



global thinking



local delivery



## Military & Armament Contaminations:

- Propellants & Explosives
- Gasoline, Heavy Metals, Solvents & PCB
- CWA : Chemical Warfare Agents
- Radioactive Materials
- Biological Agents as Anthrax, Butolinus F..





# Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites



## Goal:

## Safety

- HRA: Health Risk Assessment for future Site use.
- Implementation of Toxicology for Real Estate & Urbanization Projects (Residential, etc.),
- Verification of acceptable Risks.
- Definition of RG: Remediation Goals.
- Site Remediation by Application of RG or Site Use Modification (and/or Use Restrictions = Servitudes).
- Transparency concerning Health Hazards for the site Owner or Operator, Future Users, Investors, Banks, Insurance Companies and Authorities.
- Health, Environment, Legal and financial Budget-Safety.



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### Typical Military Pollutants:

- **Propellants**: NC, Perchlorate, Diphenylamine, NGI, Nitro-guanidine, DNT, Hydrazine, Dimethyl-hydrazine (Snow from Kazakhstan / Beikunur), etc.
- **Explosives**: Nitro-aromatics as: TNP, TNT, TNB, RDX, HMX, etc. & Metabolites as Amino-nitro-aromatics, etc.
- **CWA**: S-Mustard, Lewisite, Clark 1&2, Adamsite, Sarin, Soman, Tabun, VX, TCNM, Phosgene, etc.
- **Detonators**: Hg-Fulminate, Pb-azide, etc.



## CWA-Origin: 1914-1918:



- World War I: ~16 million Toxic Shells (10-15 % did not explode).
- > 1.5 to 2.4 million CWA Shells remain in sub-soil in N & E France, Belgium, Germany, Russia, Baltic Sea Floor, Atlantic, etc.





## CWA-Origin: 1918-1940 (WW II):

- **Munition Stocks & Waste:** Dumped or “Recycled”
- **Recycling:** In a very polluting way: Explosives and Propellants (NC) were reused and CWA were buried (drums, shells, etc.).
- New Organo-phosphorous CWA were developed



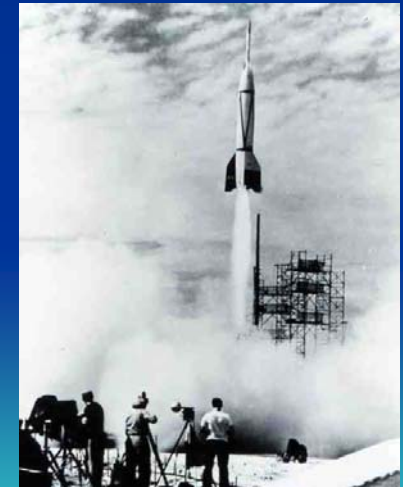
## Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites



Hallschlag

### CWA-Origin: 1940-1945:

- During WW II, CWA were not used (except in China: Japanese Army abandoned 0.7- 2 Million CWA Shells).
- Artillery Units were equipped up to 15% with CWA Ammunition.
- The German, American & British Armies left Munitions Waste & CWA in France, UK, Germany & USA.



V2: Hydrazine →



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### CWA-Origin: > 1945:



- After the WW II, any Weapon Waste found was Recycled, or Exploded by State Services or Private Companies.
- Storage, Recycling & Destruction Sites are extremely highly Contaminated by heavy metals toxic Explosives and CWA.
- Since the UN-Paris Convention 1993: CWA Production Stop.





## **Potential Contaminated Sites:**

- Combat Zones between 1914 & 1918,
- Military camps between 1890 & 1993 (or later),
- Military Training zones,
- Ammunition Destruction or Recycling Sites,
- Military waste Dumps,
- Ammunition, Explosives, Fertiliser, Pesticides, Propellants & CWA Production Sites

→ **Thousands of sites with low Historical Knowledge**



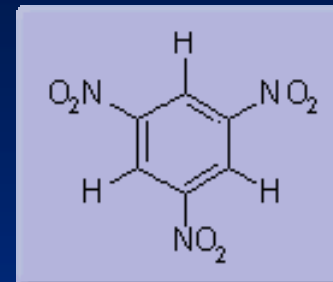
## Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites



### Site Investigations:

- Historical Survey & Identification of potential Military Pollution,
- UXO: Electromagnetic detection & Securing of Explosive Objects (Bombs, Shells, Mines, Drums...),
- Samplings of Soil, Water, Air under needed PPE (NBC masks, waterproof & gastight clothing, “B-W” decontamination unit...) ,
- Health & Environmental Risk Assessment for future Site use scenarios.



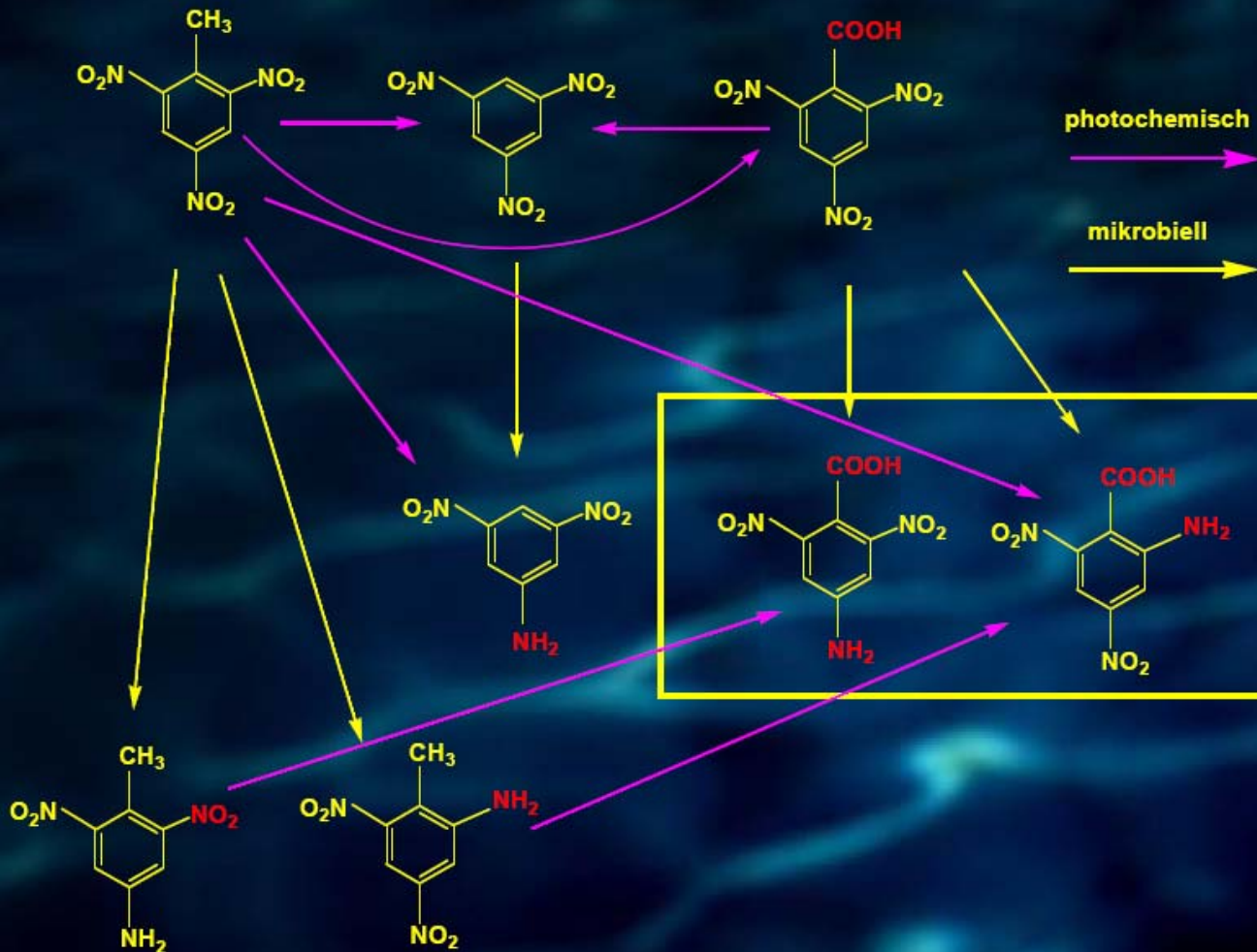


## Environmental Chemistry:

- Explosives: TNT, TNB, TNN, TNP, etc.,
- Intermediary Synthesis Compounds and
- Toxic Breakdown-Products (Micro-biological Metabolites, hydrolysis products...).

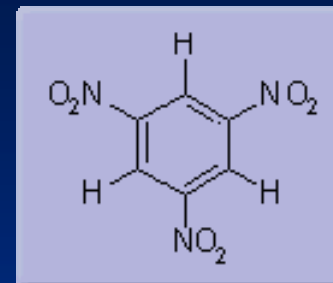


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Environmental Chemistry:  
Degradation of TNT





## Environmental Chemistry:

- Toxic Breakdown-Products (Micro-biological Metabolites, hydrolysis products...),
- 900 to 980 “active products” of CWA were produced during WW I,
- Additionally Pesticides were used (Agent Orange: 2,4,5-T...).



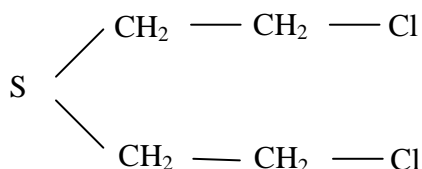
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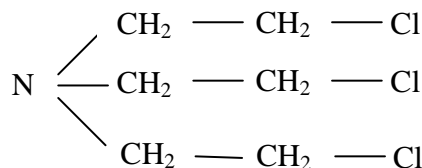
Impact Craters:  
WW I →

## Yperite type products:

**S-Mustard or  
S-Yperite (S-Lost):**



**N-Yperite (N-Lost) :**



**Many other “Yperites” exist (S-, N- and O- Yperite)**

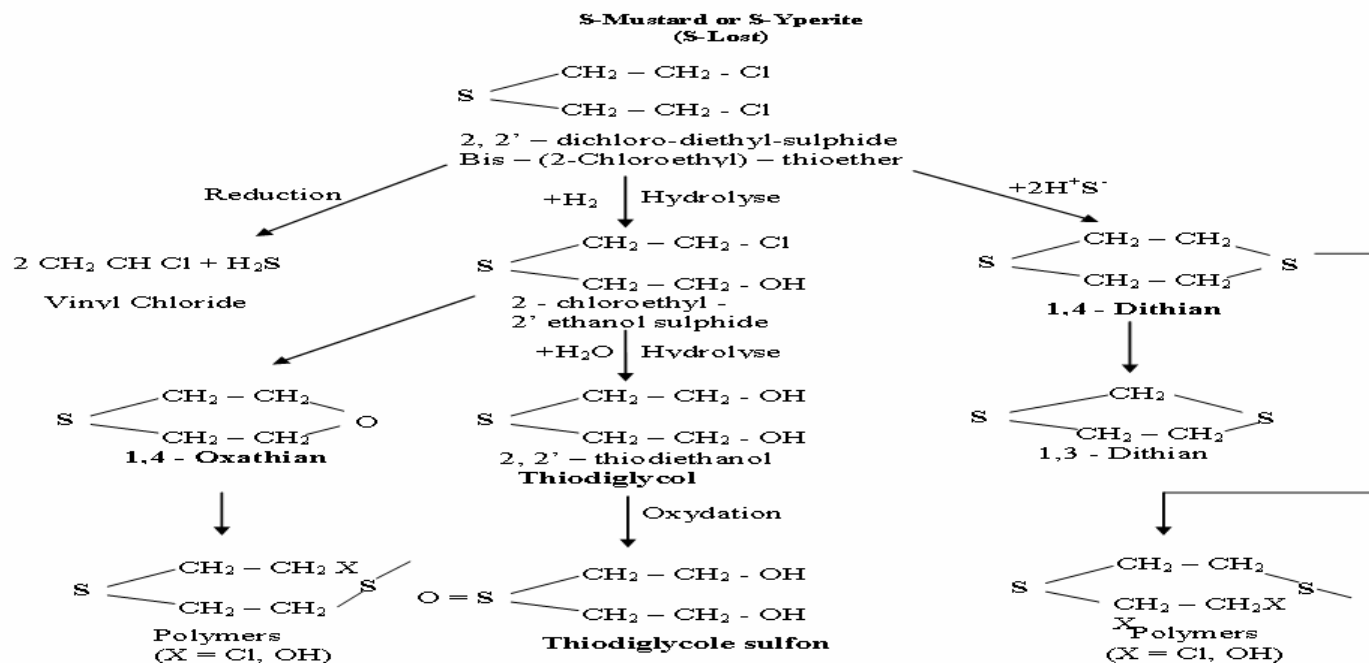




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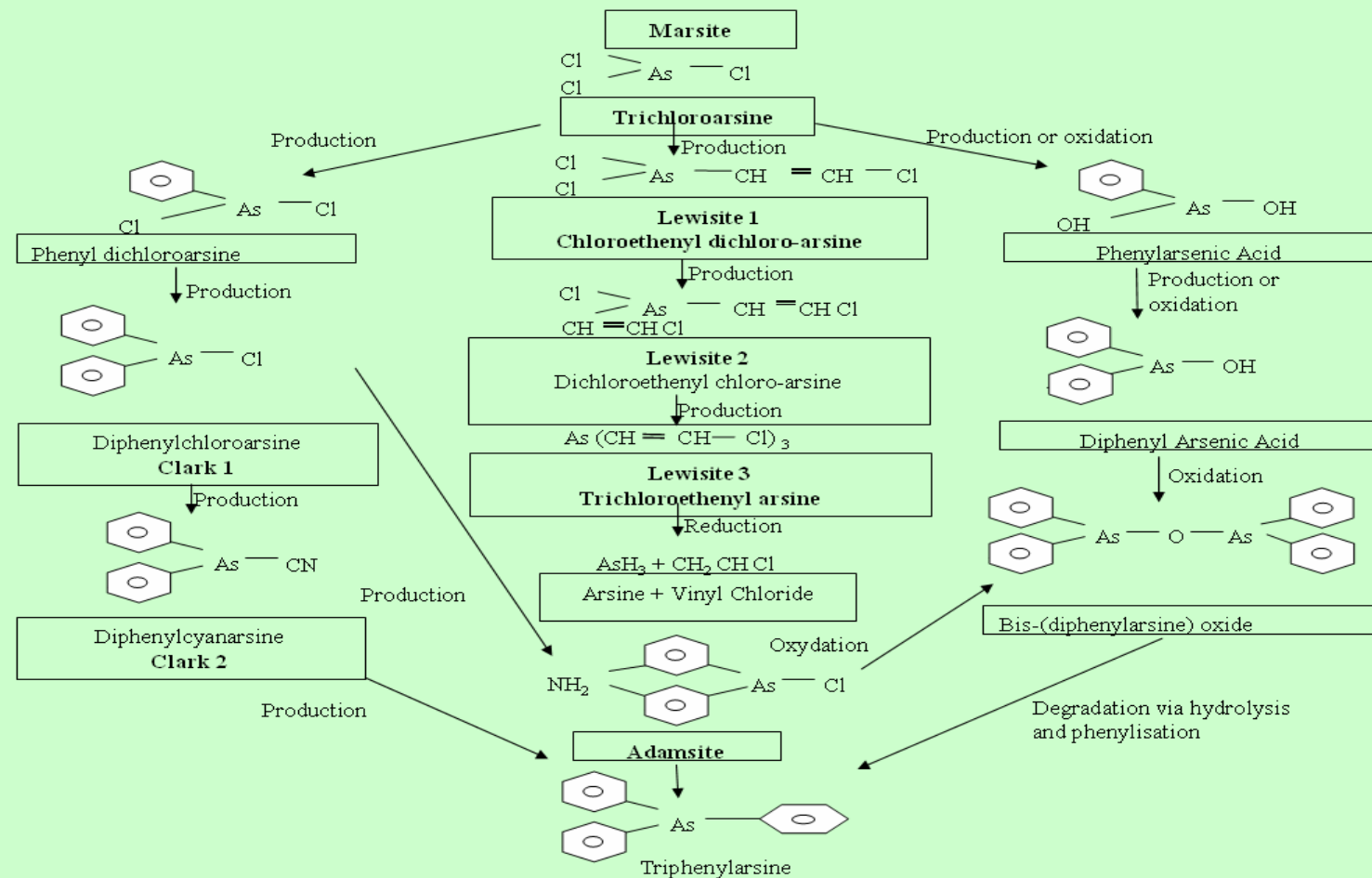
## Environmental chemistry of S-Yperite and toxic metabolites



"Winter Yperite" was a mixture of S-Yperite + Marsite + Phenyl dichloroarsine + Diphenylchloroarsine + Triphenylarsine



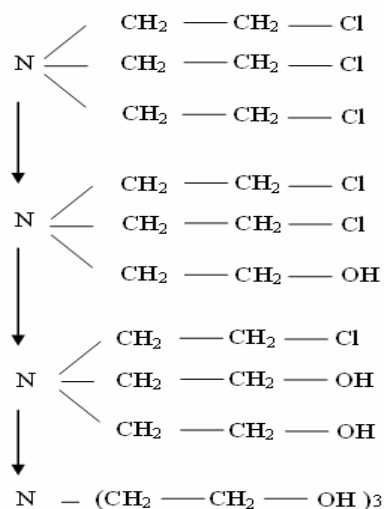
# Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites





# Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites

## Hydrolysis of N-Yperite in Environment



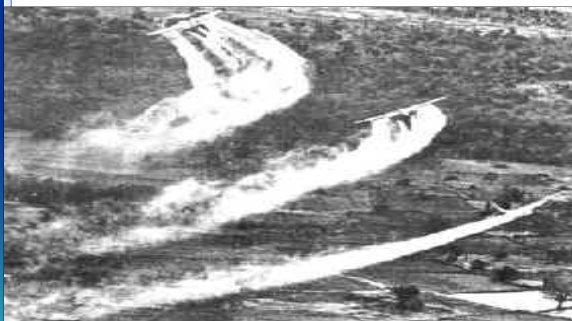
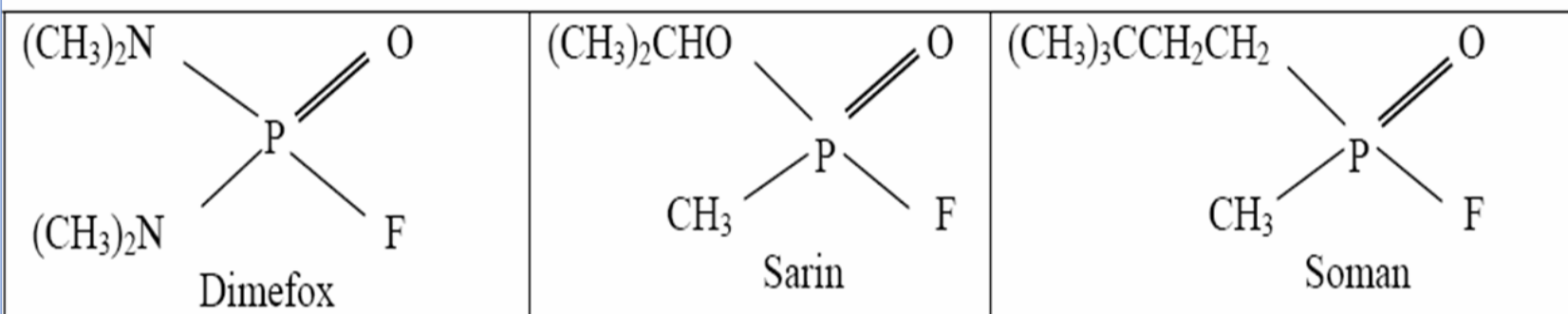
**N-Yperite:**  
Hydrolysis and  
formation of  
chlorinated  
amino alcohols



**CWA- Attack Halabjah (Iraq) : 1988 →**



## Pesticides & Chemical Warfare Agents: Similitude



← Agent Orange Use (2,4,5-T) in Vietnam War



## Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites



### HRA: Health Risk Assessment:

The first Step of HRA, is to Ensure that all Contaminants are identified.

For ex. Organo-Arsenic Compounds:

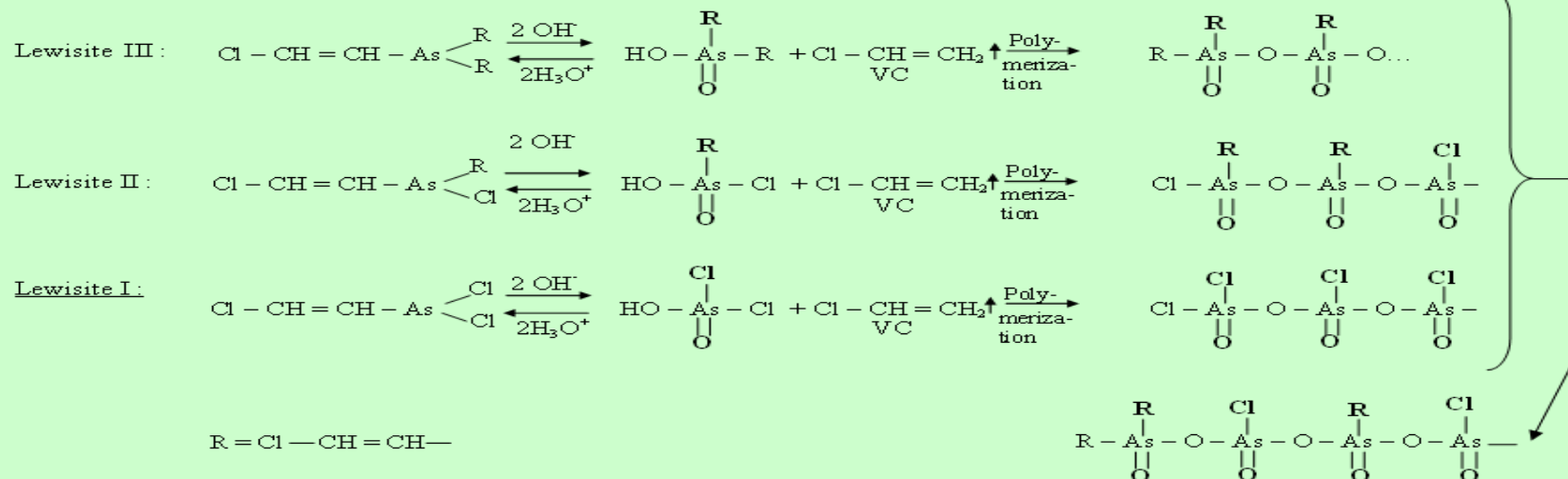
- As III and As V Ions,
- The possible Alkyl Arsenic Compounds and Alkyl Arsenic Acids,
- Intermediate products such as Marsite, Phenyl-dichloro-arsine, Phenyl-arsenic- acid and Diphenyl-arsenic-acid,
- CWA such as Clark 1 & 2, Adamsite, and Lewisites 1, 2 and 3,
- Degradation products such as Triphenyl-arsine, Bis-(diphenylarsine)-oxide, Arsine and vinyl chloride,
- Co-Contaminants such as Explosives, Propellants and Co-CWA S-Yperite, etc.



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## Environmental chemistry of Lewisites and the Inversion of hydrolysis/oxidation/polymerisation and Evaporation





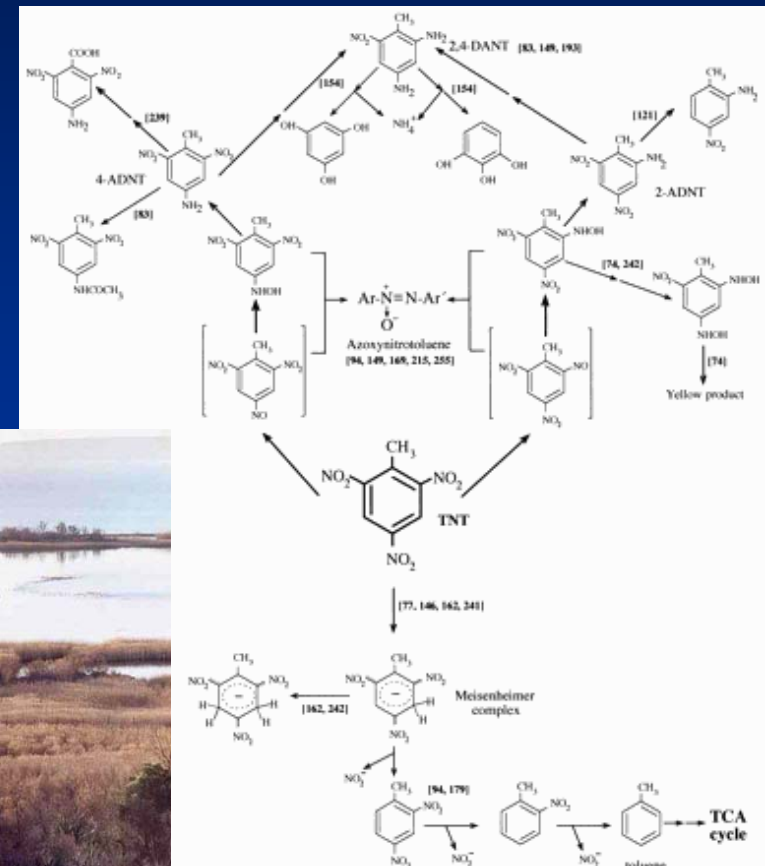
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## TNT Degradation



Saint Chamas

3 – 6 % TNT





## HRA Health Risk Assessment (chronic Risks )

- **Toxicity Reference Values** (TRVs = Dose/effect-Values) often only available from Military-medical Institutions in the US, Canada, Sweden or from other European States.
- Example: **USACHPPM** (US Army Center for Health Promotion and Preventive Medicine: Toxicity Evaluation Program (TEP) (410) 436-3980 E-mail [TEP](#)



## Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites



### Military Guidelines for HRA:

- Review of the U.S. Army's Health Risk Assessments for Oral Exposure to Six Chemical-Warfare Agents (1999),
- TG 185: US-Army: Commander's Guide to the Health Risk Assessment Process (USACHPPM POC: D. Daughdrill, DSN 584-8177),
- TG 202: US-Army: Field Environmental Science Officer Checklist,
- TG 204: US-Army: Glossary of Terms for Nuclear, Biological and Chemical Agents and Defense Equipment (CHPPM POC: Gail Gibson, DSN 584-3254),
- TG 239: US-Army: Radiological HRA's (CHPPM POC: CPT R. Reyes, DSN 584-2670),
- TG 273: US-Army: Diagnosis and Treatment of Diseases of Tactical Importance to U.S. Central Command,
- TG RD 236A: US-Army: The Technical Foundation for Basic Radiological Dose Estimation (USACHPPM POC: CPT R. Reyes, DSN 584-2670)



# Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites



## Acceptable Risks:

- Individual Cancer Risk :  $ICR \leq 10^{-5}$

- **WHO 1996: International Symposium** Exposure and Risk Assessment with Respect to Contaminated Soil: YOUNES.  
Munich (28-29/02/1996),
- **Germany: BA 161a : 28/08/1999,**
- **France: Ministry Circular** DPPR/SEI/BPSE/BS/MB: 10/12/1999,
- **U.S.A. / DOH: Department of Health: 2006:** There is no overall DEP (Data Execution Policy) on acceptable cancer risk level; this varies by program. Act 2 authorizes a range of 10E-4 to 10E-6 for the Land Recycling program.  
The calculation of the generic Statewide health standards used a level of 10E-5 :  
<http://www.dep.state.pa.us/dep/subject/advoun/cleanup/2006/TCEIssues.doc>
- $ICR = DED \cdot UR$  (Daily Exposure Dosis • Unit Risk = Slope Factor)

- Non-Cancer-Risk: Risk Index:  $RI \leq 1$

- $RI = TRV / DED$  (Toxic Reference Value / Daily Exposure Dose)



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## TRV Examples:

Compound	Type of TRV	Exposure Pathway	TRV	Institute
2,4,6-Trinitro-Toluene (TNT)	ADI	Ing.	0,0005 mg/kg/j	IRIS1993
		Inh.	-	-
	UR	Ing.	0,03 [mg/kg/j] <sup>-1</sup>	IRIS1993
		Inh.	-	-
1,4-Dithiane	ADI	Ing.	0,01 mg/kg/j	IRIS1993
		Inh.	-	-
2,4-Dinitro-toluène	ADI	Ing.	0,002 mg/kg/j	IRIS1992
		Inh.	-	-
	UR	Ing.	0,68 [mg/kg/j] <sup>-1</sup>	IRIS1990
		Inh.	0,089 [mg/m <sup>3</sup> ] <sup>-1</sup>	OEHH 2003



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## TRV Examples:

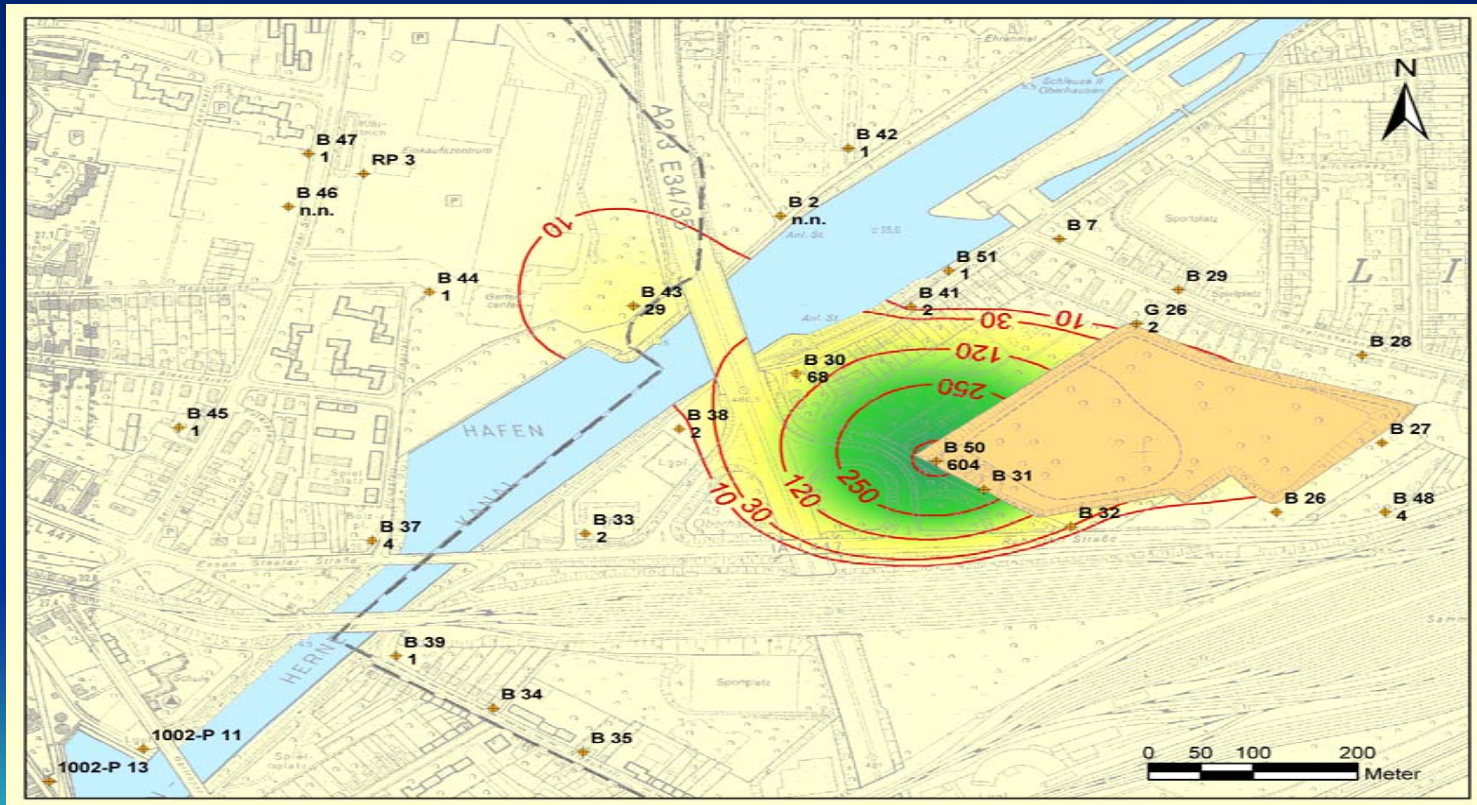
Compound	Type of TRV	Exposure Pathway	TRV	Institute
Nitroguanidine	ADI	Ing.	0,1 mg/kg/j	IRIS 1993
		Inh.	-	-
N,N-Diphenylamine	ADI	Ing.	0,025 mg/kg/j	IRIS 1990
		Inh.	-	-
2,6-diamino-toluene	ADI	Ing.	0,2 mg/kg/j	HEAST199 4
		Inh.	-	-
Hydrazine	UR	Ing.	3 [mg/kg/j] <sup>-1</sup>	IRIS 1991
		Inh.	4,9 [mg/m <sup>3</sup> ] <sup>-1</sup>	IRIS 1991
	ADI	Ing.	-	-
		Inh.	0,005 mg/m <sup>3</sup>	ATSDR199 7



# Risk Assessment Methodology for Military Pollutants & Toxic Metabolites on future Residential Sites



- Contaminants Mapping in Exposure Zones

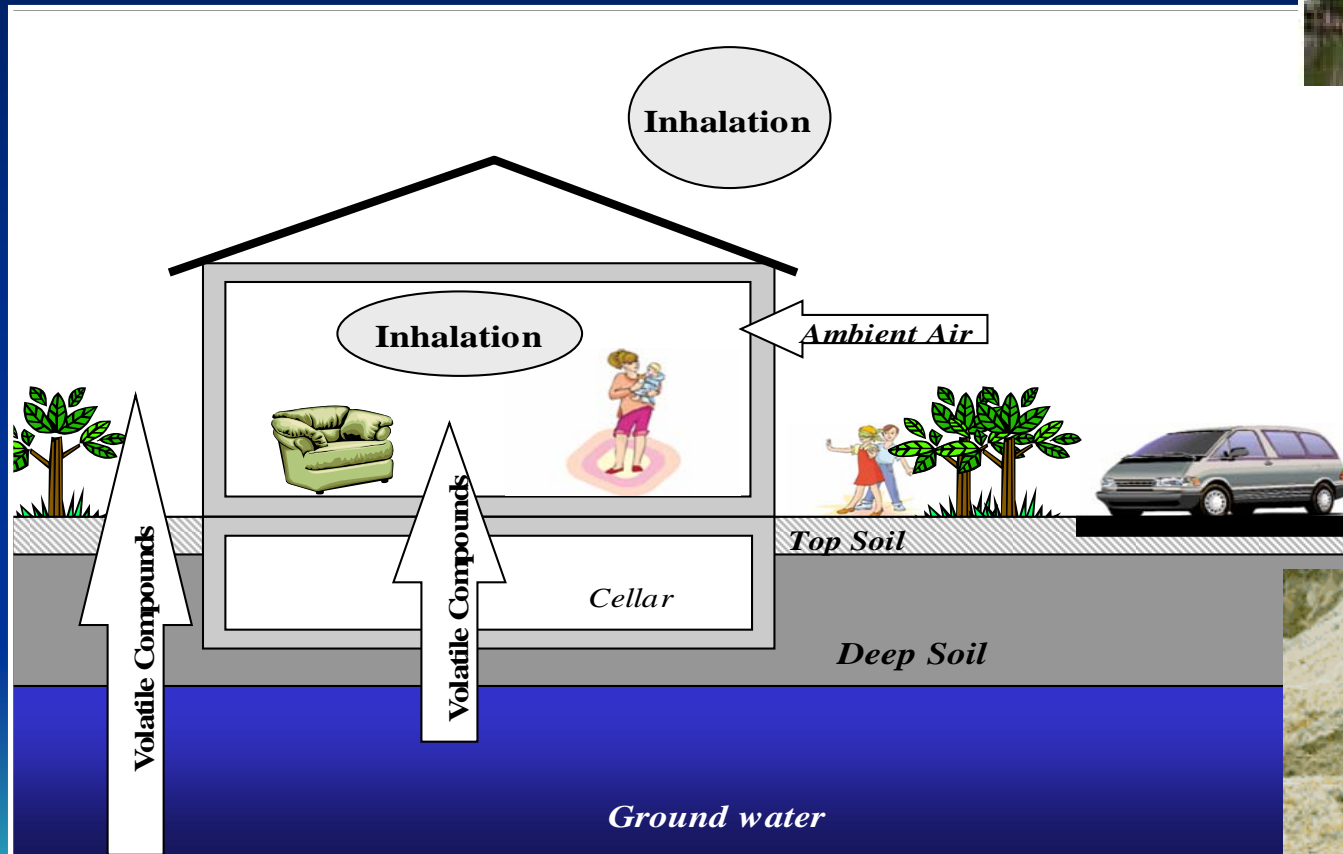




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## Exposure Pathways: Conceptual Scheme



Excavation





## Exposure Quantification: Ingestion of soils, water or food:

$$DED_{ing} = C_m \cdot \frac{Q_{ing}}{P} \cdot F_a \cdot \frac{Ex}{Ve} \cdot F_{exa} \cdot F_{exd}$$

DED<sub>ing</sub> = Daily Exposure Dose [mg/kg/d]

C<sub>m</sub> = Concentration Pollutants Concentration in the exposure medium : C<sub>soil</sub> [mg/kg], C<sub>water</sub> [mg/l], C<sub>food</sub> [mg/kg]

Q<sub>i</sub> = Ingested Soil quantity and/or food [kg/d] or water [L/d], distinct from the Adults (Q<sub>ing.A</sub>) and the Children (Q<sub>ing.C</sub>)

P(a) = Adult Body Weight [70 kg]

P(e) = Child Body Weight [15 kg]

F<sub>a</sub> = Absorption Factor (if failing: 100 % = [1])

Ex = Exposure years in Lifetime (Adult or Child) [y]

Ve = Lifetime: Adult or Child [y]. In case of carcinogenic Pollutants: Ve = Ex [y]

F<sub>exa</sub> = Yearly Exposure [d/365 d]

F<sub>exd</sub> = Daily Exposure [hrs/24 hrs]







# Saving: Health, Environment & Live Quality

