Fate and Transport of Explosives in Soil and Ground Water

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Origins of Explosives in the Environment

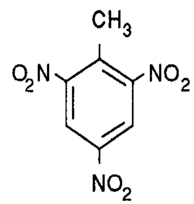
- Manufacturing of explosives
- “Load-and-Pack” operations/filling munitions with explosives
- Live-fire soldier training
- Weapon systems testing
- Commercial enterprises

Status of Explosives Contamination

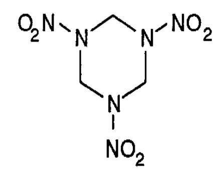
- **Manufacture and load-and-pack sites**
  - **Focus of clean-up efforts since early 1980s**
  - **Most heavily contaminated soils and ground water have been or are currently under treatment**
    - **Incineration** • **Composting** • **Pump-and-treat** • **In situ**
- **Live-fire training and weapon systems testing ranges**
  - **Characterization has only recently begun**
  - **Massachusetts Military Reservation**
  - **More distributed source; solid material**

Explosive Compounds

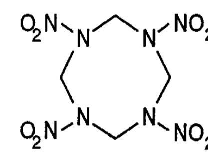
- TNT
- RDX
- HMX
- Others



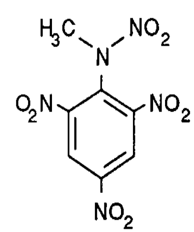
TNT
(2,4,6-trinitrotoluene)



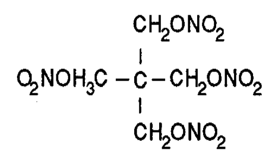
RDX
(hexahydro-1,3,5-trinitro-1,3,5-triazine)



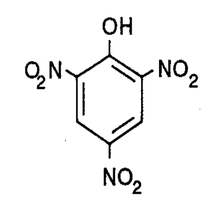
HMX
(octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)



Tetryl
(n-methyl-n,2,4,6-tetranitroaniline)



PETN
(pentaerythritol tetranitrate)



picric acid
(2,4,6-trinitrophenol)

General Properties

- Character: Crystalline solids
- Solubility: $\leq$120 ppm at 25^{o}C
- Dissolution rate: slow
- Environmental stability
  - TNT is unstable
  - RDX and HMX are stable
  - All degrade under anaerobic conditions
- Phytosensitivity
  - TNT degrades to complex red products
  - RDX and HMX less light sensitive

TNT from a 155-mm artillery projectile

Photodegradation of TNT

Transport Properties

- Soil partitioning

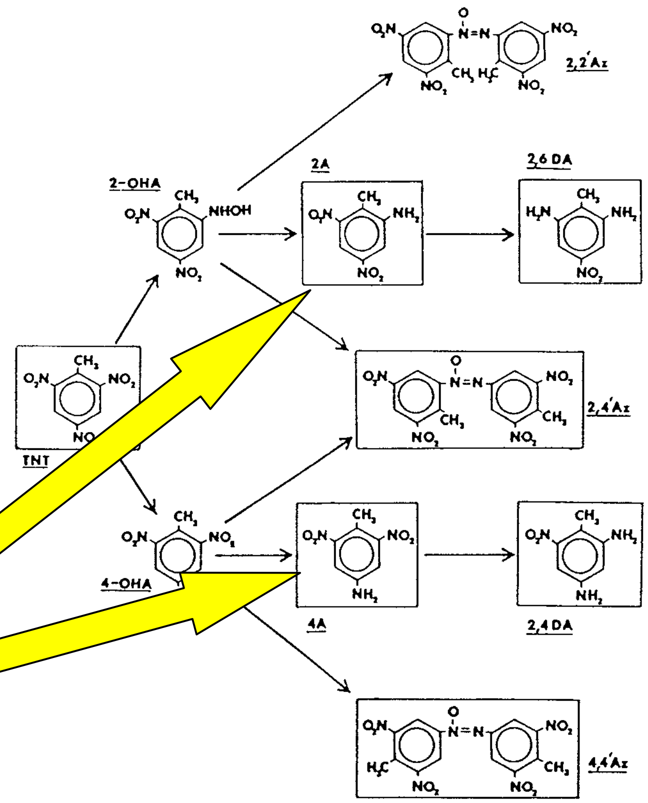
	K_d (L Kg^{-1})
TNT typically	< 10
4ADNT	6
2ADNT	6
TNB	3
RDX	<10
HMX	<10

Brannon et al. 1998

Soil adsorption is limited.

Transformation to mono amino products can be rapid.

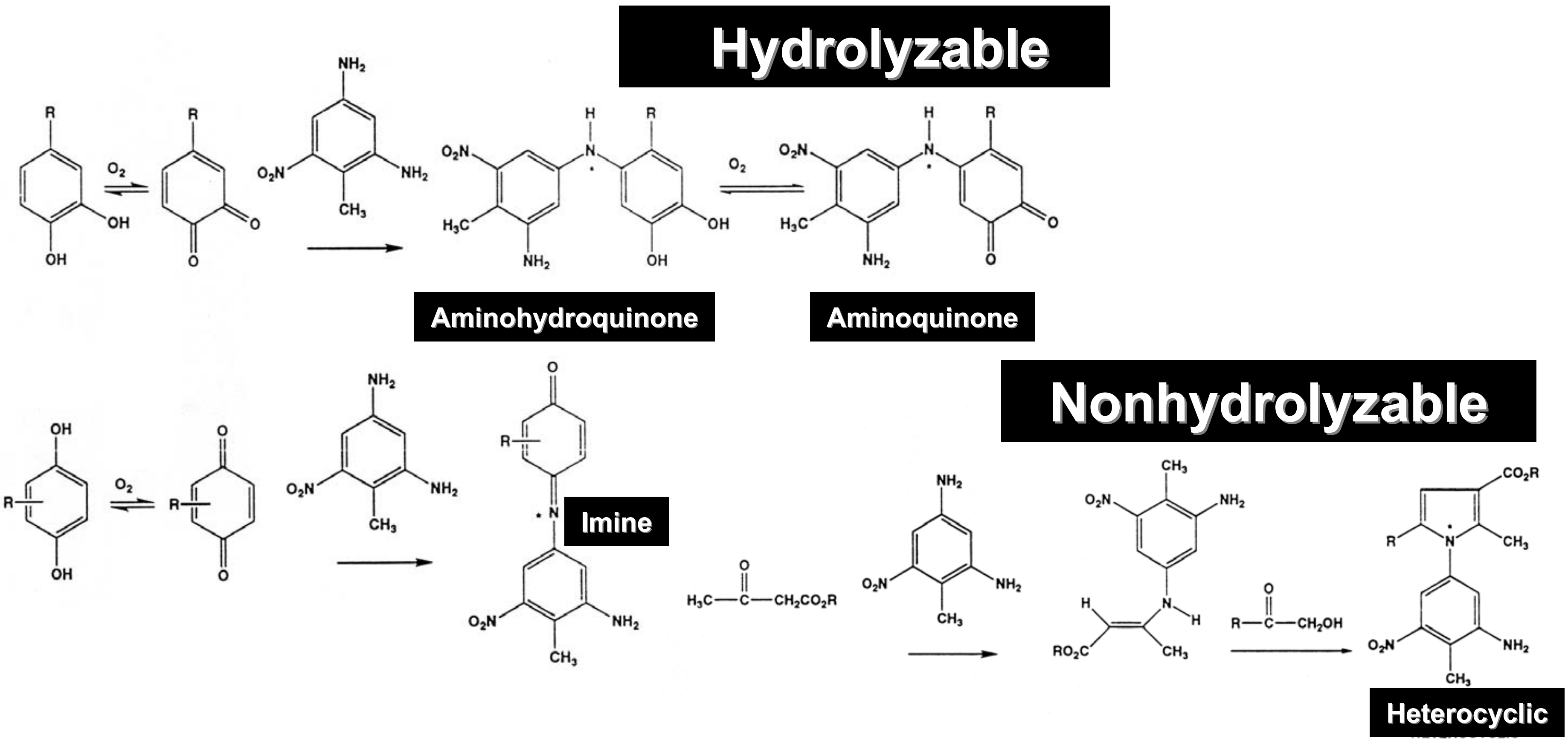
- TNT Transformation



Kaplan and Kaplan 1982

Transport Properties

Fate of TNT in surface soils



Thorn et al. 2002

- **Reactions result in immobilization**

Transport of TNT to Ground Water

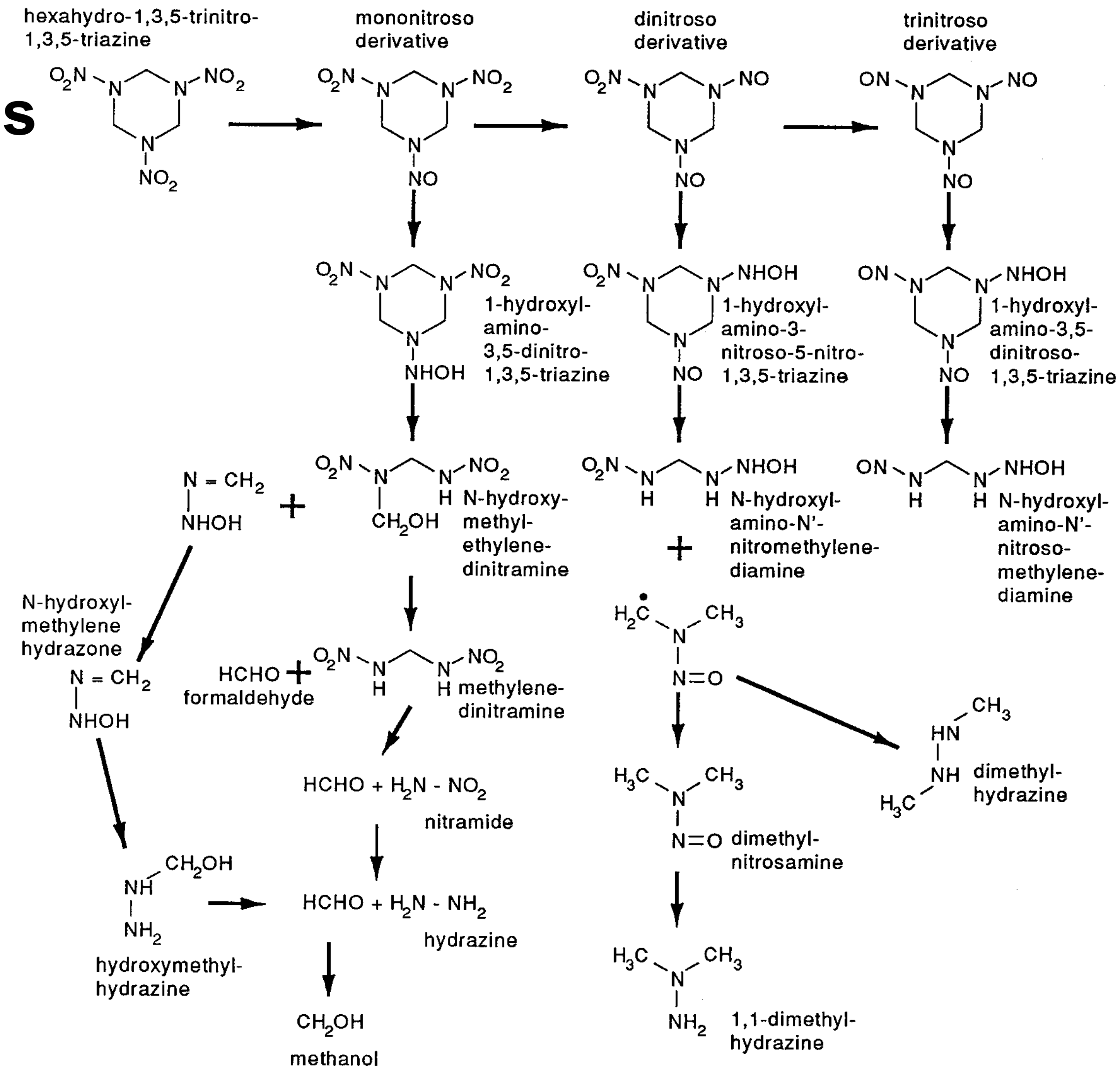
- Occurs when volume of contamination exceed capacity of soil to attenuate, e.g., manufacturing sites, load-and-pack sites

- Transformation products are common when TNT is present

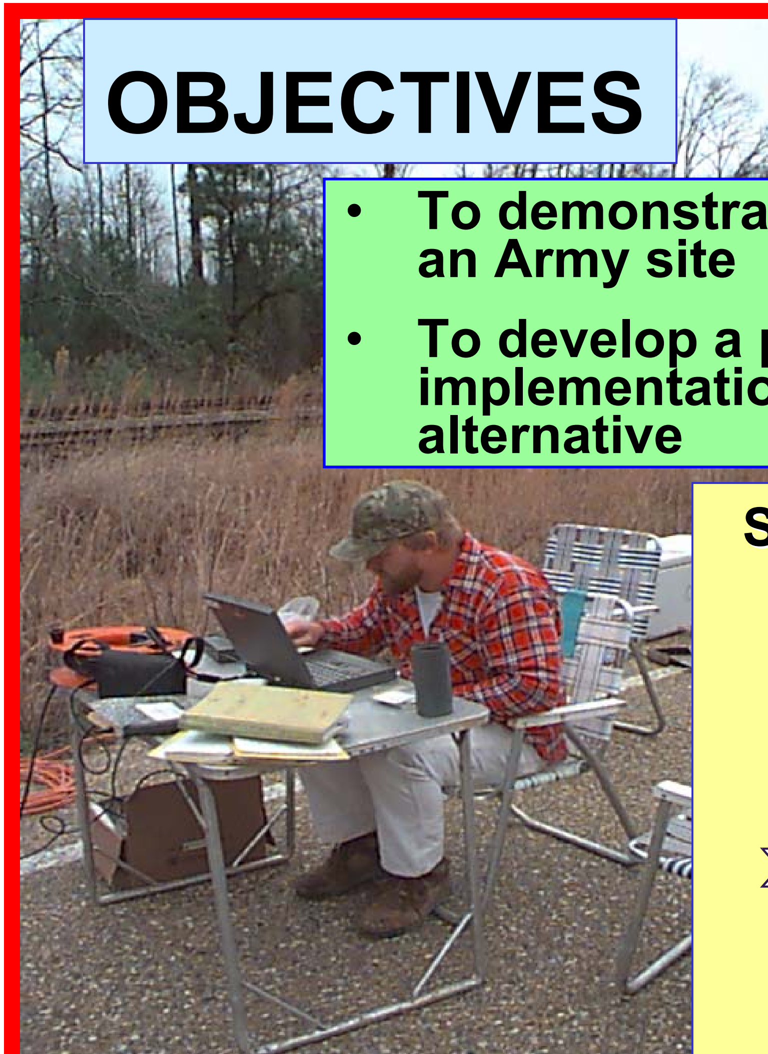
- Ground water associated with live-fire training typically does not contain TNT (data are limited)
    - Sources are small points
    - Sources are widely distributed
    - Sources are initially in solid form
    - Attenuation in surface soils is significant

RDX Transport/Degradation

- Degradation requires anaerobic conditions
- Readily transported from soil to ground water
- Transport behavior is similar to that of a conservative tracer



Monitored Natural Attenuation



OBJECTIVES

- To demonstrate natural attenuation of explosives at an Army site
- To develop a protocol for selection and implementation of natural attenuation as a remedial alternative

Sponsors:

Strategic Environmental Research and Development Program

Environmental Security Technology Certification Program

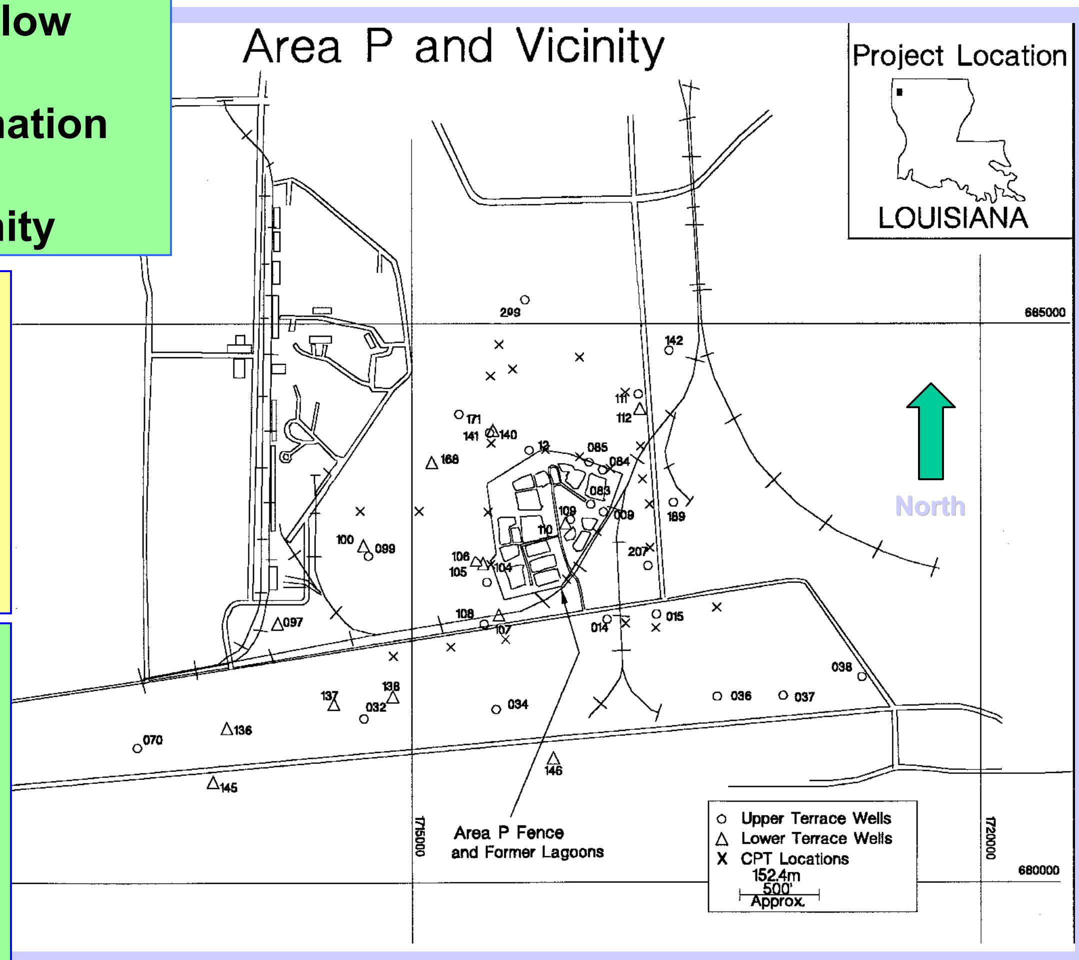
U.S. Army Environmental Center

LOUISIANA
ARMY AMMUNITION PLANT

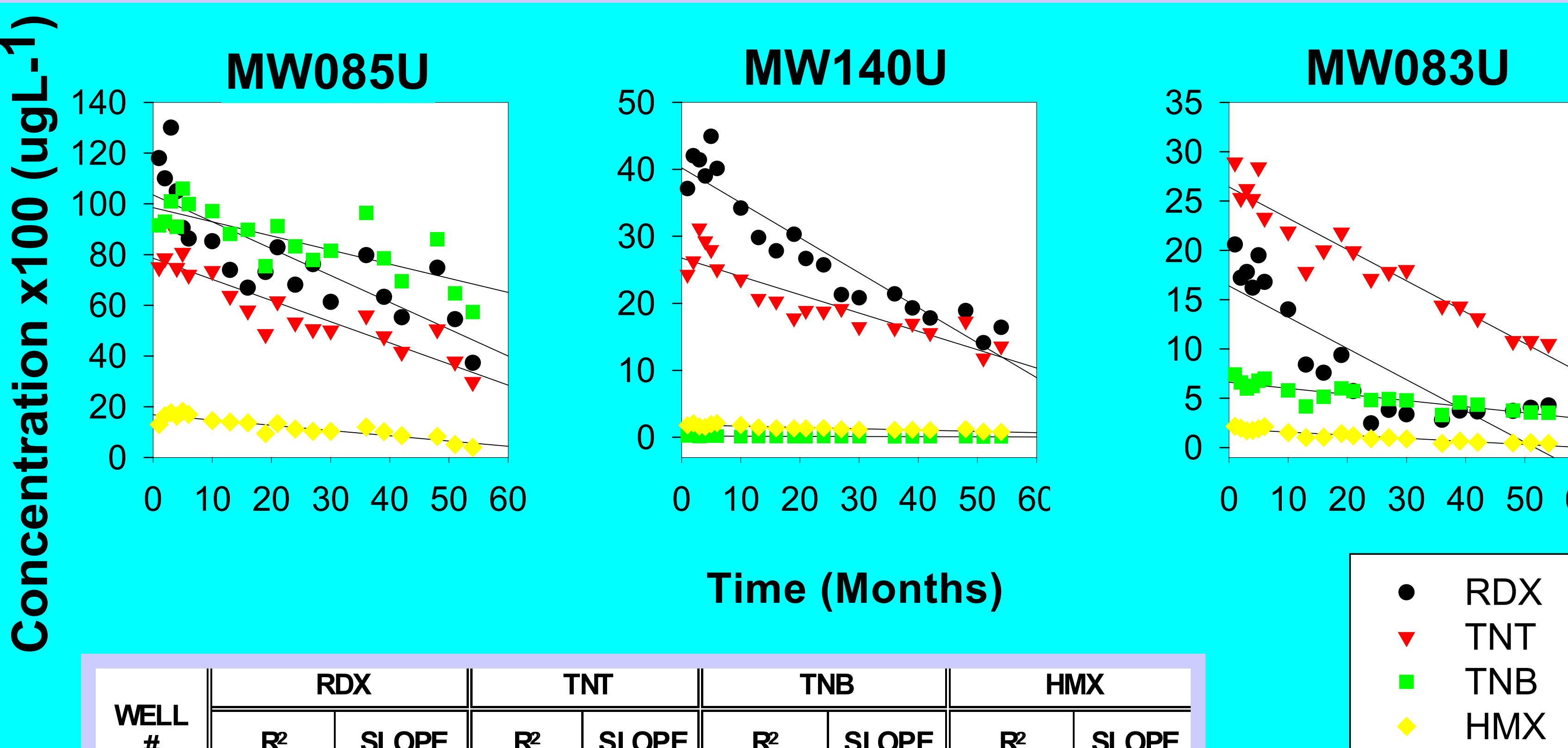
Site selection criteria
- Sufficient residence time to allow attenuation
- Limited or no risk of contamination of local receptors
- Receptive regulatory community

Characteristics of LAAP
- Source removed
- Extensive historical data
- Extensive existing monitoring wells
- Installation support

Approach
- Groundwater Monitoring
- Site Capacity Measurement
- Groundwater Modeling
- Biomarker Development
- Stable Isotopes Development
- Protocol



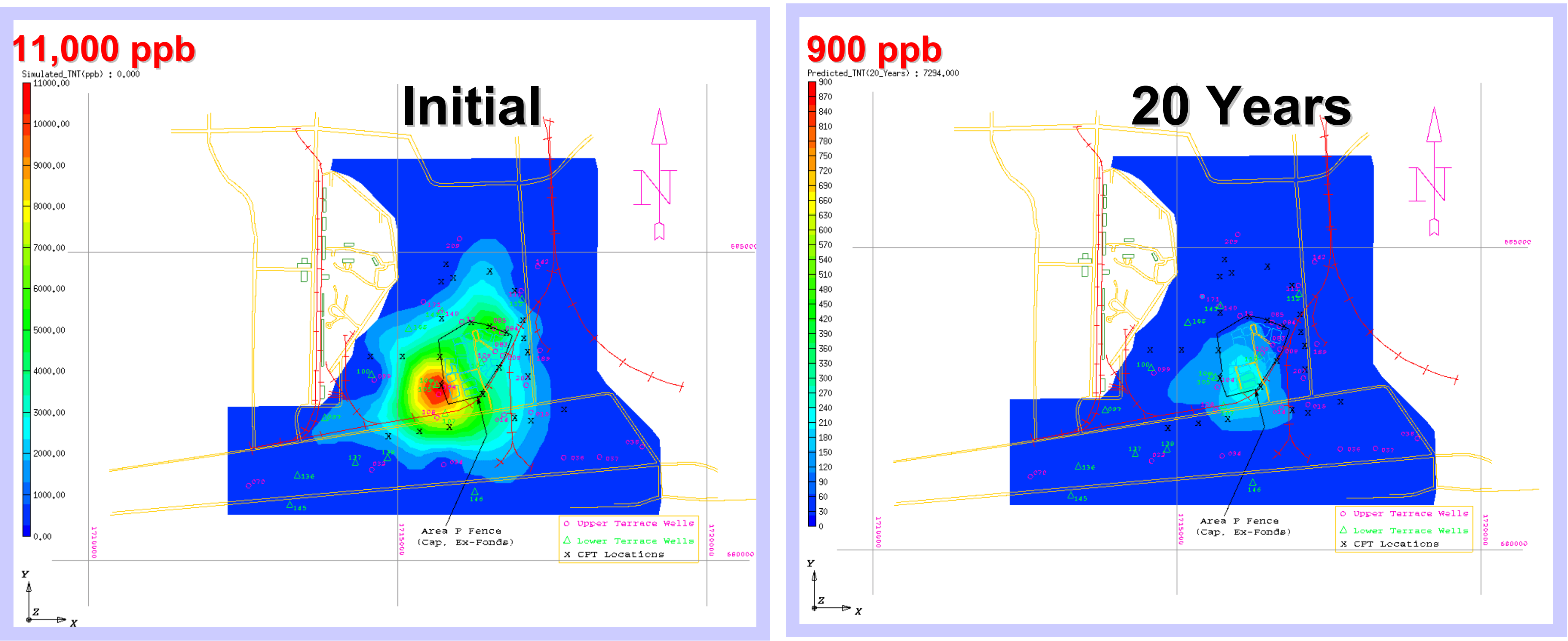
Concentrations in LAAP Ground Water Over Time



WELL #	RDX		TNT		TNB		HMX	
	R^2	SLOPE	R^2	SLOPE	R^2	SLOPE	R^2	SLOPE
0.85U	0.669	-105.864	0.822	-83.337	0.606	-55.781	0.824	-20.597
140U	0.890	-52.185	0.805	-27.363	0.559	-0.236	0.783	-1.952
083U	0.725	-31.665	0.914	-31.710	0.767	-6.201	0.861	-3.166

Modeling Ground Water Attenuation of TNT at LAAP

TNT Concentration



Monitored Natural Attenuation

Advantages

- Significant cost savings
- Less waste
- Less risk of exposure during remediation
- Less intrusive

Limitations

- Process monitoring difficult
- Slow attenuation rate
- Requires “weight of evidence”

Implementation Considerations

- Hydrologic, geologic, and contaminant characterization
- Risk determination
- Long-term monitoring
- Groundwater modeling
- Periodic reevaluation
- Contingency planning

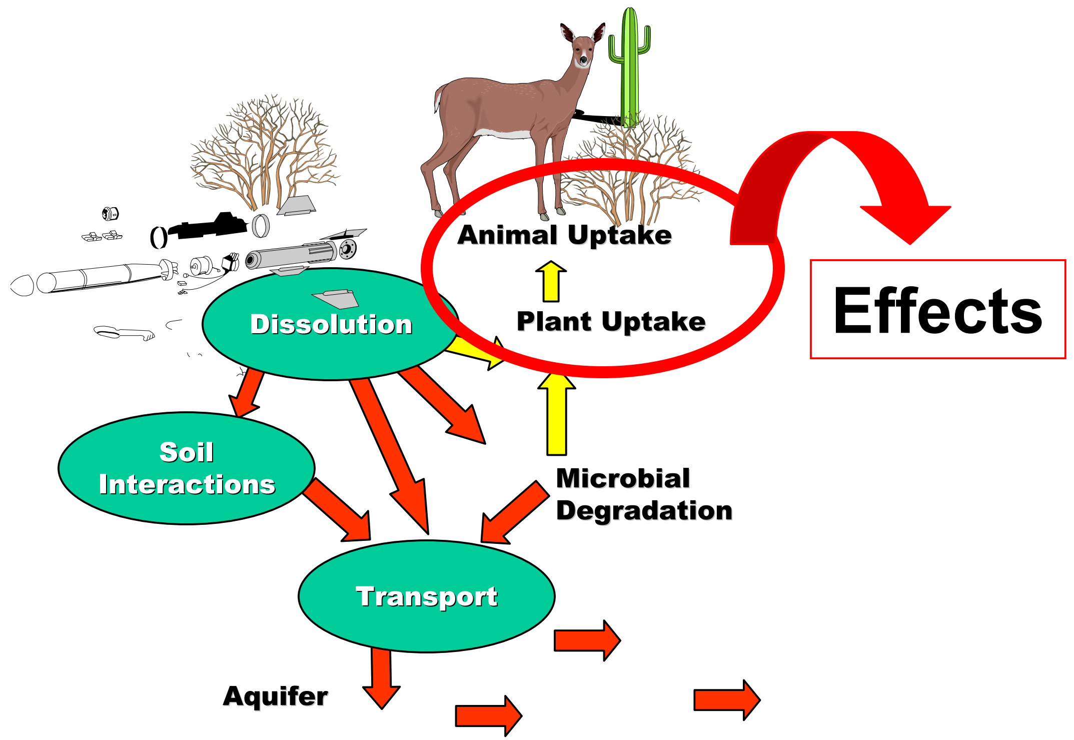
Monitored Natural Attenuation

COST SAVINGS ESTIMATES

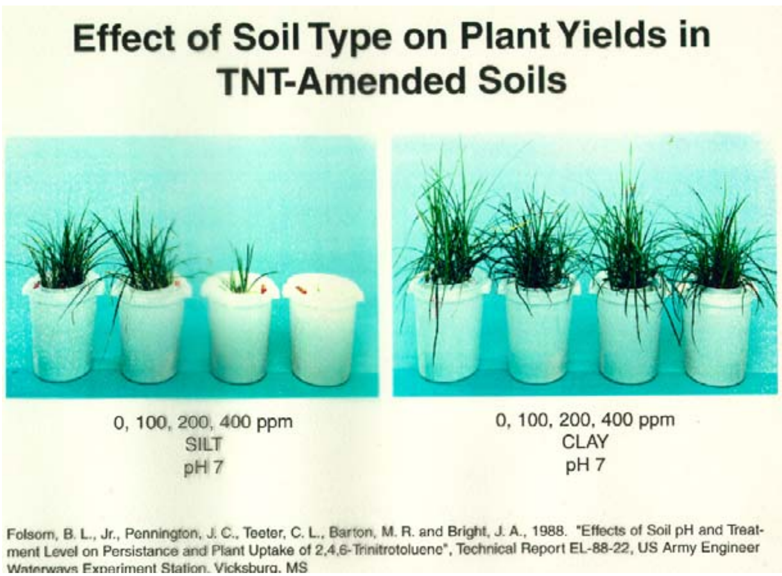
- **20 years**
  - 25 % less than in-situ bioremediation
  - 50 % less than granular activated charcoal (GAC)

- **60 years**
  - 82 % less than in-situ bioremediation
  - 88 % less than granular activated charcoal (GAC)

Effects of Explosives on Plants and Animals



Effects of explosives on vegetation

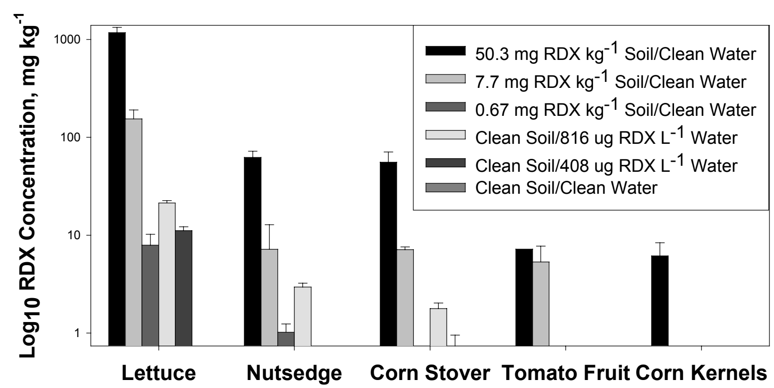


TNT

- TNT is rarely translocated beyond plant roots
- TNT toxicity to vegetation is species-specific
- Bioavailability of TNT is governed by soil properties, esp. organic carbon content

RDX

- RDX is readily taken into leave and fruits
- RDX bioaccumulates in plants
- HMX is not readily taken up (data are limited)



Effects of explosives on animals

- Toxicity varies with species (data are limited)
- Mammals seem more sensitive than birds or amphibians
- TNT is typically more toxic than RDX and HMX
- Mono amino transformation products of TNT are typically more toxic than TNT

Insect larva
Chironomus tentans

Amphipod
Hyalella azteca

Fathead minnow
Pimephales promelas

Screening Level Values

Table 2. Screening Benchmarks for Nitroaromatic Munitions[1]

Receptor	TNT	RDX	HMX	Tetryl
Wildlife Species (diet, mg/kg food)	5.6-23	15-58	5.6-22	4.4-18
Terrestrial Plants (mg/kg)	30	100	ID[2]	25
Terrestrial Invertebrates (mg/kg)	140-200	ID	ID	ID

[1] Adapted from Talmage et al. 1999. "Environmental Screening Values for Nitroaromatic Munition Compounds," *Review of Environmental Contamination and Toxicology*.

[2] Insufficient data.

Examples of Soil PRGs

Table 1. Preliminary Remedial Goals for Soils (mg/kg soil and/or sediment)			
Explosive	**Site 1**	**Site 2**	**Site 3**
TNT	290	22	200
RDX	78	6.1	ND[1]
HMX	10,000	14,000	ND
Tetryl	7,400	2,800	ND
NC	ND	ND	ND
NG	ND	ND	ND
Nitrate	1,000,000	ND	ND
Nitrite	370,000	ND	ND

[1] Not done.

Terrestrial Screening Benchmarks

Table 3. Terrestrial Screening Benchmarks [1]

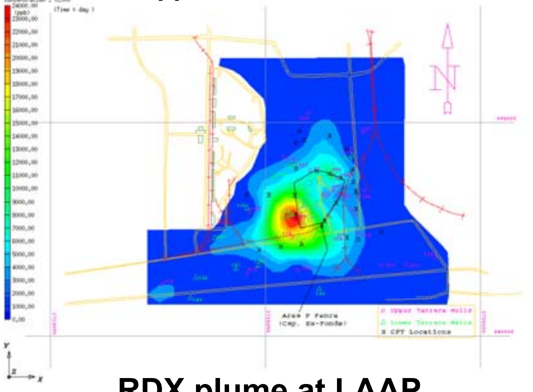
Munition	**Chronic NOAELs[2] (mg/kg/day)**	**Plant LOECs[3] (mg/kg soil)**	**Invertebrate LOECs (mg/kg soil)**
TNT	1.6	30	140[4], 200[5]
RDX	7.0	100	ID[6]
HMX	3.0	ID	ID
Tetryl	1.3	25	ID

[1] Adapted from Talmage et al. 1999. "Environmental Screening Values for Nitroaromatic Munition Compounds," *Review of Environmental Contamination and Toxicology*.
[2] No-observed-adverse-effect level.
[3] Lowest-observed-effect concentration.
[4] Value is for earthworms.
[5] Value is for soil invertebrates.
[6] Insufficient data.

Conclusions

- Fate and Transport
  - Dissolution from solid sources is slow
  - TNT tends to be attenuated by soils
  - RDX is readily transported
  - Toxicity: TNT products>TNT>RDX>HMX
- Manufacture and load-and-pack sites
  - Historical activities produced significant contamination of soils and ground water
  - These sites have been or are currently being addressed by the Army
- Live-fire training and weapon systems testing
  - Contamination typically much less than at manufacture and load-and-pack sites
  - Contamination is widely distributed point sources that are specific to range activities
  - Range management practices and periodic remedial actions are under development to control contamination

RDX 24,000 ppb



RDX plume at LAAP

Training range artillery targets