LESSONS LEARNED

Generation of Biodegradation-Sorption Barriers for Munitions Constituents

ESTCP Project ER-201123

DECEMBER 2018

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REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 15-12-2018	**2. REPORT TYPE** ESTCP Technical Report	**3. DATES COVERED** *(From - To)* March 2011 – March 2016

4. TITLE AND SUBTITLE Generation of Biodegradation-Sorption Barriers for Munitions Constituents	**5a. CONTRACT NUMBER** W912HQ-11-C-0039
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Borden, Robert C. Knappe, Detlef T. U. Won, Jongho Yuncu, Bilgen	**5d. PROJECT NUMBER** ER - 201123
	5e. TASK NUMBER
	1.0 2.0 **5f. WORK UNIT NUMBER**
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) North Carolina State Univ. 2711 Founders Dr. Raleigh, NC 27695 Solutions-IES, Inc. 1101 Nowell Rd. Raleigh, NC 27607	**8. PERFORMING ORGANIZATION REPORT NUMBER** ER-201123
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Environmental Security Technology Certification Program 4800 Mark Center Drive, Suite 17D08, Alexandria, VA 22350	**10. SPONSOR/MONITOR'S ACRONYM(S)** ESTCP
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER-201123

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Unlimited Distribution

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Explosive residues can accumulate from low order detonations. In this project, the transport and attenuation of TNT and RDX are evaluated in variably saturated soils at an active hand grenade range. The impact of natural attenuation and enhanced attenuation are evaluated in a series of laboratory experiments and in a 27 month field study. TNT was extensively degraded in all laboratory studies and never accumulated in the field. RDX did not biodegrade in well mixed batch microcosm studies but did degrade in laboratory columns and in the field under mixed aerobic/anaerobic conditions. Soil redox conditions were sensitive to soil moisture and organic carbon. In one bay, natural attenuation processes greatly reduced RDX leaching in both laboratory columns and in the field. In the other bay, natural attenuation was less effective in reducing leaching. However, addition of glycerin and lignosulfonate simulated oxygen consumption, enhancing RDX biodegradation, and reducing RDX leaching.

15. SUBJECT TERMS
grenade ranges, TNT, RDX, HMX, natural attenuation, biodegradation

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Robert C. Borden
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	UU	93	**19b. TELEPHONE NUMBER** *(include area code)* 919-873-1060

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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ACRONYMS AND ABBREVIATIONS

AIC	Akaike's Information Criterion
BAZE	Biologically Active Zone Enhancement
bgs	Below Ground Surface
BL	Bucket Lysimeter
CEC	Cation Exchange Capacity
CI	Confidence Interval
Comp B	Composition B
DoD	Department of Defense
DRDC	Defense Research and Development Canada
E	Model Efficiency
EA	Enhanced Attenuation
ECD	Electron Capture Detector
EOD	Explosive Ordnance Disposal
EOTI	Explosive Ordnance Technologies, Inc.
Eh	Oxidation Potential
ERDC	Environmental Research and Development Center
ESTCP	Environmental Security Technology Certification Program
ET	Evapotranspiration
Fe(II)	Ferrous Iron
Fe(III)	Ferric Iron
FID	Flame Ionization Detector
FME	Frozen Micro-Extraction
FS	Field Sand
g	gram
GC	Gas Chromatography
GL	Glycerin
GRG	Generalized Reduced Gradient
HE	High Explosive
HM	Humic Matter
HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Times
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
IM	Insensitive Munition
K_{oc}	Soil Partition Coefficient Normalized to Organic Carbon

K_{ow}	Octanol-water Partition Coefficient
K_{sat}	Saturated Hydraulic Conductivity
Kg	Kilogram
LDs	Lignin Derivatives
LS	Lignosulfonate
MC	Munitions Constituents
MCL	Maximum Contaminant Level
MNA	Monitored Natural Attenuation
NA	Norlig A
NCDEQ	North Carolina Department of Environmental Quality
OARS	Occupational Alliance for Risk Science
OB	Open Burn
OC	Organic Carbon
OD	Open Detonation
OSWER	Office of Solid Waste and Emergency Response
PAHs	Polynuclear Aromatic Hydrocarbons
PMSO	Peat Moss Plus Soybean Oil
PSI	Per Square Inch
PSRG	Preliminary Soil Remediation Goals
PVC	Polyvinyl Chloride
RMSE	Root-Mean-Square Error
RPM	Rotation Per Minute
RS	Range Soil
SCONC	State Climate Office of North Carolina
SE	Standard Error
SERDP	Strategic Environmental Research and Development Program
SOC	Soil Organic Carbon
TC	Total Carbon
TCD	Thermal Conductivity Detector
TOC	Total Organic Carbon
UCA	Ultrazine CA
U.S.	United States
USEPA	US Environmental Protection Agency
USDA	US Department of Agriculture
USGS	US Geological Survey
UXO	Unexploded Ordnance
WEEL	Workplace Environmental Exposure Level

WSS	Web Soil Survey

ABBREVIATIONS FOR COMPOUNDS AND ELEMENTS

Ag	Silver
Al	Aluminum
As	Arsenic
Be	Beryllium
Br	Bromine
Ca	Calcium
$Ca(OH)_2$	Calcium hydroxide
Cd	Cadmium
CH_4	Methane
Cl	Chlorine
ClO_4	Perchlorate
CO_2	Carbon Dioxide
Cr	Chromium
Cu	Copper
Fe	Iron
Hg	Mercury
HCHO	Formaldehyde
HCl	Hydrochloric acid
K	Potassium
Mg	Magnesium
Mn	Manganese
N	Nitrogen
Na	Sodium
NaBr	Sodium bromide
NaOH	Sodium hydroxide
Na_2S	Sodium sulfide
Ni	Nickel
N_2	Dinitrogen
N_2O	Nitrous oxide
NO	Nitrogen oxide
NO_2	Nitrite
NO_3	Nitrate
O_2	Oxygen
Pb	Lead
Sb	Antimony
Se	Selenium
SO_4	Sulfate
Th	Thallium
Zn	Zinc

2,4-DANT	2,4-diamino-6-nitrotoluene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
2-ADNT	2-amino-4,6-dinitrotoluene
4-ADNT	4-amino-2,6-dinitrotoluene
AH2QDS	Anthrahydroquinone-2,6,-disulfonate
ADNT	Amino dinitrotoluene
AQDS	Anthraquinone-2,6-disulfonate
ATO	3-amino-1,2,4-triazol-5-one
DNAN	2,4-dinitroanisole
DNT	Dinitrotoluene
DNX	Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (High-Melting Explosive)
IMX	Insensitive Munitions eXplosive
MNX	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
NC	Nitrocellulose
NQ	Nitroguanidine
NTO	3-nitro-1,2,4-triazol-5-one
PTFE	Polytetrafluoroethylene
RDX	Royal Demolition Explosive
TNT	2,4,6-Trinitrotoluene
TNB	1,3,5-Trinitrobenzene
TNX	Hexahydro-1,3,5-trinitroso-1,3,5-triazine

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial and technical support provided by the Environmental Technology Certification Program including the guidance provided by Andrea Leeson, Hans Stroo and Marvin Unger. We gratefully acknowledge the generous support of all the Fort Bragg Range Control staff throughout this project.

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EXECUTIVE SUMMARY AND LESSONS LEARNED

Residues of 2,4,6-Trinitrotoluene (TNT), Royal Demolition Explosive (RDX), and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetreazocine (High-Melting Explosive) (HMX) can accumulate on military ranges and open burn/open detonation (OB/OD) areas. These high explosives (HEs) are moderately soluble in water and weakly bind to soil and therefore can be transported to groundwater under certain conditions. HEs in soil also can be degraded, biologically or abiotically, under natural or engineered conditions, thereby limiting their transport and the risks to groundwater quality.

This project evaluated the transport and attenuation of TNT, RDX, and HMX in variably saturated soils at an active hand grenade range located at Fort Bragg, NC. Two different management approaches were evaluated in adjoining grenade throwing bays: (a) monitored natural attenuation (MNA); and (b) enhanced attenuation (EA). MNA relies on the use of natural attenuation processes to control off-range migration of HEs to environmentally acceptable levels. MNA is most effective in fine textured soils that occasionally become saturated during high rainfall periods, reducing oxygen (O_2) transfer through gas filled soil pores. EA involves the addition of soluble, biodegradable organic substrates that increase O_2 consumption, generating reducing conditions to stimulate anaerobic biodegradation of HEs.

The soils in the two throwing bays are mapped as Vaucluse loamy sand, but much of the surface soil was removed to form containment berms, and the remaining subsoil is less permeable. A detailed field characterization showed that soils in both bays were primarily sand with 9 - 16% silt and 1.4 - 2.6% clay. Soil pH (5.4 ± 0.2), silt content (13.4 ± 2.7%), and median grain size (D_{50} = 296 ± 70 µm) were not statistically different between the two bays. However, the organic carbon (OC) and clay contents were significantly higher in Bay C where MNA was evaluated than in Bay T where EA was evaluated.

Work included: (1) laboratory studies to identify factors controlling the fate of TNT and RDX in batch incubations and variably saturated column experiments, and (2) a field evaluation of HE migration and attenuation at an operating hand grenade range. Experimental treatments for the laboratory and field included: (1) ambient conditions (MNA), and (2) amendment with glycerin (GL) plus lignosulfonate (LS) in the EA plot.

LABORATORY STUDIES

A series of laboratory studies were conducted to help design and interpret the field demonstration. Screening studies were conducted initially to identify inexpensive organic materials that could be spray applied on ranges and would be transported 0.5 - 1.0 m into the soil profile. Subsequent studies showed that LS sorbed to soil and then biodegraded slowly, enhancing TNT, RDX, and HMX biodegradation. Laboratory column tests were conducted to evaluate the TNT and RDX transport and attenuation in soil from the two grenade bays with and without organic amendments.

Based on the results of the initial screening studies, GL and LS were selected for further development and evaluation. The readily biodegradable GL, produced as a byproduct of biodiesel production, was intended to rapidly consume O_2 in soil, generating anoxic conditions and leading to enhanced anaerobic biodegradation of explosives. The LS, produced during paper production, was expected to consume O_2 more slowly, helping to maintain anoxic conditions established by GL degradation. GL and LS are water soluble and can be applied to ranges by spraying, and then be transported into the soil by rainfall or artificial irrigation.

TNT was extensively degraded in both batch microcosm and column experiments, consistent with prior reports (Fuller and Manning, 1997; Singh, 2012). In microcosm experiments with field sand (FS) and soil from two active grenade bays, TNT rapidly biodegraded under aerobic conditions (Won and Borden, 2016). While some TNT degradation products (2-amino-4,6-dinitrotoluene [2-ADNT] and 4-amino-2,6-dinitrotoluene [4-ADNT]) increased during the aerobic phase, these intermediates were further degraded during the anaerobic phase to less than 2.5 µg/L within 42 days. In both the treated and control columns, less than 0.1% of the added TNT was discharged in the effluent. The fraction of TNT sorbed to soil was much lower in treated columns (0 - 2% in Bay C, 7 - 11% in Bay T) than in the controls (13 - 14% in Bay C, 26 - 28% in Bay T), indicating GL+LS addition enhanced TNT degradation. There was no significant accumulation of TNT degradation products (Dinitrotoluenes [DNTs] and Amino dinitrotoluenes [ADNTs]) in any column.

There was no evidence of RDX or HMX biodegradation in aerobic microcosms. Under anaerobic conditions, RDX and HMX were rapidly degraded in live control microcosms (no amendment) with Bay T soil (RDX = 0.130 d^{-1}, HMX = 0.076 d^{-1}), with somewhat slower degradation with Bay C soil (RDX = 0.050 d^{-1}, HMX = 0.027 d^{-1}). The addition of GL and/or LS significantly increased RDX degradation rates in Bay C soil. However, RDX degradation rates were already very high in the Bay T controls and the organic amendments did not further accelerate degradation. During anaerobic RDX degradation, the aqueous concentrations of dissolved nitroso derivatives (Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine [MNX], DNX, and Hexahydro-1,3,5-trinitroso-1,3,5-triazine [TNX]) increased initially and then declined. The final concentrations of DNX and TNX were below detection limits (<1 µg/L), and MNX concentrations were much lower in the amended microcosms than in the live controls.

Variable saturation column experiments demonstrated that RDX may be attenuated under ambient conditions without any amendments. However, relatively small differences in soil properties can result in large differences in RDX removal. Control Bay T soil columns were unsaturated and remained aerobic. By the end of the experiment, effluent RDX concentrations were elevated, indicating substantial RDX leaching. However, mass balance results showed that over half of the initial RDX was degraded in the control Bay T columns although O_2 was present in the soil gas. This RDX degradation was likely associated with the short-term anoxic conditions or development of anoxic microsites. In control Bay C columns, there was extensive degradation of RDX, likely due to the higher clay and OC contents, which generated anoxic conditions in the upper portion of the columns. Very little RDX was discharged in effluent with a small amount sorbed to Bay C soils. Substantial amounts of RDX degradation products (MNX, DNX, and TNX) were produced in both the Bay T and Bay C columns without any organic amendment, confirming natural attenuation of RDX. MNX and TNX were distributed throughout the vertical soil profile, while DNX concentrations rapidly declined with depth.

The GL+LS amendment stimulated RDX degradation in both replicate Bay T columns. In the first replicate (T-A), organic amendment rapidly migrated through the column, generating anoxic conditions, and stimulating RDX biodegradation. In the second replicate (T-B), O_2 levels remained close to atmospheric, which somewhat reduced RDX degradation. By the end of the experiment, effluent RDX concentrations in aerobic replicate T-B were two orders of magnitude greater than in the more reduced replicate T-A. However, mass balance results showed greater RDX degradation in both amended columns (86 and 88% removal) compared to the untreated controls (64 and 77% removal).

In Bay C columns, GL+LS addition reduced the amount of RDX and RDX degradation products remaining in the soil at the end of the experiments. GL+LS addition did not substantially reduce the RDX leaching in the Bay C columns because leaching was already very low in the untreated Bay C controls.

Amendment addition did not have a significant impact on HMX leaching or final HMX concentrations in the soil, for either the Bay C or Bay T soils. The limited HMX removal is probably due to high RDX concentrations which are reported to inhibit biodegradation of HMX (Uchimiya et al., 2010).

FIELD DEMONSTRATION

Two complementary technologies for controlling the leaching of HEs in grenade ranges were evaluated in adjoining throwing bays at a grenade range on Fort Bragg: (1) MNA; and (2) EA.

Consistent with prior work (Jenkins et al., 2006; Larson et al., 2008a), there was no evidence of significant TNT accumulation in surface soils or soil pore water in either the grenade Bay T or C. Both bays have been used regularly for training for over 20 years. Over the course of this project, approximately 5,000 fragmentation grenades containing Comp B explosive (39% TNT) were detonated in each bay. Yet TNT concentrations in the soil remain low and TNT concentrations in pore water were below detection (<1 µg/L) for most of the monitoring period.

In the untreated Bay C, there is strong evidence for natural attenuation of RDX. At the start of the project, significant concentrations of RDX were observed in pore water (1 to 454 µg/L) and soil (3 to 100 µg/kilogram [kg]). These elevated RDX levels are hypothesized to be due to a period of intense training combined with lower than average rainfall. During the low rainfall period, the low soil moisture likely resulted in more oxidizing conditions with accumulation of nitrate (NO_3) and RDX. In June 2013, the site experienced a period of high rainfall combined with warm summer temperatures resulting in reducing conditions (low Oxidation Potential [Eh]), an increase in dissolved Manganese (Mn), with rapid decline in nitrate and RDX. With the return of drier conditions and lower temperatures, soil Eh increased. However, NO_3 and RDX levels recovered much more slowly due to the low drainage rates and long travel time through the soil.

In Bay T, addition of GL and LS (GL+LS) was effective in generating reducing conditions and stimulating RDX biodegradation. At the start of the project, elevated RDX levels were also present in Bay T. The higher Saturated Hydraulic Conductivity (K_{sat}) of the soil allowed more rapid drainage even during wet periods, maintaining oxidizing conditions. Several months after amendment addition, Total Organic Carbon (TOC) concentrations in the bucket and suction lysimeters increased. With the arrival of TOC, the pore water became reduced with a decline in Eh and NO_3, an increase in Mn, and a decline in RDX. There is strong evidence that the increase in TOC was due to substrate application since TOC increased at the same time Cl and Br increased. At 500 days after amendment application, TOC declined, resulting in a rebound in Eh and NO_3, and a decline in Mn. At two years after amendment application, RDX may be beginning to rebound.

CONCEPTUAL MODEL OF EXPLOSIVES LEACHING AND ATTENUATION

A conceptual model is present of the major factors that control leaching of HE through the vadose zone beneath grenade bays including: (a) the amount of HE deposited by low order detonations; (b) the chemical properties of the individual HE compounds which control their aqueous solubility, sorption to soil, and biodegradability under aerobic and anaerobic conditions; and (c) the rate of O_2 transport and consumption in the soil. O_2 transport in soil is controlled by the soil physical properties (permeability and water retention characteristics), precipitation and evapotranspiration. O_2 consumption is controlled by the amount and type of organic carbon (OC) and soil temperature.

TNT naturally attenuates in the vadose zone at most sites due to the ease of biodegradation under both aerobic and anaerobic conditions. Natural attenuation of RDX is more variable due to its' resistance to biodegradation under aerobic conditions. At some sites (e.g., Fort Bragg grenade Bay C), the soil undergoes extended anoxic periods leading to extensive RDX removal with very limited leaching to groundwater. However, in soils with lower fines and/or organic content (e.g., Fort Bragg grenade Bay T), the soils are generally aerobic, resulting in greater RDX leaching. At many ranges, it may take several years for RDX to migrate through the upper two meters of soil due to slow infiltration and sorption to soil. If the soil becomes anaerobic for even a few weeks during this period, a significant fraction of the RDX may be degraded, reducing leaching to groundwater. Organic amendment addition can be effective in reducing RDX leaching. Given the relatively long travel time for munitions through soils, it may not be necessary to maintain continuously anaerobic conditions and periodic amendment application could be effective in reducing leaching.

LESSONS LEARNED

1. Natural attenuation processes may be more important in reducing RDX leaching than previously assumed. At Fort Bragg, minimal leaching of RDX was observed in Bay C where soil Eh was naturally low.

2. Spray application of the organic amendment (GL+LS) on the soil surface was effective in generating reducing conditions and reducing RDX leaching. Once TOC concentrations declined, soil Eh began to increase. However, RDX levels remained low for two years after amendment application.

3. There were large spatial variations in soil drainage rates between the two bays due to differences in soil permeability, and within the bays due to the presence of explosion craters. These differences can have a dramatic impact on the amount of RDX transported to groundwater.

4. Large spatial and temporal variations in geochemical conditions were observed in this project. The large spatial variations were due to relatively small differences in soil physical and chemical properties. The large temporal variations were due to short and longer term variations in rainfall, evapotranspiration, and soil temperature. Numerous studies have reported similar results for denitrification in soils. These large variations will make it much more difficult to predict when MNA processes are sufficient to prevent RDX leaching and when active control measures are required.

5. Organic amendment addition can be effective in stimulating anaerobic biodegradation. However, there are important technical challenges in this approach. In unsaturated sandy soils, O_2 transfer is very rapid and high amendment loading rates would be required to generate and maintain anaerobic conditions. In lower permeability soils, substrate loading rates are lower. However, effectively transporting the amendment into the soil profile can be challenging. When GL+LS was spray applied onto the surface of Bay T, some portion was likely washed off the soil surface by a high intensity rainstorm that occurred shortly after amendment application.

6. On many grenade ranges, Unexploded Ordnances (UXOs) are routinely cleared and a skid-steer loader or other small earth moving equipment is used to fill explosion craters and smooth the bay surface. During routine maintenance, the organic amendment could be sprayed on the surface, then tilled into the soil to reduce the potential for wash off. Alternatively, a small loader or tractor could be used to inject the amendment a few inches below the soil surface using injection nozzles similar to that used for land application of biosolids.

7. Periodic reinjections will probably be needed if relying on EA. RDX degradation can be delayed for several months after applying amendments, until after the TOC increases and Eh decreases. Once after the TOC increases and Eh levels rebound, dissolved RDX concentrations can remain low for several months.

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1.0 INTRODUCTION

The United States (U.S.) Department of Defense (DoD) faces the long-term challenge of maintaining warfare readiness while at the same time protecting and using natural resources in a sustainable manner. Firing ranges and open burn/open detonation (OB/OD) areas are used by DoD for personnel training, practice, and testing of new ordnance. However, continued use of these facilities can result in accumulation of high explosive (HE) and propellant residues (2,4,6-Trinitrotoluene [TNT], 2,4- and 2,6-Dinitrotoluene [2,4-DNT and 2,6-DNT, respectively], hexahydro-1,3,5-trinitro-1,3,5-triazine [TNX], octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine [High-Melting Explosive (HMX)] and perchlorate [ClO_4]). These munitions constituents (MC) have relatively high aqueous solubility and weak binding affinity for soil. As a result, these materials can be transported to groundwater in high permeability soils. Wani et al. (2003) reported 583 sites where groundwater contamination with explosives had been confirmed. At the Massachusetts Military Reservation, large plumes of Royal Demolition Explosive (RDX) and ClO_4 contaminated groundwater have been identified. While concentrations in groundwater are typically low (RDX < 20 µg/L), concentrations approaching 400 µg/L have been observed (Yamamoto et al., 2004). While explosives and propellants can penetrate some very high permeability soils, there are extensive data showing that these materials are biodegradable under anaerobic conditions.

This project evaluates the transport and attenuation of TNT, RDX and HMX in variably saturated soils at an active hand grenade range located at Fort Bragg, NC. Two different management approaches are evaluated: (1) monitored natural attenuation (MNA); and (2) enhanced attenuation (EA). MNA is most effective in fine textured soils that occasionally become saturated during high rainfall periods, reducing oxygen (O_2) transfer through gas filled soil pores. EA involves addition of soluble, biodegradable organic substrates that increase O_2 consumption. Both approaches result in periods of anoxic or anaerobic conditions that enhance HE biodegradation, greatly reducing leaching to the water table.

1.1 OBJECTIVES

This project evaluates two different approaches for reducing the leaching of HE constituents to groundwater at a hand grenade range at Fort Bragg, NC. In one bay within the grenade range, the natural attenuation of HE and the impact of changing redox conditions on biodegradation is examined. In the second bay, the impact of glycerin (GL) and lignosulfonate (LS) addition is evaluated to stimulate EA processes that are already occurring and reduce contaminant migration by increasing soil organic carbon (SOC) levels, increasing contaminant residence time in the soil, and generating reducing conditions to stimulate anaerobic biodegradation processes.

1.2 REGULATORY DRIVERS

Exposure of humans to these contaminants can generate significant adverse health effects. TNT can cause liver and blood damage, anorexia, and anomia. RDX and HMX can bring about systematic poisoning generally affecting bone marrow and the liver (Lynch et al., 2001). These compounds are also toxic to mammalian systems and bioaccumulate in crop plants, leading to potential exposure by eating or direct contact (Spain et al., 2000; Pennington and Brannon, 2002). TNT and RDX are classified as possible human carcinogens by US Environmental Protection

Agency (USEPA) (USEPA, 2014a; USEPA, 2014b). In contrast, HMX is not currently classified as human carcinogen, but does have adverse impacts on the liver and nervous system (Agency for Toxic Substances and Disease Registry [ATSDR], 1997).

There are currently no federal maximum contaminant levels (MCLs) for TNT, RDX, and HMX. Life-time health advisory levels in drinking water vary from 2 µg/L for TNT, 2 µg/L for RDX, and 400 µg/L for HMX (USEPA, 2012).

2.0 TECHNOLOGIES

In this project, two complementary technologies are evaluated for controlling the migration of HEs from hand grenade ranges: (1) MNA; and (2) EA.

2.1 MNA

MNA relies on the use of natural attenuation processes in combination with a careful monitoring to control off-range migration of munitions related contaminant concentrations to environmentally acceptable levels. Important attenuation processes that occur at most ranges include advection, dispersion, dilution, sorption, ion exchange, precipitation, and both abiotic and biotic degradation.

In 1999, USEPA's Office of Solid Waste and Emergency Response (OSWER) issued a Directive (USEPA, 1999) on the use of MNA for the remediation of soil and groundwater that is already contaminated. However, there is little or no guidance on how to determine if MNA processes will be effective in controlling or preventing current and future contaminant migration from ranges.

The primary advantages of using MNA for management of explosives deposited on ranges are:

- Lower volume of remediation derived wastes;
- Reduced potential for cross-media transfer of contaminants;
- Reduced risk of human exposure to contaminants, contaminated media, and other hazards;
- Some natural attenuation processes result in *in situ* destruction of contaminants;
- Less disturbance to site operations and ecological receptors;
- No artificial impact to groundwater geochemistry and biology;
- Can be applied to all or a portion of a site depending on site characteristics and goals;
- Can easily be used in combination with other technologies; and
- Lower capital costs and low, if any, maintenance costs.

The primary limitations of MNA include:

- Potential longer life cycles to reach goals compared to active remediation measures;
- More detailed site characterization is needed to demonstrate attenuation which may result in a more complex and costly up-front investigation;
- Institutional controls may be required to ensure long-term protectiveness;
- Performance monitoring may be more expensive and for a longer time period;
- Potential exists for contaminant migration, and/or cross-media transfer of contaminants; and
- May not be applicable to all sites.

2.2 EA

EA aims to stimulate the natural attenuation processes already occurring on ranges to reduce contaminant migration by increasing SOC levels, increasing contaminant residence time in the soil, and generating reducing conditions to stimulate anaerobic biodegradation processes.

Hatzinger et al. (2004) and Fuller et al. (2004) showed that peat in combination with other more biodegradable amendments (e.g., soybean oil) can be effective in enhancing the sorption and biodegradation of TNT, RDX, and HMX in soils. Biotransformation of TNT, RDX, and HMX exceeded 50% in soil slurry microcosms over a 130-day incubation period, but a maximum of 39% of the added RDX and 11% of the added HMX was mineralized (Fuller et al., 2004). Based on this work, Fuller et al. (2004, 2005, 2009) demonstrated that a 10-cm thick layer of peat moss amended with soybean oil could be effective in controlling the migration of RDX from Composition B (Comp B) detonation residues. RDX and its breakdown product, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), were greatly reduced after passage through the pilot-scale soil columns. No other explosive compounds in the detonation residues were detected in the leachate in over 95% of the aqueous samples collected. These results show that organic amendment addition can be effective in limiting migration of explosive/propellant residues to groundwater. Unfortunately, the peat-soybean oil approach developed by Fuller et al. (2009) had significant operational problems making it impractical for deployment at most ranges, OB/OD and burn areas. Weapons firing and OB/OD activities can cause the peat to catch fire. There are also questions about the physical integrity of the peat moss layer and the potential for dust problems in arid areas.

In the EA portion of this project, an alternative approach is being evaluated that builds on the basic science generated by Fuller and colleagues but overcomes the operational problems they encountered. The overall objective of this work is to develop and demonstrate a process to enhance the sorption and/or degradation of TNT, RDX, and HMX in soils by spray application of an amendment solution containing GL and a soluble humic material on the soil surface, followed by irrigation to carry the amendments deeper into the soil profile. The amendment will provide relatively rapid treatment of contaminants that have already entered the soil profile and long-term groundwater protection, significantly reducing contaminant fluxes to the water table. Amendment addition will achieve these objectives by enhancing biologically mediated reductive transformation/mineralization and sorption.

The general approach was to spray an aqueous solution containing readily biodegradable GL and much more slowly biodegradable humic material on the contaminated soil surface. The site was then irrigated with water to carry these materials deeper into the soil profile. Glycerin and humics addition to soils were expected to enhance TNT, RDX, HMX and perchlorate attenuation through several mechanisms including enhanced sorption, biotic and abiotic degradation. Explosives are known to be more rapidly and extensively removed in biologically active, higher organic carbon (OC) soils that have a low redox potential (Sheremata et al., 2001; Price et al., 2001; Ringelberg et al., 2003; Pennington et al., 2006; Larson et al., 2008a; Ronen et al., 2008). The humic materials will also maintain reducing conditions by consuming O_2, enhancing sorption, and may potentially serve as electron shuttles, enhancing abiotic degradation by ferrous iron (Fe(II)) (Kwon and Finneran, 2006).

Transport of the amendments into the soil profile will be important. By transporting these materials at least 15 cm (6 inches) into the soil profile: (a) fire hazards are dramatically reduced; (b) O_2 flux is reduced resulting in more strongly reducing conditions for contaminant degradation; and (c) the lower O_2 flux limits aerobic degradation of the humic materials, increasing treatment longevity. Physical disturbance of the amendment is not expected to be a major concern due to the depth of the material. If a large crater is formed, future applications of the amendment solution will be concentrated at that spot providing greater treatment where it is needed.

The primary advantages of using EA for management of explosives deposited on ranges are:

- Cost effective,
- Easy to maintain,
- Non-toxic and readily available materials for easy distribution over large areas,
- No adverse impact on existing vegetation,
- No unexploded ordnance (UXO) hazards,
- No dust problem,
- Does not generate a fire hazard during OB/OD activities, and
- Compatible with all on-going training activities.

The use of proposed technology may be limited by the effective life of the organic amendment, which will depend on the amount applied and the rate of O_2 diffusion through the soil. Since lignin biodegradation is a strictly aerobic process, any lignin that penetrates below the aerobic zone will be preserved. Over time, the lignin adsorbed to the surface soils will be depleted, and the aerobic zone will gradually migrate downward through the soil profile until the added material is eventually consumed. However, depending on the amount applied and the rate of O_2 diffusion through the soils, a portion of the amendment could last for years.

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3.0 TECHNICAL APPROACH AND SITE CHARACTERISTICS

3.1 APPROACH

The overall objective of this project was to develop and evaluate two alternative approaches to limit leaching of TNT, RDX and related contaminants at training ranges and OB/OD areas.

In the first approach, the use of MNA will be evaluated to limit the migration of HE from ranges. This approach is expected to be most effective in soils that undergo occasional periods of anoxic conditions that enhance HE degradation. This is more likely to occur in finer grained soils with a high-water retention capacity and/or higher levels of OC.

In the second approach, the effect of glycerin and lignin addition to soils with lower water retention capacity and/or lower levels of OC will be evaluated. Under ambient conditions, these soils are less likely to undergo extended anoxic periods. However, addition of GL and LS to these soils is expected to generate anoxic conditions, enhancing HE degradation.

Work included: (1) laboratory studies to identify factors controlling the fate of TNT and RDX in batch incubations and variably saturated column experiments, and (2) a field evaluation of HE migration and attenuation at an active hand grenade range. Experimental treatments for the laboratory and field work included: (1) ambient conditions (MNA), and (2) GL+LS addition for EA. The field evaluation was conducted at a hand grenade range located at Fort Bragg, NC. The soils used in the laboratory studies were obtained from the hand grenade range during monitoring equipment installation.

3.2 SITE CHARACTERISTICS

The field demonstration was conducted at Fort Bragg, NC. Fort Bragg is a major US Army installation located near Fayetteville and Spring Lake, NC covering over 251 square miles in four counties. Fort Bragg is known as the home of the US Army Airborne Forces and Special Forces, as well as the US Army Forces Command and US Army Reserve Command. The hand grenade range has been in active use for over 20 years.

Soils in the vicinity of the hand grenade range are mapped as Vaucluse loamy sand (fine-loamy, kaolinitic, thermic Fragic Kanhapludults) which is classified as well drained with depth to the water table > 2 m below ground surface (bgs). A typical profile for Vaucluse loamy sand consists of sandy loam (0 to 0.4 m), sandy clay loam (0.4 to 1.5 m), underlain by sandy loam (US Department of Agriculture [USDA], 2012). However, much of the Ap and E horizons have been removed from the bays and used to form blast containment berms. Parent material is loamy and sandy marine deposits.

Figure 3-1 shows the average number grenades thrown per bay per month during the field monitoring portion of this project. Grenade blown counts were higher near the beginning of the project associated with increased training prior to deployment. The great majority of HE deposited on the soil surface is from duds that are blown in-place or grenades that undergo low-order (partial) detonation (Jenkins et al., 2006). As a result, HE deposition is not directly related to blown counts.

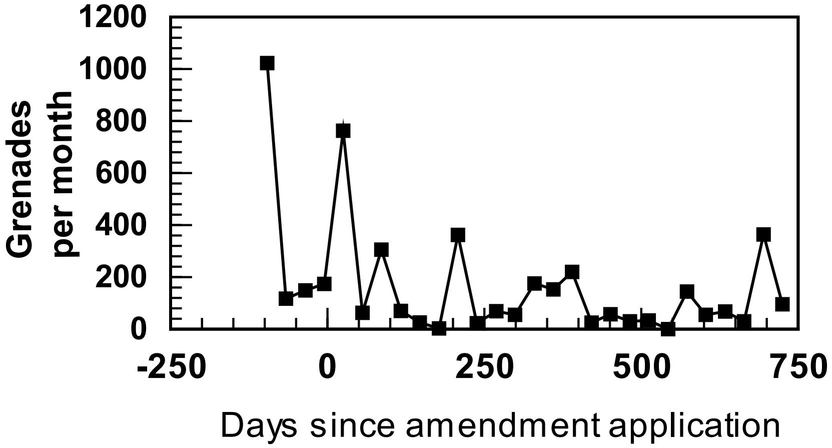

Figure 3-1. Average Grenade Throws During Monitoring

Average number of grenades thrown per bay per month during the field monitoring.

At the start of the field evaluation portion of this project, trenches were excavated down the approximate centerline of two throwing bays with the middle of the trench coinciding with the grenade targets. The trenches were excavated in lifts with composite samples collected at each depth and analyzed for a range of physical and chemical parameters. The first throwing bay was designated as Bay C and was not treated to evaluate MNA. The 2nd bay, designated Bay T, was treated with GL and LS.

Figure 3-2 shows soil characterization results including saturated hydraulic conductivity (K_{sat}), silt fraction, clay fraction, OC content, poorly-crystalline and crystalline Fe(II) and total Fe concentrations over the vertical soil profile. Overall, the physical and chemical properties of Bays C and T were similar. Soils in both bays were primarily sand with 9 - 16% silt and 1.4 - 2.6% clay. Soil pH (5.4 ± 0.2), silt content (13.4 ± 2.7%), and median grain size (D_{50} = 296 ± 70 μm) were not statistically different between Bay C and T soils. However, OC and clay content were significantly higher in Bay C (*p-values* < 0.05). Total Fe content varied from 2 to 8 gram (g)/kilogram (kg) with the large majority of the Fe present in the crystalline form. Much of the poorly crystalline Fe was present as Fe(II), which is consistent with the soils undergoing periods of anoxic conditions.

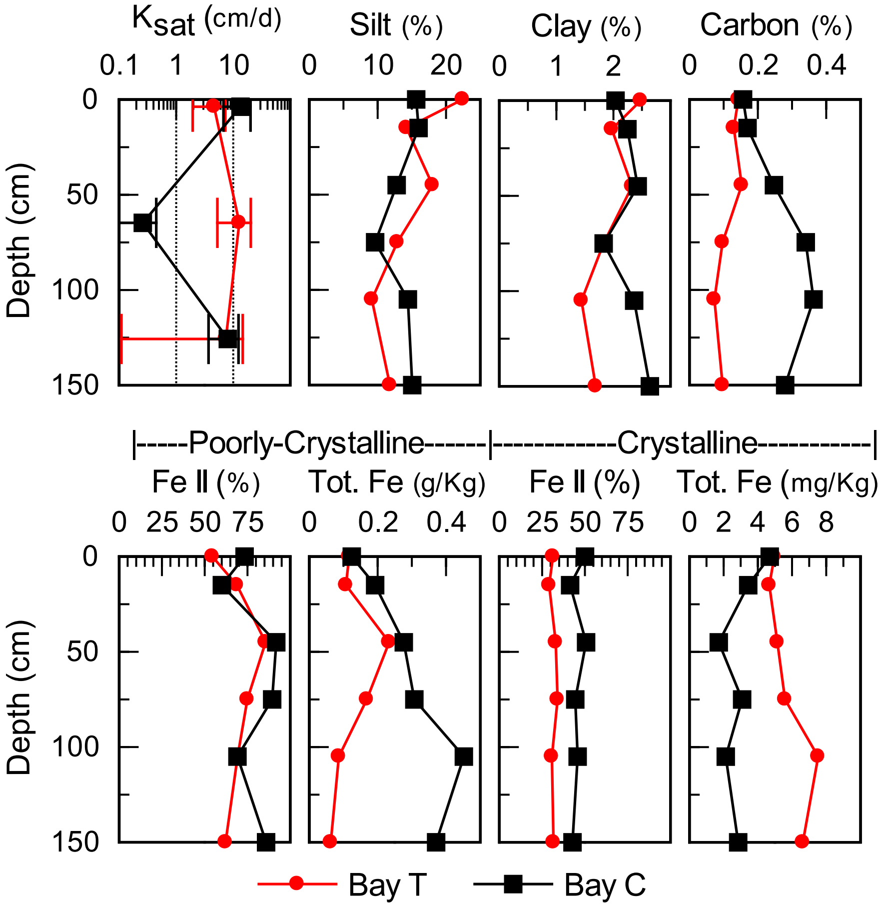

Figure 3-2. Soil Characterization Results

K_{sat}, silt, clay, OC, poorly-crystalline and crystalline Fe(II), and total Fe versus depth in Bays C and T.

HE concentrations were low at the soil surface and below surface in both bays. Average TNT and RDX concentrations in the soil surface of both Bays C and T were much lower than average concentrations (3.3 magnesium [mg]/kg TNT and 5.8 mg/kg RDX) reported by Jenkins et al. (2006) for other military grenade ranges. However, TNT was below 0.01 mg/kg in 5 of the 11 ranges, and RDX was at or below 0.01 mg/kg in 4 of 11 ranges monitored by Jenkins et al. (2006). This indicates that low TNT and RDX concentrations are not uncommon. Contrary to previous reports, TNT and RDX concentrations did not decline significantly with depth, possibly due to the very low concentration present on the soil surface.

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4.0 LABORATORY STUDIES

A series of laboratory studies were conducted to help design and interpret the field monitoring portion of the project. In the first phase of this work (Farling, 2013; Borden et al., 2013), a series of screening studies were conducted to identify low cost, organic materials that could be spray applied on to ranges and would be transported 0.5-1.0 m into the soil profile. Based on the results of these studies, crude GL and LS were selected for further development and evaluation. Subsequent studies showed that LS sorbed to soil (Won, 2016) and slowly biodegraded over time (Won, 2016; Won and Borden, 2016), enhancing RDX degradation. Laboratory column tests were then conducted to evaluate the TNT and RDX transport and attenuation in soil from two grenade bays at Fort Bragg, with and without organic amendments. Results of this work are summarized below with experimental methods presented in Appendix B.

4.1 ORGANIC SUBSTRATE SELECTION FOR EA

In the first phase of this project, a series of screening studies were conducted to identify low cost, organic materials that could be used to stimulate sorption and biodegradation of HE deposited on ranges. The general approach was to spray an aqueous solution containing readily biodegradable GL and more slowly biodegradable humic material on the range. The range would then be irrigated with water to carry these materials deeper into the soil profile. GL and humics addition to soils was expected to enhance TNT, RDX, and HMX attenuation through several mechanisms including enhanced sorption, biotic and abiotic degradation.

The readily biodegradable GL was intended to stimulate anaerobic biodegradation of the target contaminants and reduce naturally occurring ferric iron (Fe(III)) oxides and hydroxides to Fe(II). This Fe(II) also provides a long-term reservoir of reducing power to maintain anoxic conditions in the soil and enhance abiotic degradation of RDX and other contaminants. GL produced during biodiesel production is an attractive alternative for range treatment. Due to growth of the biodiesel industry, large amounts of GL are being produced (approximately 0.1 lb/lb biodiesel). Some of this material is refined into high value products. However, many small producers do not have refining capabilities and must sell it at a low cost ($0.05 to $0.15/lb). GL is completely miscible with water so it can be easily spray applied. The fire hazard for GL is classified as low due to its relatively high flash point (176 °C compared to 112 °C for lactic acid and 17 °C for ethanol) and strongly hygroscopic nature (GL will absorb water out of the air).

The humic materials will also maintain reducing conditions by consuming O_2, enhancing hydrophobic sorption, enhancing covalent binding of TNT, and may potentially serve as electron shuttles, enhancing abiotic degradation by Fe(II) (Kwon and Finneran, 2006). There are a variety of commercially available humics that could be used for range treatment including solid material (peat and humates), soluble humics chemically extracted from the solid humics, and lignin derivatives (LDs) produced during paper production. The solid humics are similar to decomposed peat and would have to be buried to eliminate the burning hazard observed by Fuller et al. (2009). Soluble humate extracts can be used but are chemically very similar to LDs from paper manufacturing and are more expensive ($2 – $3/lb in bulk). In contrast, 100 million tons of relatively inexpensive ($0.10 to $1.50/lb) LDs are produced each year. The chemical properties of the resulting LDs vary, depending on the pulping process.

The most common LDs include: (a) Kraft lignin produced through reaction with sodium hydroxide (NaOH) and sodium sulfide (Na_2S), and (b) LSs produced through reaction with metal bisulfites and other reagents (Pearl, 1967; Kirk et al., 1980).

An initial screening study was conducted to identify commercially available humic materials that: (a) can be easily spray applied, then transported 0.5 – 1.0 m into the soil profile; (b) will strongly sorb/bind/precipitate within the soil, providing long-term treatment with minimal leaching; (c) do not increase fire hazards; (d) are widely available at low cost; (e) are approved for direct contact with food and/or food crops; and (f) do not contain polynuclear aromatic hydrocarbons (PAHs) at excessive levels (Farling, 2013). The humic substances characterized included Norlig A (NA), Ultrazine CA (UCA), Borresperse CA, BorreGro HA1, BorreGro HA 2, Dry Soluble 80, Organo Liquid Hume, REAX 83A, REAX 85A, and Indulin AT. Leaching experiments conducted by Farling (2013) showed that the LSs (NA, UCA, and Borrespere CA) were more strongly retained (50-30% discharged) than other materials tested. The soluble humates (Dry Soluble 80, Organo Liquid Hume, and BorreGro HA-1, HA-2) were very poorly retained, indicating these materials would not be appropriate for the proposed application. Kraft lignins produced through reaction with NaOH and Na_2S during pulping processes, could also be transported into the soil by raising the pH to above 10 using a mixture of NaOH and calcium hydroxide $Ca(OH)_2$. While this approach can be effective in the laboratory, it will be more complicated to implement in the field. Based on the ease of field implementation, further laboratory and field work focused on the use of GL and LS.

4.2 BATCH SORPTION MEASUREMENTS

Batch isotherm experiment studies were conducted to evaluate the extent of TNT and RDX sorption to field sand (FS) collected from a nearby sand quarry, and range soil (RS) collected from Bay T.

Sorption results were fit to Linear ($S = K_dC$), Freundlich ($S = K_FC^n$), and Langmuir ($S = (K_LC)/(1 + nC)$) isotherms where S is the sorbed concentration (μg/g), C is the aqueous concentration (μg/mL), and K_d, K_F, K_L, and n are empirically derived coefficients. Goodness of fit was determined by the Nash-Sutcliffe model efficiency coefficient (*E*) indicating that the highest *E* is considered as the best model (Nash and Sutcliffe, 1970; Bolster and Hornberger, 2007). Figure 4-1 shows best fit Freundlich isotherms for TNT and RDX sorption to FS and RS. Best fit isotherm parameters for Linear, Freundlich, and Langmuir isotherms are shown in Table 4-1.

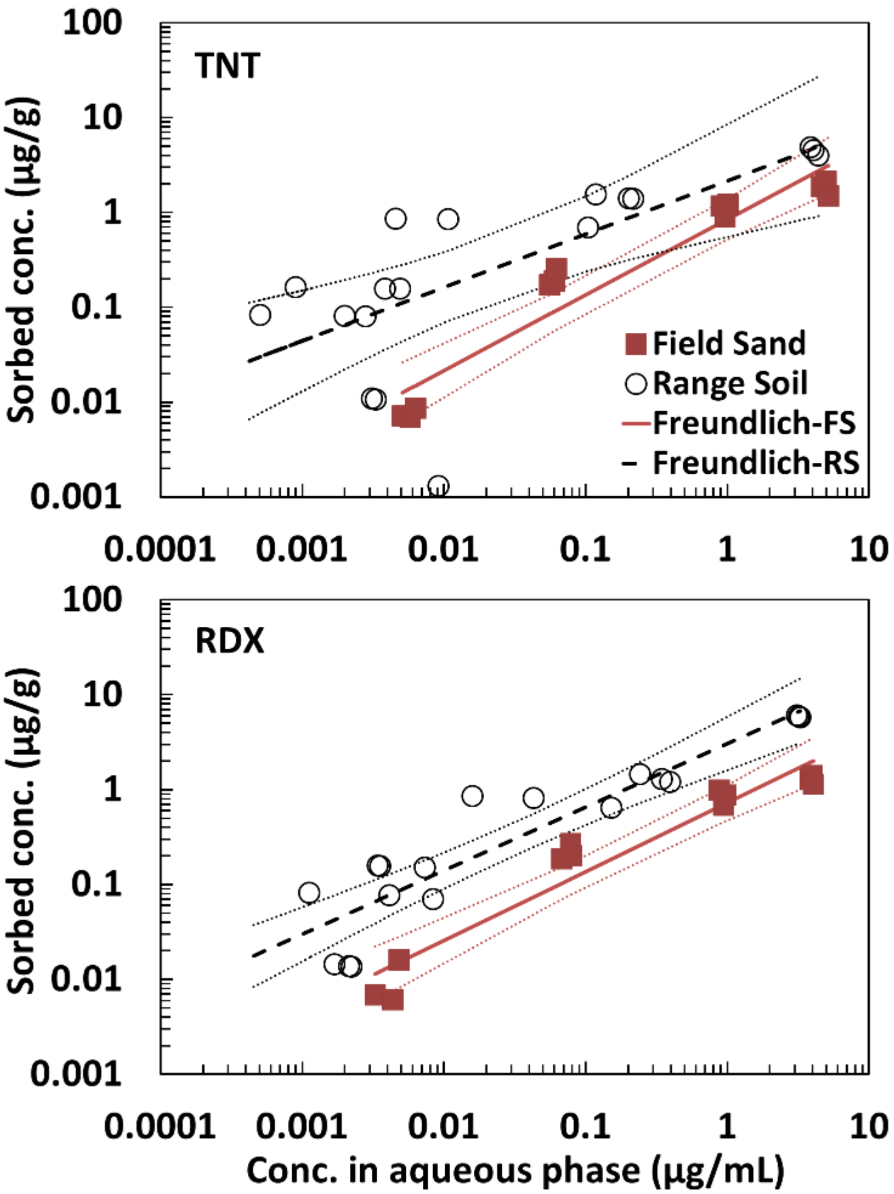

Figure 4-1. Freundlich Isotherms for TNT and RDX Sorption

Sorption isotherms for FS and RS.
Dotted lines are upper and lower 95% confidence intervals (CIs).

Both TNT and RDX sorbed more strongly to RS than FS, presumably due to the higher OC content, clay content, and cation exchange capacity of this material (Appendix B).

Table 4-1. Linear, Freundlich, and Langmuir Isotherm Parameters

Linear, Freundlich, and Langmuir isotherm parameters (± 95% confidence limits)
for TNT and RDX sorption to FS and RS.
Bold values are parameters for the model with the best fit.

HE	Soil	Linear		Freundlich			Langmuir			
		K_d[§]	*E*[‡]	K_F[§]	n	*E*	K_L[§]	n[§]	S_{max}[§]	*E*
TNT	**FS**	1.17±0.52	-6	0.84±0.54	0.80±0.16	0.33	**2.15±1.07**	**0.94±0.62**	**2.28**	**0.96**
	RS	10.98±5.07	-110	**2.16±6.09**	**0.56±0.29**	**0.92**	22.83±19.76	6.65±6.63	3.43	0.85
RDX	**FS**	1.16±0.54	-9	0.73±0.39	0.73±0.14	0.49	**2.60±1.28**	**1.83±1.13**	**1.42**	**0.97**
	RS	9.37±3.84	-21	**3.06±2.75**	**0.67±0.15**	**0.96**	18.25±25.38	4.67±7.77	3.91	0.75

‡ *E* = model efficiency; 1 = perfect fit to the measurements, $E < 0$ = average of the measurements better than model prediction.

§ Units: K_d = mL/g, K_F = $mL^n\mu g^{1-n}/g$, K_L = mL/g, Langmuir n = mL/µg, S_{max} = µg/g.

In our studies, sorption of RDX was similar to TNT in both soils tested. These results differ from prior studies that reported that TNT sorbed more strongly to soils than RDX (Brannon and Pennington, 2002; Hatzinger et al., 2004; Yamamoto et al., 2004; Jaramillo et al., 2011; Ariyarathna et al., 2016). The relatively high affinity of these soils for RDX may be due to the higher silt-clay content of the FS (3.7%) and RS (15%). Sunahara et al. (2009) suggested that interactions with clay minerals might govern RDX sorption rather than association with OC in soil.

There is some disagreement in the literature about whether sorption of TNT and RDX to soil is typically linear (Selim and Iskandar, 1994; Myers et al., 1998; Brannon et al., 2002) or non-linear (Pennington and Patrick, 1990; Selim and Iskandar, 1994; Townsend et al., 1996; Hatzinger et al., 2004; Yamamoto et al., 2004; Morley and Fatemi, 2010; Chappell et al., 2011). In this work, sorption of both TNT and RDX was non-linear to both FS and RS. The Freundlich model provided the best fit for both TNT and RDX sorption to RS, while the Langmuir model provided the best fit for TNT and RDX sorption to FS. Freundlich exponents (n) varied from 0.56 to 0.80 indicating greater relative sorption at lower concentrations.

Addition of LS was hypothesized to increase sorption of TNT and RDX by increasing SOC. However, there was no significant difference in either TNT or RDX sorption to both FS and RS with and without prior LS treatment (Won and Borden, 2016).

4.3 BATCH BIODEGRADATION MEASUREMENTS

A series of laboratory microcosm experiments were conducted to measure TNT and RDX biodegradation under transient aerobic and anaerobic conditions using soil from Bays C and T at Fort Bragg, NC. In these experiments, the microcosms had an initial 56-day aerobic phase followed by an 85-day anaerobic phase. Treatments included autoclaved control, live control (no added substrate), GL addition, NA addition, and GL+NA addition. A combination of GL and NA was selected to provide an easily biodegradable substrate (GL) to rapidly consume O_2 and a more slowly degradable substrate (NA) to maintain anaerobic conditions, while reducing the need for frequent substrate addition. Three replicate microcosms were run for each treatment. Details of experimental methods are presented in Appendix B.

Figure 4-2 shows the variation in concentration of TNT, RDX, and HMX degradation products (MNX, Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine [DNX], TNX) over time. Based on prior results (Won and Borden, 2016), the HEs and degradation products were only monitored at the beginning and end of the aerobic phase. TNT was extensively degraded in soil from both Bays C and T under aerobic conditions. At the completion of the aerobic phase, 2,6-DNT and 2,4-DNT) were below the analytical detection limit of 2.5 µg/L, whereas 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT) were increased as TNT was degraded, followed by further degradation of the Amino dinitrotoluenes (ADNTs) under anaerobic conditions (data not shown).

Consistent with prior observations (Bradley and Chapelle, 1995; Felt et al., 2009; Won and Borden, 2016), RDX was not substantially degraded in the Bay C and T soils during the aerobic phase. HMX, MNX, DNX, and TNX were not added to the incubations, but were present at low levels in the soil used to construct the microcosms. Small increases in each of these compounds were observed in some incubations during the aerobic phase, presumably due to release of this material from the soil. There is no evidence of HMX, MNX, DNX, or TNX degradation during the aerobic phase.

With the onset of anaerobic conditions, both RDX and HMX were extensively degraded in the Bay C and T microcosms. Both compounds were rapidly degraded in the soils amended with GL+NA and in the Bay T live control. However, degradation appeared to be somewhat slower in the Bay C live control. MNX, DNX, and TNX concentrations increased during the period of most rapid RDX degradation, then declined as RDX became depleted.

To provide a more quantitative evaluation of the data, lag periods and first-order degradation rates were estimated for RDX and HMX (Table 4-2). For the live control incubations (no added GL+NA), RDX and HMX degradation rates were significantly higher (*p-values* < 0.05) in the Bay T soil microcosms compared to Bay C soil microcosms, possibly associated with the higher Fe(II) content of this soil. In Bay C soil, the additional amendment treatments of GL, NA, and GL+NA significantly increased RDX degradation rates compared to the live control. However, there was no significant difference between the different amendment treatments. In Bay T, the additional amendment treatments did not significantly increase degradation rates compared to the live control, presumably because the rates in the live control were already very high.

Each of the different organic amendments stimulated HMX degradation in one of the bays. However, the results were not consistent between the bays. GL and GL+NA stimulated HMX degradation in Bay C, while NA addition simulated HMX degradation in Bay T.

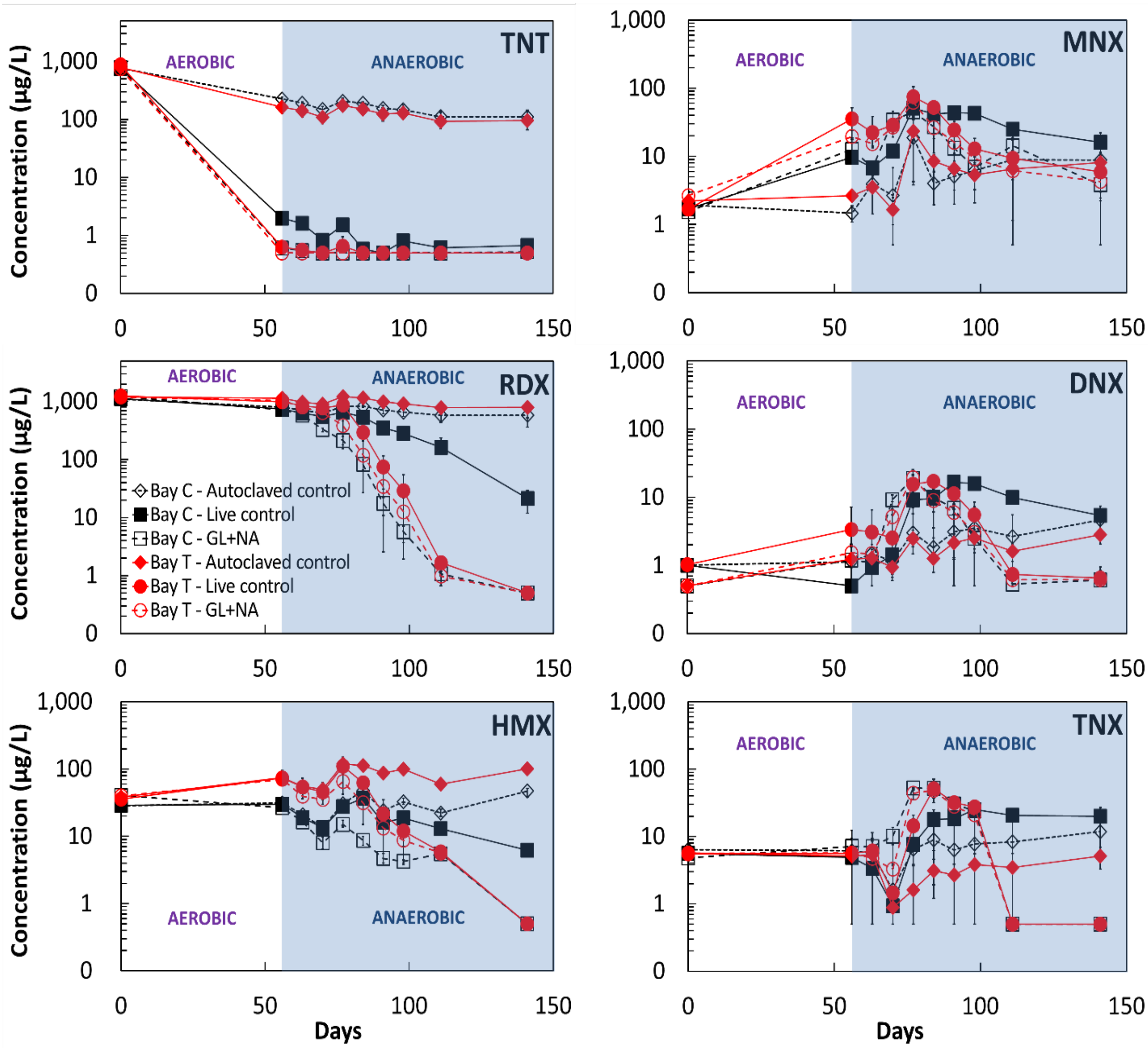

Figure 4-2. HE Biodegradation in Bay T and Bay C Microcosms over Time

TNT, RDX, HMX, MNX, DNX, and TNX in autoclaved controls, live controls, and GL+NA added microcosms. Error bars represent range of values in triplicate microcosms.

Table 4-2. RDX and HMX Lag Periods and Degradation Rates

Average lag periods and 1st order degradation rates in Bay C and T soil microcosms with different treatments. Values in parentheses are standard deviations of replicates.
Bold values are statistically different from live control (p-value < 0.05).

	Treatment	RDX		HMX	
		Lag (d)	Rate (d^{-1})	Lag (d)	Rate (d^{-1})
Bay C	Autoclaved control	21 (0)	0.010 (0.002)	35 (0)	-0.011 (0.003)
	Live control	14 (12)	0.050 (0.020)	28 (12)	0.027 (0.003)
	GL*	0	**0.120 (0.020)**	14 (12)	**0.049 (0.006)**
	NA**	7 (12)	**0.100 (0.030)**	14 (12)	0.050 (0.02)
	GL+NA	0	**0.110 (0.020)**	7 (12)	**0.044 (0.005)**
Bay T	Autoclaved control	21 (0)	0.010 (0.004)	26 (8)	0.007 (0.011)
	Live control	14 (12)	0.130 (0.040)	14 (12)	0.076 (0.008)
	GL*	0	0.147 (0.006)	0	0.100 (0.040)
	NA**	5 (8)	0.130 (0.040)	0	**0.058 (0.001)**
	GL+NA	12 (11)	0.155 (0.007)	14 (12)	0.070 (0.010)

* GL - glycerin
** NA LS

In addition to directly stimulating HE biodegradation, substrate addition should increase O_2 consumption rates, increasing the likelihood of anaerobic conditions. Laboratory soil microcosms were constructed with soil and pore water collected from Bay C and Bay T, then monitored to estimate O_2 consumption with and without organic amendments. Cumulative masses of O_2 consumed and carbon dioxide (CO_2) produced in untreated and treated microcosms with Bay C or T soils are shown in Figure 4-3. Overall, all three replicate microcosms for each treatment exhibited the same behavior in O_2 consumption. In untreated microcosms (live controls), cumulative mass of O_2 consumed was low (< 1.0 millimoles), indicating low O_2 consumption by natural carbon and microbial respiration in soils. However, O_2 consumption was significantly enhanced by addition of GL+NA, resulting in increases of 367% in Bay C and 232% in Bay T soil microcosms. The increased O_2 consumption in substrates-treated microcosms is primarily due to addition of GL rather than NA. Microcosms treated with GL only showed 286% and 195% increased O_2 consumption in Bay C and T soils respectively, whereas NA-treated microcosms showed 33% higher and 7% lower O_2 consumption in Bay C and T soils compared to untreated live controls. The O_2 consumption in the GL+NA treated Bay C soil was significantly higher than in the treated Bay T soil, possibly due to the higher initial OC content of the Bay C soil.

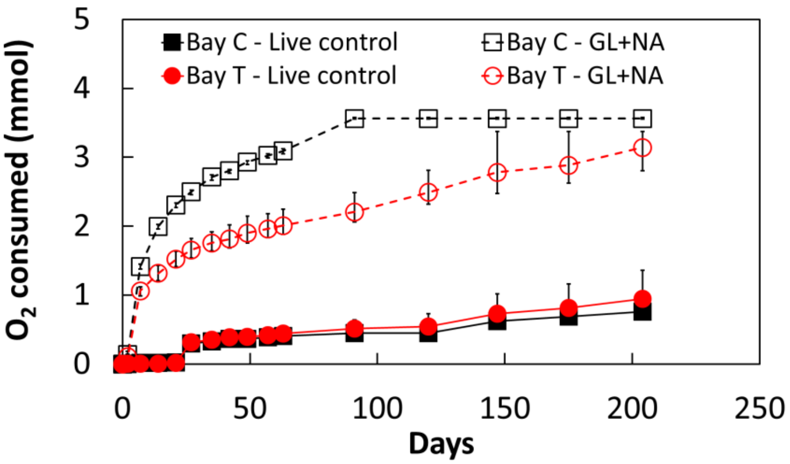

Figure 4-3. O_2 Consumption in GL+NA Treated and Untreated Soils

Cumulative O_2 *consumption versus time in live control (untreated) and GL+NA treated microcosms with Bay C or T soils. Error bars represent range of values in replicate microcosms.*

4.4 VARIABLY SATURATED COLUMN EXPERIMENTS

Column experiments were conducted using soils from grenade Bays C and T at Fort Bragg, NC, with and without organic amendment to identify factors controlling generation of anaerobic conditions and HEs attenuation in soil. A combination of crude glycerin (GL) and the LS NA was selected to provide an easily biodegradable substrate (GL) to rapidly consume O_2 and a more slowly degradable substrate (NA) to maintain anaerobic conditions, while reducing the need for frequent substrate addition. Experimental treatments included Bay C soil with no amendment (Control Bay C), Bay C soil with GL+NA (Treated Bay C), Bay T soil with no amendment (Control Bay T), Bay T soil with GL+NA (Treated Bay T), and HEs leaching columns (Leaching). Duplicate columns (A & B) for each treatment were monitored for 555 days after amendment application to evaluate the impact and longevity of the treatments on HEs leaching. Details of experimental methods are presented in Appendix B.

4.4.1 Soil Column Hydraulics

Total porosity (θ) and water-filled porosity (θ_w) were calculated from soil bulk density, moisture content, and average specific gravity (2.57 g/mL) measured at the end of the monitoring period (Figure 4-4). θ was relatively consistent in all Bay C columns (range = 0.22 to 0.32 excluding drainage layer), but more variable in the Bay T columns (0.22 to 0.39). The reason for this variability is not known, since identical procedures were used to pack all the columns. At the end of the monitoring period, the Bay C soil columns were nearly saturated with $\theta_w/\theta > 95\%$ throughout the profile, while θ_w/θ was below 82% throughout the Bay T soil columns. The average θ_w in Bay C soils was significantly higher than Bay T soils at the end of column experiment (*p-values* < 0.05), resulting in lower air-filled porosities (θ_a). The higher water-filled porosities in Bay C soils are probably associated with relatively higher clay and organic carbon fraction leading to lower K_{sats} on intact cores from the field site (Figure 3-4). Rawls et al. (2003) reported a positive relationship between OC content and water retention in soil, exhibiting higher correlation in sandy and silty soils.

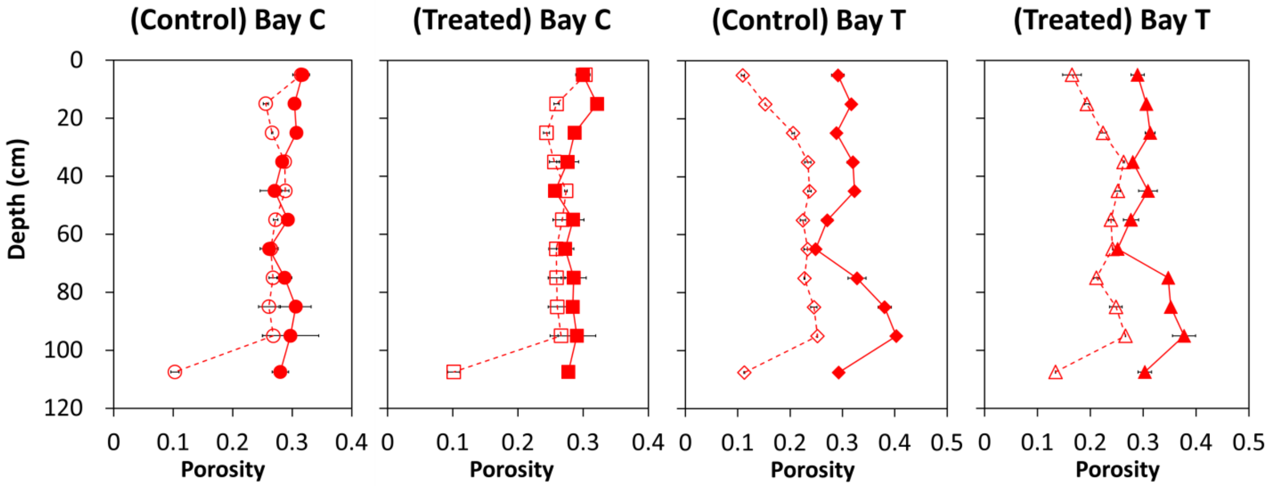

Figure 4-4. Average Total and Air Filled Porosity versus Depth Profiles

Total porosity (θ) *(filled) and water-filled porosity* (θ_w) *(open) at the end of monitoring period. Error bars represent range of values in duplicate columns.*

Organic amendment addition resulted in a substantial increase in θ_w in the upper half of the Bay T columns, with the greatest increase in the top layer (0 - 20 cm) (*p-values* < 0.05), presumably due to enhanced water retention and/or lower K_{sat} associated with LS addition. This increased θ_w and reduced θ_a is expected to have reduced O_2 transport through the soil surface of the amended Bay T columns, increasing the likelihood of anaerobic conditions. Amendment addition did not have a substantial impact on θ_w in the Bay C columns, presumably due to the very high θ_w in the Bay C controls.

Two centimeters of water was applied to the surface of each soil column every other week over the course of the experiment. The applied water was not allowed to runoff and remained on the column surface consistent with the observed presence of ponded water in numerous craters on the Fort Bragg grenade ranges (Section 5). Water infiltrated into the Bay T columns with minimal ponding, but began to accumulate on the surface of the Bay C columns between 26 and 86 weeks due to the lower K_{sat} (Won and Borden, 2016). The presence of ponded water increased evaporation from the Bay C columns, reducing the total amount of water discharged in the effluent, compared to the Bay T columns. Similarly, the higher water retention in the surface layer of the amended Bay T columns enhanced evaporation and reduced the amount of water discharged from these columns. During the last year of the experiments, the average flowrate was 15 cm/yr (range = 12.5 - 17.9) in the Bay C columns and 37 cm/yr (range = 35.9 - 37.5) in the Bay T columns (Table 4-3). These values are reasonably consistent with the net groundwater recharge rate of 32 cm/yr for the Fort Bragg area reported by Heath (1994).

The average hydraulic retention times (HRT) during the last year of the experiment were computed from the water discharged and the average θ_w (Table 4-3). Average HRT varied from 266 days in the control Bay T columns to 1,623 days in the amended Bay C columns. The larger HRTs were the result of higher water retention in these columns combined with greater evaporation (reduced discharge). Given the high HRTs in the Bay C columns, amendments and explosives added to the top of the columns would not be expected to reach the effluent in the ~600 day monitoring period.

Table 4-3. Effluent Volume and HRT during Last Year of Column Experiment

Columns	**Bay C**				**Bay T**			
	Control		**Treated**		**Control**		**Treated**	
Replicate	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
Effluent Volume (cm)	17.9	12.5	5.9	9.4	35.9	37.5	29.1	33.5
HRT (d)	699	966	1,972	1,273	273	258	366	314

4.4.2 O_2 Distribution in Soil Columns

To identify the impact of soil texture and organic amendment addition on redox conditions, soil gases were monitored monthly. Figure 4-5 shows the variation in soil gas O_2 content at 25, 50, 75, and 100 cm depths in each column. In both of the duplicate control Bay T columns, O_2 concentrations remained close to atmospheric throughout the monitoring period. However, in both of the duplicate treated Bay T columns, O_2 concentrations rapidly declined at a depth of 50 cm following organic amendment addition. In one of the treated Bay T replicates (column T-A), O_2 concentrations remained below 5% by volume at the 75 cm depth for over 280 days. However, in the treated Bay T-B replicate column, there was only a small decline in O_2, and levels rebounded to near atmospheric by 200 days. The large difference in O_2 levels in the duplicate soil columns may be associated with more rapid O_2 transport through slightly higher air-filled porosities (θ_a) in the top layer (0 - 30 cm) of the treated Bay T-B column (0.09 - 0.14) compared to the treated Bay T-A column (0.05 - 0.08). However, θ_a at the end of the monitoring period were not significantly different at the 95% level (*p-values* = 0.06).

In Bay C soils, gas samples could not be collected from the 25 cm and 50 cm sampling ports due to nearly water saturated soil conditions. The measured O_2 levels at 75 and 100 cm depths in Bay C soils were close to the atmospheric, probably due to air entry through the bottom of columns. The O_2 transport through the upper portion of the Bay C columns was probably limited due to the high water saturation, greatly increasing the potential for development of anoxic conditions. However, the bottom half of the Bay C columns remained aerobic for most of the monitoring period.

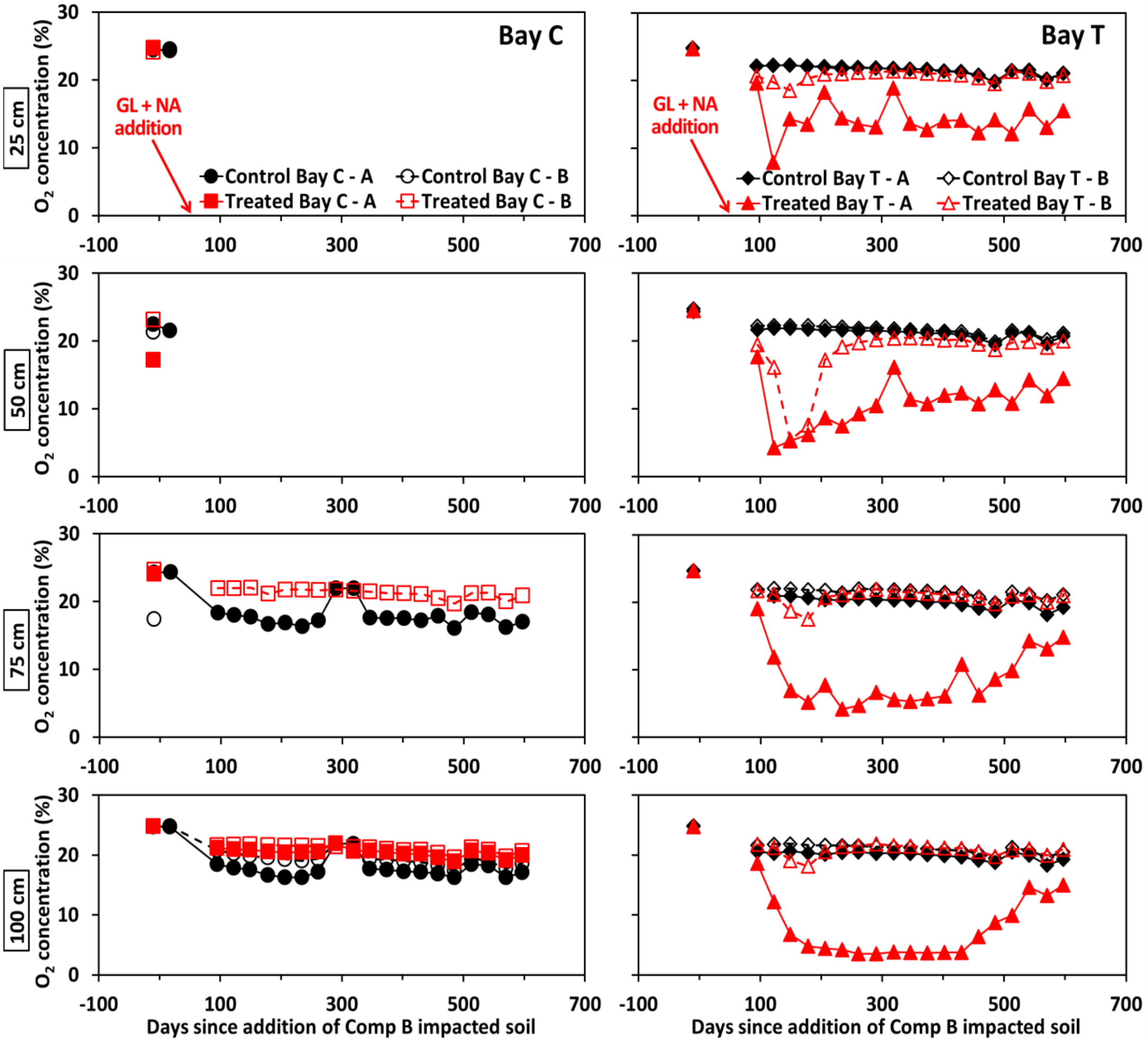

Figure 4-5. Soil Gas O_2 Concentrations Versus Time

Soil gas O_2 *concentrations (%) at 25, 50, 75, and 100 cm below the surface.*

4.4.3 Soil Column Geochemistry

Column effluents were monitored monthly to evaluate the impact of organic amendment addition on geochemical parameters including Total Organic Carbon (TOC), anions (Chlorine [Cl], Nitrate [NO_3], Nitrite [NO_2], and Sulfate [SO_4]), and cations (manganese [Mn] and Fe). Carbon content and Fe(II/III) in soils packed in columns were also measured at the end of the monitoring period. Figure 4-6 shows the variation in Cl, TOC, NO_3, and Mn in the soil column effluents. TOC concentrations were initially elevated, potentially due to TOC released during column packing. In the treated Bay T columns, Cl present in the waste GL (2.7% Cl) began to arrive in the effluent at 280 days, increasing to a maximum of 283 mg/L at 420 days (364 days after GL addition), which is consistent with the computed average HRT of 340 days. By this time, TOC concentrations were low (0.9 to 12.7 mg/L) indicating negligible OC transport through the columns. However, there were significant variations in Cl migration between duplicate treated Bay T columns as shown in Figure 4-6. Cl concentration in effluent reached a maximum more rapidly in the T-A column (283 mg/L at 420 days) compared to the T-B column (151 mg/L at 588 days). This difference may have resulted from the slightly lower θ_w in the upper 0 - 30 cm of the T-B column (average = 0.18, range = 0.15 - 0.22) than the T-A column (average = 0.20, range = 0.18 - 0.23) since Cl migrates through the water-filled portion of soil pores.

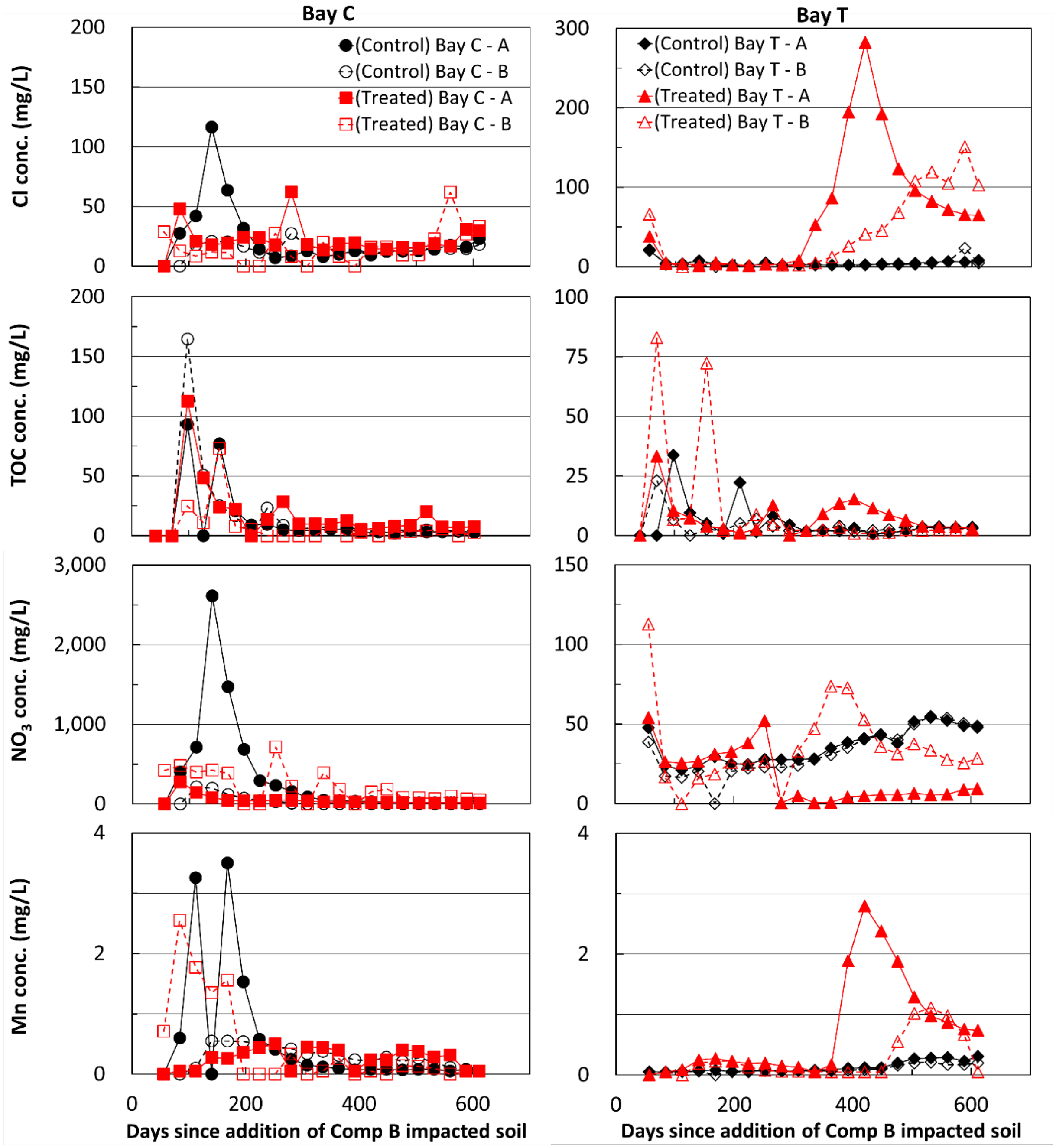

Figure 4-6. Cl, TOC, NO_3, and Mn in Column Effluents Versus Time

Inner graphs present log-scale concentrations over time.

In the treated Bay C columns, there was a small increase in Cl towards the end of the experiment. It is unlikely this is the beginning of Cl breakthrough, since computed HRT of these columns were 1,292 and 1,972 days. Similar to the Bay T columns, OC breakthrough in the Bay C columns was negligible. In all treated columns, less than 1% of the added carbon was discharged in the effluent. In contrast, over 60,000 mg/L of TOC was discharged in the effluent of washed sand (3.7% silt-clay) columns amended with GL (Farling, 2013). The much more limited TOC breakthrough in the Fort Bragg soil columns is presumably due to the higher silt-clay content (15.1 ± 3.5% silt-clay) and longer HRT.

NO_2 was initially detected in the effluent of all columns at concentrations ranging from 0.7 to 1.8 mg/L and then declined below detection (< 0.5 mg/L) within 168 days (data not shown). NO_2 concentrations in the leaching column effluent varied from 0.5 to 5.5 mg/L (data not shown), indicating substantial NO_2 attenuation in Bay C and T columns, either by oxidation to NO_3 or anaerobic NO_2 reduction.

In both control Bay T columns and one treated Bay T column (T-B), NO_3 concentrations increased over the course of the experiment, presumably due to oxidation of NO_2 released from the Comp B on the column surface. However, in the treated Bay T-A column, NO_3 concentrations slightly increased by 252 days then declined over time, presumably due to denitrification under anoxic conditions (Figure 4-6). Initial NO_3 concentrations in both the treated and control Bay C effluents were much higher than those in the Bay T columns. The reason for this difference is not known, but it might be associated with deposition of nitrogenous compounds following explosives detonation followed by oxidation to NO_3. Over time, NO_3 concentrations in all the Bay C effluents declined.

Mn concentrations increased in the amended Bay T-A and T-B columns, concurrent with Cl. This implies that the organic amendment addition generated Mn reducing conditions in the treated Bay T soils. Organic amendment addition did not result in a measurable increase in dissolved Fe in either the Bay C or Bay T columns, with dissolved Fe concentrations remaining below the analytical detection limit of 0.05 mg/L in all column effluents throughout the monitoring period (data not shown).

Amendment addition increased the OC content in the upper portion of both the Bay C and T soils (Figure 4-7), compared to the controls (*p-values* < 0.05). The greater increase in the Bay C columns is likely due to the reduced water flow and O_2 transport in these columns. Poorly crystalline Fe(II) content increased in the upper portion of the Bay C and middle portion of Bay T columns (Figure 4-8), compared to the controls (*p-values* < 0.05). Amendment addition did not result in a measurable increase in crystalline Fe(II) for either soil.

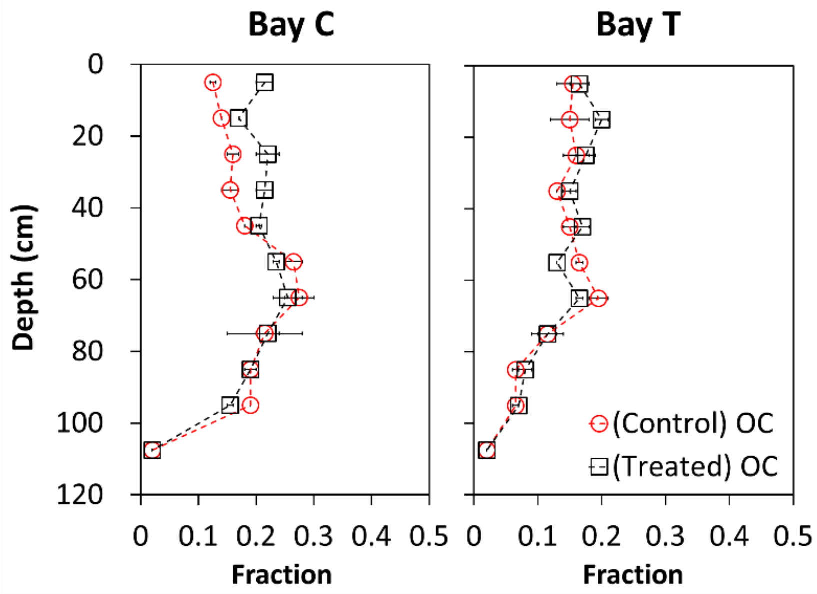

Figure 4-7. Average OC Versus Depth in Columns

OC measured at the end of the experiment.
Error bars represent range of values in replicate columns.

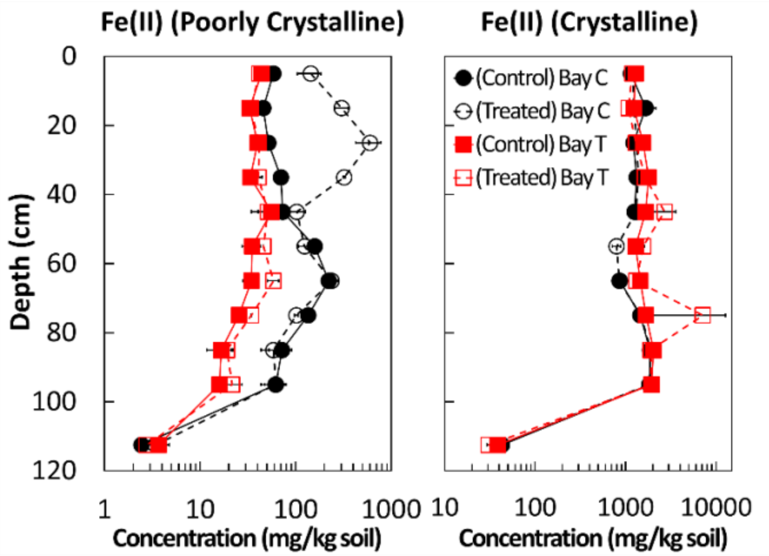

Figure 4-8. Average Fe(II) of Crystalline and Poorly Crystalline Fe Versus Depth

Fe(II) measured at the end of the experiment.
Error bars represent range of values in replicate columns.

4.4.4 Explosives in Soil Columns

Column effluents were analyzed monthly to evaluate the impact of soil texture and organic amendment addition on changes in HE concentrations (Figure 4-9). At the completion of the experiment (the end of the monitoring period), the soils were extracted and analyzed to determine the distribution of HEs (Figure 4-10) and develop a mass balance for HEs in each column (Figure 4-11). The mass associated with the Comp B soils was calculated from the mass discharged from parallel leaching column experiments reported by Won and Borden (2017). As shown in Figure 4-9, effluent TNT concentrations varied from 5.7 to 56.4 mg/L (average = 23.4 mg/L) and RDX varied from 6.0 to 31.4 (average = 27.8 mg/L) in the Comp B leaching columns with no long-term trend. HMX concentrations reached a maximum of 0.23 mg/L at about 150 days and then gradually declined with time to 0.05 mg/L (average over monitoring period = 0.11 mg/L). Low levels of MNX, DNX, and TNX were initially present in the leaching column effluent, then gradually declined over time, suggesting these degradation products were initially present in the soil and leached out over time (Won and Borden, 2017).

TNT was extensively degraded in both Bay C and T soils with effluent concentrations consistently below the detection limit (< 1 µg/L) (TNT data not shown in Figure 4-9 since all values were below detection). TNT daughter product concentrations also remained low. Dinitrotoluenes (DNTs) (2,4-DNT and 2,6-DNT) were below the detection limit (< 2.5 µg/L) and concentrations of ADNTs (2-ADNT and 4-ADNT) were less than 10 µg/L in all columns over the most monitoring period (data not shown). The total mass of TNT discharged in the Bay C and Bay T soils was less than 0.1% of the mass released from the leaching columns for both organic amended (treated) and control columns (Figure 4-11).

TNT concentrations in soil were highest at the soil surface and then declined with depth in all columns (Figure 4-10). In both the Bay C and Bay T soils, soil bound TNT levels were significantly lower (*p-values* < 0.05) in the amended columns than the untreated controls, indicating organic substrate (GL+NA) addition enhanced TNT degradation in both Bay C and T soils. These low levels of TNT and its degradation products in the effluent and soil are consistent with results from batch microcosm experiments using Bay C and T soils which showed extensive TNT biodegradation under both aerobic and anaerobic conditions (Won and Borden, 2016).

RDX leaching behavior was significantly different between Bay C and T soil columns. Figure 4-9 shows the variation in RDX and RDX nitroso degradation products (MNX, DNX, and TNX) in column effluents over the monitoring period. In the treated and control Bay T columns, RDX, MNX, DNX, and TNX were relatively consistent over the first 250 days, reaching a maximum at approximately 100 days and then declining. In the control Bay T columns, RDX concentrations began to increase at 250 days to 350 days, reaching a maximum of ~10,000 µg/L by the end of the experiment, similar to the RDX concentrations discharged from the leaching columns. In the treated Bay T columns, RDX concentrations began to rebound at about 450 days in treated Bay T-B column and at 550 days in treated Bay T-A column. The more rapid rebound in column B was likely due to the more rapid return to oxidizing conditions in this column (Figure 4-9). Similar results were observed for MNX and DNX, where organic amendment addition appeared to delay degradation product increases in the Bay T column effluents by about 200 days.

RDX concentrations were more variable in the Bay C column replicates (Figure 4-9). In one control column (C-A) and one treated column (C-B) with Bay C soil, RDX concentrations were relatively high (100 - 1000 µg/L) and remained almost constant with time. In the other replicate Bay C column, RDX concentrations were lower and declined more rapidly with time. As a result, total mass of RDX released from the Bay C treated and control columns were similar (Figure 4-11).

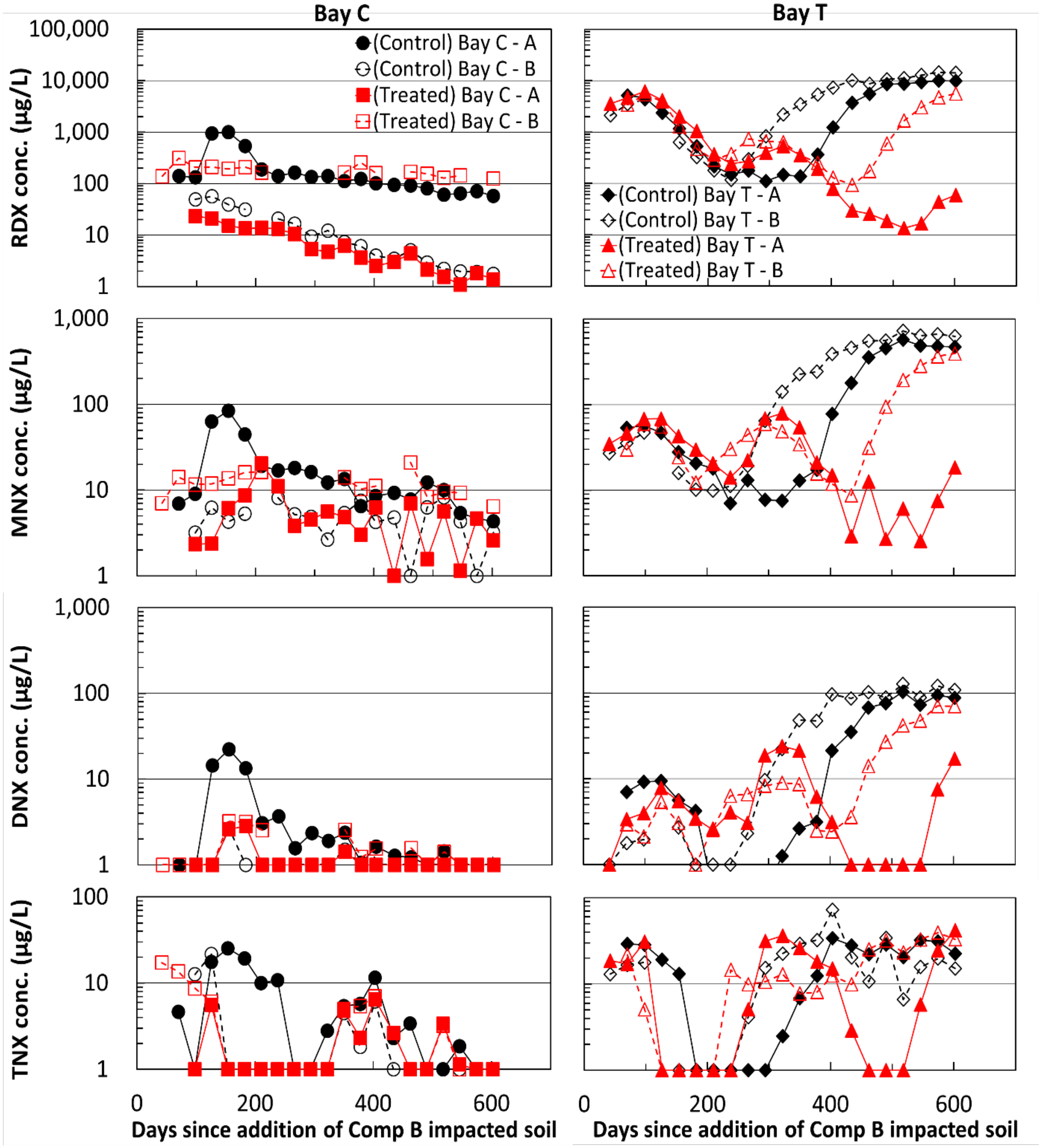

Figure 4-9. RDX, MNX, DNX, and TNX in Column Effluents Versus Time

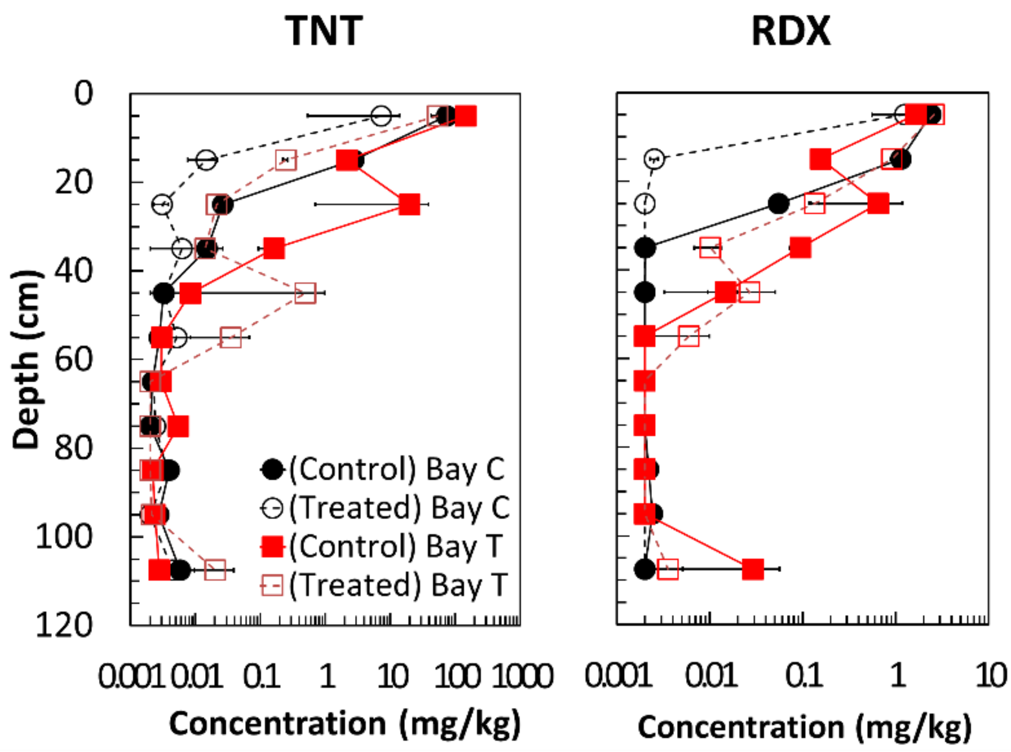

Figure 4-10. Average TNT and RDX Versus Depth

HE concentrations measured at the end of monitoring period.
Error bars represent range of values in replicate columns.

In Bay C columns, RDX concentrations were highest near the soil surface and declined rapidly with depth (Figure 4-10). Mass balance results (Figure 4-11) demonstrate that RDX was extensively degraded in both the control and treated Bay C columns, with 10% to 22% of the RDX recovered as nitroso degradation products. RDX removal was slightly higher in the treated Bay C columns than the controls. However, RDX degradation product mass (sum of MNX, DNX and TNX) was higher in the treated Bay C columns so overall removal of RDX and degradation products was similar in the treated and control Bay C columns. The large majority of the degradation products recovered was sorbed to the soil with TNX present in the highest concentrations, followed by MNX and DNX (Figure 4-11).

The distribution of RDX and its degradation products in the Bay T soil at the end of the experiment was similar to the Bay C columns (Figure 4-10). The highest RDX concentrations were present near the soil surface, and levels declined rapidly with depth. 13 to 33% of the RDX mass was recovered as nitroso degradation products sorbed to soil, with TNX present in the highest concentrations. In the Bay T columns, amendment addition reduced both the mass of RDX released in the column effluent and the mass of RDX degradation products in the soil.

Amendment addition did not have a significant impact on HMX leaching or final HMX concentrations in the soil, for either the Bay C or Bay T soils (Figure 4-11). The limited HMX removal is probably due to high RDX concentrations which are reported to inhibit biodegradation of HMX (Uchimiya et al., 2010).

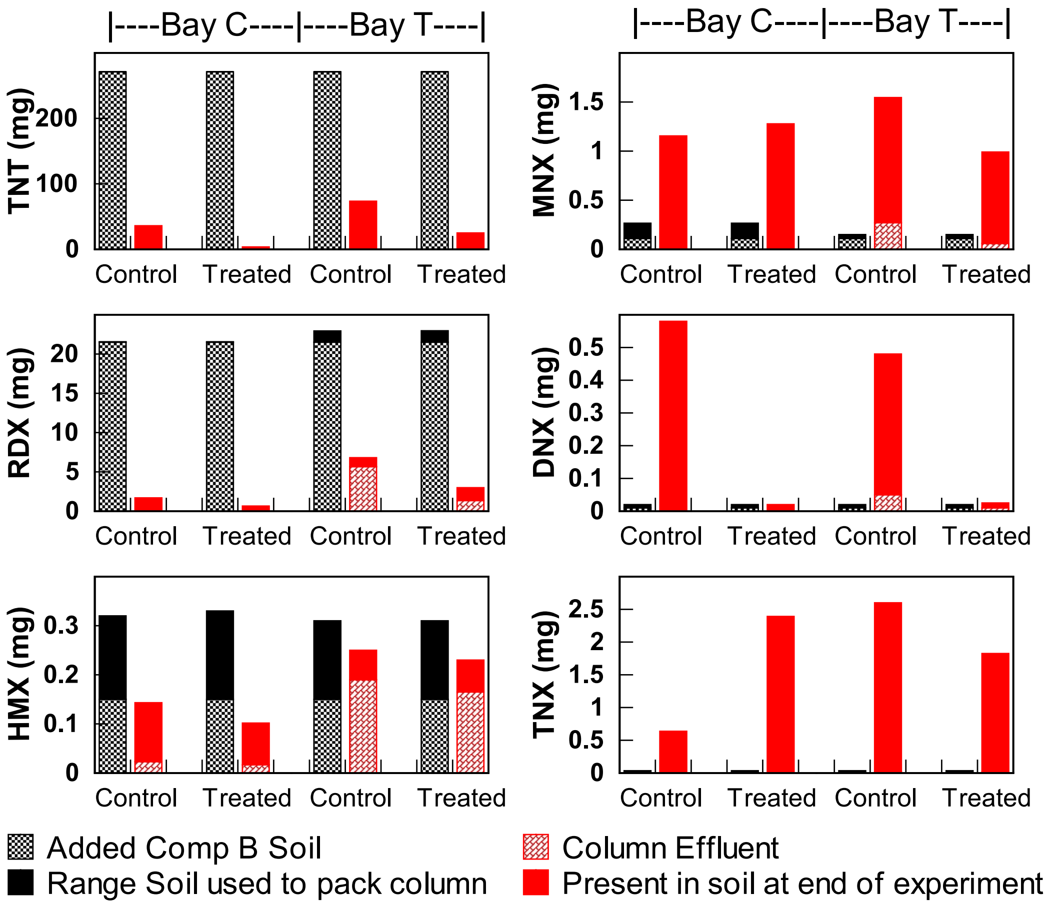

Figure 4-11. Average Mass Balance Results for TNT, RDX, HMX, MNX, DNX, and TNX

Mass present in the soil at the start of the column experiment (black) and recovered in the column effluent or soil at the end of the experiment (red). The difference between the black and red columns is the mass degraded or produced.

4.5 DISCUSSION AND CONCLUSIONS

TNT was extensively degraded in both batch microcosm and column experiments, consistent with prior reports (Fuller and Manning, 1997; Singh, 2012). In microcosm experiments with field sand (Won and Borden, 2016) and soil from two active grenade throwing bays, TNT rapidly biodegraded under aerobic conditions. While some TNT degradation products (2-ADNT and 4-ADNT) increased during the aerobic phase, these intermediates were further degraded during the anaerobic phase, and were reduced below 2.5 µg/L within 42 days. In both the treated and control columns, less than 0.1% of the mass added in Bay C and Bay T soils was discharged in the effluent. The fraction of TNT sorbed to soil were much lower in treated columns (0 - 2% in Bay C, 7 - 11% in Bay T) than controls (13 - 14% in Bay C, 26 - 28% in Bay T), presumably due to further degradation of TNT, indicating GL+NA addition was effective in enhancing TNT degradation. There was no significant accumulation of TNT degradation products (DNTs and ADNTs) in any column.

There was no evidence of RDX or HMX biodegradation in aerobic microcosms. Under anaerobic conditions, RDX and HMX were rapidly degraded in live control microcosms (no amendment) with Bay T soil (RDX =0.130 d^{-1}, HMX = 0.076 d^{-1}), with somewhat slower degradation with Bay C soil (RDX =0.050 d^{-1}, HMX = 0.027 d^{-1}). Addition of GL and/or NA significantly increased RDX degradation rates in Bay C soil. However, the organic amendments did not accelerate degradation in Bay T soil, possibly because the rates were already high. During anaerobic RDX degradation, dissolved nitroso derivatives initially increased then declined, resulting in final aqueous concentrations of DNX and TNX below 1 μg/L. While MNX was still present in all microcosms, organic amendment addition reduced MNX levels compared to live controls.

Variable saturation column experiments demonstrated that RDX may biodegrade under ambient conditions without any amendments (natural attenuation). However, relatively small differences in soil properties can result in substantial differences in RDX removal. Control Bay T soil columns were unsaturated and remained aerobic. RDX concentrations reached the concentrations discharged from the leaching columns after approximately 546 and 430 days in the replicates, which are somewhat later than computed HRT during last year (273 and 258 days). The somewhat slower breakthrough of RDX was likely due to low, but significant sorption to the soil. Most RDX was discharged in effluent with small portion of RDX sorbed onto soils. However, the great majority of the RDX degradation products were retained in the soil columns and were not discharged in the than effluent (Figure 4-11). The large amount of MNX and TNX present in the soil indicates that RDX was degraded in control Bay T soils under anoxic conditions, presumably in the 50 - 70 cm depth interval where the soils were nearly saturated (average $\theta_w/\theta > 97\%$) (Figure 4-4). RDX concentrations were highest near the soil surface and declined rapidly with depth (Figure 4-10).

In control Bay C soils with relatively higher clay and organic carbon contents, anoxic conditions were likely established in the upper portion of columns due to the nearly water saturated soil conditions, while the lower portion remained aerobic (Figure 4-5). Very little RDX was discharged in effluent with a small amount sorbed to Bay C soils (Figure 4-11). The mass of RDX discharged in effluent was expected to be low, based on the long HRT of the column (833 days). However, the mass remaining in the soil was also low, indicating the majority of RDX was degraded. As a result of RDX degradation, RDX degradation products were elevated in soil. MNX and TNX were distributed throughout the vertical soil profile, while DNX concentrations rapidly declined with depth (Won and Borden, 2017).

Mass balance results showed significant RDX removal (Figure 4-11) in the control Bay T columns that contained free O_2 for most of the monitoring period (Figure 4-5). The observed RDX degradation might be associated with the short-term anoxic conditions or development of anoxic micro-niches (Christensen and Tiedje, 1990; Smith, 1980; Sexstone et al., 1985; Whalen and Sampedro, 2010; Chen and Strous, 2013). In the Bay C control columns, RDX extensively degraded, presumably due to anoxic conditions resulting from the high water saturation. Ringelberg et al. (2003) reported extensive RDX attenuation in sandy loam (silt-clay content = 42%) under the saturated conditions compared to limited degradation under the unsaturated conditions RDX is typically more resistant to aerobic biodegradation than TNT (Bradley and Chapelle, 1995; Hawari et al., 2000; Felt et al., 2009). Farling (2013) showed extensive TNT removal and no substantial RDX degradation in his aerobic column study using sandy soil.

The mixture of crude GL and LS was selected as an organic amendment in this study. The readily biodegradable GL, produced as a byproduct of biodiesel production, was intended to rapidly consume O_2 in soil, generating anoxic conditions and leading to enhanced anaerobic biodegradation of explosives. The LS, produced during paper production, was expected to much slowly consume O_2 due to its slow biodegradability, helping to maintain anoxic conditions established by GL degradation. GL and LS are highly water soluble and could be applied to the contaminated site by spraying without entering the range to remove UXO. The amendment applied would be transported into the soil by rainfall or artificial irrigation.

The impact of amendment addition was variable between replicates in Bay T soil columns. In replicate T-A, organic amendment rapidly migrated through the column with a travel time of 366 days, generating anoxic conditions at the bottom half of the column for about a year (Figure 4-5). With the arrival of Cl present in the GL at the bottom of the column, TOC and Mn concentrations increased, while RDX and its degradation products substantially declined with a concurrent NO_3 decrease, indicating enhanced RDX biodegradation under anoxic conditions. However, in replicate T-B, O_2 levels remained close to atmospheric for much of the experiment (Figure 4-5), NO_3 remained high, Mn remained low, and there was very little TOC discharged in the effluent (Figure 4-6). Due to the more oxidizing conditions in replicate T-B, RDX degradation was more limited. By the end of the experiment, RDX concentrations in replicate T-B were two orders of magnitude greater than in the more reduced replicate T-A (Figure 4-9).

In Bay C columns, amendment addition was not effective in reducing RDX leaching since very little RDX was discharged even in the controls. However, amendment addition enhanced reductive degradation of RDX, reducing the amount of RDX in soil and increasing the amount of RDX degradation products at the end of the experiment (Figure 4-11). There was no evidence that amendment addition reduced HMX leaching or enhanced degradation.

5.0 FIELD EVALUATION

Two complementary technologies for controlling the migration of HEs from hand grenade ranges were evaluated in adjoining throwing bays at the grenade range at Fort Bragg, NC: (1) MNA; and (2) EA. The spatial distribution of HE in the soil within each bay was initially determined by excavating a soil monitoring trench down the approximate centerline of each throwing area, running from 20 to 30 m from each throwing box. Soil samples collected from these trenches were analyzed for explosives, metals, and soil characteristics. Soil redox probes and pore water samplers were installed during trench backfill to allow continued monitoring without actually entering the throwing bays. After monitoring pore water for three months to establish baseline conditions, a 15 m x 30 m area in Bay T was treated by spray application of an organic amendment solution containing GL and LS to evaluate EA. Bay C was treated with an equal volume of water and served as an untreated control to evaluate MNA. After monitoring soil pore water concentrations for 24 months, the trenches in both bays were re-excavated and sampled to look for changes in HE in the soil. Details of experimental methods are presented in Appendix B.

5.1 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

Actual treatment of the grenade bays was very simple. After monitoring pore water for three months to establish baseline conditions, a 15 m x 30 m area in one of the bays (designated Bay T) was treated by spray application of 755 kg of crude GL (Piedmont Biofuels, Pittsboro, NC), 800 kg of NA LS (Lignotech USA, Rothschild, WI.), and 542 L of water, resulting in a net application of 1.7 kg/m^2 of LS, 1.6 kg/m^2 of GL, and 0.5 cm of fluid (mixture of LS's, GL, and water). GL *(CAS # 56-81-5)* serves as an easily biodegradable carbon source for microorganisms to consume O_2, stimulating anaerobic biodegradation of the target contaminants, is completely miscible with water, and has a high flash point reducing fire hazards. LS serves as a slowly biodegradable humic material that provides a large reservoir of reducing power to maintain long-term anoxic condition and will not propagate combustion. LS contains traces of naphthalene (0.18 mg/kg). All other PAHs were below the reporting limit of 0.1 mg/kg (Columbia Analytical Services, Inc.). At the application rate used in this project, naphthalene present in the LS would have increased the soil concentration by 0.16 µg/kg which is below the 3.8 mg/kg Residential Health Based Soil Remediation Goal (North Carolina Department of Environmental Quality [NCDEQ], 2016). The physical and chemical characteristics of waste GL and LS are summarized in Table 5-1.

Table 5-1. Characteristics of Waste GL and LS

Parameter	Unit	GL	LS
Carbon %	%	47.1	25.2
Moisture Content %	%	26.7	48.4
Volatile Solid Content %	%	61.5	41.3
Ash Content %	%	11.8	10.3
Solubility in water		Over 99%	Over 99%
Antimony (Sb)	mg/kg	0.02	< 0.01
Arsenic (As)	mg/kg	0.05	< 0.01
Beryllium (Be)	mg/kg	< 0.01	< 0.01
Cadmium (Cd)	mg/kg	< 0.01	0.16
Total Chromium (Cr)	mg/kg	0.83	0.28
Copper (Cu)	mg/kg	0.97	0.53

Table 5-1. Characteristics of Waste GL and LS (Continued)

Parameter	Unit	GL	LS
Lead (Pb)	mg/kg	0.13	0.04
Mercury (Hg)	mg/kg	< 0.01	< 0.01
Nickel (Ni)	mg/kg	0.64	0.20
Selenium (Se)	mg/kg	0.02	0.03
Silver (Ag)	mg/kg	< 0.01	< 0.01
Thallium (Th)	mg/kg	< 0.01	< 0.01
Zinc (Zn)	mg/kg	1.71	6.82

The second throwing bay (Bay C) was treated with an equal volume of sodium bromide (NaBr) solution and served as an untreated control to evaluate MNA of explosives under ambient conditions. Bay T was selected for amendment addition because the initial oxidation potential (Eh), TNT, and RDX concentrations were higher. NaBr was not added to the organic amendment applied to Bay T since the crude GL contains a substantial amount of potassium (K) Cl that can be used as a tracer. After monitoring soil pore water concentrations for 24 months, the trenches in both bays were re-excavated and sampled to evaluate changes in HE in the soil. K_{sat} was measured in the laboratory (Mohanty et al., 1994) on intact 7.5 cm dia. x 7.5 cm long cores collected at two locations and three depths within each trench. Figure 5-1 shows the grenade bays prior to amendment application.

The original plan was to spray apply the material with impact sprinklers. However, during the application process, the impact heads ‘gummed up’, preventing the head from rotating and causing all the material to be applied in a small area. To overcome this problem, the field crew spray applied the material with a simple hand-held spray nozzle. For the pilot test, this was not a problem and all the material was spray applied in one day. However, for full-scale application, an alternative spraying approach should be developed.

Figure 5-1. Grenade Bays Prior to Amendment Application

Image shows pooled water in grenade craters.

5.2 PERFORMANCE MONITORING RESULTS

5.2.1 Site Hydrology and Biogeochemistry

Spatial and temporal variations in precipitation and evapotranspiration (ET) had a significant influence on soil moisture. This in turn, influenced O_2 transfer through air filled soil pores and soil redox potential. Figure 5-2 shows cumulative drainage and cumulative rainfall over time in the bucket lysimeters (BLs) installed in Bay C and Bay T. Drainage rates were measured by monitoring the total volume of water recovered from each BL normalized to the bucket surface area. Rainfall and reference crop ET data are from weather station NFBR – Fort Bragg, located 2.2 km north of the grenade range (data from the State Climate Office of North Carolina [SCONC]).

There were large variations in drainage rates within each bay and between the two throwing bays. Measured drainage rates in Bay T BLs B-5 and D-5 were very high, equivalent to 60 - 70% of cumulative rainfall, while other Bay T lysimeters (A-3, A-5, B-3, C-3, C-5, and D-3) were much lower (equivalent to 12 - 26% of rainfall). The cause of the large differences is likely the result of grenade detonation craters that formed over different lysimeters, focusing infiltration in different locations. The surface of the bays is periodically regraded to fill the craters, so the areas of concentrated infiltration may shift over time.

In Bay C there were also significant variations in drainage between the different BLs. However, total drainage rates were much lower, with cumulative drainage varying from less than 1% to up to 6% of cumulative rainfall. The low drainage rates in Bay C are likely due to the lower K_{sat} of these soils (Figure 3-2).

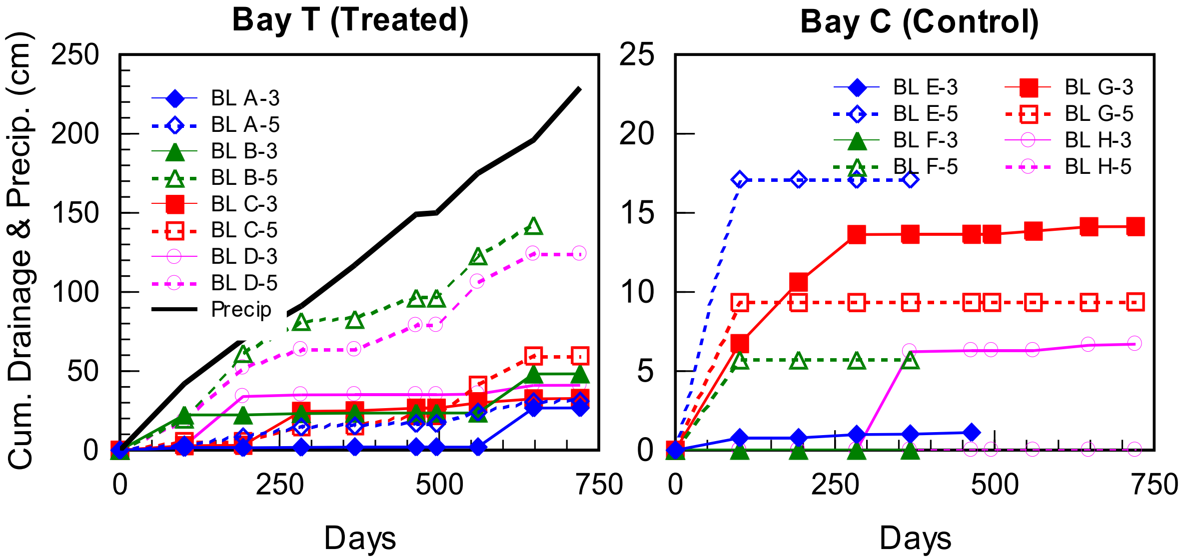

Figure 5-2. Cumulative Drainage and Precipitation Versus Time

Cumulative drainage measured in BLs in throwing bays in comparison to cumulative rainfall. Precipitation data from SCONC.

Figure 5-3 shows precipitation, reference crop ET, and soil moisture for the study period. Electrical resistance in the moisture sensors was converted to soil moisture using a measured characteristic curve generated with soil from the site. Climate data are for weather station NFBR – Fort Bragg. ET was estimated using the Modified Penman-Monteith equation (Allen et al., 1998). High rainfall and low ET in spring and winter of 2013 resulted in high soil moisture contents in both Bays C and T. June 2013 was very wet (total precipitation = 27 cm) resulting in near saturated soil conditions during substrate application. Drier conditions in August through October 2013 allowed the soil in Bay T to dry, while moisture content remained high in Bay C. High ET and relatively low rainfall from April 2014 through October 2014 resulted in a decline in soil moisture in both Bays C and T. Higher rainfall with low ET from Dec-14 to Mar-15 caused soil moisture to rebound.

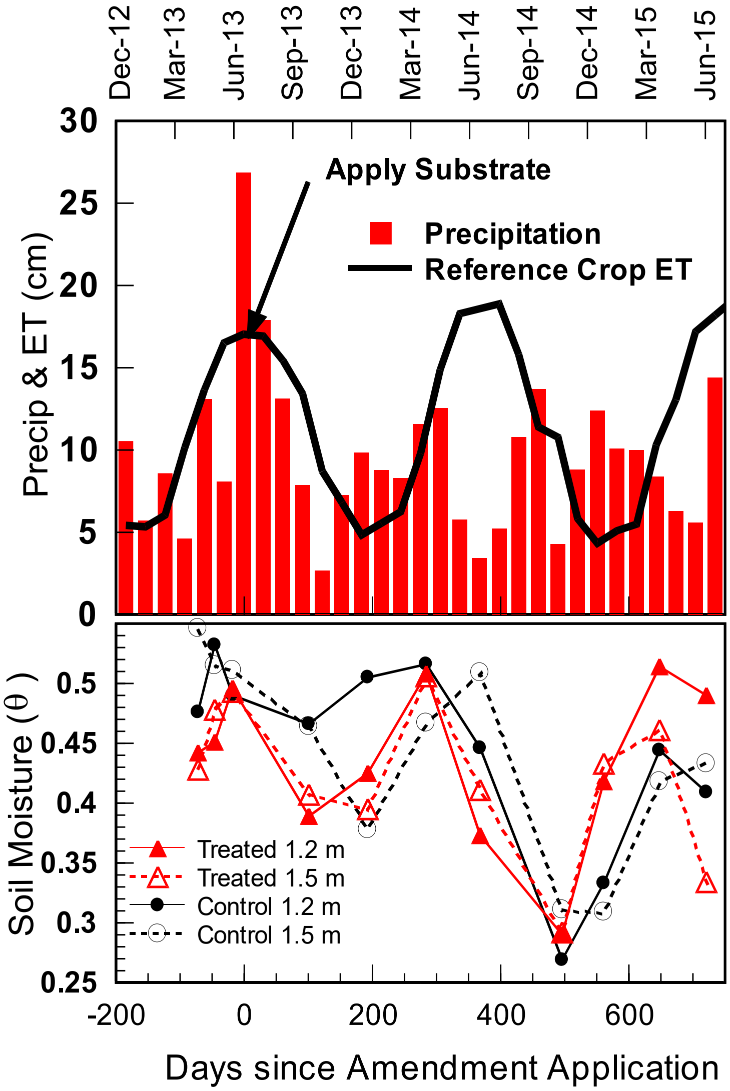

Figure 5-3. Precipitation, ET, and Soil Moisture Versus Time

Precipitation and potential ET from SCONC and average soil moisture for December 2012 to June 2015.

Figure 5-4 shows average concentrations of Cl and Bromine (Br) in BLs at 0.9 and 1.5 m bgs and suction lysimeters at 1.2 m. In the treated Bay T, Cl and Br present in the waste GL began to breakthrough at 1.2 m after 90 days, reaching a peak at one year after amendment addition. In control Bay C, Br breakthrough from the tracer addition was more variable with two separate pulses observed in the 0.9 m BLs. Samples could not be collected from the control bay 1.5 m BLs during most sampling events, so Br breakthrough could not be monitored at this depth. Cl was not applied to the control bay, so concentrations remained low (8 ± 2 mg/L).

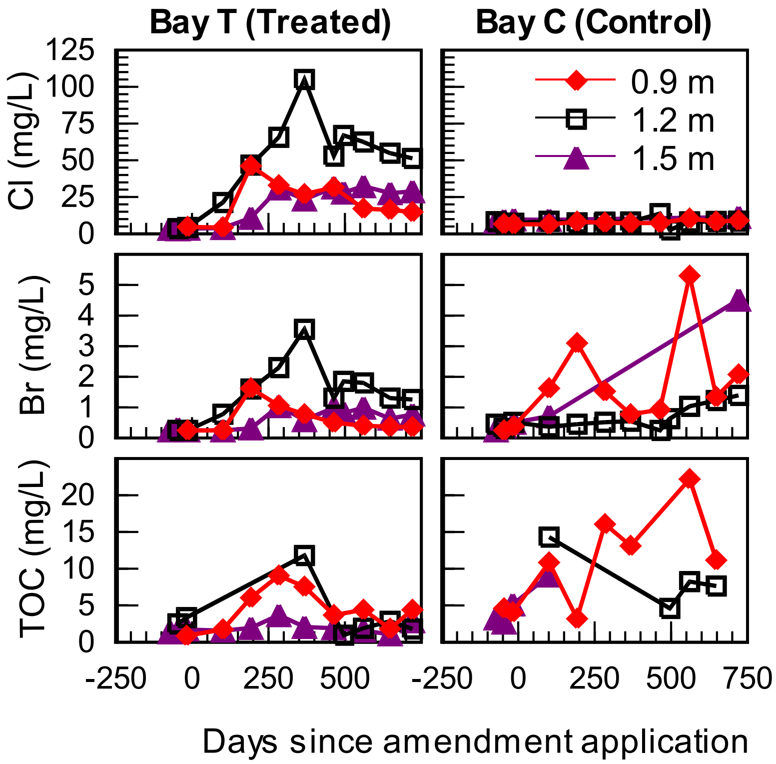

Figure 5-4. Cl, Br, and TOC Versus Time in Bays C and T

Measurements at 0.9, 1.2, and 1.5 m bgs.

OC breakthrough in the treated bay followed a similar pattern to Cl and Br, with peak TOC concentrations observed at about one year after amendment application (Figure 5-4). TOC concentrations in the control bay were more variable and did not follow any clear pattern. The elevated levels of TOC in Bay C are presumably associated with the higher OC content of these soils (Figure 3-2).

Substantial variations in soil oxidation potential (Eh), NO_3, Mn, and Fe (Figure 5-5) were observed in response to variations in soil moisture and amendment application. In Bay C (control), Eh initially declined (reducing conditions) with a concurrent drop in NO_3, presumably due to the high soil moisture, warmer summer temperatures, and higher OC content of the Bay C soils. In Bay T, Eh declined with the arrival of OC (Figure 5-5) following organic amendment application, and then rebounded as TOC declined. NO_3 followed a similar pattern to Eh in Bay T, but changes in NO_3 lagged Eh by several months. Mn increased in Bay T concurrent with the NO_3 decline. Fe concentrations in Bay T remained below 0.15 mg/L throughout the monitoring period, indicating only moderately reducing conditions. In Bay C, Mn and Fe were occasionally elevated, indicating more strongly reducing conditions. However, there was no obvious pattern to the variations in Mn and Fe over time. There was no significant change in the fraction of Fe(II) present in the poorly-crystalline or crystalline phases in either bay, in soil profiles measured in March 2013 (prior to amendment application) and July 2015 (two years after amendment application) (data not shown).

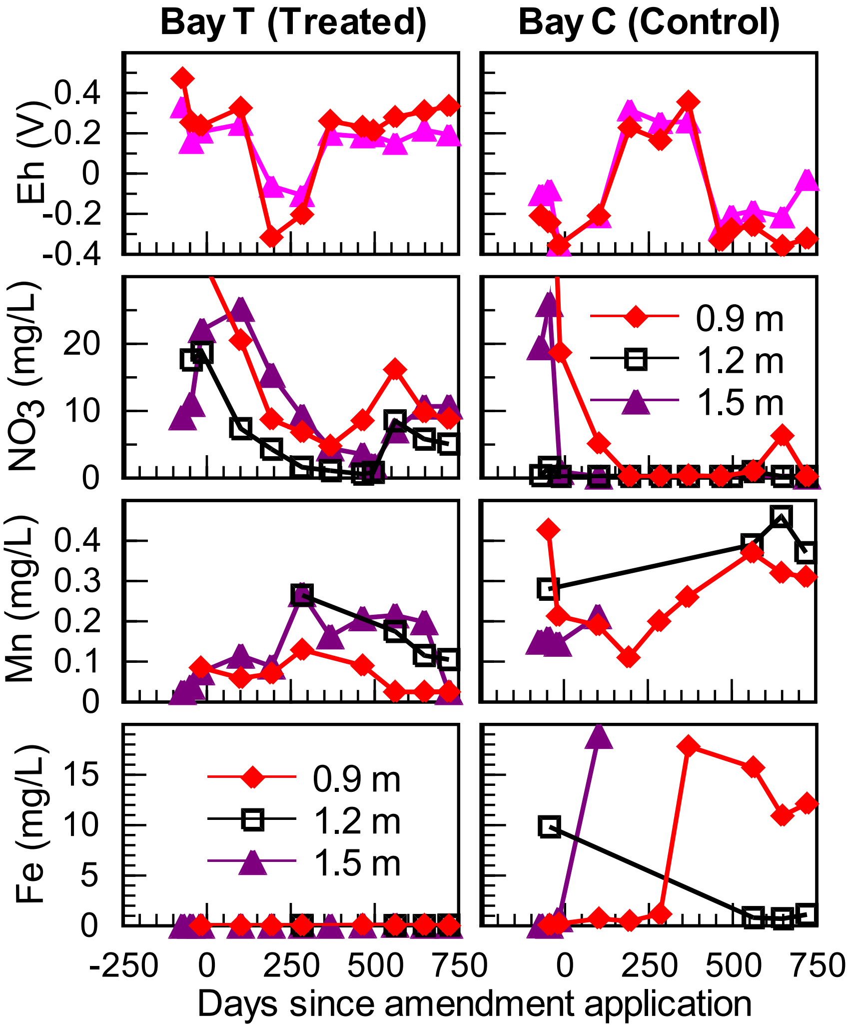

Figure 5-5. **Eh, NO_3, Mn, and Fe Versus Time in Bays C and T**

Measurements at 0.9, 1.2, and 1.5 m bgs.

5.2.2 Explosives in Pore Water

Figure 5-6 shows the variation in the average concentrations of TNT, RDX, HMX, MNX, DNX, and TNX in the BLs (0.9 and 1.5 m) and suction lysimeters (1.2 m) in Bays C and T. Detectable levels of TNT were initially observed in several different lysimeters in both bays. However, TNT levels dropped below the detection limit (1 µg/L) in all samples by 100 days, and concentrations remained near or below the detection limit for the remainder of the project.

RDX was also present in pore water samples collected throughout both Bay T and C at the start of the project. In Bay C, RDX levels declined with the onset of reducing conditions and remained low for the duration of the project. In Bay T, RDX levels declined with the arrival of TOC from the organic amendment and depletion of NO_3. Low levels of RDX nitroso degradation products (MNX, DNX, and TNX) were detected throughout the monitoring period in both bays, indicating anaerobic biotransformation of RDX. HMX levels varied throughout the monitoring period in both bays and did not follow any obvious patterns.

Annual drainage and RDX leaching rates (mass flux per unit area = concentration * drainage) are shown in Figure 5-7 for each of the 1.5 m BLs in Bays T (lysimeters A, B, C, and D) and Bay C (lysimeters E, F, G, and H). In both Years 1 and 2, drainage and RDX leaching rates were much higher in Bay T than in Bay C. There were also large variations in drainage and RDX leaching rates between the different lysimeters in Bay T, presumably due to the presence of explosion craters. In Bay T, average drainage rates were similar in Year 1 (44.2 cm) and Year 2 (44.9 cm), while average RDX leaching rates declined from 30 to 9 $\mu g/m^2/yr$, indicating the amendment addition did have some longer-term benefits.

5.2.3 Explosives in Soil

Soil sampling results from March 2013 and July 2015 (Figure 5-8) demonstrated extensive TNT attenuation in both treated and control bays. At the start of monitoring (March 2013), TNT was present at very low levels in both Bays C and T, varying between 5 and 13 µg/kg with TNT degradation products (2,4-DNT, 2,6-DNT, 2-ADNT, and 4-ADNT) below detection in most samples (data not shown). Over two years later (July 2015), TNT levels continued to be low in Bay T, and had declined below the detection limit in most samples in Bay C with no accumulation of degradation products.

Soil sampling results (Figure 5-8) showed low RDX concentrations in Bay C with higher concentrations in Bay T. In Bay C, soil RDX concentrations were essentially unchanged from March 2013 (average = 28 µg/kg) to July 2015 (average = 25 µg/kg). However, average MNX levels in Bay C increased from 4 to 273 µg/kg (data not shown), indicating substantial anaerobic degradation of RDX over the monitoring period. In Bay T, average soil RDX levels increased from 90 to 249 µg/kg and MNX increased from 5 to 42 µg/kg, indicating more limited RDX degradation.

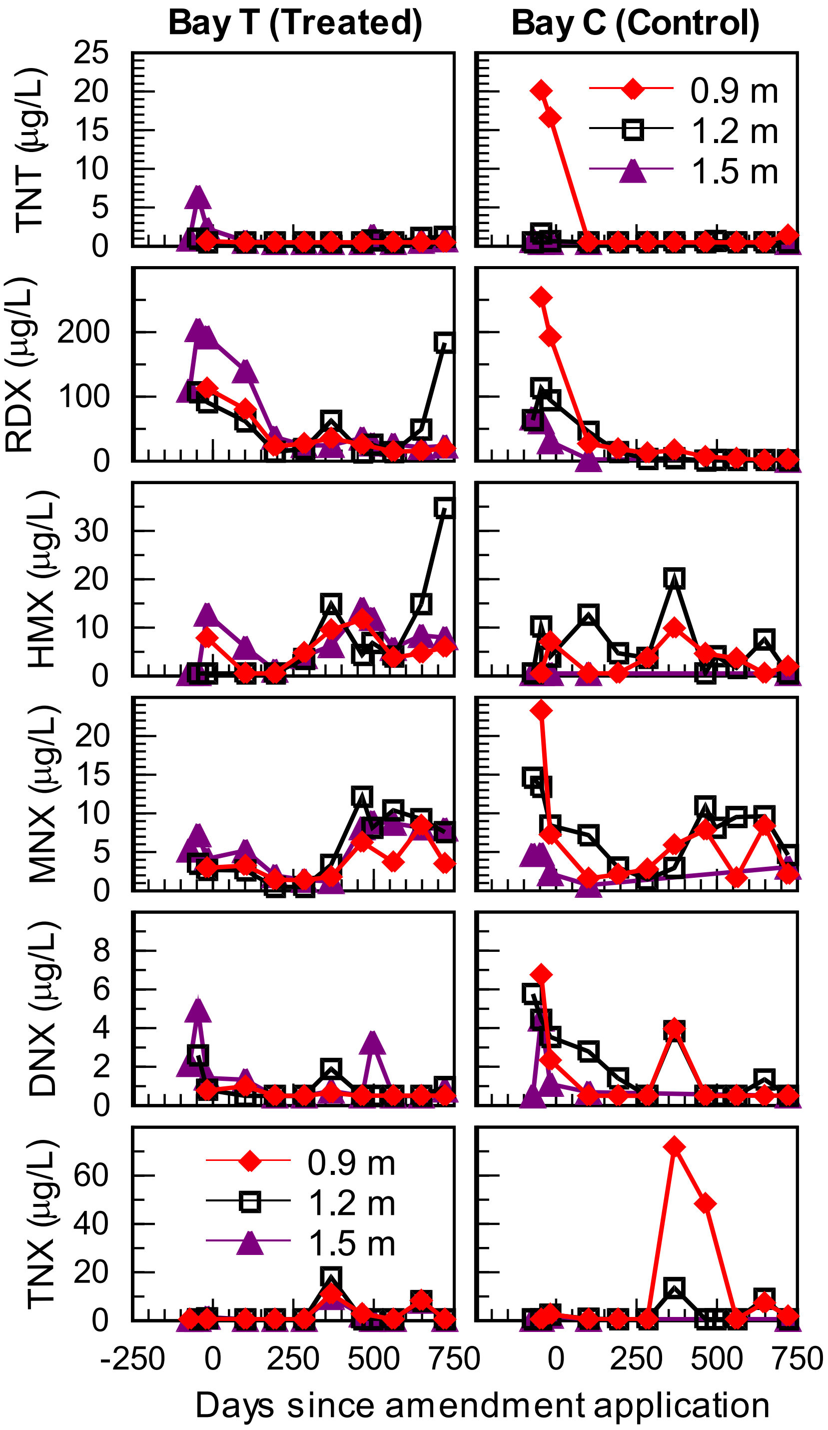

Figure 5-6. TNT, RDX, HMX, MNX, DNX, and TNX Versus Time in Bays C and T

Measurements at 0.9, 1.2, and 1.5 m bgs.

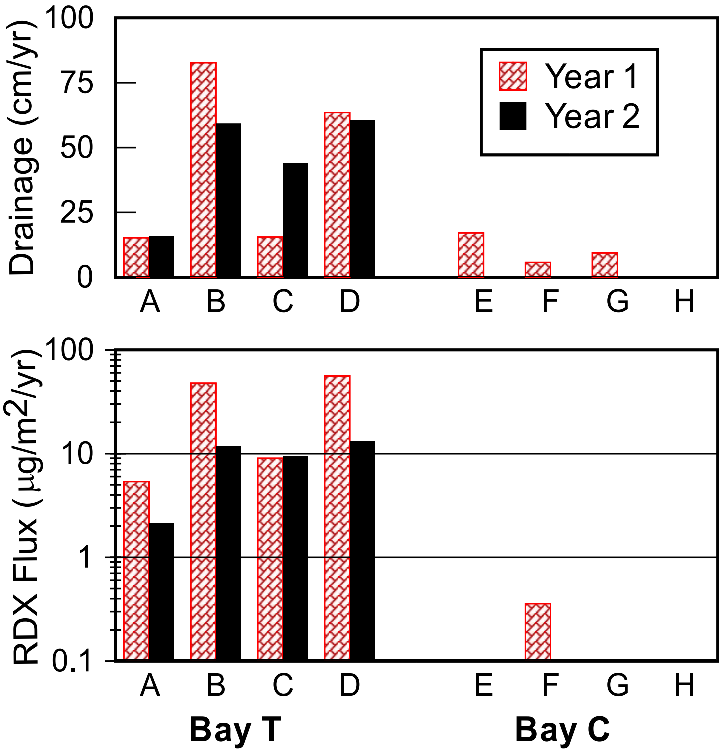

Figure 5-7. **Annual Drainage and RDX Leaching Rates in Bays C and T**

Measurements from 1.5 m BLs during Years 1 and 2 after amendment application.

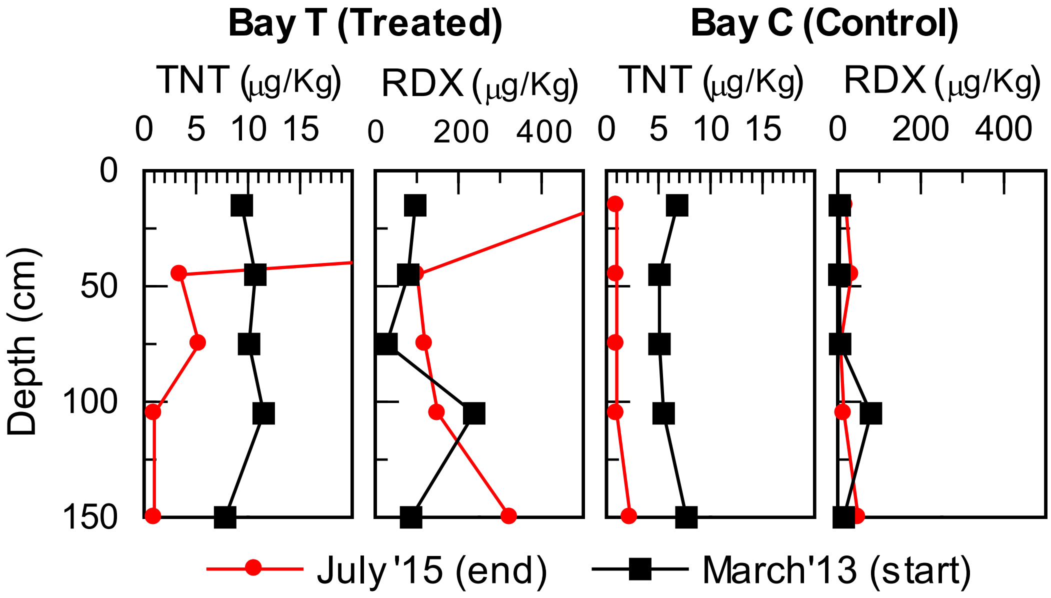

Figure 5-8. **Average RDX and TNT Versus Depth**

Measurements at the start (March 2013) and end (July 2015) of monitoring.

5.3 DISCUSSION OF PERFORMANCE MONITORING

5.3.1 Monitored Natural Attenuation

Consistent with prior work (Jenkins et al., 2006; Larson et al., 2008b), there was no evidence of significant TNT accumulation in surface soils or soil pore water in either the grenade Bay T or C. Both bays have been used regularly for training for over 20 years. Over the course of this project, approximately 5,000 fragmentation grenades containing Comp B explosive (39% TNT) were detonated in each bay. Yet TNT concentrations in the soil remain low and TNT concentrations in pore water were below detection (<1 µg/L) for most of the monitoring period. This is consistent with laboratory microcosm results which showed extensive removal of TNT in both aerobic and anaerobic laboratory microcosms containing soil from Bay C, Bay T, and a nearby sand quarry (Section 4.3, Won and Borden, 2016). Similar results were found at two grenade bays at Fort Jackson, SC, where TNT concentrations in soil were very low and TNT in pore water samplers were consistently below 1 µg/L (Larson et al., 2008b).

In the untreated Bay C, there is strong evidence for natural attenuation of RDX. At the start of the project, significant concentrations of RDX were observed in pore water (1 to 454 µg/L) and soil (3 to 100 µg/kg). These elevated RDX levels are hypothesized to be due to a period of intense training combined with lower than average rainfall. During the low rainfall period, the low soil moisture likely resulted in more oxidizing conditions with accumulation of $NO_3$and RDX. In June 2013, the site experienced a period of high rainfall combined with warm summer temperatures resulting in reducing conditions (low Eh), an increase in dissolved Mn, with rapid decline in $NO_3$and RDX. With the return of drier conditions and lower temperatures, soil Eh increased. However, $NO_3$and RDX levels recovered much more slowly due to the low drainage rates and long travel time through the soil. Similar results were observed in laboratory column experiments containing Bay C soil, where saturated, anoxic conditions reduced RDX leaching by 93% (Section 4.4, Won and Borden, 2017). Larson et al. (2008b) observed similar results at Fort Jackson, SC, where RDX levels varied from < 1 µg/L to 3,200 µg/L (avg. = 435 µg/L) in suction lysimeters installed below an untreated grenade bay. Similar to Bay C at Fort Bragg, RDX levels were high in winter and spring, declining to low levels in summer. Concurrent with the decline in RDX, redox potential decreased and soluble Fe increased (Larson et al., 2008b).

Anaerobic RDX degradation is a reductive process, similar to biological denitrification, where naturally occurring microorganism reduce NO_2- groups to nitrogen oxide (NO)- groups. Denitrification in soils has been shown to result in large losses of reactive nitrogen (N) (Howarth et al., 1996; Groffman, 2008), suggesting anaerobic degradation could be an important process controlling RDX leaching.

In this project, there was evidence of large temporal and spatial variations in RDX leaching. Similar temporal (Myrold, 1988; Christensen, 1985) and spatial (Christensen et al., 1990; Parkin, 1987) variations in soil denitrification rates have been observed. Denitrifiers are known to be sensitive to variations in O_2, carbon, NO_3, temperature, and pH (Tiedje, 1988; Firestone, 1982). Much of the observed spatial and temporal variability in denitrification is believed to result from variations in geochemical conditions including development of anaerobic zones within soil aggregates (Smith, 1980; Sexstone et al., 1985) and rapid biodegradation of labile organic matter (Parkin, 1987; Christensen and Tiedje, 1990).

5.3.2 EA

In Bay T, addition of GL and LS were effective in generating reducing conditions and stimulating RDX biodegradation. At the start of the project, elevated RDX levels were also present in Bay T. The higher K_{sat} of the soil allowed more rapid drainage even during wet periods, maintaining oxidizing conditions. Several months after amendment addition, TOC concentrations in the bucket and suction lysimeters increased. With the arrival of TOC, the pore water became reducing with a decline in Eh and NO_3, increase in Mn, and decline in RDX. There is strong evidence that the increase in TOC was due to substrate application since TOC increased at the same time Cl and Br increased. At 500 days after amendment application, TOC declined, resulting in a rebound in Eh, NO_3, and decline in Mn. At two years after amendment application, there is some evidence that RDX is beginning to rebound.

Similar results were observed in laboratory column experiments with Bay T soil (Section 4.4, Won and Borden, 2016). At 6 - 12 months after GL and LS addition, small amounts of TOC and Cl were discharged in the column effluent, followed by a rapid decline in NO_3, increase in Mn, and removal of RDX. However once TOC was depleted in the columns, NO_3 recovered, Mn declined, and RDX started to rebound. While the GL+LS addition did not provide permanent treatment, the total mass of RDX discharged from the Bay T columns was reduced by an average of 76% compared to untreated control columns.

While organic amendment addition was effective in stimulating RDX biodegradation, several operational problems were identified. Some portion of the spray applied amendment was likely washed off the soil surface by a high intensity rainstorm that occurred shortly after amendment application. Alternative application approaches should be considered. Methods of increasing the amendment longevity to reduce application frequency and costs would also be beneficial.

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6.0 CONCEPTUAL MODEL OF EXPLOSIVES TRANSPORT AND ATTENUATION

Munitions contain a small amount of primary explosives that are highly susceptible to initiation and a larger volume of secondary or HEs that are less susceptible too initiation. Because of the much larger amount used, the explosives of concern on ranges are HEs including TNT, TNX, RDX, and HMX. In addition to these explosives, common impurities and degradation products of explosives include 2,4-DNT, 2,6-DNT, 2-ADNT, 4-ADNT, MNX, DNX, and TNX. TNT, 2,4-DNT, 2,6-DNT, 2-ADNT, and 4-ADNT are nitroaromatics. RDX, HMX, MNX, DNX, and TNX are nitramines.

The US military is replacing many of the traditional explosive materials with Insensitive Munitions (IMs) to reduce risks of accidental or unintended detonation. The IM materials will burn, rather than explode, when subjected to fast or slow heating, bullets, shrapnel, shaped charges, or the detonation of another nearby munition. Important components of IM include 2,4-dinitroanisole (DNAN), nitroguanidine (NQ), 3-nitro-1,2,4-triazol-5-one (NTO), and other traditional munitions components (RDX, HMX).

The structure, physical and chemical, of explosive materials control their fate and transport in the environment. Figure 6-1 shows the chemical structure of common HE.

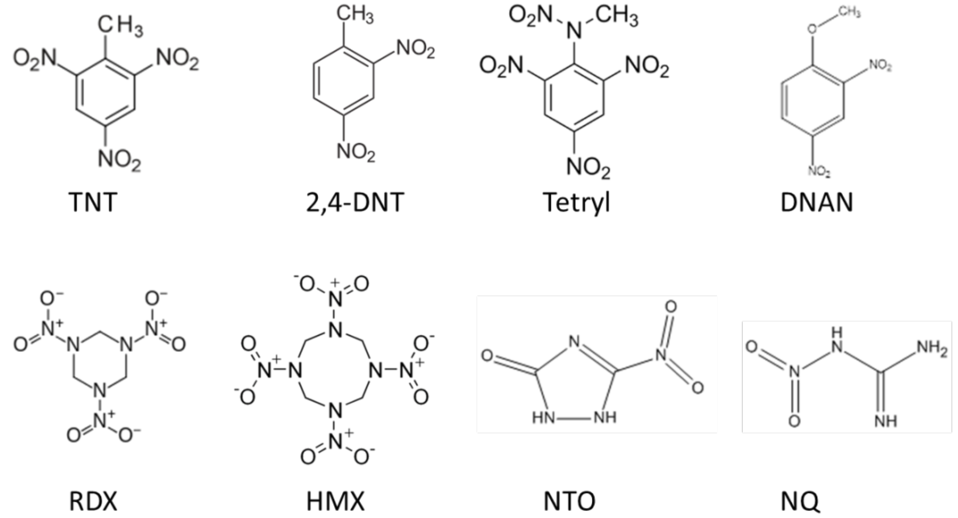

Figure 6-1. Chemical Structures of Common Explosives

Chemical structures of TNT, 2,4-DNT, Tetryl, DNAN, RDX, HMX, NTO, and NQ.

Important physical and chemical properties influencing the fate of these materials are summarized in Table 6-1. The major HEs and degradation products are solids at ambient temperatures. Aqueous solubility varies dramatically between the different materials and can have an important influence on their mobility in the environment. Octanol-water partition coefficients (K_{ow}) are moderate to low suggesting that hydrophobic partitioning to soil organic matter will be limited. Due to their low vapor pressures, volatilization is not an important loss mechanism.

Table 6-1. Physical and Chemical Properties of HE Compounds

Explosive	CAS	Formula	Molecular Weight [g/mol]	Aqueous Solubility at 25 C [mg/L]	Log K_{ow}	Vapor Pressure at 20 C mm Hg
TNT	118-96-7	$C_7H_5N_3O_6$	227.13 [b]	130 [b]	1.60 [b]	1.99E-4 [b]
RDX	121-82-4	$C_3H_6N_6O_6$	222.26 [c]	56.4 [e]	0.87 [c]	1 to 4 E-9 [c]
HMX	2691-41-0	$C_4H_8N_8O_8$	296.16 [a]	4.5 [e]	0.165 [e]	3.3E-14 [a]
Tetryl	479-45-8	$C_7H_5N_5O_8$	287.14 [a]	80 [a]		5.7E-9 (25 C)[a]
2,4-DNT	121-14-2	$C_7H_6N_2O_4$	182.15 [a]	300 (22 C) [d]	1.98 [d]	1.47E-4 [d]
2,6-DNT	606-20-2	$C_7H_6N_2O_4$	182.15 [a]	180 (22 C) [d]	1.72 or 2.10 [d]	5.67E-4 [d]
2-ADNT	35572-78-2	$C_7H_7N_3O_4$	197.17 [a]	2800 [a]		4.0E-5 [a]
4-ADNT	19406-51-0	$C_7H_7N_3O_4$	197.17 [a]	2800 [a]		2.0E-5 [a]
NTO	932-64-9	$C_2H_2N_4O_3$	130.08	2000 [h]	0.858 [h]	
DNAN	119-27-7	$C_7H_6N_2O_5$	198.13 [g]	213 [j, k]	1.58 [j, k]	1.E-4 (25 C) [f]
NQ	556-88-7	$CH_4N_4O_2$	104.07	4,400 [i]	-0.89 [f] 0.21 [g]	1.00E-9 (est)[f]

a = Thiboutot et al., 2002
b = USEPA, 2014b
c = USEPA, 2014a
d = USEPA, 2014c
e = Monteil-Rivera et al., 2004
f = Occupational Alliance for Risk Science (OARS), 2014a.
g = Defense Research and Development Canada (DRDC), 2011
h = OARS, 2014b.
i = Van der Schalie, 1985
j = Hawari, 2014
k = Hawari et al., 2015

6.1 MUNITIONS DEPOSITION ON RANGES

When munitions function as designed and undergo a high-order detonation, greater than 99.99% of the explosive is consumed, leaving traces of micron size particles on the range (Hewitt et al., 2005, Walsh et al., 2005). However, when the munition undergoes a low-order (partial) detonation or does not detonate, then a substantial portion of the explosive load may be deposited on the range as particles or chunks of explosive material or as UXOs. In tests on five types of munitions (60-mm, 81-mm, and 120-mm mortars, and 105-mm and155-mm howitzer projectiles), Pennington et al. (2006) found that 27 to 49% of the original explosive mass was deposited on the range following low-order detonation.

In some cases, blow-in-place detonations are used to destroy surface UXOs by military EOD (explosive ordnance disposal). These blow-in-place detonations do not use the built-in detonation train, and so may be more likely to result in low-order detonations. When blow-in-place results in a high-order detonation, the deposition is much lower than from low-order detonations (Pennington et al., 2006; Walsh et al., 2007.

Table 6-2 shows mean concentration of HE in surface soil at 12 active and three closed hand grenade ranges reported by Jenkins et al. (2006). These ranges are typically a few acres in size containing several throwing bays with targets near the middle of each bay. A large portion of the grenades detonate near these targets, resulting in the development of craters over time. The most commonly used ordinance was the M67 fragmentation grenade containing 185 g of Comp B including RDX, TNT, HMX, and other minor constituents such as 1,3,5-trinitrobenzene (TNB), 4-ADNT, and 2-ADNT. HE sampling results fell into two groups. In the upper portion of the table, HE concentrations are higher with RDX levels varying from 51 to 0.45 mg/kg. In the lower portion of the table, HE concentrations are much lower with RDX varying from 0.12 to < 0.01 mg/kg. This range of concentrations is potentially the result of differing detonations. When only high-order detonations occurred recently, HE levels were expected to be low. However, when there has been a relatively recent low-order detonation, HE residue levels can be much higher. Jenkins et al. (2006) reported that remnants of grenades were observed that did not completely detonate resulting from partial (low order) detonation or duds that were blown-in-place. The highest HE concentrations are typically found in the top few cm of soil (Jenkins et al., 2006). However, particles of HE could be incorporated into the soil by subsequent explosions or by periodic regrading of the grenade range to fill in craters.

Table 6-2. Explosives Concentrations in Surface Soils at Hand Grenade Ranges (Jenkins et al., 2006)

	Current Use	Discrete Samples	Multi-Increment Samples	RDX (mg/Kg)	HMX (mg/Kg)	TNT (mg/Kg)	TNB (mg/Kg)	4ADNT (mg/Kg)	2ADNT (mg/Kg)
Range G	Active		3 (30)*	51	9.1	36	0.28	0.4	0.03
Range F	Active		25 (1, 5, 10, 20, 40)	11	2	1.2	0.15	ND	ND
Range A	Active	23		7.5	1.8	9.3	0.05	0.15	0.13
Range H	Active		7 (30)	5.6	0.53	0.78	<0.01	<0.01	<0.01
Range I - Old	Closed	11		5.1	ND	0.4	ND	ND	ND
Range A	Active		5 (50)	4.4	1	1.5	ND**	ND	ND
Range E	Active		15 (20)	0.71	0.05	0.06	<0.01	0.02	0.02
Range K	Active		9 (25, 100)	0.65	0.18	0.16	<0.01	<0.01	<0.01
Range D	Active		18 (30)	0.45	0.19	<0.01	<0.01	<0.01	<0.01
Range I - Old	Closed		5 (30)	0.12	0.02	0.12	<0.01	<0.01	<0.01
Range B	Active	27		0.08	0.02	0.03	ND	0.01	ND
Range J	Active		2 (30)	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Range I - New	Active		15 (25)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Range I - New	Active		5 (30)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Range C	Closed	48		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

* (n) increments per sample

** Not determined

6.2 EXPLOSIVES DISSOLUTION AND SORPTION

Once deposited on a range, the HE will dissolve and be transported into the soil with infiltrating precipitation. The rate that the HE dissolves is a function of the aqueous solubility of the individual components (Table 6-1), the mass deposited, the size or surface area of the particles or chunks, and the three-dimensional structure of the HE formulation. Dissolution drip tests have shown that single component explosives (e.g., TNT) retain their general shape as they dissolve, while multicomponent formulations (e.g., Comp B used in grenades) quickly become lumpy as the surface TNT dissolves, leaving less soluble RDX and HMX crystals on the surface. Over time, the TNT is leached away leaving a mass of RDX crystals held together by TNT below the surface

(Taylor et al., 2009). During outdoor dissolution tests, HE chunks have been observed to crack, split into pieces, and/or spall off small flakes of material, increasing the surface area (Taylor et al., 2010). IM rounds often deposit more of their fill onto the range during high-order and blow-in-place detonations than do traditional HE filled rounds (Walsh et al., 2015; Richard and Weidhaas, 2014) and are more friable so they dissolve more quickly.

Once HEs enter the soil, they can partition or sorb to the solid phase though a variety of different processes including hydrophobic partitioning, hydrogen bonding, ion exchange, and chemisorption (Pichtel, 2012) and can be influenced by the soil and pore water physicochemical properties including clay content, SOC, ionic strength, pH, cation exchange capacity (CEC), and pore water composition (Kalderis et al., 2011).

Nitroaromatic compounds including TNT, 2,4-DNT, and DNAN can initially sorb through hydrophobic partitioning to soil organic matter. Soil partition coefficients normalized to organic carbon (Koc) are relatively high with values of 2.48 - 3.04 for TNT (US Department of Health and Human Services, 1995) and 2.24 - 2.45 for DNAN (Dontsova et al., 2014; Hawari et al., 2015). TNT, 2,4-DNT, and DNAN can also sorb to certain clay minerals (Haderlein et al., 1996; Linker et al., 2015). When the nitro groups on TNT and DNT are reduced to amino-groups, the transformation products can permanently bind to organic matter in soil (Thorn and Kennedy, 2002; Thorn et al., 2008; Hawari et al., 2015). Yamamoto et al. (2004) and Chappell et al. (2011) demonstrated linear sorption of TNT to soils, while other studies (Pennington and Patrick, 1990; Selim and Iskandar, 1994; Hatzinger et al., 2004) have reported nonlinear sorption.

Cyclic nitramines including RDX and HMX are more polar, with smaller K_{ow} values (Table 6-1) than the nitroaromatics, resulting in a lower affinity for hydrophobic sorption (Brannon and Pennington, 2002; Tucker et al., 2002) and partitioning to clays and iron oxides (Haderlein et al., 1996; Dontsova et al., 2009a). Several different modeling approaches have been employed to describe RDX and TNT sorption. Selim and Iskandar (1994), Myers et al. (1998), and Brannon et al. (2002) reported that a linear model provided a good fit for RDX sorption to soil. However, other investigators reported nonlinear sorption of RDX to clayey soil and activated carbon (Townsend et al., 1996; Morley and Fatemi, 2010; Hatzinger et al., 2004).

6.3 EXPLOSIVES PHOTODEGRADATION AND HYDROLYSIS

HE particles deposited on the soil surface can be degraded by reactions with sunlight (photodegradation) (Taylor et al., 2010). TNB is the primary stable photodegradation product of TNT in environmental systems (Sandus and Slagg, 1978). Some photodegradation products are highly colored and can be washed off the HE surface by precipitation, leading to a reddish brown residue on the soil surface surrounding TNT-containing particles. However, once the HEs are transported below the soil surface, photodegradation is not an important attenuation mechanism.

At high pH, HE can be rapidly degraded by alkaline hydrolysis. System pH above 11 has proven most effective at hydrolyzing dissolved-phase TNT, RDX, and HMX (Emmrich, 1999; Balakrishnan et al., 2003). Brooks et al. (2003) found that the reaction rates were fastest for TNT, followed by RDX, and then HMX in soil microcosms at pH between 8 and 12. However at pH less than 8, hydrolysis rates are much lower. In neutral to acidic soils, alkaline hydrolysis is not expected to be a significant attenuation mechanism.

6.4 BIOLOGICALLY MEDIATED EXPLOSIVES DEGRADATION

TNT can be biodegraded by a wide variety of microorganisms under both aerobic and anaerobic conditions. Under aerobic conditions, TNT can serve as both a carbon and N source (Kalderis et al., 2011). However, TNT is often transformed more rapidly under anoxic/anaerobic conditions (Pennington and Brannon, 2002). Under both aerobic and anaerobic conditions, TNT is generally transformed to amino derivatives via nonspecific extracellular enzymes, such as nitroreductase producing 2-ADNT, 4-ADNT, and 2,4-diamino-6-nitrotoluene (2,4-DANT). These amino degradation products will then undergo irreversible covalent binding to soil surfaces (Achtnich et al., 1999a, 1999b; Thorn and Kennedy, 2002). Although TNT can be used as a primary substrate by microorganisms, TNT removal was more rapid when pyruvate was provided as co-substrate compared to when TNT was the sole carbon source (Boopathy and Manning, 1996).

Both pure and mixed cultures of both aerobic and anaerobic microorganisms have been shown to biodegraded RDX (Cupples, 2010). However, RDX and HMX degradation are often low or zero in aerobic environment (Boopathy and Manning, 1996; Hawari et al., 2000; Pennington and Brannon, 2002; Bhushan et al., 2006; Kwon and Finneran, 2008; Morley et al., 2002; Cupples 2010). In contrast, RDX has been shown to rapidly biodegrade under anaerobic conditions. Ringelberg et al. (2003) reported maximum RDX rate of 0.15 mg/L/d in saturated sandy loam (silt-clay content = 42%). Under anaerobic conditions, RDX is transformed to MNX, DNX, and then TNX sequentially which are eventually degraded to nitrous oxide (N_2O) and formaldehyde (HCHO).

Similar to RDX biodegradation, HMX can be degraded by reduction of nitro groups (NO_2-) to nitroso groups (-NO). The intermediates can be subsequently transformed to N_2O and HCHO that are indicators of ring cleavage (Bhushan et al., 2006; Pichtel, 2012). Relatively less information on HMX biodegradation is available compared to RDX and TNT degradation. HMX and RDX were effectively degraded in Makua Military Reservation in Oahu, HI, by application of molasses-water mixture as a carbon source (Payne et al., 2013). Fournier et al. (2004) showed that 97% of HMX was degraded after 25 days by reduction under N-limiting conditions. Morley et al. (2002) also demonstrated use of HMX and RDX as a N source under anaerobic conditions.

In addition to direct microbial attack, microbial processes can indirectly enhance HE degradation through reduction of Fe(III) to Fe(II) and reduction of electron shuttles. RDX and HMX can then be abiotically degraded by microbially reduced Fe, humic acid, and Anthrahydroquinone-2,6,-disulfonate (AH2QDS), resulting in HCHO production (Bhushan et al., 2006). Free Fe(II) alone did not react with RDX or HMX, but Fe(II) bound to magnetite, siderite, hematite, and goethite were reactive with both RDX and HMX (Gregory et al., 2004; Bhushan et al., 2006). Certain compounds including humic materials, cytochromes, flavines, cobalamins, porphyrins, pyridines, phenazines, and quinones can act as shuttles to transport electrons from Fe(II) and/or other sources of reducing equivalents, accelerating HE reduction (Bhushan et al., 2006; Hoferkamp and Weber, 2006; Van der Zee and Cervantes, 2009).

6.5 O_2 TRANSPORT AND CONSUMPTION IN SOILS

The concentration of O_2 in soil pores is controlled by the rate of O_2 transfer through the soil pores and the rate of O_2 consumption by organic carbon. In the saturated zone, O_2 transport is low since the O_2 diffusion rate in water is four orders of magnitude less than in air. In the vadose zone, O_2 is primarily supplied by diffusion through gas-filled pores. The diffusive flux of O_2 through soil pores (J_O) is

$$J_O = D_O^e \, {\partial O}/{\partial x}$$

where D_O^e is the effective diffusion coefficient of O_2 through the soil and ${\partial O}/{\partial x}$ is the O_2 concentration gradient. D_O^e is calculated as

$$D_O^e = \tau \, \theta_a \, D_O$$

where the τ is the tortuosity, θ_a is the air filled porosity, and D_O is the free air diffusion coefficient of O_2. Soil moisture content has a major impact on O_2 transport through soils. As moisture content increases, the individual air bubbles become separated greatly reducing D_O^e. Capillary forces can cause soils with greater organic content or silt and clay minerals to strongly retain water leading to near saturated conditions.

In general, O_2 content is highest near the surface and decreases with depth due to larger diffusion distance to the free atmosphere. In partially saturated soils, the largest soil pores may drain allowing O_2 to transport deep below the surface. However, soil aggregates can remain saturated, greatly reducing O_2 transfer rates into the aggregate, allowing anaerobic microsites to develop even in soils where the larger soil pores contain O_2 (Smith, 1977; Smith, 1980; Sexstone et al., 1985; Zausig et al., 1993). Anaerobic microsites can also develop within or near organic particles where O_2 consumption rates are high (Jones and Hinsinger, 2008).

The O_2 consumption rates are primarily controlled by temperature, moisture content, and OC. Kirschbaum (1995) reported that respiration rates decline by an average factor of 2.5 as the soil temperature declines from 30 to 20 °C, a factor of 4.5 from 20 to 10 °C, and a factor of 8 from 10 to 0 °C. As soil moisture drops below a critical value (commonly 20 - 30% by volume), respiration rates decline as diffusion of nutrients through the soil slows and bacteria undergoes osmotic stress. Soil respiration rates are a function of both the quantity and quality of OC (Yiqi and Zhou, 2010). The low density, uncomplexed fraction is most easily degraded, while the higher density fraction associated with soil minerals is much more resistant (Alvarez and Alvarez, 2000). First order NO_3 removal rates in 30 different soils varied from 0.001 to 0.04 hour^{-1} and were correlated with both total soil OC and an index of readily decomposable C (Stanford et al., 1975). Incorporation of organic material can substantially increase soil respiration and O_2 demand (Meek and Grass, 1975; Flessa and Beese, 1995).

Soil redox potential measurements are commonly used to evaluate biogeochemical conditions in soil and the potential for different redox conditions to occur (Flessa and Beese, 1995). At Eh values > +400 mV, O_2 will be the dominant electron acceptor (Reddy et al., 2000). Denitrification can occur when the bulk Eh drops below 340 mV (Pearsall and Mortimer, 1939; and Patrick, 1960). Eh values can vary dramatically in time and space due to temporal variations in precipitation and soil moisture and spatial variations in organic content and soil characteristics (Mansfeldt, 2004; Fiedler et al., 2007; Gao et al., 2002; Vepraskas et al., 1999). The time required for development of anoxic or anaerobic conditions depends on the respiration rate and presence of other electron acceptors. In flooded soils, O_2 may be depleted in less than 36 hours (Turner and Patrick, 1968) and Fe can be reduced in a few weeks (Vepraskas and Faulkner, 2001).

6.6 EXPLOSIVES ATTENUATION IN THE VADOSE ZONE

TNT naturally attenuates in the vadose zone at most sites due to the ease of biodegradation under both aerobic and anaerobic conditions. Natural attenuation of RDX is more variable due to its' resistance to biodegradation under aerobic conditions. At some sites (e.g., Fort Bragg Grenade Bay C), the soils undergo extended anoxic periods leading to extensive RDX removal with very limited leaching to groundwater. However, in soils with lower fines and/or organic content (e.g., Fort Bragg Grenade Bay T), the soils are generally aerobic, resulting in more extensive RDX leaching. At many ranges, it may take several years for RDX to migrate through the upper two meters of soil due to slow infiltration and sorption to soil. If the soil becomes anaerobic for even a few weeks during this period, a significant fraction of the RDX may be degraded, reducing leaching to groundwater.

There are many similarities between natural attenuation of NO_3 and RDX. Both materials are readily biodegradable under anaerobic conditions, with very limited removal under aerobic conditions. While NO_3 leaching to groundwater is common (Spalding and Exner, 1993), numerous studies have documented substantial denitrification for a wide range of conditions (Howarth et al., 1996; Groffman, 2008). Stable isotope studies have shown that denitrification losses are extremely variable and can exceed one-third the N applied as fertilizer. A mass balance analysis of large watersheds in the northeastern US estimated that 40% of the total N input was removed, with most of this loss associated with denitrification (Van Breemen et al., 2002). Other studies report total N losses due to denitrification of 40% for Europe, 30% for Asia, and 32% for the U.S. (Boyer et al., 2006). While anaerobic degradation of RDX is probably an important removal mechanism at many sites, there are major challenges associated with estimating the extent of degradation. Studies of denitrification in soils have documented large temporal (Myrold, 1988; Christensen, 1985) and spatial (Christensen et al., 1990; Parkin, 1987) variations in soil denitrification rates.

Transport and natural attenuation of the nitro-aromatic compound DNAN, a component of Insensitive Munitions eXplosive (IMX)-101, may be similar to TNT. Similar to TNT, DNAN, is rapidly reduced to under anaerobic conditions to aromatic amines (Perreault et al., 2012; Olivares et al., 2016). However, aerobic biodegradation in soil is slow without addition of a supplemental carbon source (Perreault et al., 2012; Olivares et al., 2016). The aromatic amines produced by aerobic and anaerobic DNAN biodegradation can then irreversibly bond to soil and be immobilized.

NTO transport and attenuation may be similar to RDX. NTO was readily reduced to 3-amino-1,2,4-triazol-5-one (ATO) under anaerobic conditions with seven different soils but was not aerobically transformed in any incubation (Krzmarzick et al., 2015). The aqueous solubility of NTO is 2000 mg/L, over an order of magnitude greater than RDX, which could accelerate leaching.

Natural attenuation processes may be more important in reducing RDX leaching than previously assumed. At Fort Bragg, minimal leaching of RDX was observed in Bay C where soil Eh was naturally low. In a study examining lime addition to a hand grenade bay at Fort Jackson, SC (data from Larson et al., 2008b), pore water Eh was correlated to Log RDX concentration in both the bay treated with lime ($r^2 = 0.33$, $p<0.01$) and the untreated control bay ($r^2 = 0.34$, $p<0.01$).

Organic amendment addition was effective in reducing RDX leaching in Fort Bragg Grenade Bay T for over one year and could potentially be effective in reducing leaching of RDX, DNAN, and NTO on other ranges. Given the relatively long travel time for munitions through soils, it may not be necessary to maintain continuously anaerobic conditions and periodic amendment application could be effective in reducing leaching. However, additional research is needed to better understand the processes controlling O_2 transport and anaerobic biotransformation on ranges.

7.0 CONCLUSIONS AND RECOMMENDATIONS

Under certain conditions, natural attenuation processes can greatly reduce leaching of TNT and RDX deposited on hand grenade ranges. TNT is readily biodegraded under both aerobic and anaerobic conditions and was extensively degraded in both grenade Bays C and T with no significant leaching. In general, RDX biodegradation is very limited under aerobic conditions. In Bay C, high rainfall, warm temperature, low K_{sat}, and/or higher soil OC resulted in reducing conditions (low Eh) for part of the year. The development of reducing conditions resulted in NO_3 removal, dissolved Mn release, and stimulated RDX biodegradation which greatly reduced RDX leaching. However, in Bay T, the higher K_{sat} and/or lower OC of the soil resulted in more oxidizing conditions, limiting RDX biodegradation.

Spray application of the organic amendment (GL+LS) on the soil surface in Bay T was effective in generating reducing conditions as indicated by a rapid decline in Eh and NO_3, and an increase in Mn, for about one year after amendment application. The shift to more reducing conditions was likely a direct result of amendment application since the decline in Eh and NO_3 coincided with the arrival of TOC and Cl present in the GL. With the onset of reducing conditions, RDX concentrations in pore water decreased, reducing RDX leaching. However, once TOC concentrations in pore water declined, the Eh increased, NO_3 began to increase, and Mn began to decline. At two years after amendment application, RDX concentrations may have been starting to rebound.

The difference in geochemical conditions between the two grenade bays is believed to be due to relatively small differences in soil physical and chemical properties. In Bay C, the somewhat lower K_{sat} and higher clay content resulted in near saturation conditions with reduced O_2 transport for long periods. The somewhat higher OC of the Bay C soil in combination with reduced O_2 transport resulted in development of reducing conditions, stimulating RDX biodegradation. In Bay T, the higher K_{sat} and lower clay content allowed more rapid soil drainage and greater O_2 transport. The somewhat higher OC of the Bay T soil in combination with greater O_2 transport resulted in more oxidizing conditions, inhibiting RDX biodegradation.

Over the 24 month monitoring period, there were large temporal variations in moisture content and Eh in Bay C. At the start of monitoring, NO_3 and RDX levels were elevated in Bay C, presumably due to an extended dry period combined with intensive use of the bays for training. Following a high rainfall period, the soil became saturated, with a subsequent drop in Eh, NO_3, and RDX. The following winter, Eh increased and remained high during the subsequent dry summer. However, NO_3 and RDX remained low from 0.9 - 1.5 m below the surface, presumably to slow transport through the soil profile.

In BLs spaced 1-2 m apart, there were large variations in water drainage rates and associated RDX leaching. These large differences are believed to be due to development and later filling of explosion craters that focus infiltration in small areas. It is not known how the focused infiltration impacts O_2 transport and geochemical conditions beneath the craters.

Organic amendment addition can be effective in stimulating anaerobic biodegradation. However, there are major technical challenges in this approach. In unsaturated sandy soils, O_2 transfer is very rapid and high amendment loading rates will be required to generate and maintain anaerobic conditions. In lower permeability soils, substrate loading rates are lower.

However effectively transporting the amendment into the soil profile can be challenging. When GL+LS was spray applied onto the surface of Bay T, a portion of the amendment appears to have penetrated the surface and was effective in generating reducing conditions. However, a portion of the amendment probably washed off during a high intensity rainstorm that occurred shortly after application.

On many grenade ranges, UXO is routinely cleared and a skid-steer loader or other small earth moving equipment is used to fill explosion craters and smooth the bay surface. During routine maintenance, the organic amendment could be sprayed on the surface, then tilled into the soil to reduce the potential for wash off. Alternatively, a small loader or tractor could be used to inject the amendment a few inches below the soil surface using injection nozzles similar to that used for land application of biosolids.

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APPENDIX A POINTS OF CONTACT

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APPENDIX B LABORATORY AND FIELD METHODS

B.1 MATERIALS

Two soils collected from near Fort Bragg, NC, were used in this work. Grenade RS used in the sorption experiments was collected from 0 to 1.0 m bgs in Bay C within the hand grenade range at Fort Bragg. FS was obtained from the Four-O-One Sand quarry, located approximately 27 km from the grenade range at Fort Bragg. Soils were air-dried, passed through a No.4 (4.76 mm) mesh sieve, and homogenized prior to use. Selected properties were measured on homogenized samples (Table B-.1). Soil OC, CEC, humic matter (HM), and silt-clay fraction were significantly higher in RS than those in FS. Explosive concentrations were 0.012 ± 0.005 mg/kg for RDX and 0.015 ± 0.006 mg/kg for TNT in RS, while all explosives were below the detection limits (< 0.002 mg/kg) in FS.

Table B-1. Selected Properties of Soils Used in Sorption Isotherm Study

Properties		(FS	RS*
OC	(%)	0.06	0.19
CEC	(meq/100 cm^3)	0.9	1.6
Base Saturation	(%)	48	44
HM	(%)	0.04	0.12
Sand	(%)	96.3	85.0
Silt-Clay	(%)	3.7	15.0
pH		4.6	4.9

* Average values for range soils from 0 to 1 m bgs.

Calcium LSs (Ultrazine CA and Norlig A) were from Lignotech USA (Rothschild, WI) and crude GL was from Piedmont Biofuels (Pittsboro, NC). Acetonitrile and toluene used in soil and water sample extractions for explosives were High Performance Liquid Chromatography (HPLC) grade and purchased from J.T. Baker and Fisher Scientific respectively. Hydrochloric acid (HCl) and hydroxylamine hydrochloride used in soil Fe(II/III) extraction were American Chemical Society grade and purchased from Fisher Scientific and Acros Organics respectively.

Analytical standards for TNT, RDX, 2,4-DNT, 2,6-DNT, 2-ADNT, 4-ADNT, and HMX were purchased from AccuStandard, Inc. (New Haven, CT), and standards for RDX nitroso degradation products (MNX, DNX, and TNX) were purchased from SRI International (Menlo Park, CA) then prepared by dissolution in acetonitrile.

B.2 ANALYTICAL METHODS

Analytical methods are described in Won (2016) and Won and Borden (2016). Briefly, explosives concentrations were determined by gas chromatography (GC) with electron captured detector (ECD) following U.S. Environmental Protection Agency (USEPA) Method 8095 to minimize interferences with humic materials and lignin present in soil and aqueous samples. Prior to GC-ECD analysis, water samples were extracted in toluene by a modified frozen micro-extraction (FME) method (Li et al., 2011) followed by analysis of the filtered supernatant by GC-ECD. Water samples were first filtered through 0.2 µm Polytetrafluoroethylene (PTFE) syringe filters. Liquid-liquid was extracted with 1 mL of both sample and toluene placed in 4 mL Teflon-capped PTFE target vials, followed by shaking on a vortex for 30 seconds and mixing on a table shaker for 2 hours after packed in an insulated box filled with ice to minimize thermal decomposition of explosives. Vials were placed in a -80 ºC freezer for 30 minutes to separate toluene by freezing water. The toluene was transferred to amber target vials and stored at -20 ºC until analyzed by GC-ECD. 300 g soil samples were dried at room temperature, grounded by puck mill for 60 seconds to reduce the particle size to less than 75 µm, homogenized by random subsampling, and then extracted with acetonitrile for 18 hours in a cooled (< 4 °C) ultrasonic bath following USEPA Method 8330b. 2 µL extracted toluene was injected into an Agilent 7890A GC equipped with a cool-on-column inlet, 7.5 m long - 0.53 mm diameter - 1.5 µm film thickness DB-5ms column, and 1 m long Restek retention gap column, with helium as the carrier gas (10 mL/minute) and N as the makeup gas (60 mL/minute). The different analytes were separated with the following temperature program: 75 ºC for 0.1 minute, increased at 15 °C per minute to 200 ºC, then increased at 20 ºC per minute to 300 °C, then held for 5.5 minutes, and the detector temperature was 325 ºC. The cool-on-column injector and the autosampler tray cooled to ~ 4 ºC were used to minimize thermal decomposition of the explosive components. TOC in water was analyzed using Shimadzu 5000A TOC analyzer. Anions (Cl, NO_3, Br, NO_2, and SO_4) were analyzed by ion chromatography (IC) following EPA Method 9056A (SW-846). Cl, NO_3, NO_2, and SO_4 were analyzed by IC following USEPA Method 9056A (SW-846). Fe and Mn were analyzed on a Perkin-Elmer Plasma II Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) following methods equivalent to USEPA Method 6010C (SW-846).

Soil particle size distribution was measured using a Beckman Coulter LS 13-320 laser particle size analyzer equipped with a Universal Liquid Module. Soil total carbon (TC) content was analyzed using Perkin Elmer 2400 CHNS (carbon, hydrogen, nitrogen, sulfur) Analyzer. Soil moisture content and volatile solids were determined by weight losses on drying at 105 °C for 24 hours and ignition in a muffle furnace at 550 °C for 2 hours respectively. Soils samples for iron analysis were extracted using 0.25 M HCl for Fe(II) and 0.25 m HCL + 0.25 M hydroxylamine hydrochloride for total Fe (II + III). Extractions were performed in 40 mL USEPA vials flushed with N gas to minimize Fe oxidation, then the extracts were analyzed by ICP-AES. Samples were extracted for 30 minutes to measure poorly crystalline and sediment-bound iron oxides, and for 96 hours to measure crystalline reactive iron oxides.

B.3 LABORATORY EXPERIMENTAL PROCEDURES

B.3.1 Sorption Measurements

Explosive sorption measurements were conducted in 50 mL disposable glass centrifuge tubes containing 25 g of soil, 40 mL artificial groundwater, and varying amounts of TNT and RDX (10 to 5,000 µg/L). To inhibit biological activity, all tubes were autoclaved at 121 ºC and 20 per square inch (psi) for an hour prior to spiking TNT and RDX. Triplicate tubes were prepared for each concentration in each soil. Tubes were capped, sealed with parafilm, and shaken on a tumbler for 14 days, then centrifuged at 2500 rotations per minute (rpms) for 20 minutes, followed by decantation of aqueous phase. The collected water samples at 0 and 14 days were extracted using toluene by the modified FME method (Li et al., 2011). The extracts were analyzed by Agilent 7890A GC with an ECD. The amount sorbed to soils was determined by mass lost from the aqueous phase. The extracts were stored at -20 ºC until analyzed by GC-ECD. Tube controls were run in parallel containing 40 mL artificial groundwater and 100 µg/L of explosives, but their sorption was negligible. The amount of explosives released from sediment was also negligible. Sorbed concentration was calculated as (initial aqueous concentration - final aqueous concentration)/soil mass.

Desorption of TNT and RDX was not evaluated due to loss of clay and silt material while supernatant was removed after centrifugation, and difficulties in re-suspending sediment with fresh water. The Linear, Freundlich, and Langmuir sorption isotherm models were applied to determine the best presentation for the isotherms of LSs and explosives. The Linear isotherm has the form:

$$S_i = K_d C_i$$

where S_i is the sorbed concentration (µg/g), C_i is the aqueous concentration (µg/mL), and K_d is the linear sorption coefficient (mL/g). The Freundlich isotherm has the form:

$$S_i = K_F C_i^n$$

where S_i is the sorbed concentration (µg/g), C_i is the aqueous concentration (µg/mL), and K_F is the Freundlich sorption coefficient ($mL^n µg^{1-n}/g$), and n is a constant. The Langmuir isotherm has the form:

$$S_i = (KC_i)/(1 + nC_i)$$

where S_i is the sorbed concentration (µg/g), C_i is the aqueous concentration (µg/mL), K is the ratio of sorbed and solute concentrations, and n is the equilibrium constant (mL/µg). Coefficients for Linear, Freundlich, and Langmuir isotherms were obtained by fitting the model to the observed sorption results in each soil using the Generalized Reduced Gradient (GRG) Nonlinear solver in MS Excel to minimize root-mean-square error (RMSE) of log transformed sorbed concentrations. RMSE was defined as $[\Sigma(\text{Log } S_{estimated} - \text{Log } S_{observed})^2/n]^{0.5}$ which gives approximately equal weight to low and high concentration data. Goodness of fit was determined by the Akaike's Information Criterion (AIC) indicating that the lowest AIC is considered as the most correct model. 95% CI and t-test with 95% confidence level were applied to determine the statistical significance. 95% CI was defined as [$S_{estimated}$ ± Critical t x Standard Error (SE) of $S_{observed}$]. SE was computed by dividing the sum of squares of the residuals by the degrees of freedom, and critical t-value was calculated by Excel built-in function (TINV) to minimize underestimation of the true uncertainty in nonlinear estimation (Hossain et al., 2013).

B.3.2 Batch Biodegradation Measurements

Microcosms were constructed to evaluate HE biodegradation under the transient aerobic and anaerobic conditions that might occur in grenade range soils. Microcosms were constructed by addition of 50 g of blended grenade range soil, 100 mL of pore water collected from BLs at the site, and RDX/TNT stock solutions to generate approximately 1,000 µg/L of each component in the microcosm. The experimental treatments included: (1) autoclaved control, (2) no treatment (live control), (3) 0.074 g of crude GL, (4) 0.074 g of NA, LS, and (5) 0.074 g of both crude GL and NA. All treatments were run in triplicate. The organic amendment loading per g soil was identical to the substrate loading used in a field evaluation of organic substrate addition to the Fort Bragg hand grenade range. Microcosms for the autoclaved controls were constructed by placing soil and groundwater into serum bottles, autoclaving at 121 ºC and 20 psi for an hour to remove viable microorganisms, and then spiking RDX and TNT stock solutions to avoid thermal decomposition of those explosives. Bottle controls were constructed without sediment by transferring groundwater and spiking explosives, and operated in parallel with other microcosms. For the first 56 days, all microcosms were shaken on a tumbler and the headspace was flushed each week with 500 mL of pure O_2 using a gas syringe to maintain aerobic conditions in aqueous phase. At day 56, all bottles were flushed with pure N gas for 30 minutes to switch from aerobic conditions to anaerobic conditions in microcosms. After 56 days, the microcosms were incubated with no shaking since rapid O_2 exchange was no longer required. Gas samples from each microcosm were analyzed by GC with a thermal conductivity detector (TCD) and flame ionization detector (FID) in series to monitor changes in O_2, CO_2, N, and methane concentrations. When gas samples were analyzed, gas pressure in each bottle was neutralized using a gas syringe, followed by adding 3 mL of pure N gas into each bottle prior to collecting 3 mL of gas sample for the analysis in order to avoid negative pressure inside the bottles.

Soil microcosms were constructed and monitored to evaluate the impact of organic substrates (crude GL and/or NA) on O_2 consumption in microcosms using sediment collected from both Bays C and T at Fort Bragg. The soil microcosms were constructed by transferring 100 g of air-dried, mixed soil and 100 mL of pore water into three different 250 mL serum bottles for each treatment. The microcosm headspace was flushed with 500 mL of pure O_2 to displace the air, sealed with a butyl rubber stopper, and shaken on a tumbler for two days to saturate the liquid phase with O_2 prior to the O_2 consumption experiment. Each microcosm was flushed with another 500 mL of pure O_2, followed by neutralizing gas pressure in bottles using a gas syringe. Experimental treatments were the same as in the HEs biodegradation incubations. The only difference between the HEs biodegradation and O_2 consumption experiments was the use of greater amount of soil with more amendment addition to evaluate the kinetics of O_2 consumption by organic amendments more efficiently. Gas samples from each microcosm were periodically analyzed by GC-TCD to monitor changes in concentrations of O_2, CO_2, and N. When gas samples were analyzed, gas pressure in each bottle was neutralized using a gas syringe, followed by adding 3 mL of pure N gas into each bottle prior to collecting 3 mL of gas sample for the analysis in order to avoid negative pressure inside the bottles. The added N gas was subtracted in the calculation of gaseous masses. The amount of O_2 consumed and CO_2 produced in each bottle was determined by accounting for the mass removed during sampling and correcting for gas partitioning to the aqueous phase based on the Henry's Law constant. Gas concentrations (%) by volume determined by GC-TCD were converted to mass using the molecular weight and ideal gas molar volume. O_2 consumption in bottles containing a sodium (Na) sulfite solution matched within a range of 108 - 114% of the theoretical value, confirming the accuracy of this approach.

B.3.3 Column Experiments

Experimental columns were constructed with 5 cm diameter x 1.5 m long clear Polyvinyl chloride (PVC) pipe and packed with 0.15 m of coarse sand and 0.1 m of washed fine sand as a water drainage layer, followed by 1 m of grenade bay soil. Prior to use in columns, soils were passed through a No. 4 (4.76 mm) sieve to remove clumps. Soils were excavated in 0.25 m vertical increments and packed in the columns in the same order. Infiltrating water drained by gravity through 0.64 cm inner diameter x 0.2 m long low-density polyethylene tubing connected the bottom of columns into aerobic sampling vials. Soil gas sampling ports were installed at 0.25, 0.5, 0.75, and 1 m below the soil surface. Four replicate columns were prepared for each throwing bay soil (Bays C and T), followed by biweekly groundwater application. Three months after the start of water application, the surface of each column was amended with 50 g of Comp B explosive impacted soil. The columns were wrapped with aluminum (Al) foil to prevent the photoreduction of Fe(III) and photodegradation of explosive compounds (Brannon and Pennington, 2002). Two leaching columns were prepared with a water drainage layer (0.15 m coarse sand + 0.1 m fine sand) and received the same amount of Comp B contaminated soil as other columns. These leaching columns were operated and monitored in parallel with the columns containing active range soils to measure the explosives concentrations released by the Comp B contaminated soil and entering the Fort Bragg soil.

Two cm (40.6 mL) of Nitrocellulose (NC) groundwater was applied every other week to the column soil surface. At 56 days after addition of the Comp B amended soil, 0.15 g/cm^2 crude GL and 0.15 g/cm^2 NA, LS were applied to the soil surface. The GL and NA loading rates are the same as employed in a field evaluation of substrate addition being conducted at the grenade range at Fort Bragg (Borden and Won, 2017). Experimental treatments evaluated included: (1) Bay C soils with no amendment, (2) Bay C soils with GL+NA, (3) Bay T soils with no amendment, and (4) Bay T soils with GL+NA. Duplicates were prepared for each treatment. Column effluents and soil gases were monitored monthly for explosives (RDX, TNT, HMX, and their degradation products), Cl, NO_3, NO_2, SO_4, Mn, Fe, TOC, pH, and gas concentrations (N_2, O_2, CO_2, and CH_4). At the end of column operation, columns were cut into 0.1 m sections, homogenized, and soils were analyzed for explosives, TOC, Fe(II/III), moisture, volatile solids, and ash contents.

B.4 FIELD PROCEDURES

Prior to amendment application, an extensive array of soil monitoring instrumentation was installed in Bays C and T to evaluate the performance of MNA and EA in limiting migration of HE through the soil profile. Trenches were installed down the approximate centerline of each throwing bay with the middle of the trench beneath the grenade targets. Throughout the excavation process, the soil was monitored for the presence of UXOs. Soil samples collected from these trenches were analyzed for explosives, metals, and soil characteristics. During excavation, the soil was segregated in 0.3 m lifts, then backfilled in the same sequence. During backfill, instrumentation clusters were installed and spaced 2 m on-center at four locations in Bay T (lysimeters A, B, C, and D) and Bay C (lysimeters E, F, G, and H). Each cluster consisted of two BLs (Soil Moisture Equipment, CA; top of bucket at 0.9 (labeled -3) and 1.5 m (labeled -5) bgs), one suction lysimeter with the intake at 1.2 m bgs (Model 1922 Ultra Soil Water Samplers, Soil Moisture Equipment), two electrical resistance moisture sensors (Irrometer Model 200SS WATERMARK at 1.2 and 1.5 m bgs), and two oxidation-reduction potential (Eh) probes at 1.2 m and 1.5 m bgs (Vepraskas and Cox, 2002). No instrumentation was installed shallower than 0.9 m bgs to prevent damage by grenades during ongoing training exercises. Sampling and monitoring lines were run to the central berm to allow continued monitoring without actually entering the throwing bays. Samples could not be collected from some BLs during certain monitoring events due to low water volume. During those events, averages were computed from the lysimeters that could be sampled. Figure B-1 shows photographs of the instrumentation being installed in a trench and a sampling access point on the berm.

Figure B-1. Monitoring Instrumentation and Sampling Access Point

During installation in grenade bays - March 2013.