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The Fate of Munition Constituents (MC) on Military Ranges

Jay Clausen

Physical Research Scientist

Hanover, NH

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US Army Corps of Engineers®

MC used by the Military

- Propellants

  Nitrocellulose (NC), **Nitroglycerin (NG), 2,4-Dintrotoluene (2,4-DNT)**, Nitroguanadine (NQ), ethylcentralite (EC),

- Explosives

  RDX, 2,4,6-Trinitrotoluene (TNT), HMX, ammonium picrate (AP), Tetryl, pentaerythritol tetranitrate (PETN)

- Pyrotechnics

  Perchlorate, White Phosphorous (WP), Metals (Al, Sb, Ba, B, Cr, Ce, Cu, Fe, Pb, Mg, Mn, Ti, W, Zn, Zr)

- Armor/Casings

  Pb, Sb**, W,** Cu, Zn, Fe, Mn, Al, B, Mg

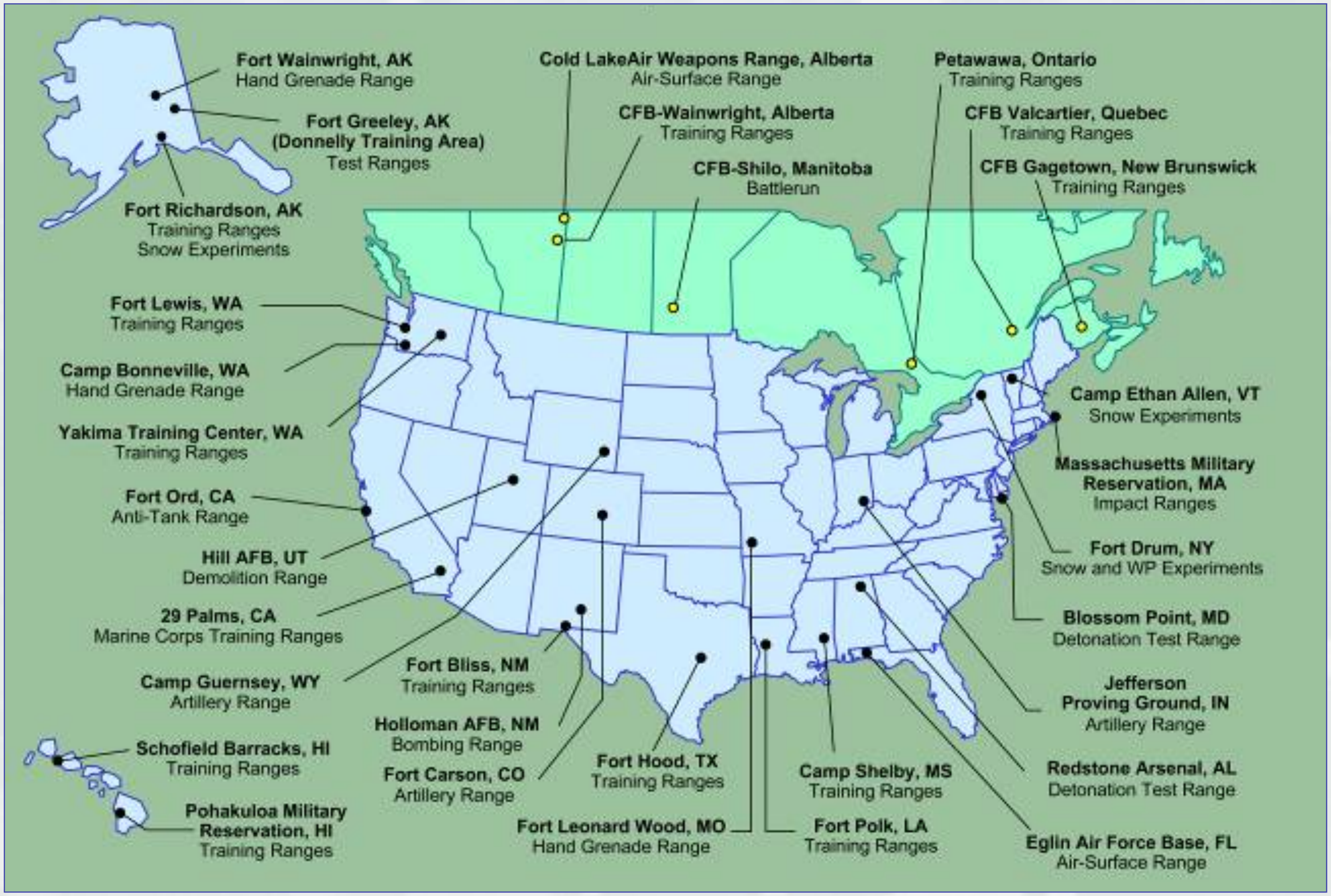
- Fillers

  Phthalates, Polychlorinated Naphthalenes (PCNs), Diphenylamine

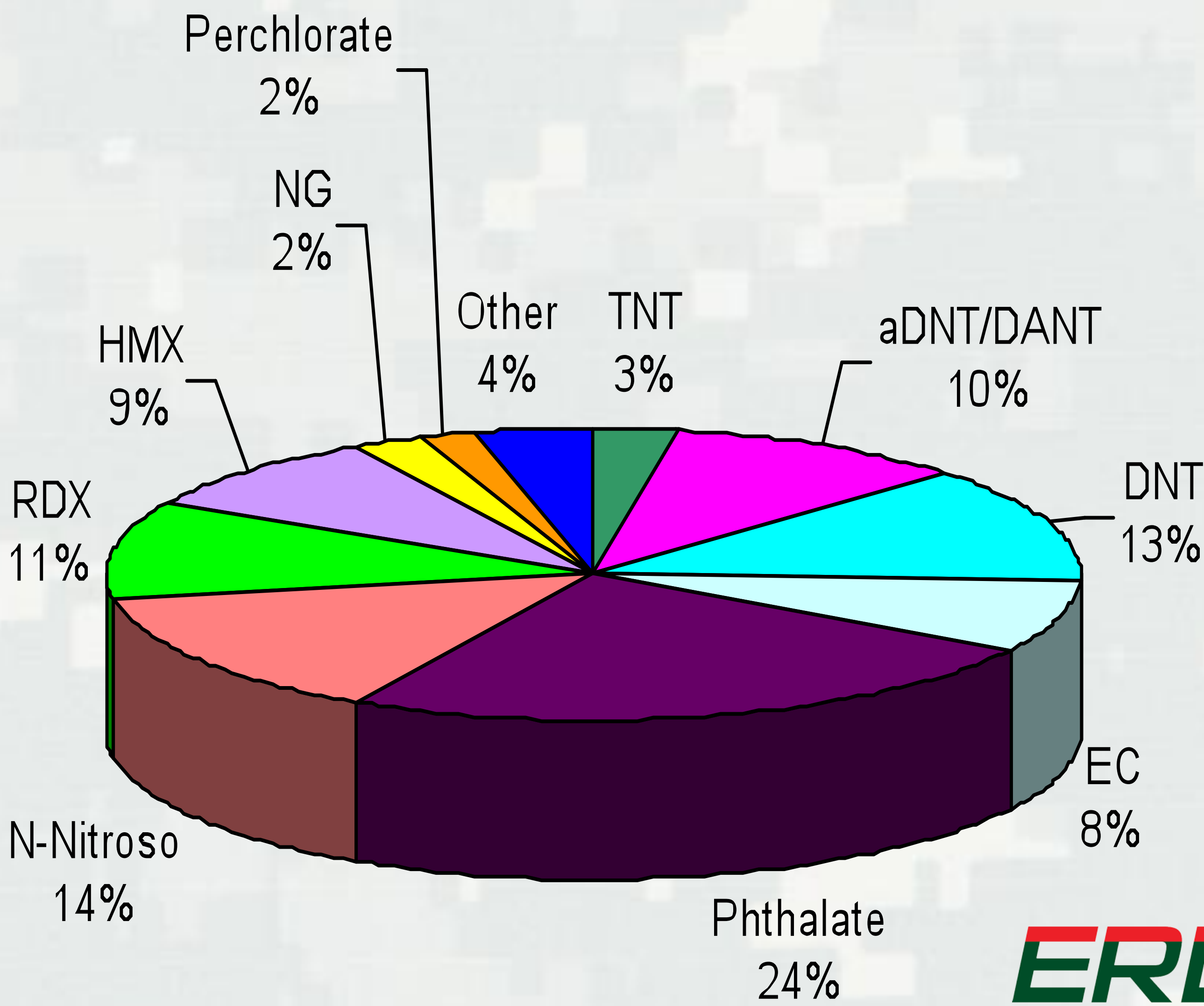
General Physical and Chemical Properties of MC

- Most are solids at environmental temperatures
- Sources on ranges are particulates deposited on soil surface
- Surface contamination of "chunks" can persist for long periods (50-100 years) - particularly in arid areas
- Most MC is adsorption or dissolution dependent
- Propellant residues consist of discrete fibers
- Metals can be in the metallic form or as salts

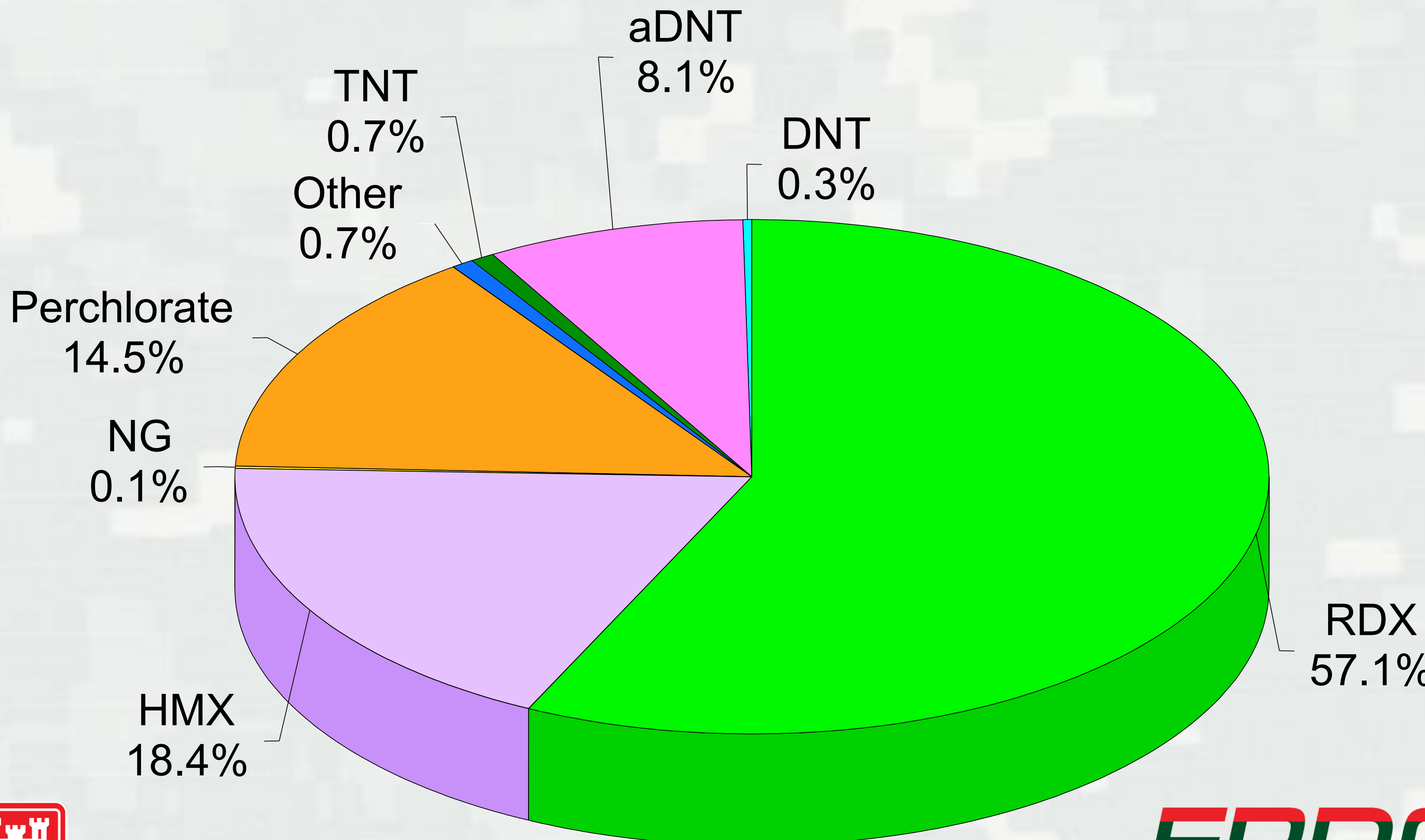
Field Study Sites



Munition Constituents in Soil



MC in Ground Water



MC Distribution by Range Activity

Range Activity	MC Anticipated
Artillery/Mortar Impact Area	RDX, HMX, TNT, 2a-DNT, 4a-DNT, perchlorate
Artillery/Mortar Firing Position	2,4-DNT, 2,6-DNT, NC, NQ, EC, diethyl phthalate, di-n-butyl phthalate, di-n-octyl phthalate, N-nitrosodiphenylamine
Rocket Target	RDX, HMX, TNT, 2a-DNT, 4A-DNT, NG
Rocket Firing Point	NG, NC, EC
Small Arms Range Firing Point	Pb, NG, DNT
Small Arms Range Impact Area	Pb, Zn, Cu, Sb, W
Demolition Area	Explosives, metals, PAHs, perchlorate, PCNs, dioxins
Weapons Test Ranges	Explosives, metals, perchlorate, PCNs,

RDX/HMX

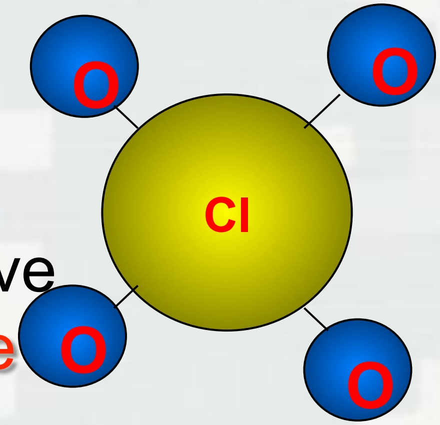
- Initial heterogeneous release of MC particulates to environment
- Dissolution is the key transport mechanism
- Dissolves slowly and rapid migration to groundwater (recalcitrant)
- Natural bio-, abiotic-, and phototransformation insignificant
- Once in solution little residual soil contamination remains (sorption insignificant, i.e. < 7 L/kg)
- Insufficient pore-water concentration relative to soil mass to be detectable in subsurface soil

2,4,6-trinitrotoluene (TNT)/aDNTs

- Initial heterogeneous release of MC particulates to environment
- TNT is rapidly dissolved
- Dissolution/sorption are key transport mechanisms
- Sorption to soil of NG, DNT >> TNT > aDNT >>> RDX, HMX, > Perchlorate
- Transformation is the key fate mechanism and 2a-DNT and 4a-DNT are important isomers
- Photomediated, abiotic, and biotic processes important
- Insufficient pore-water concentration relative soil mass to be detectable in subsurface soil

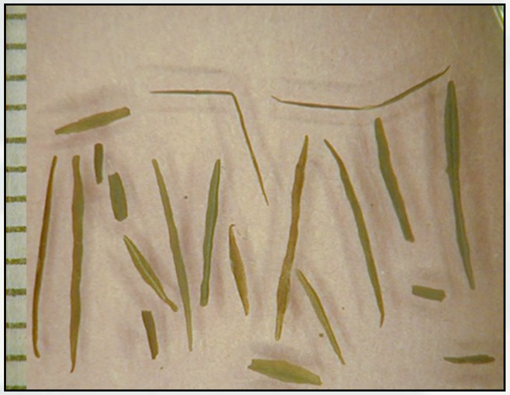
Perchlorate

- Initial heterogeneous release of MC particulates to environment
- Dissolution is the key transport mechanism
- Rapidly dissolves and has high solubility, e.g. ammonium perchlorate = 200,000 mg/L
- Rapidly migrates to groundwater (recalcitrant) due to lack of abiotic-biotransformation and minimal sorption
- Once in solution little residual soil contamination remains
- Insufficient pore-water concentration relative to soil mass to be detectable in subsurface soil



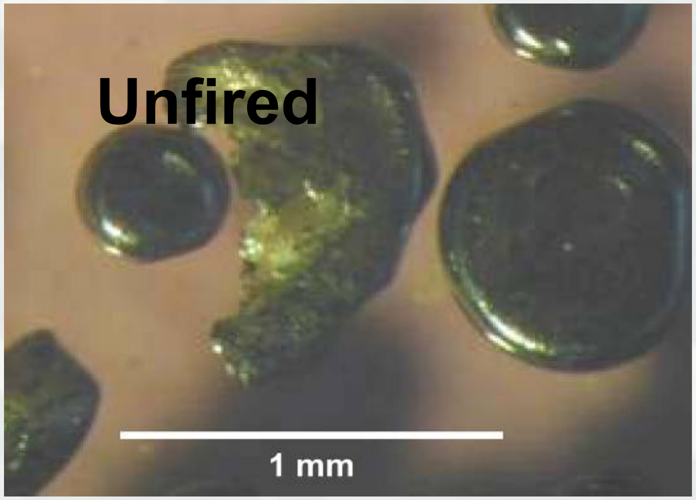
Dinitrotoluene (DNT)

- Two isomers of interest 2,4-DNT and 2,6-DNT
- Initial heterogeneous release of MC particulates to environment
- Dissolution is the key transport mechanism
- Rapidly dissolved from surface but NC limits dissolution via diffusion processes
- Once the available surface DNT has dissolved the remaining DNT is locked up in the NC and is not bioavailable or transportable
- Transformation is the key fate variable followed by soil sorption
- Highly susceptible to biotransformation and phototransformation
- Soil profiling and lysimeter and groundwater monitoring indicate minimal transport (< 1m)

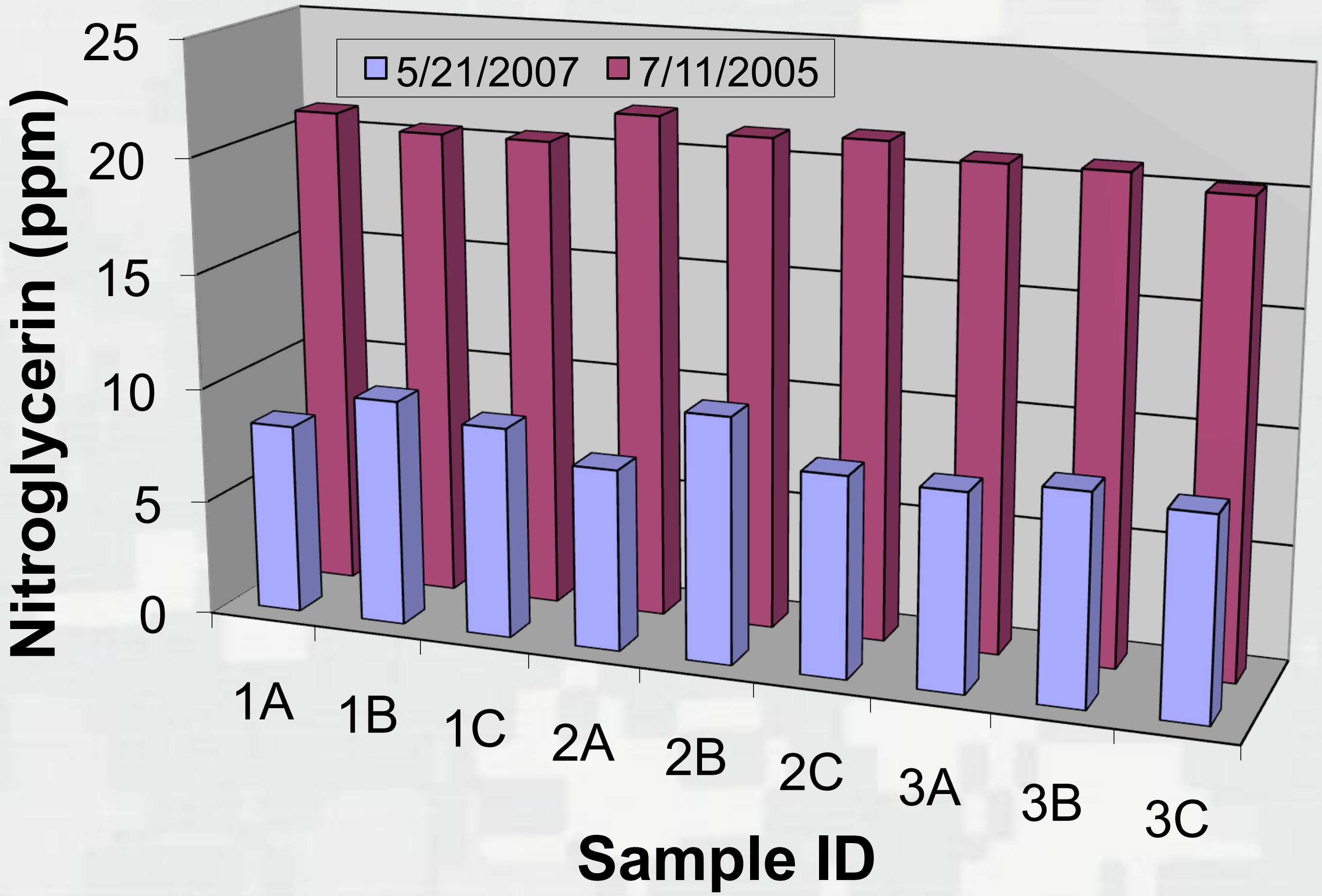


Nitroglycerin (NG)

- Initial heterogeneous release of MC particulates to environment
- Dissolution is the key transport mechanism; Rapidly dissolved from surface but NC limits dissolution via diffusion processes
- Once the available surface NG has dissolved the remaining NG is locked up in the NC and is not bioavailable or transportable
- Highly susceptible to biotransformation and strongly sorbed to soil
- Soil profiling and lysimeter and groundwater monitoring indicate minimal transport (< 1m)
  - Solubility = 1,250 mg/L



NG Field Observation



White Phosphorous (WP)

- Rapidly oxidized on soil surface, i.e. not persistent
- Stable under anoxic/reducing conditions (i.e. swamp, wetland)
- Does not readily dissolve
- Transport not significant

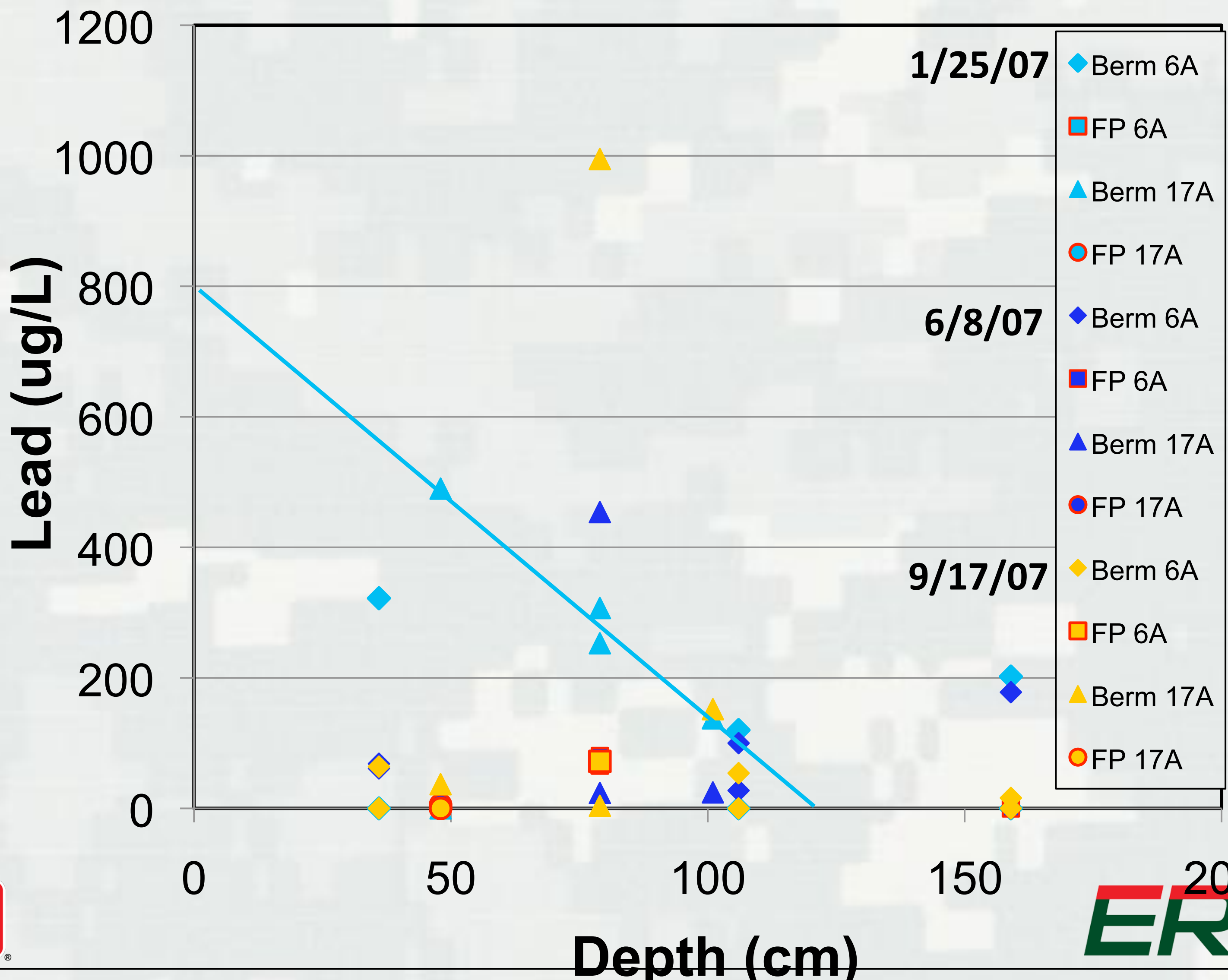
Oxidation of White Phosphorous

Metallic Residues

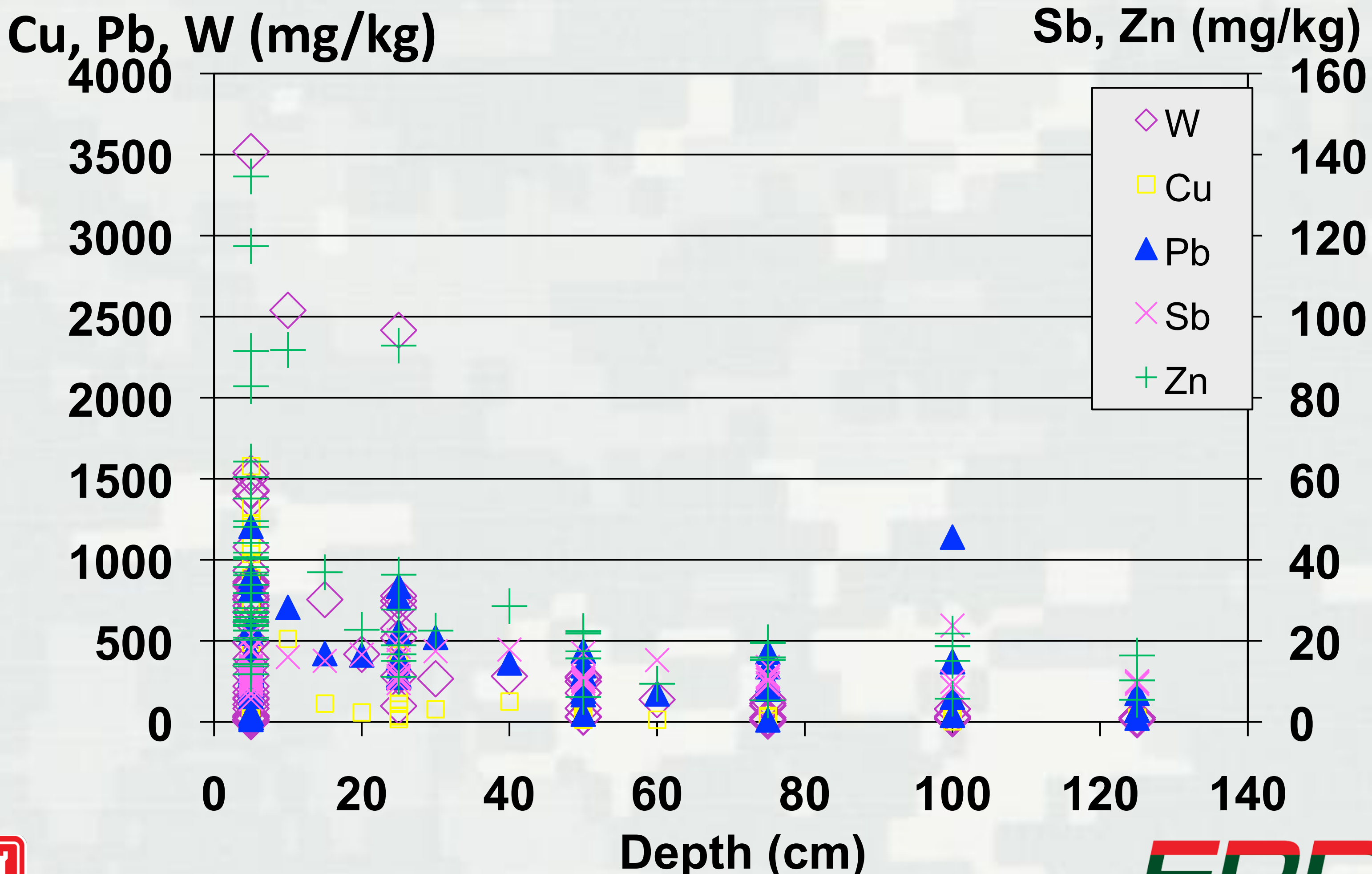
Lead

- Key fate mechanism is dissolution-precipitation reactions followed by sorption/desorption
- Not mobile under most geochemical regimes
- Metallic lead oxidizes to form insoluble lead carbonates and sulfates
- Dissolved form, Pb^{2+}, controlled by redox, pH, and geochemical conditions
- Dissolved form scavenged by Fe and Mn oxide and oxyhydroxide surfaces
- No peer-reviewed evidence of groundwater impacts from leaded ammunition

Lead in Soil Pore Water

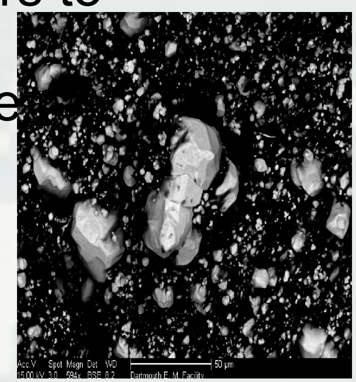


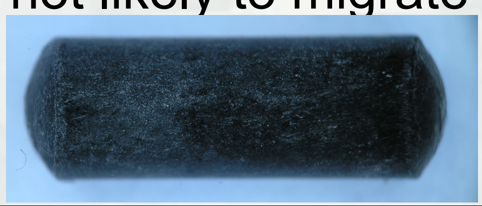
Metal Concentrations in Soil



Tungsten

- Exists in 0, $^{+}2$, $^{+}3$, $^{+}4$, $^{+}5$, & $^{+}6$ oxidation states
- Metallic tungsten rapidly oxidizes
- Forms condensed complex ions of polytungstates or polyoxometallates (POMs - $H_3PW_{12}O_{40}$) in low pH environments
- Mobility from highest to lowest is : Tungstate → Polytungstate → POM → Tungsten Oxide → Metallic Tungsten
- Tungstate, consistent with its low sorption potential and susceptibility to polymerize, is not a dominant soil species. What little adsorption that occurs appears to be on iron oxide surfaces such as ferrihydrite.
- The most prevalent forms of oxidized W in surface soils appear to be one or more polytungstates.
- POMs are relatively stable and likely to persist in surface soils but not likely to migrate significantly.





MC Distribution by Range Activity

Range Activity	Soil	Groundwater
Artillery/Mortar Impact Area	RDX, HMX, aDNT, TNT, perchlorate, WP,	RDX, perchlorate, HMX, aDNT
Artillery/Mortar Firing Position	NG, DNT, Phthalates, N-Nitroso, EC, NQ	None
Rocket Target	RDX, HMX, TNT, aDNT, DNT, NG	RDX, HMX
Rocket Firing Point	NG, DNT	None
Small Arms Range Firing Point	NG, DNT	None
Small Arms Range Impact Area	Pb, Cu, W, Zn, Sb, PAH	W, Sb
Demolition Area	Explosives, metals, perchlorate, PAH, dioxins	RDX, perchlorate, HMX, aDNT, TNT
Weapons Test Ranges	Explosives, perchlorate, PCNs	RDX, perchlorate, HMX, aDNT, TNT

Fate-and-Transport Conclusions

- Mobility for HMX, RDX, perchlorate, W >>> aDNT, TNT, Sb >> EC, NG and DNT >>> Lead, PCN, WP
- RDX and HMX slowly dissolved, not sorbed to soil, unreactive, rapid migration through soil and in groundwater
- Perchlorate is rapidly leached from soil and transported in groundwater, unreactive; soil sampling of limited value
- RDX, HMX, and perchlorate can be expected in groundwater at most ranges (desert areas the exception)
- TNT and aDNT can be present in soil and groundwater but mobility is limited by transformation and sorption processes
- DNTs and NG can be present in soil but presence in groundwater is unlikely due to transformation, sorption, and diffusion from NC processes

Metals Fate-and-Transport

- Initial deposition on soil surface up to percent levels
- Metal concentrations rapidly decrease in soil with increasing depth
- Soil geochemical properties (pH, redox, chemistry, OM) control dissolution and formation of subsequent metal species
- Metals present dissolved in soil pore-water
- Metals transport in pore-water is dependent on speciation forms
- Pore-water concentrations decrease with increasing depth
- Soil profiling and lysimeter monitoring indicate minimal transport (< 1m) under most geochemical conditions for lead, copper, and zinc
- Tungsten only element resulting in groundwater impacts
- Soil geochemistry key to W mobility
- Mobility Potential (W >> Sb > Zn > Cu > Pb)
- No evidence for significant Pb movement; tends to form insoluble species

References

- Clausen, J. and N. Korte. 2009. The distribution of metals in soils and pore water at 3 U.S. military training facilities. *Soil Sed Cont J.* **18**(5):546-563. http://www.tandfonline.com/doi/abs/10.1080/15320380903085683
- Clausen, J. and N. Korte. 2009. Environmental fate of W from military use. *Sci Total Env.* **407**(8):2887-2893.
- Clausen, J. *et al.* 2011. Fate of NG and DNT in soil at a small arms training range. *Soil Sed Cont J.* **20**(6):649-671. http://www.tandfonline.com/doi/abs/10.1080/15320383.2011.594108#preview
- Clausen, J. *et al*. 2011. Migration of Pb in surface water, pore water and ground water with emphasis on firing ranges. *Crit Rev Env Sci Tech.* **41**(15)1397-1448. http://www.tandfonline.com/doi/abs/10.1080/10643381003608292
- Clausen, J. *et al.* 2012. *Metal Residue Deposition from Military Pyrotechnic Devices and Field Sampling Guidance.* ADA562327. http://handle.dtic.mil/100.2/ADA562327
- Clausen, J. et al. *Phase II Tungsten Fate-and-Transport Study for Camp Edwards.* ERDC-CRREL TR-10-3. Hanover, NH. http://acwc.sdp.sirsi.net/client/search/asset/1001760

References (Continued)

- Morley, M.C., H. Yamamoto, G.E. Speitel Jr., and **J.L. Clausen**. 2006. Dissolution kinetics of high explosives particles in a saturated sandy soil. *Journal of Contaminant Hydrology.* **85**:141-158.
- Yamamoto, H., M.C. Morley, G.E. Speitel Jr., and **J. Clausen**. 2004. Fate and transport of high explosives in a sandy soil: Adsorption and desorption. *Soil and Sediment Contamination Journal: An International Journal.* **13**(5): 1-19.
- Clausen, J.L., J. Robb, D. Curry, B. Gregson, and N. Korte. 2004. A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA. *Environmental Pollution.* **129**:13-21.
- Clausen, J. et al. 2007. *Conceptual Model for the Transport of Energetic Residues from Surface Soil to Groundwater by Range Activities.* ERDC-CRREL TR-06-18. Hanover, NH. http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-06-18.pdf

Email: Jay.L.Clausen@us.army.mil