<b>HMX</b>	4.80	1.46
<b>TEGDN</b>	7,430	6.17
<b>NQ</b>	3,200	0.21
<b>DNAN</b>	216	38.1
<b>NTO</b>	17,200	0.02

# Future MC: What to Promote

## Best scenario

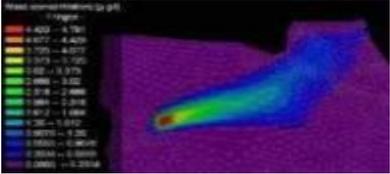
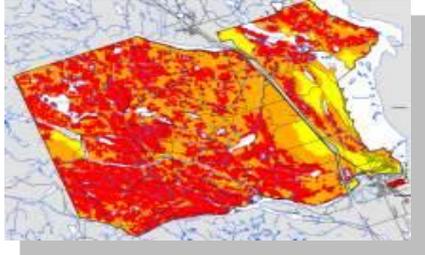
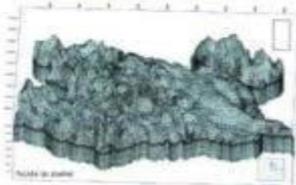
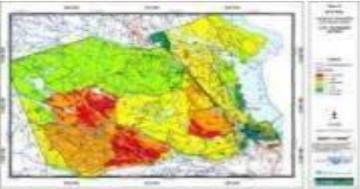
- Non toxic, low water solubility, not bioavailable (e.g. NC)
- Favourable biotic and abiotic transformations
- High sorption to soil/humic material
- Low volatilization
- Benign gaseous emissions (e.g. nitrogen-based explosives)
- Non UXO producing munitions (high-order scenarios)
- Propellants: Modular charges !
- Design for demil
- Metals: Mitigation measures in ranges if unavoidable



# Conclusions

- MC are dispersed heterogeneously in RTAs
- Composite systematic sampling must be used
- Treatment and homogenization are critical
- Fate and transport studies are critical
- Knowledge lead to risk management through mitigation measures
- Future IM are a challenge
- **Green component must be taken into consideration early in the development process**

# The End - Thank You



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FOR CANADA'S DEFENCE AND SECURITY

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POUR LA DÉFENSE ET LA SÉCURITÉ DU CANADA

