SELINUS UNIVERSITY
OF SCIENCES AND LITERATURE

CHARACTERIZATION OF EXPLOSIVES TESTING RANGES: ENVIRONMENTAL IMPACTS AND REMEDIATION CONSIDERATIONS

By Stacy Theonne Kuykendall

Supervised by
Professor Salvatore Fava PhD

A DISSERTATION

Presented to the Department of
Geotechnical Engineering
Program at Selinus University

Faculty of Geotechnical Engineering
in fulfillment of the requirements
for the degree of Doctor of Philosophy
in Geotechnical Engineering

2023

DECLARATION

I do hereby attest that I am the sole author of this Dissertation titled "Characterization of Explosives Testing Ranges: Environmental Impacts and Remediation Considerations", which is submitted for the Award of Doctor of Philosophy (PhD) in Geotechnical Engineering to the Faculty of Geotechnical Engineering, Selinus University of Sciences and Literature. Its contents are only the result of the readings and research I have done.

Student's signature Stacy Theonne Kuykendall
Department of Geotechnical Engineering
Date 17 July 2023

Stacy Kuykendall

Table of Contents

List of Figures

List of Tables

ABSTRACT

Developing an integrated framework of explosive detection in soil and determination of site-specific treatment strategies for locations with explosive use is an ongoing issue in arid regions around the world. Currently, this framework utilizes limited data analysis regarding various explosive compounds after continuous use, including subsequent explosive impacts on the surrounding landscape. Local environmental features dominate the region in desert areas, mainly soil compaction, soil erosion, and aridity, which are significantly accelerated after explosive use. Although these regions are usually ideal for explosive testing due to their remoteness and relatively stable climatic conditions, little data is widely distributed to provide robust data on explosive impacts in arid regions.

In this study, a comprehensive investigation of locations where active and continuous use of explosives provides significant data that can be correlated between similar areas around the world. Soil sample analysis from explosive testing ranges confirms that a suite of explosive compounds used in conventional explosives and munitions can be detected for some time after use. These compounds include various explosive residues, namely ammonium nitrate fuel oil (ANFO), octogen (HMX), 1,3,5-trinitro-1,3,5-triazinane (RDX), and 2,4,6-trinitrotoluene (TNT). Physical impacts from explosive use include alteration of landscape equilibrium, changes in natural drainage patterns, and increased erosive processes on nearby hillslopes and in downgradient locations. Other observable impacts of explosive use indicate the disturbance of soil horizons and adverse effects on vegetative structure, species composition, and plant production. Site-specific management methods to correct explosive damage and avoid new impacts must be implemented, including maintaining historical use and site-specific sampling records, on-going maintenance and preservation of explosively impacted areas, and the removal of excess debris and unexploded ordnance (UXO), accomplished once an area is deemed safe for restoration. Implications of this study will allow for more correlations to be made across arid regions of the world, particularly those involved in military operations, and provide better understanding of how explosive use impacts both the soil environment, and, ultimately, the global climate.

CHARACTERIZATION OF EXPLOSIVES TESTING RANGES: ENVIRONMENTAL IMPACTS AND REMEDIATION CONSIDERATIONS

CHAPTER 1 INTRODUCTION

1.1 Statement and significance of the problem

Explosives have been used continuously for over 100 years, from the historical use of black powder as propellant in guns to the modern inventions of dynamite and nitrocellulose, created as a more stable propellant for use in firearms. Evidence of fire pots being used as incendiary devices, thrown upon intruders attacking Assyrian settlements around 900 BC, can be found depicted on artifacts from that period in the British Museum (Brown, 1998). The invention of the blasting cap by Alfred Nobel allowed an operator to detonate dynamite from a distance with a fuse, which advanced modern expansion with nitroglycerin explosives for rock demolition, tunneling, and highway construction in the United States. Presently throughout the U.S. and on a global scale, there exists numerous explosive testing ranges, combat zones, and other areas where explosives have been used in various operations, from military activities to mining operations to road construction. Although explosive use is a necessary component of defense and military operations, the activities associated with detonation can impact, modify, and often pollute the environment, alter soil morphology and composition, and cause landscape change over time. Modern explosive testing and use and its resulting environmental impacts can pose a serious threat to ecosystem function and stability.

To control the damage that can be imparted by explosives to metal tanks and ships and to concrete structures, experimental studies on increasing the strength of such materials to defend and protect both military personnel and civilian populations must be performed in controlled environments. Different types of explosives can be tested against various materials in a controlled manner to ensure their proper functioning and operation. Energetic materials can also be tested in controlled environments to determine parameters such as safe handling procedures, detonation pressure, detonation velocity, and sensitivity. Usually this involves detonating the energetic material in an area located far from public access, called an explosive testing range. The testing range is outfitted with various instrumentation equipment to obtain the necessary testing data, along with image forming instruments, such as other high-speed imaging to obtain numerous views of the explosive event as it detonates.

Explosive use, especially on testing ranges and in other conflict locations throughout the world, along with improper storage and disposal of waste material from explosive manufacture and production, can contribute to environmental impacts and contamination. Ammunition firing ranges and explosive testing ranges present costly issues for remediation and reclamation, as soil in these locations can contain a diverse suite of both inorganic and organic pollutants (Tauqeer, et al., 2021). The deterioration of metal bullets and projectile fragments and their explosive constituents in military range soils along with the release of metals and hazardous materials into surrounding ecosystems has been widely documented (Sanderson, Qi, Seshadri, Wijayawardena, & Naidu, 2018). Explosive-laden effluent and site run-off from contaminated testing ranges can be leached to underlying aquifers, which then serve to transport compounds some distance from the original site. The movement of metals, explosives, and explosive transformation products from firing ranges to underlying aquifers and their identification in irrigated soil from nearby agricultural fields has also been reported (Fayiga, 2019). The primary environmental contaminants typically found in testing range soils include arsenic (As), antimony (Sb), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), selenium (Sn), zinc (Zn), nitrate esters such as nitrocellulose and nitroglycerine, nitro compounds including 2,4,6-trinitrotoluene (TNT), organic classes of explosives including nitroso compounds, lead azide, and ammonium nitrate (AN) (Fayiga, 2019).

Long-term effects of explosive use can be easily recognized in areas where they have been continuously used. These effects include landscape alteration and soil disruption, caused by the movement of military vehicles and warfare traffic and large-scale shelling and bombing of locations near critical habitats and ecosystems, which serve as a stark contrast to nearby areas with no impacts. Explosive testing ranges can contain large volumes of military scrap and other waste materials, including spent projectiles and bullets, plastics, and sharp metallic fragments. These materials can not only pollute soil with toxic metals and explosive residues but also can present an unsightly hazard in the local landscape. After detonation, explosive compounds can leach through the soil profile, contaminating precious water resources in underlying aquifers (Robinson, 1979). These compounds can also be transported off site through weathering or fluvial processes or during slope and surface stability processes such as surface subsidence or soil desiccation. Eolian deposits, such as sand, silt, and clay, can then transport materials whenever wind moves over barren regions, like those found on explosive testing ranges. Mass wasting, the downslope movement of soil under the influence of gravity through heave, slide, and flow, can serve to move materials off site, especially during periods of heating and cooling, wetting and drying, freezing and thawing, and water pressure from periodic saturation (Thomas, 2011). Explosive testing and use can have thermal impacts on vegetation, leading to a significant reduction in vegetative cover and exposing soil to the erosive effects of wind and water. Such alteration of a site’s topography can influence the type, variety, and amount of pioneer and each successive plant community that is available for site recolonization.

Traditional methods of explosive site remediation typically involve processing with large volumes of chemicals as used in leaching treatments on soil or its physical removal through excavation and transport of explosive-laden soil to a suitable landfill, often at some distance from the original site. McDonald et al. (2005) postulated that excavation of a one-foot layer of soil across a 7,000-acre site in New Jersey, U.S., was estimated to cost more than €226,000,000 ($250 million). Current cost estimates for excavation and disposal of soil typically range from $300 to $510 per metric ton ($270 to $460 per ton) depending on the nature of the hazardous contaminants and methods of excavation employed (Remediation Technologies Screening Matrix and Reference Guide, 2023). These estimates include excavation and removal of soil, transportation, and disposal at a specialized and permitted facility. Additional cost of treatment at the facility may also be required. Other costs may include soil characterization after treatment to meet final site disposal requirements. Therefore, it is evident that the absence of affordable and feasible remediation and reclamation technologies show that continued explosive use will be an issue in future environmental restoration, both for contaminated locations around the world. This issue is especially true for ongoing management and the continued use of explosive testing ranges and other military sites used for training exercises. The exorbitant price associated with explosively contaminated soil disposal demonstrates that the increasing cost of excavation and the shrinking amount of usable landfill space will likely prohibit the use of this disposal method in the future.

Recent studies involving energetic materials impact on ecosystems show that explosives are persistent in surface soils and ground water (Bordeleau, Martel, Ampleman, & Thiboutot, 2008). Explosive compounds can be identified in soil from formerly used munitions processing plants to ammunition storage facilities, often many years after use. In many areas around the world, explosives can be found at former battle sites, clearly identified from small crystals to large chunks in soil and sediment. Several locations where explosive disposal occurred over 20 to 50 years ago still show high levels of explosive content in the environment. Commonly identified compounds in soils at such sites include monoamino-dinitrotoluenes, such as 2-amino-4,6-DNT and 4-amino-2,6-DNT, and diamino-nitrotoluenes, including 2,4-diamino-6-NT and 2,6-diamino-4-NT (Serrano-Gonzalez, et al., 2018) .

This study will determine the physical and chemical disturbances that can be expected from explosive testing and use in an arid environment. Explosive residues and other harmful compounds that will commonly be identified in areas where explosives have been used and the environmental impacts that can be expected from their presence and transport through the soil will be determined. This study will expand the existing literature by identifying cost-effective, reliable, and viable management and treatment techniques for explosive testing ranges. By developing an understanding of the environmental issues related to the management and use of testing ranges, this study will help determine and develop approaches that can be implemented at other explosively impacted locations. This study will emphasize that environmental impacts and landscape disturbance will be reduced by minimizing the amount of soil that requires remediation, especially in arid regions. Applying these principles will ensure the continued use and environmental health and sustainability of existing explosive testing ranges.

The study will first determine the presence or absence of explosives and their transformation products in soil from explosive testing ranges to develop an initial site assessment and to begin an exploration of landscape change over time. Previous research that examined different explosive munitions in the environment indicate that various factors such as temperature, salinity, oxygen, and water content of soil at each site can greatly influence the rate of corrosion of the munition (Koske, et al., 2020). The main contaminants found at many bombing ranges where explosives are continually used include metals and energetic materials (Brochu, et al., 2005). By investigating the properties of soil potentially contaminated with explosive compounds should provide an indication of the probable distribution of explosive compounds around a contaminated site. Different locations in the surrounding area near a contaminated site should also be analyzed to investigate the possible spread of contamination off site. The priority for environmental protection of any explosive testing range will be to develop a baseline understanding of how development and testing activities using energetic materials can impact and change both soil and landscape. Determining the presence or absence of explosive residues and their concentrations in test range soils is important if optimal environmental management practices are to be developed for continued use of the site.

Overall, explosive use in testing activities and its impact on the surrounding environment is a key issue that requires critical analysis to identify site and soil conditions likely encountered at similar locations. Based upon the history of explosive use in the area and nearby landscape impacts, a baseline for planning site remediation as well as restoration can be developed. This research serves to contribute to current knowledge regarding the impact of explosive testing and use on the environment. This study will develop an understanding of key issues related to the management of explosive testing ranges. This in turn will help identify and clarify the best approaches for maintaining site conditions while at the same time reduce future costs by minimizing the area of land that requires remediation and restoration.

1.2 Research questions

The location for this study will be an explosive testing range in the desert Southwest of the U.S. The study will involve the collection of soil samples near the site of detonation on active explosive testing ranges. The samples will be analyzed using high performance liquid chromatography (HPLC) to determine the type and concentration of energetic materials and explosive compounds, to include a suite of typical explosives used in conventional explosives and munitions. The analysis will be used to identify which compounds are likely to identified in soil after continuous use of explosives. The analytical results will be compared with explosive concentrations commonly identified in soil at similar locations. These areas include locations impacted either by military activities or from explosive testing operations. They are commonly located in desert climates such as Arizona or Nevada in the U.S. or in desert countries around the world.

This study will be guided by the following research questions:

1. How does explosive testing and use affect soils and the physical landscape?
2. How can explosive use accelerate land degradation and contribute to desertification? In what ways does explosive use contribute to anthropogenic disturbance of the environment?
3. What technical measures and management strategies can be implemented to reduce impacts from explosive testing and use? How can these concepts be easily implemented for suitable management in arid locations around the globe?

In order to better understand the impact that explosives can have on soil and on landscapes, a broad overview of the different types of explosives and the process of explosive detonation will be provided in Chapter 2.

CHAPTER 2 EXPLOSIVES

The detonation of an explosive creates a sudden increase in volume along with a release of energy in a violent manner, generating extreme temperatures and releasing gases (Cooper, 1996). This exothermic, violent process can serve to introduce metals, energetic compounds, and other materials into soil and the surrounding environment. This chapter will provide an overview of explosives to help develop an understanding of how explosives work to better understand how explosive testing and use can impact the environment. A brief discussion of what comprises an explosive and how explosives function, along with an introduction to the various types of explosives used in military operations and in commercial applications will be covered. The sections of this chapter will be comprised of examinations of the following topics. First the various classifications of what determines a material is an explosive will be considered. This will be accomplished by studying the various chemical structures that encompass energetic materials. Next, how to achieve the detonation of explosives will be analyzed. The various types of explosives and the composition of commonly used explosives in military applications and commercial explosives will be compared. Finally, the composition of commonly tested and used explosive ordnance and the resulting predominant explosives of environmental concern will be discussed.

2.1 Classification of explosives

An explosive must be capable of doing useful work on the target, whether that target is a rock face, a building, or a metal vehicle. For most practical purposes in military or industrial operations, this requires that the explosive compound be capable of converting heat energy and compressed gas output from its decomposition into kinetic energy in air in the form of a blast wave, into a rocket or a bullet, or into rock or soil. All explosives consist of a mixture of several ingredients, including a metallic fuel to enhance energy output, a polymer binder to impart mechanical integrity to the device and to act as a fuel, a plasticizer to facilitate processing, a curing agent to cure the binder, and other additives to increase the energy output (Brown, 1998).

2.1.1 Classification according to U.S. ATF specifications

Classification of explosives usually is based on their source, use, or application. The United States Bureau of Alcohol, Tobacco, and Firearms (ATF) classifies explosives into three categories: low explosives, high explosives, and blasting agents. Low explosives are composed of an explosive material that can freely burn when unconfined. Smokeless powder and black powder are examples of low explosives. They are typically used as propellants in pyrotechnics and in rockets and in ammunition for firearms. High explosives are explosive materials that must be detonated with a blasting cap. A common high explosive is dynamite, found in granular, gelatin, and semi-gelatin forms. Dynamite can be nitroglycerin-based or ammonium nitrate-based. A blasting agent is defined as a mixture consisting of a fuel and oxidizer, intended for blasting operations for industrial purposes, such as mining or demolition. Blasting agents can be either dry and free-flowing or wet and pourable, which eases its addition into blastholes for commercial operations such as large-scale open pit mines. The shock wave produced by commercial explosives on detonation provides the characteristic brisance, or rock breaking capability.

Ammonium nitrate fuel oil (ANFO) is a common commercial explosive, composed of 94% ammonium nitrate and 6% fuel oil. Today ANFO is the most widely used explosive in the blasting industry because it is relatively inexpensive and safe to handle (Meyer, Kohler, & Homburg, 2016).

High explosives can be further subdivided into primary and secondary explosives. Primary explosives are initiators that easily detonate in the presence of heat, friction, or mechanical shock. Figure 1 provides a summary of the various categories of explosives.

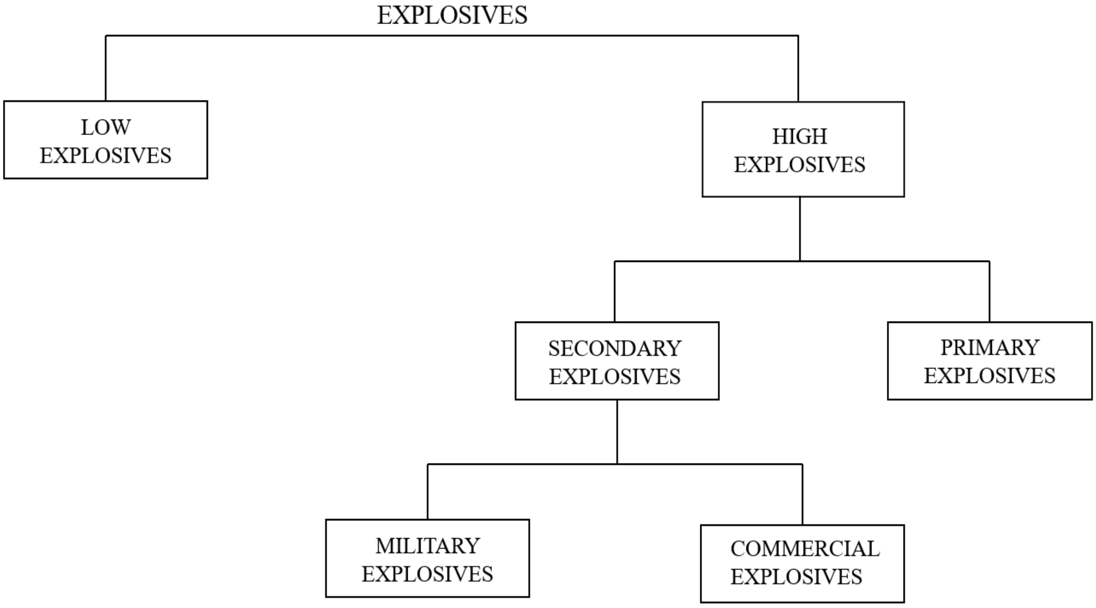


Figure 1: General categories of explosives.

2.1.2 Classification according to explosive chemical structure

The chemical structure of an explosive is important because it can affect the stability of the explosive in soil (Hasanuzzaman & Prasad, 2021). If an explosive contains cyclic aromatic ring compounds, it may remain unchanged in soil for some time and not be easily biodegraded. Explosives are composed of various ingredients, but most include mixtures of C (carbon), N (nitrogen), H (hydrogen), and O (oxygen). The end products of the exothermic detonation reaction include harmless gases such as H_2O (water vapor), CO_2 (carbon dioxide), and N_2 (nitrogen). Other end products can be potentially toxic gases, including NO (nitric oxide), N_2O (nitrous oxide), NOx (nitrogen oxides), NO_2 (nitrogen dioxide), CO (carbon monoxide), NH_4 (ammonia), and CH_4 (methane).

Based upon their chemical structure, explosive compounds can also be broadly classified into three classes: nitroaromatics, nitramines, and nitrate esters. Nitroaromatic explosives include TNT. These compounds contain an aromatic ring with multiple NO_2 groups linked to carbon atoms. Nitramine explosives such as RDX and HMX contain a cyclic ring with NO_2 groups associated with nitrogen atoms. Nitrate esters contain NO_2 groups attached to an oxygen atom with hydrogen and carbon linked together to form nitrate esters such as PETN.

Nitroaromatic and nitramines explosive compounds are extensively utilized and can be considered potential environmental contaminants. As an example, nitramines have a higher aqueous solubility compared with nitroaromatics and thus can be expected to be highly mobile in soils (Batnagar, Kamath, & Potoff, 2013). Nitrate esters can remain in soil unchanged and are thus considered recalcitrant in nature. Nitrate ester explosives are often found as co-contaminants with other xenobiotic compounds in soil (Arbeli, et al., 2016).

Breaking the aromatic ring in explosive compounds, severing a nitrogen bond, or breaking a strong oxygen bond in an explosive is what provides that compound with its explosive power. As the number of nitrogen groups increases, the overall energetic content of the compound also increases (Matyas & Pachman, 2013). Knowledge about the chemical composition of explosives can provide information to both identify the explosive used some time after detonation and to determine trace explosive materials remaining in soil.

Based upon their chemical structures, explosives commonly contain seven types of chemical bonds, which also serve to provide explosive properties when the bond is severed:

- $N{=}O$ bonds, found in nitro compounds and various salts, such as those of benzofuroxan,
- $N{=}N$ bonds, found in diazo compounds, including diazodinitrophenols,
- $N{\equiv}N$ bonds, found in copper, lead, and silver azides,
- $O{-}Cl$, found in chlorates and perchlorates,
- $N{=}C$, found in mercury and silver fulminates,
- $N{-}Cl$, found in nitrogen chlorides,
- $O{-}O$, found in peroxides, such as triacetone triperoxide (TATP),
- $-NX_3$ where X is halogen, such as nitrogen trichloride,
- $C{\equiv}C$, found in acetylene and acetylides, such as silver acetylide (Akhavan, 2004).

2.2 How to initiate explosives to detonation

Explosives are compounds that when subjected to heat, impact, or shock can undergo a rapid decomposition. The resulting exothermic reaction releases large quantities of heat and gas, expanding under high temperature to a high state of pressure. A detonation is defined as a shock wave with a rapid exothermic chemical reaction occurring just behind a shock front (Cooper, 1996). A detonation occurs when an explosive is properly designed, and initiation of the explosive is performed under ideal physical and chemical conditions. This is important because the detonation process can not only introduce explosive compounds into the surrounding environment, but the detonation also itself can tear apart metallic components of the explosive device and distribute them away from the point of detonation. The high heat and thermal energy produced from the exothermic reaction can alter the chemical composition of energetic materials, plasticizers, polymers, and plastics that comprise the explosive device. These materials can also become potential environmental contaminants in soil.

The application of what is considered an “explosive train” is vital in the proper and effective detonation of an explosive device. A schematic diagram of an explosive train is provided in Figure 2. As indicated in the diagram, the explosive train can consist of many parts, each with different explosive constituents. The types of explosive materials that comprise the explosive train can influence the power and brisance of an explosive. The shock energy required to set off the components of an explosive is obtained using an explosive train consisting of an initiator and booster.

An explosive train works as follows. A small impulse such as a detonator sets off the main charge. Often the detonator must be “boosted” to amplify its effect on the main charge. The explosive train acts to begin activation of the detonation process by inputting low levels of energy from the primary explosive, causing a chain reaction to initiate the final main charge, the secondary explosive. The proper initiation of the main charge is important because the overall effect is to detonate the entire explosive device. Incomplete detonation leads to the formation of unexploded ordnance (UXO), which can cause problems for both human and animal due to unintended detonation at some time later. Incomplete detonation can also lead to the formation of explosive chunks of material that can be scattered about the surrounding area, also leading to widespread contamination and the creation of additional UXO.

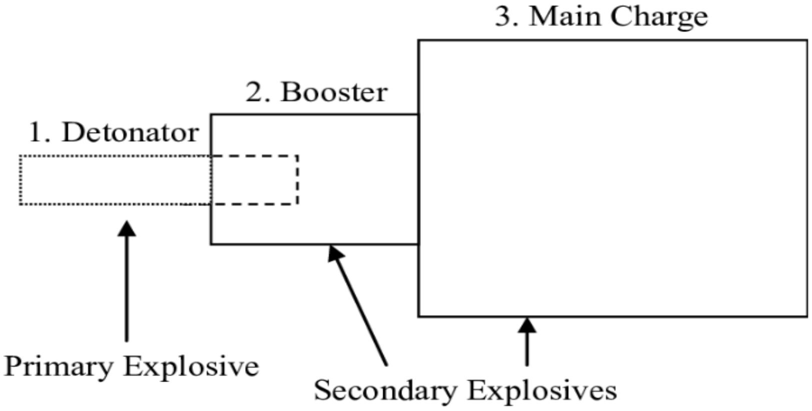


Figure 2: Typical explosive train.

Boosters and primers

Boosters and primers are used to initiate the main charge, the explosive. Boosters and primers are initiated by detonators such as No. 8 blasting caps, detonating cord, and other initiating devices. Common blasting caps are shown in Figure 3. The most commonly used booster is a cast pentolite booster, containing a mixture of pentaerythritol tetranitrate (PETN) and TNT. A primer is a booster into which a detonator has been inserted. A booster does not contain a detonator; it only serves to boost explosive energy. Boosters are initiated by adjacent primers or by detonating blasting agents. Boosters are typically used in mining operations in blastholes where there is excess moisture and water, in areas with excess rock fragments and overburden, and in areas with hard geological strata (Hudson & Harrison, 1997).

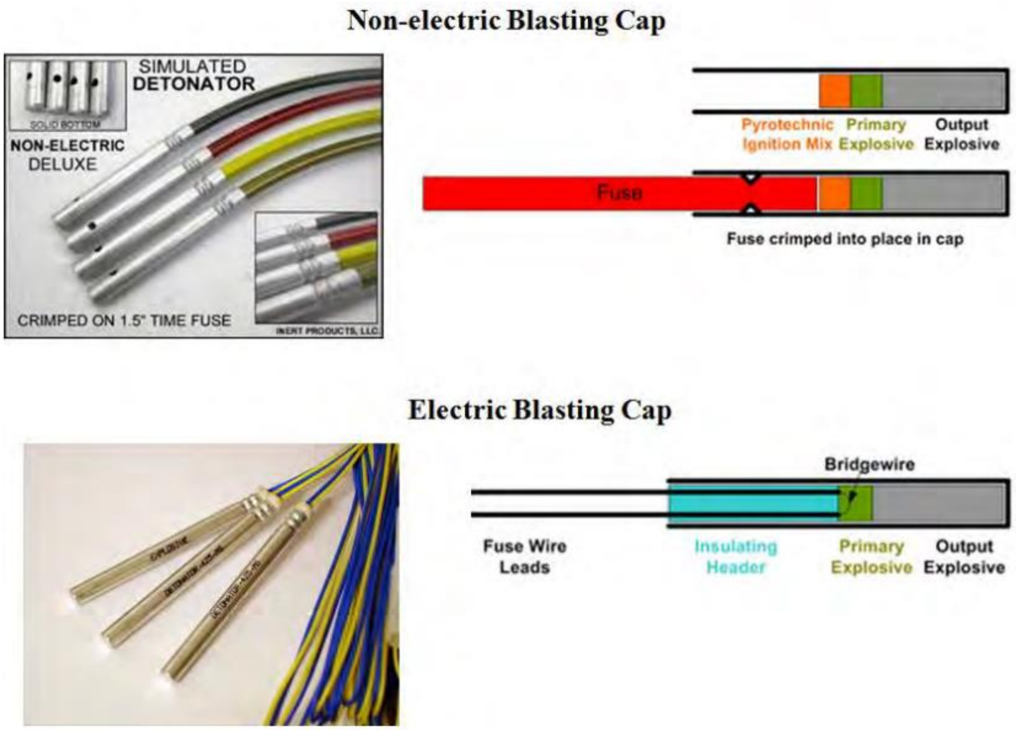


Figure 3: Blasting caps.
(Source: Overview of Explosive Initiators by Dr. K. Oyler)

2.3 Composition of explosives used in military operations and for testing purposes

There are many types of explosive materials that can introduce energetic materials and metals into the environment from testing activities and from military use. The following discussion will identify the various uses of different explosive devices. Military applications use high explosives in terms of their performance, functionality, and safe handling and transport. These applications require that the explosive be powerful, while insensitive to intense shock and vibration.

The composition of ordnance can help to develop a better understanding of how explosive testing and use impact the environment. This can be achieved by identifying the types of materials that are introduced into the environment upon detonation. Such types of ordnance material contain significant quantities of explosive components that are intended to fragment upon detonation, to achieve a wide area effect, and to maximum accuracy and precision (Cross, Dullum, Jenzen-Jones, & Garlasco, 2016). These devices cause damage primarily through explosive blast and through material fragmentation and thermal effects upon detonation. Most explosive ordnance are designed and employed to achieve maximum effects against a large area upon detonation. There exist many different types of munitions that contain a variety of energetic formulations. The composition of ammunition and explosives for military applications is varied. Medium to large caliber projectiles are composed of steel and aluminum. Small caliber bullets are composed of lead, antimony, arsenic, copper, and zinc. Grenades are composed of brass. TNT is the most common military explosive because of its ease of manufacture, its low melting point which makes it suitable for melt-casting or loading operations, its low cost from available raw materials, and its safety in handling. Overall, there are many types of military ordnance and associated materials that can introduce explosives into the environment from testing activities and from military use. The following discussion will identify the various uses of these specific components. The different types of ordnance that will be introduced include explosive shells, bombs, grenades, torpedoes, shaped charges, warheads, other pyrotechnic materials, and radioactive weapons.

2.3.1 Explosive shells

A shell is a hollow projectile filled with an explosive and fired from artillery. A shell has a dual function of producing fragments as an anti-personnel weapon and producing blast effects against enemy installations. Explosives include TNT or RDX and TNT mixtures. Shells used for penetrating armor have heavier steel bodies with the nose made of specially hardened metal. The explosive is resistant to detonation by impact so that the shell penetrates the armor before the explosive is initiated. Armor-piercing projectiles contain no explosives but have high-density cores made of tungsten alloy.

A cartridge case is an explosive shell cover that contains a projectile, the primer, and the propellant in a single unit for convenience of handling and loading. Usually, the cartridge case is composed of metal. In the case of combustible cartridge cases, the contents are based on nitrocellulose, cellulose, or nitroguanidine ($CH_4N_4O_2$). It offers specific advantages over the conventional metallic or brass case. Combustible cartridge cases are made of cellulose fibers with suitable explosives to ensure debris-free combustion inside a gun barrel.

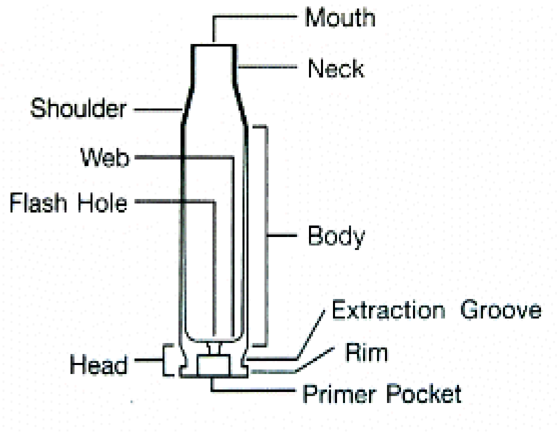


Figure 8: Typical Cartridge Case.

2.3.2 Bombs

Bombs are containers filled with explosives, chemicals, or other nuclear, biological, and chemical warfare agents, along with an explosive train. Bombs intended to produce a blast effect against buildings have a lighter casing and are usually filled with an explosive containing aluminum. Anti-personnel bombs have a relatively heavy casing and are filled with an explosive strong enough to break the casing into fragments on impact. Armor-piercing bombs for use against warships have heavy bodies with a small explosive charge and resemble armor-piercing shells in their construction.

2.3.3 Grenades

Hand-thrown and rifle-projected anti-personnel grenades are self-contained fragmenting, blast, smoke, or gas munitions. The steel grenade body is thin so that it is broken into fragments of pre-determined size to provide shrapnel. Small metal objects, such as nuts and bolts, can be used in the explosive fillings. Grenades projected from rifles have a longer range. Smoke grenades are canister-type and are used as signaling devices, targets, landing zone marking devices, and as screening devices for troop movements. Riot control grenades create barriers of tear gas in order to prevent movement of large groups of people and to maintain law and order.

2.3.4 Torpedoes

The explosive charge in a torpedo is carried in the nose, with the rear compartments containing fuel and a motor with control equipment. Because the torpedo is required to penetrate a ship, the nose is constructed of heavy steel and the fuse operates with a delay. The explosive charge must be of maximum density and power to ensure a high velocity of detonation.

2.3.5 Shaped charges

The penetrating power of a shaped charge is proportional to the cube of its diameter and proportional to the detonation pressure of the explosive used (Cooper, 1996). Suitable fillings for shaped charges are cast pentolite, RDX/TNT mixtures, or HMX/TNT mixtures. Shaped charges are capable of perforating and cutting various types of targets, like reinforced concrete structures, bunkers, steel plates, and bridges. Large caliber shaped charges can be used to demolish unexploded ordnance (UXO) buried in the soil. Shaped charges are frequently used in warheads for anti-tank missiles. They can also be used to initiate nuclear weapons.

2.3.6 Warheads

A warhead is an explosive mass enclosed in a suitable casing assembled with a fuse, which consists of an initiation mechanism. The warhead is in the rocket or missile, which is used to deliver it to the target and the target is damaged on the detonation of the warhead. Warheads are specifically designed for different roles and for different target effects. They can be used for anti-tank and anti-armor applications and in fragmenting type warheads. Incendiary type warheads are used against fuel and ammunition dumps.

2.3.7 Radioactive weapons

Radioactive materials used in weapons are broadly divided into two classes, including fission weapons and fusion weapons. Fission weapons derive their power from nuclear fission when heavy nuclei such as uranium (U) or plutonium (Pu) are bombarded by neutrons and split into lighter elements, more neutrons, resulting in an energy release. The newly generated neutrons then bombard other nuclei, which then split and bombard other nuclei. This process continues and leads to a nuclear chain reaction which releases large amounts of energy. These weapons are known as atomic bombs. Fusion weapons are based on nuclear fusion when light nuclei, such as deuterium or tritium, combine into heavier elements and release large amounts of energy. Weapons which have a fusion stage are known as hydrogen bombs because of their primary fuel or thermonuclear weapons because fusion reactions require extremely high temperatures to occur. The extreme temperatures and densities necessary for a fusion reaction are generated with energy from a fission explosion.

Nuclear weapons which use nuclear fusion have far greater yields than fission weapons, as fusion releases more energy per kilogram. The light weight of the elements used in fusion makes it possible to build extremely high yield weapons, which are still portable enough to deliver. Compared to large fission weapons, fusion weapons are cheaper and much less at risk of accidental explosion. The simplest nuclear weapons are pure fission bombs. They were the first type of nuclear weapons built during the American Manhattan Project and are considered as a building block for all advanced nuclear weapons.

TATB (1,3,5-triamino-2,4,6-trinitrobenzene) and hexanitrostilbene (HNS) are the main explosive components in nuclear weapons, as they are insensitive to impact, friction, and can provide additional safety to prevent accidental explosion during mixing, processing, and fabrication. Cyclotol (75% RDX + 25% TNT) is another main explosive used in nuclear weapons with a high RDX content to promote a better weapon performance.

The development of nuclear technology has contributed to environmental contamination with radioactive materials. Major sources include mining and milling, nuclear weapons and munitions testing, and accidental introduction into the soil from nuclear facilities such as Chernobyl. Radioisotopes present in the surrounding environment of such areas include ^{222}radon, ^{238}uranium, ^{230}thorium, ^{226}radium, ^{210}lead, ^{131}iodine, ^{90}strontium, ^{137}cesium, and ^{239}plutonium.

One radioactive element of concern from weapons and explosives testing is depleted uranium (DU). Depleted uranium, composed almost entirely of ^{238}uranium and less than 5% ^{235}uranium, is a by-product of uranium enrichment in the nuclear power industry. Due to its high density, DU is used as counterweights in aircraft, as radiation shields in medical radiation therapy instruments, and in the transportation of radioactive materials. Military applications of DU include tank shielding and armor-penetrating bullets and missiles. Uranium has a long half-life (4.47 x 10^9 years) and so is persistent in the environment. Little is known about the ecological transport mechanisms that govern the movement of this element.

2.4 Composition of commercial explosives

A commercial explosive is an explosive designed, produced, and used for commercial or industrial applications other than military (Meyer, Kohler, & Homburg, 2016). Ammonium nitrate-based explosives, dynamite, and nitroglycerin are all examples of commercial explosives. ANFO, ammonium nitrate fuel oil, is a commonly used blasting agent composed of ammonium nitrate and liquid hydrocarbons. Commercial explosives are used in the mining industry, in demolitions, and as firearms and rocket propellants.

Commercial explosives are characterized by their heaving action created by gas volume and pressure. They are usually mixtures of ingredients such as oxidizers, fuels, absorbents, sensitizers, and stabilizers. Commercial explosives are characterized by their capability to move rocks, soil, buildings, etc., through the effects of its detonation (Zukas & Waters, 1985).

In most mining applications, the goal is to perform rock fragmentation through blasting. The most effective method to do this is to use timed energetic charges and explosives, uniformly spaced throughout, that provide high gas pressures to provide cracks and fissures in a rock mass. Conversely, in the case of the military application of explosives, the goal is to provide the most effective explosive compound to achieve the highest shock and vibration, thereby imparting the most damage to structures.

In the mining industry, controlled blasting using explosives is the key step for successful rock breaking. The term controlled blasting is used to describe several blasting techniques to preserve the stability and competency of rock walls at the perimeter of an excavation. Controlled blasting reduces cracking within perimeter walls and increases the stability of the openings (Wyllie & Mah, 2004). In open pit mines and quarries, controlled blasting is used to maintain safe walls and allow for steeper slopes, increasing the ratio of ore to waste removed, decreasing rock fall hazards, and minimizing the need for rock bolting and other supports. Another application of commercial explosives is in the production of rip rap or dimension stone, where controlled blasting techniques are required to produce material of exact shape and sizes.

2.5 Predominant explosives of environmental concern

Many explosive testing ranges and training ranges in the U.S. and Canada have been found to contain explosive residues and transformation products in soil, often at some time after use, as indicated in Figure 4 (U.S. Army Corps of Engineers, 2006). These include hand grenades, rifle grenades, antitank rockets, demolition explosives, tank firing ammunition, mortars, various artillery, and explosive testing and bombing ranges. Training at many of these ranges is conducted with different types of explosive devices that contain a variety of energetic formulations.

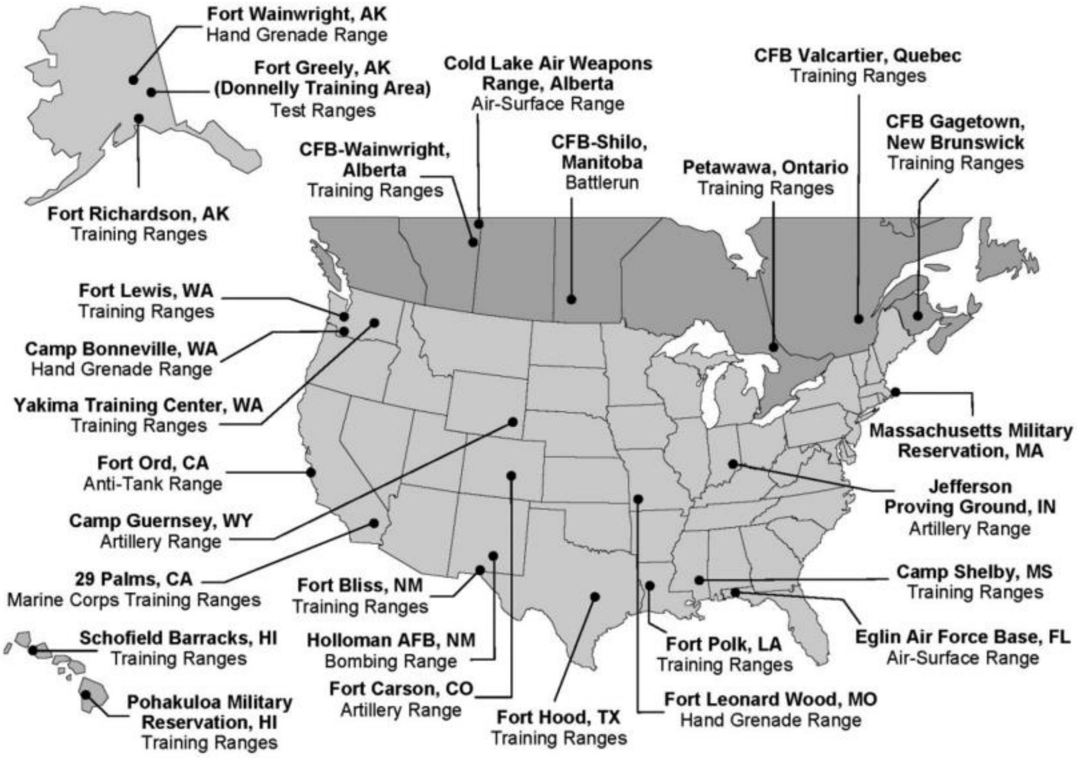


Figure 4: United States and Canadian explosive testing ranges where explosives have been identified in soil.
(Source: U.S. Army Corp of Engineers, 2016).

There are certain explosives identified in the literature as being commonly identified in soil and groundwater samples from locations where explosives have been continuously used. These compounds are often organic in nature which will persist in the environment and degrade very slowly under natural conditions. These compounds are often fat soluble and can accumulate in the food chain (Henry & Heinke, 1989). Explosives can also contain inorganic compounds such as lead which can accumulate in soil and sediments and can be taken up by plants. The predominant explosives of environmental concern commonly found in contaminated soils include TNT, picric acid, PETN, TATP, RDX, and HMX, along with the commercial explosive ANFO.

2.5.1 TNT ($C_6H_2(NO_2)_3CH_3$))

TNT, $C_6H_2(NO_2)_3CH_3$, is commonly used as a filling for artillery shells, as it easily can be melted by steam at 80-90°C and can be poured into shell cases at about 80-85°C. The amino reduction products of TNT are commonly encountered in both soil and groundwater. The mono amino transformation products of TNT, 4-amino-2,6-dinitrotoluene (4ADNT) and 2-amino-4,6-dinitrotoluene (2ADNT), are more common than the diamino products, 2,4-diamino-6-nitrotoluene (2,4DANT) and 2,6-diamino-4-nitrotoluene (2,6DANT). The triamino product, 2,4,6-triaminotoluene (TAT), has been reported in the laboratory, but is not observed in the environment. A photodegradation product of TNT, 1,3,5-trinitrobenzene (TNB), is also common in contaminated soil and groundwater, especially on sites where wastes received exposure to sunlight. The bioaccumulation of TNT and its biodegradation products in living organisms is much greater than the bioaccumulation of TNT by itself (Belden, Ownby, Lotufo, & Lydy, 2005).

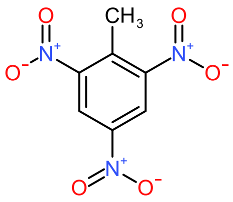


Figure 5: TNT molecule.

The chemical reaction for the detonation of TNT is provided in Equation 1 (Brown, 1998):

$$C_7H_5N_3O_6(s) \rightarrow 3.5CO(g) + 2.5H_2O(g) + 1.5N_2(g) + 3.5C(s) \quad \text{[Equation 1]}$$

2.5.2 Picric acid (2,4,6-trinitrophenol, $C_6H_2(NO_2)_3OH$)

Picric acid is one of the most acidic and strongly nitrated organic compounds. Munitions containing picric acid can found in sunken warships. Over time, the buildup of metal picrate complexes makes them extremely hazardous as they are easily shock sensitive to detonation. It is recommended that shipwrecks that contain such munitions not be disturbed in any way. The hazard may be reduced when the cartridge casings become corroded enough to admit seawater, because picric acid is water-soluble. Picric acid is found more commonly in groundwater than in soil due to its high aqueous solubility.

There are several significant problems associated with the use of picric acid, due to its acidity. It forms sensitive compounds with metals such as copper, which were used in parts of fuses and detonators. Its major drawback in historical use was that picric acid did not always detonate completely. The U.S. improved the performance with a material which detonated more effectively and reliably and was not likely to form sensitive compounds with parts of the fuse. This is ammonium picrate, Explosive D, and is extremely safe and reliable as an explosive and has a very long shelf-life but is not particularly powerful (Explosive Effects and Applications by Zukas).

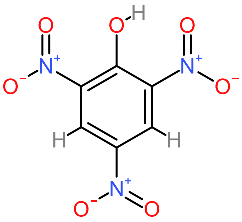


Figure 6: Picric acid molecule.

2.5.3 PETN (Pentaerythritol tetranitrate, ($C(CH_2ONO_2)_4$)

PETN is a nitrate ester of pentaerythritol. PETN contains five carbon atoms and a neopentane skeleton. It is commonly used in detonating fuses. PETN has low volatility and low solubility in water, and will therefore present a low bioavailability risk for most organisms. Its toxicity and transdermal absorption are both relatively low. PETN is not usually found in large amounts on military ranges and in explosive testing ranges, as it not produced in large amounts (Williams, Reddy, Quinn, & Johnson, 2015).

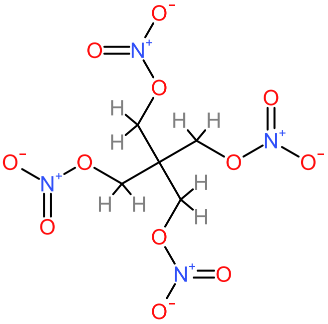


Figure 7: PETN molecule.

2.5.4 TATP (Triacetone triperoxide, $C_9H_{18}O_6$)

TATP, acetone peroxide, is an both organic peroxide and a primary explosive. The type of acid used during TATP preparation has a significant impact on its environmental stability (Matyas & Pachman, 2013). TATP prepared using sulfuric or perchloric acid will decompose more quickly in the environment than TATP prepared with other acids. TATP does not react with water or heavy metals (Oxley, Smith, Bowden, & Rettinger, 2013). TATP has not been used historically in many industrial or military applications. The precursors for preparing TATP can now be purchased individually from internet sources. This has led to the increased use of TATP by terrorists and extremists for the preparation of detonators and main explosive charges in homemade devices (Michalske, Edelstein, Sigman, & Trewhella, 2007). Until about 2015, explosive detecting instruments, such as those in airports, were not typically set to detect nonnitrogen based explosives, including TATP. Due to its increased use in several terrorist bomb attacks, the need for research and testing into this explosive compound to develop counter-terrorism measures will also increase. Therefore, it is likely that TATP will increasingly be detected in soil from active explosive testing ranges. The cyclic trimer form indicative of TATP is shown in Figure 8.

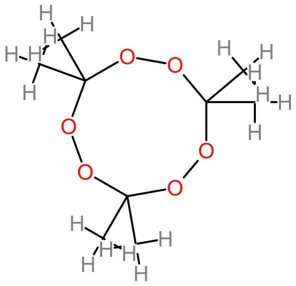


Figure 8: TATP molecule.

2.5.5 RDX (1,3,5-trinitro-1,3,5-triazinane, ($O_2N_2CH_2)_3$)

RDX is a white solid without smell or taste and is widely used as a military explosive. Chemically, it is classified as a nitroamine and is considered a more energetic explosive than TNT. It was used widely in World War II and remains common in military applications. RDX is often used in mixtures with other explosives and can be found as the explosive agent in C-4 plastic explosive. It is stable in storage and is considered one of the most energetic of high explosives.

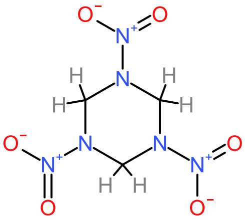


Figure 9: RDX molecule.

The chemical reaction for the detonation of RDX is provided in Equation 2 (Brown, 1998):

$$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g) \quad \text{[Equation 2]}$$

2.5.6 HMX (Octogen or Tetramethylenetetranitramine, $C_4H_8N_8O_8$)

HMX, also called octogen, is a powerful and relatively insensitive nitroamine high explosive, chemically related to RDX. The molecular structure of HMX consists of an eight-membered ring of alternating carbon and nitrogen atoms, with a nitro group attached to each nitrogen atom. Because of its high molecular weight, it is one of the most potent chemical explosives manufactured.

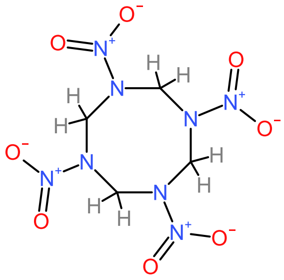
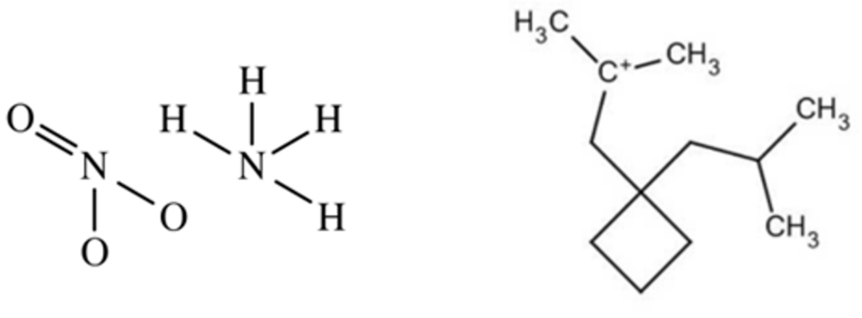


Figure 10: HMX molecule.

2.5.7 ANFO

Ammonium nitrate fuel oil (ANFO) consists of prilled ammonium nitrate to which has been added a stoichiometric quantity of fuel, in the form of a petroleum derivative such as diesel oil (7% w/w). As ANFO is a commonly used commercial explosive used in many modern activities, from mining to road construction to demolition, it should be readily identified in many locations where explosives use has occurred. This can be connected to the current study as it will probably be identified in soils from active explosive testing ranges.



Ammonium nitrate (NH_4NO_3)
(source: Encyclopedia Britannica, 2023)

Diesel fuel
(source: Meraj Oil, 2023)

Figure 11: ANFO chemical structure.

(Source: Investigating the differences between diesel fuel and gasoline, MerajOil.com, April 14, 2023; Ammonium nitrate, Encyclopedia Britannica, April 14, 2023.)

In conclusion, there are various explosive materials that can be used in military operations, research and development testing operations, and in commercial applications that will introduce explosives into soil and into the surrounding environment. The composition and mode of action of each explosive is varied, but all are spread out across the landscape during the process of detonation. This can introduce explosive compounds, metals, plastics, and other materials into soil, often remaining in place unaltered for long periods of time. Modern explosives testing is used to not only demonstrate key considerations such as long-term stability of the explosive compound, limited sensitivity to accidental stimuli, initiation efficiency, safe handling, and storage compatibility with other materials, but also to measure key properties including detonation pressure and velocity and impact dynamics of explosive fragments. Many explosive compounds are also embedded inside more complex explosive devices and must be insensitive to extreme temperatures, moisture, and atmospheric carbon dioxide (Matyas & Pachman, 2013). All of these reasons indicate that continued use and need for explosive testing ranges and their associated research and development activities.

Chapter 3 provides a literature review and will provide a broad overview of the current research into explosives and how they serve to contaminate the environment.

CHAPTER 3 LITERATURE REVIEW

3.1 Introduction

Several sources of explosive contamination, including partial detonations, improper storage, and release during production and transport, lead to pollution, negative plant health, and threats of acute and chronic health concerns (Manley, Sagan, Fritschi, & Burken, 2019). Prolonged exposure to gunfire and high-explosive blasts also lead to auditory complaints among professionals in the military service (Kubli, Pinto, Burrows, Littlefiedl, & Brungart, 2017). In this context, researchers have investigated the development of green explosives that can replace traditional explosive materials((Bolter, 2018); (Li, et al., 2017); (Zhang, et al., 2019)). Scholars have also explored the emerging materials, devices, and ignition principles behind a safer and more controlled use of energetic materials as primers (Lundgaard, et al., 2019). However, in order to appropriately advance to green explosives, it is critical to first understand the specific nature of contamination by various kinds of explosives during their manufacture and testing. In this context, Oluwoye (Oluwoye, Dlugogorski, Gore, Oskierski, & Altarawneh, 2017) noted that a detailed understanding of the formation mechanism and the survival of pollutants from the detonation of explosives is critical. Further, Broomandi (Broomandi, Guney, Kim, & Karaca, 2020) suggested that a comprehensive scientific framework be developed and used to examine the human health risks posed by these contaminants. The aim of this study is to explore the specific contaminants and pollutants that are released into the environment during the testing of different classes of explosive materials and to analyze the associated health impacts.

For the review of literature, Google Scholar search engine was used to gather the relevant research works. Search terms included “explosives,” “primary explosives,” “secondary explosives,” “tertiary explosives,” “propellants,” “explosive testing,” “environmental impacts of explosives,” “military explosives,” “commercial explosives,” “green primary explosives,” “green secondary explosives,” “green propellants,” “emulsion explosives,” “green emulsion explosives,” “explosive pollution,” “air pollution by explosives,” “water pollution by explosives,” “soil pollution by explosives,” “explosive contamination,” and “explosive contamination treatments.” The identified articles were critically reviewed, and the ones relevant to the research phenomenon under study were included in the literature review. A total of 75 research works were included in the literature review; out of these, 66 (88%) were published between 2016 and 2021 and 9 (12%) were published before 2016 and not before 2012.

This chapter will be organized as follows. A systematic review of literature will be presented. The literature review begins with a discussion on the different types of explosives’ classifications and a description of the recent advances in different kinds of explosives. Next, the characterization of different explosives will be discussed, followed by a description of the different kinds of pollution caused by explosive materials. Finally, the existing detection and treatment technologies for addressing explosive material-related contamination will be elaborated on, and the dearth of studies on the testing of different kinds of explosives will be highlighted. The chapter will end with a conclusion to demonstrate how the review of literature ultimately led to the identification of the research gap to be addressed.

3.2 Literature review

An explosive is defined as a chemical substance or mixture of chemical substances, which when subjected to heat, percussion, detonation, or catalysis, undergoes a very rapid decomposition accompanied with the production of a large amount of energy. A large volume of gases, considerably greater than the original volume of the explosive, is also liberated (Agrawal, 2010). Explosives are utilized for several applications in different sectors. A number of researchers have focused on different aspects of explosives and their anthropological uses. In this regard, Klapec (Klapec, Czarnopys, & Pannuto, 2020) conducted a review to illustrate that researchers in the field had extensively investigated theoretical and commercial explosive manufacturing, explosive detection technologies, performance and physics of explosives, sampling improvements, and novel or improved analytical techniques for the identification of explosives. In the following sections, the above topics as well as other aspects of explosives are explored in detail.

3.2.1 Classification of explosives

A number of researchers have put forward different classification basis of explosive materials. For instance, Chatterjee (Chatterjee, Deb, Datta, Walther, & Gupta, 2017) presented the classification of explosives based on their functionalities: low explosives and high explosives. According to the authors, low explosives or deflagrating explosives, such as gunpowder, are majorly used for propelling as these materials ignite spontaneously and undergo quick combustion. On the other hand, high explosives or detonating explosives, like trinitrotoluene (TNT), are primarily used for generating shock waves that propagate across the explosive at a high speed. This type of explosives sets off spontaneously without the need of any external source of oxygen (Chatterjee et al., 2017). Chatterjee (2017) further divided high explosives into primary and secondary explosives; the former detonates on application of heat, friction, or mechanical shock and do not burn, while the latter are relatively insensitive to heat, shock, or friction and they deflagrate in small unconfined quantities and detonate when confined.

The classification of explosives into low and high explosives was also made by Zou (Zou, 2016). However, unlike Chatterjee (2017)'s classification based on the explosives' functionalities, Zou (2016) made their classification on the basis of detonation velocity. Low explosives were defined as compounds where the associated rate of decomposition proceeds through the material at speeds lower than the speed of sound, and high explosives were defined as compounds where the associated explosive shock front passes through the material at speeds higher than the speed of sound, i.e., at supersonic speeds (Zou, 2016). Zou (2016) further presented the classification of explosives with respect to their sensitivity as primary, secondary, and tertiary explosives, and the classification of explosives based on their applications as commercial and military explosives.

In an approach very similar to that adopted by Zou (2016), Zapata and García-Ruiz (Zapata & Garcia-Ruiz, 2020) provided a classification of explosives based on their velocity of detonation. The classes were high energy explosives that were further divided into primary, secondary, and tertiary explosives and low energy explosives. Zapata and García-Ruiz (2020) also provided another commonly used classification depending on the application of explosives: military explosives, commercial explosives, and homemade explosives. Military explosives were defined as high explosives that had to meet the required levels of performance, functionality, and safety during handling, transport, and storage, and these materials had to be powerful, insensitive to weak- and medium- intensive stimuli, and requiring detonators to detonate. Commercial explosives were defined as those materials used for commercial purposes, such as in mining, for demolitions, and in firearm, rocket, and pyrotechnic propellants. Finally, homemade explosives were defined as those that can be prepared at home and are not available commercially because of their extreme instability and sensitivity (Zapata & Garcia-Ruiz, 2020).

An additional classification of explosive materials based on their chemical composition was also made by both Zou (2016) and Zapata and García-Ruiz (2020). Zou (2016) presented a relatively simple classification on this basis, which included single explosive substances and composite explosive mixtures. Single explosive materials were described as chemical compounds containing a single well-defined molecule, which primarily decomposes into gaseous reaction products, such as N_2, CO_2, and H_2O, while composite explosive materials were a mixture of two single explosive materials, a mixture of a fuel and an oxidizer, or an intermediate mixture comprising one or more single explosives with a fuel, an oxidizer, or both (Zou, 2016). Zapata and García-Ruiz (2020) presented an updated and substantially more elaborate classification of explosives based on their chemical composition. Explosives were divided into (i) pure individual/single explosives and (ii) explosive mixtures. Pure individual/single explosives were further classified as organic and inorganic explosives; organic explosives could be peroxide explosives, nitro-explosives, organic azides, halogen amino compounds, or azo/diazo compounds, and inorganic explosives could be metal-containing or metal-free compounds. Explosive mixtures could contain two or more single explosive materials, one or more single explosive materials and fuels, oxidizers, binders, or plasticizers, or only fuels and oxidizers (Zapata & Garcia-Ruiz, 2020).

The review of literature thus shows various classifications of explosives depending on their nature, properties, characteristics, and applications. Classifications made by different researchers seemingly overlap at certain instances. While these intersections between different classes of explosives may seem complex, a thorough examination of the various groups of explosives illustrates that all explosive materials have certain similarities as well as distinctions. A number of specific types of explosives and their recent progress are described in the next few sections.

3.2.2 Primary explosives

Several researchers have investigated primary explosives in detail, including their history and recent progress. Oyler (Oyler, 2014) defined primary explosives as explosive materials that can be relatively easily initiated through external stimuli, such as impact, shock, heat, friction, or electrostatic discharge. The primary objective of these powerful explosives is to trigger the more potent and harder to initiate secondary energetics, and an important property of an effective primary explosive is a swift deflagration to detonation transition (DDT); this implies that once the explosive is initiated, it proceeds rapidly from combustion to detonation (Oyler, 2014). Oyler (2014) further discussed traditional primary explosives commonly used for military and commercial applications and described their harmful environmental and health-related impacts. The compounds lead azide and lead styphnate, which are the majorly used primary explosive materials in both the commercial and military sectors, were noted to be harmful to the environment owing to their heavy metal lead content (Oyler, 2014). This critical issue was cited by Oyler (2014) to provide a segue to the need for developing green explosives as an alternative to traditional primary lead-based explosives.

Subsequently, a number of researchers have investigated green primary explosives. For instance, Li (Li, et al., 2017) synthesized four potassium-based primary green explosives and demonstrated their promising characteristics. The researchers developed the four salts based on nitraminofurazan using a simple preparation method, and based on their systematic analyses, demonstrated that all the synthesized salts exhibited desirable impact sensitivities (1–2 J), fairly low electrostatic discharge sensitivities (0.030–0.196 J), and comparably low friction sensitivities (12–168 N), making them attractive and suitable candidates to be used as primary explosives (Li, et al., 2017). In a similar study on green primary explosives, Zhang (Zhang, et al., 2019) described an environmentally friendly method to prepare primary green explosives with highly potential characteristics, and they used this method to develop five novel green primary explosives without metal ion and organic pollution. The synthesized green primary explosives had thermal decomposition temperatures above 200°C, and two of the developed materials could maintain long-term stability at 100°C. The developed green explosives exhibited detonation and safety properties that were significantly better than those of traditional primary explosives, such as lead azide, and four of the synthesized explosive materials were found to demonstrate fast deflagration-to-detonation transition abilities (Zhang, et al., 2019). The above study findings demonstrated the high potential of green primary explosives as an alternative to traditional primary explosives.

A few scholars have investigated the progress of green primary explosive materials. In one such study, Manzoor (Manzoor, Cao, & Zhang, 2021) discussed the recent advances in the synthesis of primary green explosives and the existing challenges to replace traditional primary explosives with these green alternatives. The authors reported the synthesis of a number of potassium-based primary explosives in recent years, many of which had good thermal stability and good oxygen balance. Compared to traditional primary explosives, these potassium-based materials had better sensitivities and were prepared from cheap and easily available raw materials. However, the latter's complex synthesis method and low yield require further research (Manzoor, Cao, & Zhang, 2021). Through their study, Manzoor (2021) underscored the need for heavy metal-free primary explosives.

The review of literature illustrates the significance of primary explosives in both commercial and military sectors. Major research interest is currently focused on the design and development of green primary explosives in order to address the harmful environmental and health-related impacts of traditional primary explosives. Although considerable progress has been made in this regard, further research is required to synthesize more efficient green explosive materials and to study and address the challenges of introducing these materials in the market.

3.2.3 Secondary explosives

Although not quite as popular as primary explosives, a number of researchers have focused on secondary explosive materials. For instance, Shanmugaraju (Shanmugaraju, et al., 2017) synthesized a Troger's base-functionalized covalent organic polymer for the reversible adsorption and storage of secondary explosives from water. The authors synthesized a Troger's base-functionalized covalent organic polymer (TB-COP) and used it as an adsorbent for the efficient removal of picric acid (PA) from water. TB-COP was synthesized via a one-pot metal-free polymerization reaction, and it was found to be thermally stable up to 380 °C. Further, TB-COP had an excellent adsorption capacity of ~90% within a contact time of 60 minutes at a temperature of 298 K, and the adsorption efficiency was found to increase as the temperature was increased. Notably, Shanmugaraju (2017) observed that the TB-COP compound was capable of safely storing PA for a long duration, with no leakage or significant loss in the extraction efficiency. Although this study did not directly involve secondary explosive materials, the study findings presented valuable insights regarding how novel materials can be designed to detect and store these explosives.

In another study, Konovalov (Konovalov, Yudin, Kolesov, & Ul'yanov, 2019) demonstrated the high potential of using additives for enhancing the heating efficiency and ignition rate of secondary explosives. Specifically, the authors examined the possible enhancement of the heating efficiency and ignition rate of secondary explosives by the use of photo-absorbing additives under continuous near-infrared laser radiation. The authors used powders of three secondary explosive materials, PETN, TNT, and ε- CL-20, and prepared samples in the form of capsules by pressing the raw powders. Carbon black, CuO, nanoscale Al (nAl), and carbon nanotubes were used as the photosensitizers. Among these photosensitizers, the nAl photosensitizer was found to be the most suitable for use with explosives owing to its relatively high absorption properties, which were comparable to those of carbon black, and its easy and homogenous dispersion within the volume of the energetic material. The addition of nAl was found to increase the efficiency of ε-CL-20 laser heating by 10–100 times, and the optimum nAl mass fraction was found to be 0.5% (Konovalov, Yudin, Kolesov, & Ul'yanov, 2019). Through their study, the authors demonstrated that the properties of existing secondary explosive materials could be efficiently improved by considering appropriate additives and suitable methods.

A few scholars have also investigated potential green alternatives to traditional secondary explosives. In one such study, Bolter (Bolter, 2018) discussed the synthesis and characterization of novel environmentally benign secondary explosives based on azoles. The author noted that nitropyrazoles were valuable energetic materials owing to their wide variety of substitution patterns. With regard to nitropyrazoles, the mono-nitropyrazoles were noted to be low energetic, and trinitropyrazoles' intensive synthetic protocol and high sensitivity were highlighted. Due to these undesirable characteristics of mono-nitropyrazoles and trinitropyrazoles, Bolter (2018) synthesized three dinitropyrazoles and characterized and compared their properties. The synthesized compounds were demonstrated to have relatively high thermal stabilities, low sensitivity values, and suitable detonation performances, which made them potential candidates for use as high energy density materials.

The existing literature shows a limited focus on secondary explosive materials. Although these explosives have been studied by some researchers, the aspect of designing and synthesizing green secondary explosive materials has not been intensively addressed. This warrants further research in this area.

3.2.4 Propellants

Propellants are a kind of low explosive material that have attracted the interest of some researchers. According to Chaturvedi and Dave (Chaturvedi & Dave, 2019), propellants are highly energetic materials that produce high-temperature gaseous products on combustion. Solid propellants have a high material density, which results in a high energy density that is required for generating an adequate propulsive force. Based on their constituent ingredients and the conditions under which they are linked, Chaturvedi and Dave (2019) classified solid propellants into two groups: heterogenous solid propellants and homogenous solid propellants. Homogeneous propellants are those with a homogenous physical structure throughout; in these propellants, the constituent ingredients are chemically linked. Heterogenous propellants, on the other hand, have physically mixed ingredients (i.e., oxidizers and fuels), which results in a heterogeneous physical structure (Chaturvedi & Dave, 2019).

Similar to research involving primary and secondary explosives, researchers have looked into the progress of propellants. For instance, Yadav (Yadav, Srivastava, & Varma, 2021) reviewed the recent advances in catalytic combustion of ammonium perchlorate (AP)-based composite solid propellants (CSPs). The authors noted that combustion catalysts are highly suitable for applications in propellant technology as the utilization of catalytic materials in the formulation of propellants is a convenient approach that has demonstrated higher potential in improving the propulsive performance of these materials compared to other techniques. In this regard, AP was noted to be a common oxidizer that is used in CSPs due to its ability to deliver high burning rate with inclusion of combustion catalysts, improved mechanical properties, and higher performance than other inorganic oxidizers. Further, Yadav (2021) noted that catalysts containing transition metal oxides, such as ferric oxide, cobalt oxide, manganese oxide, chromium oxide, and copper chromite, significantly enhanced the decomposition process of AP-based CSPs. The observations made in the above study presented valuable insights regarding existing solid propellants and their potential improvements.

Some researchers have synthesized a number of interesting compounds that can have beneficial applications in society. In such a study, Chen (Chen, et al., 2021) investigated nitrated bacterial cellulose-based energetic nanocomposites as propellants and explosives for military applications. The authors introduced a nitrated bacterial cellulose (NBC) energetic binder in order to develop an NBC-based nanocomposite energetic material (nEM). To achieve this, a combined simple and safe sol-gel method and freeze-drying technology was utilized. The composites were found to be of the nanometer-scale, which indicated restricted crystal growth of the explosive particles. Further, Chen (2021) found that the nitramine explosive particles were homogenously dispersed and embedded in the three-dimensional porous cross-linked construction of the NBC gel matrix. According to the thermal analysis, the peak temperature of the composite was reduced and produced significant heat release during the decomposition process (Chen, et al., 2021). The findings of this study demonstrated the promising potential of NBC-based energetic composites used in explosives and propellants in the military.

Recently, a number of researchers have looked into green propellant materials. For instance, Abd-Elghany (Abd-Elghany, Klapotke, & Elbeih, 2018) prepared a novel green high energy dense oxidizer, 2,2,2-trinitroethyl-formate (TNEF), and its propellant formulation based on hydroxyl-terminated polybutadiene (HTPB) as a binder. Based on the results of non-isothermal thermogravimetric analysis and the iso-conversional (model-free) methods "Kissinger, Ozawa and Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS)," the newly developed TNEF oxidizer and its formulation based on HTPB were observed to have chlorine-free decomposition products and higher performance characteristics than the traditional propellants (Abd-Elghany, Klapotke, & Elbeih, 2018). In another study on green propellants, Luo (Luo, Xia, Zhang, Song, & Zhang, 2020) developed a hydrogen peroxide adduct of ammonium cyclopentazolate as a green propellant component. The synthesized material exhibited a high oxygen balance, high calculated detonation velocity and pressure, and an impressive specific impulse (Luo, Xia, Zhang, Song, & Zhang, 2020). The findings of the above studies demonstrate that research focusing on green alternatives to traditional propellants is gradually gaining momentum.

In the context of research on different kinds of explosives, a number of researchers have investigated different aspects of propellants. This includes providing an appropriate definition for these materials, making suitable classifications, and studying the properties of these materials to explore how they can be improved. Researchers have also focused on the development of green propellants; however, this aspect requires further research with regard to addressing the challenges of introducing green propellants as an alternative to traditional ones.

3.2.5 Emulsion explosives

Emulsion explosives are another type of explosive material that have garnered considerable research interest. Emulsion explosives are new-generation industrial explosives that do not contain nitro compounds. These explosives are multi-phase mixtures that have a gel-like consistency and are produced by blending supersaturated solutions of inorganic nitrates with paraffin hydrocarbons (Mertuszka, Fuławka, Pytlik, & Szastok, 2020). A number of researchers have investigated the properties of emulsion explosives. For example, Yao (Yao, et al., 2021) examined the explosion temperature structures of safe, water-resistant, and environmental-friendly emulsion explosives. The authors used the two-color pyrometer technique to measure the transient temperature field of emulsion explosives with different contents of TiH_2 powders. Based on their experimental results, Yao (2021) concluded that the introduction of TiH_2 powders significantly increased the explosion temperature and fireball duration of the emulsion explosives.

In the context of research on emulsion explosives, a number of scholars have studied these materials with relation to their commercial applications. In such a study, Domozhirov (Domozhirov, Pytalev, Nosov, Nosov, & Gaponova, 2019) explored the qualitative explosive characteristics of emulsion explosives with regard to the mineral deposits of the southern Urals, where open-pit mining is performed with the use of emulsion explosives. In another study involving the application of emulsion explosives, Khomenko (Khomenko, Kononenko, Myronova, & Savchenko, 2019) explored the use of these materials for drilling and blasting operations. The above studies highlighted the extensive research on several kinds of applications of emulsion explosives.

3.2.6 Manufacturing and testing of explosives

According to the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 2021), explosives manufacturing can be classified as commercial and military explosive manufacturing. The former involves the production of ammonium nitrate-based explosives, dynamite, and nitroglycerin, while the latter involves the production of military-grade explosives, such as TNT, HMX, and RDX (U.S. Environmental Protection Agency, 2021). Existing literature, particularly research conducted in the last five years, does not adequately focus on the manufacture of different classes of explosives and the associated environmental impacts. The studies that do touch on this aspect generally look at improving existing manufacturing methods. In one such study, Biessikirski (2020) studied the provenance of ammonium nitrate for the manufacture of ANFO explosives and observed that the provenance of ammonium nitrate was essential for ANFO production. Similarly, Biessikirski (Biessikirski, et al., 2021) examined the possible application of polyolefin waste-derived pyrolysis oils for the manufacture of ANFO explosives and found that post-pyrolysis FOs could be used as the flammable component in ANFOs. In another study, O'Grady (O'Grady, et al., 2020) focused on additive manufacturing (AM) of energetic materials and investigated the impacts of typical AM artifact or defect geometries on detonation propagation. Using the physical vapor deposition of explosive samples as a model system, the authors observed that the presence of a large triangular void affected the detonation front of high explosive materials (O'Grady, et al., 2020). O'Grady (2020) observed a number of associated phenomena, such as jetting, pre-shock of the material ahead of the detonation front, quenching of the detonation front, partial reaction of the material, and interaction of the detonation front with shocked material after passing the void.

The few studies that have involved the testing of explosives included conducting impact tests of these materials. For instance, Xiao (Xiao, Sun, Zhen, Guo, & Yao, 2017) designed and conducted two different low velocity impact experiments to study the impact damage behavior of polymer bonded explosives (PBXs). The authors adopted multi-axial loading experiments, in which the designed loading styles ensured easier specimen recycling and avoided secondary damage to the samples. Systematic analyses were performed wherein the PBX samples’ damage mechanisms and corresponding fracture modes under different impact loadings were analyzed, and a model with viscoelastic response and statistical fracture for PBX was developed (Xiao, Sun, Zhen, Guo, & Yao, 2017). Similarly, Manner (Manner, et al., 2020) prepared 13 distinct samples of TNT explosives and tested their particle sizes and impact sensitivities. The objective of the study was to examine whether differences in the particle sizes of TNT explosives obtained by a freshly synthesized method versus a historical lot sample resulted in different impact sensitivity values. The authors observed that although the particle sizes of the samples varied between 44 and 1502 µm, the corresponding impact sensitivities mostly fell within error (Manner, et al., 2020). In a more recent study, Marrs (Marrs, et al., 2021) compiled a data set with over 450 impact test results of the standard explosive pentaerythritol tetranitrate (PETN) from 1959 to 2020. They found that the test laboratory, test method, and use of grit paper had significant effects on the measured sensitivity of PETN (Marrs, et al., 2021). The above studies used impact testing of explosives to study different aspects of these materials.

One in-depth study that involved the testing of explosive materials was conducted by Kovacs (Kovacs, Vasilescu, Gheorghiosu, Rus, & Jitea, 2017). Kovacs (2017) discussed the findings of studies associated with the tests performed within INSEMEX explosives testing in the context of improving the security measures while using explosives in firedamp hazardous mines. The authors discussed the development of permitted (i.e., firedamp-safe) explosives and electrical detonators. The former required meeting the requirements of maximum explosion heat, work capacity, and oxygen balance, while providing good detonation performance, and the latter involved ensuring complete detonation of the explosive charges, coating the detonators with inhibiting substances, and inhibiting detonators with incandescent aluminum shells (Kovacs et al., 2017). Kovacs (2017) discussed three testing methods in the context of firedamp-safe explosives (i.e., fire-damp safe high explosives, detonating cords and electrical detonators) in detail. While this study was one of the limited ones to address the testing of explosives in a specific context, the authors failed to elaborate on the associated environmental impacts.

3.2.7 Characterization of explosives

A number of researchers have considered the characterization of different properties of explosive materials. In this regard, some researchers have focused on the detonation properties of explosives. In such a study, Li (Li, Li, Yan, Wang, & Wang, 2018) developed a novel velocity probe-based technique that could be applied for the reliable and convenient determination of commercial explosives' detonation pressure. The developed velocity probe allowed for the recording of continuous velocities of detonations and shock waves. With the use of the novel probe and the impedance matching method, Li (2018) set up a series of measuring devices to determine the velocities of shock waves in a number of inert materials, such as water, Plexiglas, and paraffin wax. Using their velocity probe-based technique, Li (2018) demonstrated the reliable and convenient determination of commercial explosives' detonation pressure. In a similar study, Balakrishnan (Balakrishnan, Pradhan, & Dhekne, 2019) investigated the detonation behavior of conventional blasting of explosives and other explosive consumption reduction techniques that induce air gaps using plastic tubes, plastic balls, or plastic bottles in the explosive columns. The authors observed that the velocity of detonation varied between 5321.6 m/s and 4544.2 m/s in conventional site mixed emulsion column and between 5123.4 m/s and 4274.2 m/s in distributed spherical air gap column. The detonation behavior was found to be stable and similar in both cases (Balakrishnan, Pradhan, & Dhekne, 2019).

In another study, Zhao (Zhao, Wang, Fang, Fan, & Du, 2021) explored the shockwave propagation characteristics of spherical and cylindrical explosives. The authors also used explosion experiments to investigate the damage features of reinforced concrete (RC) slabs under spherical and cylindrical explosives with a certain length/diameter (*L/D*) ratio. Zhao (2021) found that the shape of the explosives directly predicted the shape of upper surface crater damage and that the spall damage area of the RC slabs became larger with an increase in the *L/D* ratio. For a specific value of the *L/D* ratio, the cylindrical explosive was found to induce a larger spall damage than the spherical explosive. Through their study, Zhao (2021) underscored the significance of the effect of the cylindrical charge in the antiknock design of the RC structure. Another study involving shockwave propagation was carried out by Hargather (2013). Hargather (Hargather, 2013) conducted experimental measurements of shockwave propagation from C4 explosions, wherein they visualized the shockwave propagation through background-oriented schlieren. Hargather (2013) presented two distinct processing techniques for BOS analysis: image subtraction and image correlation. The image subtraction technique was observed to provide a higher resolution for identifying the location of a shock wave propagating into still air, while the image correlation technique was more suitable to identify shock reflections and multiple shock impacts in a region with complex flow patterns. The author used optical shock propagation measurements in order to predict the peak overpressure and overpressure duration at different locations, and these measurements were compared to experimental pressure gage measurements. A good agreement was obtained between the overpressure predictions and the pressure gage measurements; the overpressure duration prediction was observed to be within an order of magnitude of the experimental measurements. The findings of the above studies present certain interesting characteristics of explosive materials.

The characteristics of explosives materials can be used to distinguish between their different types. To illustrate this, Schachel (Schachel, Stork,, Schulte-Ladbeck, Vielhaber,, & Karst, 2020)used three analytical techniques to differentiate between military and commercial explosives based on their overall composition. A total of 36 samples of commercial and military explosives from Germany and Switzerland were tested. The authors developed an approach involving high-performance liquid chromatography and high-resolution mass spectrometry (HPLC-HRMS) and considered 27 analytes, including high-energy compounds, synthesis by-products, and additives. The methods of HPLC-HRMS and X-ray diffraction (XRD) were used to obtain molecular information on each sample, and X-ray fluorescence (XRF) spectroscopy analysis was used to determine the corresponding elemental compositions. Based on the results of all the three considered techniques (i.e., HPLC-HRMS, XRD, and XRF spectroscopy), the authors identified 41 different additives as diagnostic analytes. Further, a unique analytical fingerprint was obtained for all the samples, which allowed for differentiation of the samples (Schachel, Stork,, Schulte-Ladbeck, Vielhaber,, & Karst, 2020). Notably, the methods used in this study could be used for creating and populating a database on explosives that could be used for several commercial applications.

Some researchers have conducted comparative studies to characterize different kinds of explosive materials. For instance, Figuli (Figuli, Kavicky, Jangl, & Zvakova, 2018) compared the efficacy of homemade and industrially made ammonium nitrate fuel oil (ANFO) explosives as improvised explosive devices. The authors noted that homemade explosives had 75% lower efficacy than industrially made explosives. This was based on the preparation of the explosives. Homemade explosives were not mixed well, were made from low-quality raw material, and contained chemical impurities and water (Figuli, Kavicky, Jangl, & Zvakova, 2018). Similarly, Biessikirski (Biessikirski, Kuterasinski, Dworzak, Pyra, & Twardosz, 2019) compared the structure, morphology, and topography of different ANFO samples. Specifically, the authors used ammonium nitrate porous-prilled (AN-PP), which is a substance that is applied in the mining industry, and an ANFO material used as mineral fertilizer, AN-F. The two samples were found to have the same structure, but they differed in morphology. Notably, AN-PP had several characteristics cracks on the crystal surface, which enabled improved absorption of fuel oil, directly affecting the blasting abilities of the explosive (Biessikirski, Kuterasinski, Dworzak, Pyra, & Twardosz, 2019). In another comparative study, Lease (Lease, et al., 2021) examined the impact sensitivity of 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX) and 3,3’-diamino-4,4’-azoxyfurazan (DAAF). During impact testing of the two materials, Lease (2021) observed the formation of ignition sites in both HMX and DAAF. However, only the HMX explosive demonstrated ignition sites that propagated to a deflagration at low firing speeds. Further, the authors found that the presence of grit particles increased the occurrence of ignition sites in DAAF at lower firing speeds (Lease, et al., 2021). In the above studies, specific characteristics of explosive materials were highlighted by comparison with other similar explosives.

3.2.8 Detection of explosives

The characterization of explosive materials paves the way for the detection of these materials in different contexts. According to Kielmann (Kielmann, Prior, & Senge, 2018), spectroscopy- and spectrometry-based detection techniques are highly suitable for detecting explosive materials due to these methods’ facile interaction with chemical sensors and good detectability. As such, techniques such as colorimetrics, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), ion mobility spectrometry (IMS), Raman spectroscopy, and Fourier-transform infrared spectroscopy (FTIR) have been widely used for the detection of these materials (Kielmann, Prior, & Senge, 2018). Recently, a number of researchers have looked into using these techniques for the detection of explosive materials and explosive material-related pollutants. For instance, Ben-Jaber (Ben-Jaber, et al., 2016) examined photo-induced-enhanced Raman spectroscopy for the detection of explosives, pollutants, and biomolecules. The authors observed that the combination of plasmonic nanoparticles with a photo-activated substrate resulted in a high signal enhancement for a wide range of small molecules, even those that typically have a low Raman cross-section. Ben-Jaber (2016) demonstrated that the induced chemical enhancement was because of an increased electron density at the noble-metal nanoparticles. The authors showed that the developed system could be universally used for detecting trace levels of explosives, biomolecules, and organic dyes (Ben-Jaber, et al., 2016). Notably, the developed substrates in this study were easy to fabricate, self-cleaning, and reusable, and examined technique may be extended by applying the same concept to other engineered plasmonic substrates.

In another study, Forbes (Forbes, Krauss, & Gillen, 2020) focused on the trace detection and chemical analysis of fuel-oxidizer mixture explosives. Based on their review of existing literature, Forbes (2020) noted that although chemical analysis of inorganic species and complex mixtures has been extensively studied by using a wide range of laboratory-based analytical methods, the implementation of these established techniques for detection of trace explosives has a number of associated challenges. A majority of these obstacles were noted to arise from the instrumental needs for rapid analysis, minimal or no sample preparation, and overall system cost. Specifically, Forbes (2020) noted that the methods and techniques established for the detection of organic explosives face major obstacles in the context of inorganic fuel-oxidizer mixture detection. For instance, certain traditional analytical techniques for environmental monitoring and screening, such as thermal desorption ion mobility spectrometry (IMS) or mass spectrometry (MS), face difficulties due to the refractory nature of inorganic oxidizers. In this regard, recent advances in high-temperature desorption and reagent acidification provide potential solutions to this limitation, and at the same time, help in maintaining the techniques' ability to screen a wide range of threat materials using the large base of already deployed systems (Forbes et al., 2020). Forbes (2020) noted that currently, several promising detection approaches are being investigated, including the efficient gradient elution moving boundary electrophoresis (GEMBE) technique.

This robust electrokinetic separation technique was discussed in detail by Krauss (Krauss, Forbes, & Jobes, 2021). Krauss (2021) utilized the GEMBE approach to separate and detect common inorganic oxidizers in commonly used fuel-oxidizer mixtures. The GEMBE system consisted of a sample reservoir and a run buffer reservoir, a short capillary measuring 5 cm, an applied electric field, and a pressure-driven counterflow. The GEMBE system provided a separation approach that allowed for the continuous injection of the sample and appropriate selectivity of analytes, and it did not require sample clean-up or filtration before the analysis. Krauss (2021) detected chlorate, nitrate, and perchlorate oxidizers from low explosive propellants, such as black powder and black powder substitutes, form pyrotechnics, such as flash powder, and from tertiary explosive mixtures, such as ammonium nitrate- and potassium chlorate-based fuel-oxidizer mixtures (Krauss, Forbes, & Jobes, 2021). The GEMBE system was demonstrated as a simple and efficient analysis tool, and its direct sample-in/answer-out nature that did not require sample clean-up or significant consumable filtration, presented a highly potential alternative to conventional injection capillary electrophoresis.

A number of other explosive material detection techniques have also been investigated. For instance, Masoumi (Masoumi, Hajghassem, Erfanian, & Rad, 2018) designed and fabricated a TNT explosive detector based on graphene field effect transistors (GFETs). The authors developed the biological receptor with a graphene-based FET by transferring graphene sheets from a Cu foil to the target substrates, which were functionalized by TNT peptide receptors. The fabricated sensor demonstrated high sensitivity and selectivity for the detection of TNT (Masoumi, Hajghassem, Erfanian, & Rad, 2018). The study results showed a change in the bipolar property of the GFET depending on the TNT concentration. Thus, Masoumi (2018) demonstrated the high potential of developing an easy-to-use, robust, and low-cost TNT detection method for sensitive, reliable, and semi-quantitative detection.

In another study, Irlam (2019) (Irlam, et al., 2019) developed a detection approach for generalizable extraction of trace explosives using dual-sorbent solid phase extraction (SPE) combined with liquid chromatography-high resolution accurate mass spectrometry (LC-HRMS). The authors used seven different sorbents (i.e., Oasis HLB, HyperSep Retain PEP and Isolute ENV+, HyperSep SAX, HyperSep NH2, Strata Alumina-N and Bond Elut CN) for the recovery of 44 organic explosives from model solutions. Overall, Oasis HLB and Isolute ENV+ were observed to yield the highest recoveries (> 80%). For the evaluation of matrix effects, a range of aqueous (river- and wastewater), solid (soil), dirty (road sign swabs), oily (oven hood swabs), and biological (dried blood) samples were chosen based on complexity and forensic relevance. Except for river water, the observed matrix effects were lowest using dual-sorbent SPE, with little or no compromise in recovery. Irlam (2019) applied the method to untreated wastewater and demonstrated efficient detection of new explosives traces. The method developed in this study and its efficiency in real-life contexts demonstrated its high potential for detecting explosive-related sources of environmental toxicity. In another study, Carton (Carton, et al., 2017) focused on munitions and explosives of concern (MEC) present in United States waters as a result of live-fire testing and training, combat operations, and sea disposal. The authors developed a process for selecting appropriate MEC detection technologies by synthesizing historical research, characterizing physical sites, reviewing remote sensing technologies, and conducting in-field trials (Carton, et al., 2017).

The review of literature related to the detection of explosive-related materials illustrates that several traditional techniques are being investigated and improved and novel and efficient techniques are being developed. The methods and technologies studied in this context could be a good place to start for exploring the different explosive-related pollutants released during the manufacture and testing of different classes of explosive materials. Combining the findings of studies involving the characterization and detection of explosives could help develop strategies for identifying specific pollutants released by various explosive materials, which could ultimately be conducive towards managing the environmental impacts caused by these materials.

3.2.9 Environmental effects of explosives

The environmental impacts of explosive materials, particularly traditional explosives, have been the focus of a number of researchers. The manufacturing, testing, transportation, and degradation of explosives all lead to environmental issues in varying degrees. In this context, Trifunović and Antonijević (Trifunovic & Antonijevic, 2019) studied the impacts of the widely used TNT explosive as well as its degradation products on the environment. The authors noted that munition used for military and civilian applications severely contaminates the environment. Specifically, TNT was noted as poorly degradable and found in low concentrations in soil, surface water, and underground waters (Trifunovic & Antonijevic, 2019). Trifunović and Antonijević (2019) highlighted that not only is TNT harmful to the environment, but so are its degradation products, which adversely affect the soil, water, plants, animals, and also humans. The observations made in the above study underscored the need to extensively investigate the different types of environmental issues brought about by explosive materials. In this section, specific environmental impacts caused by explosive materials, including water pollution, air pollution, and soil pollution, are discussed in detail.

Water Pollution. Water pollution is the contamination of water by pollutants in a way that is harmful to the organisms living in the associated water body as well as in a manner that makes the water unfit for human use. The pollution of water bodies by explosive materials is widespread and has been studied by a number of researchers. In one study involving the impacts of water pollution caused by explosive compounds, Koske (2020) explored the genotoxicity of nitroaromatic compounds in fish, the metabolism of munition compounds in fish liver, and the detection of munition compounds in fish from the Baltic Sea. TNT and its two primary degradation products, 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT) were found to exhibit acute toxicity and significant genotoxic effects in zebrafish embryos. The TNT-induced genotoxicity was three to four times higher than that induced by 2-ADNT and 4-ADNT. Thus, Koske (Koske, 2020) demonstrated the critical genotoxic threat that is posed by TNT and its degradation products to fish. In a related study, Koske (Koske, et al., 2020) noted that toxic explosive materials from a dumpsite in the Baltic Sea were accumulated in flatfish, and this, in turn, could pose a risk to the health of marine organisms as well as to human food safety. Koske (2020) conducted a comprehensive investigation of the contamination status of dab (*Limanda limanda*) from a munition dumpsite and from reference sites in the Baltic Sea. The authors used bile of 236 dab from four different study sites, including a dumpsite for conventional munitions, and explosive compounds were detected by the technique of high-performance liquid chromatography-mass spectrometry. Koske (2020) identified five explosive compounds, including TNT, 4-ADNT, and hexahydro-1,3,5-trinitro-1,3,5-triazine. At least one explosive material was found in 48% of the samples from the dumpsite (Koske, et al., 2020). The findings of the above studies evidence how dangerous the situation is with regard to explosive compounds being dumped in large water bodies and consequently being ingested by marine animals.

A few researchers have studied how various environmental factors affect water bodies that have been polluted by explosive materials. In one such study, Scharsack (Scharsack, Koske, Straumer, & Kammann, 2021) reviewed the existing literature to understand how climate change may affect the contamination of marine environments and inhabiting biota with munition compounds. The authors noted that researchers have not yet modelled climate change scenarios with relation to marine pollution by munition compounds. However, based on existing knowledge, effects of climate change, such as increased global temperature and higher occurrences of extreme weather events, are predicted to accelerate corrosion rates of disposed ordnances and, in turn, the leakage rate of munition compounds (Scharsack, Koske, Straumer, & Kammann, 2021). Scharsack (2021) further noted that climate change is expected to result in elevated stress for the biota, including temperature stress, low availability of oxygen, and changes in pH and salinity levels. The combination of these factors with the increased release of munition compounds is expected to put biota under severe threat, particularly in water bodies that are highly contaminated with munitions and that have limited water exchange, such as the Baltic Sea (Scharsack, Koske, Straumer, & Kammann, 2021). The only positive aspect noted by Scharsack (2021) was that the rising temperature due to climate change was likely to result in accelerated biodegradation of organic munition compounds by biota and microorganisms. The findings of the above study underscored the long-lasting impacts of water pollution by munitions.

While the critical situation with regard to water pollution by explosive materials has been the focus of some researchers, others have looked into the possible ways to manage this issue. For instance, Strehse (Strehse & Maser, 2020) explored the use of mussels in the context of monitoring marine pollutants with a focus on dumped conventional and chemical munitions. The authors noted that the use of mussels for programs involving large scale monitoring as well as in case studies has been established as an effective tool. The authors further noted that monitoring experiments with mussels have the capability of generating large and complex data sets, and that these data sets should be mandatorily included in decision support tools (Strehse & Maser, 2020). In another study, Fawcett-Hirst (Fawcett-Hirst, Temple, Ladyman, & Coulon, 2021) examined various explosive material contaminated wastewater treatment methods with respect to their strengths, weaknesses, and application opportunities. The method of adsorption was identified as an appropriate treatment method. However, the high solubility of the insensitive high explosive material (IHE), 3-nitro-1,2,4-triazol-5-one (NTO), was noted to have the potential to exceed the adsorptive capacity of carbon adsorption systems. In this regard, Fawcett-Hirst (2021) recommended that the existing limitations of carbon adsorption systems for IHE wastewater should be urgently overcome. The above study findings illustrate that researchers are exploring several avenues to help control and minimize water pollution by explosive materials.

For the effective development of pollution control systems with regard to water contamination by explosives, it is critical to first determine efficient approaches for quantifying the amount of explosive pollutants in water bodies. In this regard, Bünning (2021) (Bunning, Strehse, Hollmann, Botticher, & Maser, 2021) developed a toolbox of methods in order to determine the amount of the explosives 1,3-dinitrobenzene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, and its metabolites in marine samples. The toolbox was developed to enhance sample preparation and analysis of several kinds of marine samples, such as water, sediment, and different kinds of biota. Bünning (2021) adapted, improved, and combined a number of established methods.

With the use of their toolbox, in the event that the concentrations of explosives in sediment or mussel samples were greater than 10 ng per g, direct extraction allowed for time-saving sample preparation, and if the concentrations were below 10 ng per g, several techniques, such as freeze-drying, ultrasonic, and solid-phase extraction, could help detect up to picogram amounts of explosives. The detection limits achieved by Bünning (2021) were among the lowest reported values to date, and their reliability was adequately confirmed by the use of large and diverse sample sets.

The review of literature related to water pollution caused by explosive materials shows that major focus has been given to the environmental impacts of dumped munition compounds. Research has also been conducted on the quantification of explosive-related pollutants and possible pollution management approaches and wastewater treatment methods. However, in-depth research on the specific water pollutants released during the testing of explosive materials has not been conducted.

Air Pollution. Air pollution is the contamination of the atmosphere by harmful gases, particulate matter, dust, and pollen, which is harmful for the planet and the organisms living on it. The blasting of explosive materials and consequent pollution of air have been investigated by a number of researchers. In one such study, Oluwoye (Oluwoye, Dlugogorski, Gore, Oskierski, & Altarawneh, 2017) presented a comprehensive account of the formation of NO_x during the blasting of ammonium-nitrate (AN)-based explosives that are employed in surface operations. The authors estimated the total NO_x emission rate from AN-based explosives to be $5×10^4$ ton nitrogen per annum, and compared it to the global anthropogenic NO_x emissions of $41.3×10^6$ ton nitrogen per annum. Although the AN-based explosive related NO_x emission value was minor in the global context, the localized plumes from blasting were found to exhibit high NO_x concentration (500 ppm), exceeding up to 3000 times the international standards. The authors noted that this level of NO_x emission had severe environmental impacts as well as health-related issues. Further, they suggested that the development and implementation of new sampling techniques, such as light-weight remote-controlled drone-sampling, could help in measuring nitrate aerosols and particulate matter as well as other pollutants like supplementary Nr species, hydrocarbons, and nitrogenated analogues. The findings of the study by Oluwoye (2017) underscored how critical the air pollution caused by blasting of explosive materials may be.

In another study, Chen (Chen, Qiu, Rai, & Ai, 2021) compared the emission characteristics of NO_x and CO from three traditional blast design models that are most commonly used during tunnelling: the NTNU, Swedish, and China models. The authors detailed the blasting parameters of the three models by using a 42.3 m^2 cross-section tunnel as reference and evaluated the emission characteristics associated with each of the models in terms of the total mission, emissions per area, and emission increment. In order to examine the impact of functional blastholes on the emitted gases, the tunnel face of all the models were divided into four functional sections: the cut zone, the stopping zone, the lifter zone, and the contour zone. Based on the study findings, Chen (2021) concluded that the CO and NO_x emissions associated with the China model were the lowest, followed by those of the Swedish and the NTNU models. Further, the authors noted that the total emissions were dominated by the stoping blastholes, and thus, environmental pollution could be effectively reduced by adjusting the stopping zone parameters (Chen, Qiu, Rai, & Ai, 2021). Chen (2021) provided a detailed analysis of the tunneling operation, its impacts on the environment, and possible remedial strategies. They demonstrated how the most common commercial blasting operations could be adjusted so as to minimize the environmental impact caused by them. Along with the blasting of explosive materials for commercial purposes, military activities' use of explosives contributes significantly to air pollution. In this context, Mehta (Mehta, et al., 2014) noted that the two most common military primary explosives, lead azide and lead styphnate, have well-established hazards to human health as well as severe environmental impacts.

Similar to the use of explosives for military and commercial applications, the manufacturing of explosive materials itself can be severely detrimental to the environment. With regard to this, Sandham (Sandham, Van der Vyver, & Retief, 2013) noted that in the context of explosives manufacturing, air quality is severely impacted as a result of the emission of hazardous gases and particulates during acid manufacture, concentration, and recovery, by the nitration process, and by exposed burning of explosives' waste and packaging. These sources of air pollutants ultimately contribute to ozone depletion, global warming, and climate change (Sandham, Van der Vyver, & Retief, 2013). Akinyemi (Akinyemi, Emetere, & Usikalu, 2016) noted that air pollutants released from explosives or blasts seem to get transported into the atmosphere within the first few seconds through forceful injection, rather than by gradual dispersion, which is the case with normal air pollutants' plume releases. The above study findings highlight that the manufacturing and blasting of explosive materials have instantaneous impacts on the environment as well as long-lasting ones.

A few researchers have looked into addressing these critical issues of air pollution owing to the manufacture and use of explosive materials. For instance, Jagtap (Jagtap, 2018) described the types and working of air pollution controller-fabric filters in the context of the manufacture of explosive materials such as TNT. A fabric filter or bag house or bag filter was defined as an air pollution control device that is used for the removal of particulates from polluted gases released from commercial and industrial processes. The commonly used fabric filters in commercial as well as industrial sectors were noted to be mechanical shakers, reverse air bag houses, and pulse jet fabric filters. The mechanical shaker filter uses the oldest technique among the three and it is based on mechanical work, where the filter fabric is shaken back and forth. In the case of the reverse air bag houses, the bags are fastened onto a cell plate that is present at the bottom of the bag houses and suspended from an adjustable hanger frame at the top. Polluted gas enters the fabric filter and the dust collects on the inside of the bags. Pulse jet bag houses utilize compressed streams of high-pressure air to remove particulate matter during cleaning (Jagtap, 2018). The observations made in the above study illustrate that a number of techniques exist for managing the air pollution caused by explosive materials used in the commercial and industrial sectors.

The existing literature on air pollution caused by explosive materials is very limited. Only a handful of studies focus on the air pollutants released during blasting caused by explosives (Chen, Qiu, Rai, & Ai, 2021), (Oluwoye, Dlugogorski, Gore, Oskierski, & Altarawneh, 2017). In-depth studies on the specific air pollutants released during the manufacture of different kinds of explosive materials and during their testing are lacking.

Soil Pollution. Soil pollution is the presence and accumulation of toxic substances in soil in concentrations that can impact the properties of the soil, the organisms living and growing in soil, and by extension, humans, and animals. Explosive materials' impacts on the quality of soil have been investigated by several researchers. For instance, Certini (Certini, Scalenghe, & Woods, 2013) explored the impact of human warfare on soil properties, including the effects of cratering by bombs and the introduction of pollutants such as nitroaromatic explosives. The authors noted that anthropological disturbances to soil in the context of wars are essentially of three types: physical, chemical, and biological. Physical disturbances to soil include excavation of trenches or tunnels, sealing due to building of defensive infrastructures, compaction by traffic of machinery and troops, or cratering by bombs. Chemical disturbances involve the introduction of pollutants in soil such as heavy metals, nitroaromatic explosives, oil, organophosphorus nerve agents, or radioactive elements. Finally, biological disturbances of soil occur as unintentional consequences of the physical and chemical disturbances caused by various warfare activities (Certini, Scalenghe, & Woods, 2013). Thus, soil pollution during wartime, including the excessive use of explosive materials during this time, is critical and has far-reaching impacts on the soil ecosystem.

Although soil pollution during wartime is severe, pollution of soil by explosive materials and munitions is widespread even in the absence of wars. A major contribution to peacetime soil pollution is from shooting ranges. In this regard, Fayiga (Fayiga & Saha, 2016) explored soil pollution in outdoor shooting ranges. The authors noted that the major sources of soil pollution at shooting ranges are bullets. These bullets, which are aimed at distant targets, get fragmented and pulverized on impact with the ground or different sections of the range. The introduction of these fragments alters the particle size distribution of the shooting range soil and result in soil contamination. Although the heavy metals used in bullets include Cu, Sb, Zn, As, and Pb, Pb metal causes the highest level of soil contamination in shooting ranges due to its higher concentration and toxicity (Fayiga & Saha, 2016). Being a strong neurotoxin, Pb in the soil poses serious threats to the wildlife, particularly those in shooting ranges located close to or in forests. Pb also has severe impacts on shooters and workers at the ranges who inhale or directly ingest Pb dust, and are at risk of lead poisoning (Fayiga & Saha, 2016).

While Fayiga (2016) focused on the detrimental effects of Pb introduced in the soil of shooting ranges, Dinake (Dinake, Maphane, Sebogisi, & Kamwi, 2018) investigated the pollution status of shooting range soils due to Cd, Cu, Mn, Ni, and Zn found in ammunition. Soil samples from five shooting ranges in Botswana were tested, and all five shooting ranges were found to have a high concentration of Cu, varying from 67.4 ± 0.05 mg/kg to 1569 ± 13 mg/kg; the next highest concentration was that of Mn, which ranged between 25.9 ± 0.1 and 953.8 ± 2.8 mg/kg. In order to quantify the environmental pollution risk that the different heavy metals posed, the authors used pollution risk indices. Although all five shooting ranges recorded low Cd concentrations, this metal was found to pose the highest risk of pollution compared to any of the other studied heavy metals. Through their study, Dinake (2018) demonstrated that a continuous assessment of the pollution status of shooting ranges is critical to establish appropriate management practices and remedial strategies.

In another study, Ahmad (Ahmad, Lee, Moon, Yang, & Ok, 2012) reviewed the environmental contamination by heavy metals in shooting range soil and discussed the corresponding remedial strategies. Similar to Dinake (2018) and Fayiga (2016), the major pollutants of soil from shooting ranges were identified as Pb, Ni, Cu, Zn, and Sb. The authors noted that soil amendments have been researched and practically applied to stabilize the heavy metals in shooting range soils. These amendments included sugar foam, red mud, poultry waste, and dolomitic residue (Ahmad, Lee, Moon, Yang, & Ok, 2012). Ahmad (2012) noted that among the several amendments, waste materials that were based on lime, such as oyster shells and eggshells, could effectively immobilize heavy metals in shooting range soil and reduce their bioavailability in the soil. The findings of this study demonstrated how the soil pollution caused in shooting ranges could be easily and effectively handled.

Military activities also form a source of soil pollution through explosive-related contaminants. In this context, Broomandi (Broomandi, Guney, Kim, & Karaca, 2020) reviewed the physical and chemical disturbances in soil due to military activities, the existing approaches for characterizing contaminated military-impacted sites, and the advances in human health risk assessment for evaluating potential adverse impacts. Based on their review, Broomandi (2020) noted that physical disturbances in the soil may significantly affect soil properties, such as its hydraulic conductivity, resulting in severe environmental issues including increased soil erosion. With relation to chemical disturbances of the soil, the authors noted that the primary cause is the introduction of several kinds of potentially toxic elements (PTEs), energetic compounds (ECs) and chemical warfare agents (CWAs). Further, the authors found that studies on human health risk assessment generally followed an agreed upon framework, but the depth and adequacy of the use of this framework varied greatly. They proposed that a comprehensive scientific framework that covered a range of contaminants was urgently needed (Broomandi, Guney, Kim, & Karaca, 2020).

In another study examining soil pollution caused by explosive materials, Panz (Panz, Miksch, & Sojka, 2013) examined the toxicity of forest soil contaminated individually with TNT, RDX, and HMX as well as with combinations of these materials. The authors observed that TNT was the most toxic material among the examined substances, and although RDX and HMX did not adversely affect the health of plants, these substances caused earthworm mortality. Further, the authors observed the synergistic effects of mixtures of these explosives. A lower concentration of the explosives' mixtures was found to be more lethal to earthworms compared to the concentration of individual explosives (Panz, Miksch, & Sojka, 2013). The findings of this study highlighted the severe and more critical effects of mixtures of explosives than that of individual explosive materials. The study findings underscored the significance of studying the fate of explosives present in soils.

In this regard, Pichtel (Pichtel, 2012)examined the presence of energetic materials in soil and discussed their fates after contact with soil. Similar to Panz (2013), Pichtel (2012) focused on TNT, RDX, and HMX explosives; Pichtel (2012) also emphasized on some propellant ingredients, namely, nitroglycerin (NG), nitroguanidine (NQ), nitrocellulose (NC), 2,4-dinitrotoluene (2,4-DNT), and perchlorate. The authors observed that the types of residues of TNT, RDX, and HMX explosives, their concentrations, and their distributions vary depending on the kind of range and munition used. Energetic compounds were found to undergo chemical and bio-chemical transformation to varying extents, depending on the nature of the compounds involved as well as environmental factors. RDX and perchlorate were observed to possibly contribute to groundwater contamination, and a number of energetic materials as well as their decomposition products were found to pose environmental and health-related risks (Pichtel, 2012). Through their study, Pichtel (2012) highlighted the global need for the removal of these contaminants to ensure public safety and for protecting natural resources in the long term.

In a more recent study, Temple (Temple, et al., 2018) investigated the environmental fate of insensitive high explosive (IHE) residues in soil. The authors explored the fate and transport of a combination of IHEs, namely, 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ), and 3-nitro-1,2,4-triazol-5-one (NTO), in two UK soil types. Temple (2018) found that DNAN and NTO began degradation within twenty-four hours in the soil with high organic content; both these IHEs were found to have completely degraded by sixty days. NQ was relatively more stable, and 80% of the original material could be recovered after sixty days. Based on the study results, the authors noted that the three explosives (i.e., DNAN, NQ, and NTO) did not interact with each other when present in soil. Thus, Temple (2018) provided valuable insights regarding the characteristics of three combined IHE materials in soil, which could help in developing strategies to reduce soil and water contamination during military training.

Literature on soil pollution caused by explosive materials has awarded some focus on the specific pollutants released in different contexts, such as in shooting ranges, (Dinake, Maphane, Sebogisi, & Kamwi, 2018) (Fayiga & Saha, 2016), from military activities (Broomandi, Guney, Kim, & Karaca, 2020), and during wars (Certini, Scalenghe, & Woods, 2013). Although this focus of existing literature is substantially more than the corresponding focus on air and water pollution caused by explosives, further research on all kinds of explosive-related pollution is warranted. Specifically, an in-depth exploration of the pollution caused by various types of explosives during their testing is critical to understand how the very development of these substances impacts the environment.

3.2.10 Treatment techniques and approaches

A number of researchers have investigated various treatment techniques and approaches for remedying the environmental impacts caused by explosive materials. For instance, Ladyman (Ladyman, et al., 2019) developed a novel decision framework for the environmental management of explosive contaminated land. This decision framework involved conducting a systematic and scientific investigation to examine the extent and severity of a potential environmental impact arising from an operational process within an organization. Based on the findings of this investigation, the organization could make a simple binary decision as to whether the specific organizational process could continue or whether it had to be modified or mitigated. Ladyman (2019) applied the framework to three case studies; the first examined the change in composition of explosive contaminated wastewater, the second looked into the environmental impacts of explosive contaminated land from open-burning, and the third studied the air pollution caused by open burning of explosives. Through all three cases, the authors demonstrated how linking environmental impacts to business risks could help manufacturers to examine and analyze a wide range of issues that might not be identified during the initial environmental assessment.

Ferreira (Ferreira, Ribeiro, Clift, & Freire, 2019) examined an alternative to destructive disposal of ammunition: the valorization of energetic material from military ammunition by incorporating it into civil emulsion explosives. The authors studied the potential primary energy avoided and the environmental benefits of the valorization of energetic material from military ammunition by incorporating it into civil emulsion explosives. A circular economy principle was adopted for this approach; a new service was provided to a residue by its incorporation into a new product. The authors found that compared to the conventional disposal process, the re-using of ammunition through valorization of energetic materials significantly decreased the environmental impacts in all aspects. The benefits of the valorization process were majorly due to its avoidance of incineration and flue gas treatment processes during ammunition disposal as well as the replacement of producing civil explosive components with the energetic materials from military ammunition (Ferreira, Ribeiro, Clift, & Freire, 2019). This study took an interesting take on the disposal of ammunition by focusing on the concept of recycling in the context of energetic materials.

Another interesting, relatively new, and extensively studied remedial technique for explosive-related pollution is phytoremediation. Phytoremediation of explosive materials primarily involves the degradation and transformation of these substances into inert forms using the inherent metabolic processes of plants (Via, 2020). The phytoremediation of explosive materials has been investigated by a number of researchers. For instance, Panja (Panja, Sarkar, & Datta, 2018)highlighted the method of phytoremediation as environmentally and economically sustainable and studied the phytoremediation potential of vetiver grass (*Chrysopogon zizanioides*) in the removal of explosive materials and nitrate from wastewater generated from an industrial munition facility. The authors observed that by using successive batches of vetiver grass, 96%, 79%, and 100% of DNAN, NQ, and RDX, respectively, could be removed. Further, greater than 95% of nitrates could be removed by four successive batches of vetiver. In another study examining the phytoremediation of explosives, Cary (Cary, et al., 2021) demonstrated the high potential of XplA/XplB-expressing switchgrass (*Panicum virgatum*) for the phytoremediation of RDX in live-fire training ranges, munitions dumps and minefields. In another study focusing on microbial-based bioremediation treatment techniques, Alothman (Alothman, et al., 2020)used microbiological assay and gas chromatography–mass spectrometry (GC–MS) analysis to examine the ability of *Trichoderma viride* in the degradation of nitrogenous explosives. The authors observed that the *T. viride* fungus had the ability to decompose TNT explosives at doses of 50 and 100 ppm. 5-(hydroxymethyl)-2-furancarboxaldehyde was identified as the major compound, and 4-propyl benzaldehyde was identified as the minor compound as the result of the biodegradation of TNT by *T. viride*. The findings of the above studies illustrate the high efficacy and sustainable nature of phytoremediation for handling explosive material-related pollution.

Considering the critical role that phytoremediation plays in addressing contamination caused by explosive materials, it is important to understand the associated mechanisms. In this regard, Rai (Rai, Kim, Lee, & Lee, 2020) explored the molecular mechanisms of phytoremediation of explosive materials and discussed the prospects of engineered transgenic plants and microbes in this context. The authors noted that no natural transporter of organic environmental contaminants exists within plant cells and that the passive uptake of these contaminants occurs in view of the man-made origin of organics/xenobiotics; the changing hydrophobic or hydrophilic nature of xenobiotics affects their uptake in plant cells (Rai, Kim, Lee, & Lee, 2020). Three major photo-remediation approaches are commonly used for remedying explosive-related pollution: rhizofiltration, phytostabilization, and phytoextraction (Via, 2020). Rhizofiltration constitutes the beginning of the phytoremediation process and involves the heightened activity of bacterial communities around a specific region in plants roots, which is called the rhizosphere; phytostabilization involves the localization of compounds in a certain area and preventing their transportation; phytoextraction involves the pumping of contaminated water from the soil and the deposition of the associated toxins in the plant tissues (Via, 2020). Following these is the phytodegradation process, where the plants degrade and transform the explosive compounds into inert substances. The transformation of organics occurs in three phases: (i) functionalization/chemical modifications through oxidation, reduction, and hydrolysis, (ii) conjugation of foreign xenobiotics with sugars, glutathione, and amino acids, and (iii) compartmentalization/compartmentation/sequestration (Rai, Kim, Lee, & Lee, 2020).

Along with this description of the phytoremediation of organic pollutants, Rai (2020) also discussed the phytoremediation process of inorganic explosive-related contaminants. Further, the authors noted that although phytoremediation is globally considered as an economic and eco-friendly method, several challenges exist with regard to its implementation by the governments of nations as well as by the industrial sectors. In addition, certain limitations associated with the phytoremediation process were noted: i) the susceptibility of the bio-agents of phytoremediation towards climatic and biotic variables, such as temperature fluctuations, seasonal constraints, and pathogens, ii) the likelihood of food-chain contamination, and iii) the possible mobilization of contaminants like radionuclides (Rai, Kim, Lee, & Lee, 2020). Nevertheless, the existing literature clearly demonstrates that the remedial approach of phytoremediation is an effective tool in the fight against explosive material-related contamination.

The contamination by explosive materials largely varies depending on the nature of the polluting material as well as the specific site that undergoes contamination. In this regard, Muter (Muter, 2014)noted that remediation strategies with regard to contamination by energetic compounds should be developed and implemented based on the nature of the sites. Energy-intensive chemical treatments, such as incineration, may not be an economically sustainable choice for the remediation of low concentrations of explosive materials; further, these may result in other environmental issues, such as NO_x emission. On the other hand, for addressing high explosive-related pollutant concentrations, the toxicity of nitroaromatics may limit the effectiveness of bioremediation or the treatment process may produce recalcitrant reaction by-products (Muter, 2014). To enable the suitable selection of remedial strategies for explosive-related pollution in different contexts, it is critical to first evaluate the different environmental parameters of that setting. In that regard, obtaining an in-depth knowledge regarding the specific pollutants released by different classes of explosive materials may be beneficial.

3.3 Conclusion

The review of literature shows a significant amount of research on several aspects of explosive materials. Researchers have presented detailed classifications of explosive materials based on their functionalities (Chatterjee, 2017), sensitivities (Zou, 2016), and detonation velocities and applications (Zapata, 2020). With regard to specific types of explosives, significant research has been conducted on primary and secondary explosives and their green alternatives (Bolter, 2018; Li, 2017; Manzoor, 2021; Zhang, 2019). Scholars have also explored and characterized several propellants (Chaturvedi, 2019; Chen,2021; Yadav, 2021) and emulsion explosives (Domozhirov, 2019; Yao,2021). Further, researchers have investigated how explosive materials lead to environmental impacts, such as soil pollution (Broomandi, 2020; Dinake, 2018), water pollution (Koske, 2020; Scharsack, 2021), and air pollution (Chen, 2021; Oluwoye, 2017).
Although substantial research has been conducted on the pollution of soil, water, and air caused by explosive-related contaminants, a comprehensive study on the specific contaminants released into the environment during the testing of different classes of explosive materials has not been conducted. The present study will address this gap in the literature and will further analyze the environmental impacts of pollutants released during testing of explosives. Chapter 4 will elaborate on the materials and methods used for the purpose of this study.

CHAPTER 4 MATERIALS AND METHODS

4.1 Introduction

Military ranges, explosive testing ranges, and shooting ranges all exhibit significant environmental concerns. The presence of diverse types of organic pollutants in their soils, including TNT, RDX, and HMX, along with inorganic pollutants such as lead, copper, cadmium nickel, chromium, zinc, arsenic, and antimony, can cause lasting damage to the environment.

The focus of the study is to determine physical and chemical disturbances and impacts indicated from explosive testing and use, particularly in an arid location. The research design of this study will investigate explosive impacts to answer the following questions:

1. How does explosive testing and use affect soils and the physical landscape?
2. How can explosive use accelerate land degradation and contribute to desertification? In what ways does explosive use contribute to anthropogenic disturbance of the environment?
3. What technical measures and management strategies can be implemented to reduce impacts from explosive testing and use? How can these concepts be easily implemented for suitable management in arid locations around the globe?

This chapter will be structured as follows. First, the research strategy of the study will be described. Next, the site-specific sampling methodology will be discussed. The data analysis methods and techniques will next be described for the study. Finally, a concluding summary of the chapter will be presented.

4.2 Research methods

The research method for this study will be an exploratory research strategy to gain insight into the impacts of explosive testing and use on soil and the surrounding landscapes. This strategy will be used to provide solutions to the guiding research questions.

The current study will use a quantitative methodology. A quantitative approach is most appropriate for the current study because the data collected will be numerical and will provide continuous measures of explosive compounds and soil quality determinants. Additionally, the research will use statistical analyses to address the research questions, which makes a quantitative methodology a good fit for this study.

4.2.1 Research design

This quantitative study will utilize a quasi-experimental desing because the explosive compounds present in soil are not randomly being assigned to conditions. Instead, the explosives in soil will be measured as they naturally occur, prior to any treatment processes. Quasi-experimental designs are common in field settings, such as this current study where random assignment of conditions is not possible (Campbell & Stanley, 2001). Quasi-experimental studies have higher internal validity than correlational studies, but lower internal validity than true experimental studies because they cannot account for confounding variables, since conditions are not randomly assigned (Campbell & Stanley, 2001).

The sampling location chosen for the study into explosives and their impact on the environment is in an arid desert environment in the American Southwest. This desert region lies on one side of an asymmetric, elongated valley bounded by mountains, dormant volcanoes, and rocky slopes.

4.3 Sampling location site description

Deserts, like the local area around the sampling site, are characterized by a great number of common features of climate, weather, geomorphology, hydrology, soils, vegetation, and animal life. Areas that are arid to semi-arid, have little to no marked season of precipitation, and have a wide range of extreme temperatures are classified as deserts. Deserts comprise 13 to 14% of the land surface of the globe (Evenari, Noy-Meir, & and Goodall, 1985).

The sampling area for the study is in the Chihuahuan desert region of the American Southwest. In North America, the Mohave, Sonoran, and Chihauhaun deserts of the American Southwest and northern Mexico are regions of dry climate. In these areas, there is a strong seasonal temperature cycle, with a dry, hot summer and freezing temperatures in late winter. Precipitation is low in all months but has peaks in late winter and late summer. Maximum precipitation in late summer is caused by the invasion of maritime tropical air masses, which bring thunderstorms to the region. High rainfall in late winter to early spring is produced by midlatitude wave cyclones following a southerly path.

4.3.1 Features of the sampling location hydrological cycle

The Chihuahuan Desert of the arid Southwestern United States receives most of its moisture largely during summer from the Gulf of Mexico to the southeast. Occurring primarily as convective storms, the rainfall arrives in events of short duration, high intensity, and limited area. January to May is generally a dry period. Annual totals range from 75 mm (3 in) in the south to 400 mm (16 in) at the northern edges of the desert. The Chihuahuan desert covers an area of around 453,000 km^2 (175,000 mi^2), or about 35.5% of all North American deserts.

Thunderstorms may cause flash flooding in normally dry drainage basins. The climate is characterized as arid with sparse rainfall, resulting in rapid runoff and sheet erosion from short-lived thunderstorms. The soil is dry much of the year. The area does not support permanently flowing streams.

4.3.2 Native vegetation

The region is characterized by light precipitation, a wide range of diurnal and annual temperatures, abundant sunshine, low relative humidity, with high evaporation rates from water surfaces. Because of the climatic conditions, the area has sparse plant cover with large sections of bare ground. Most native plants have an extensive rooting system, while the aboveground vegetation is limited in size.

This zone of desert is made up of xeric trees and shrubs that are adapted to the climate with a very long, hot dry season and only a very brief, but intense, rainy season. Some local plants are found widely dispersed over the ground. They consist of small, hard-leafed, spiny shrubs, succulent plants, including cactus, and hard grasses. Species of small annual plants only appear after rare and heavy downpours. Many of these areas have no plant cover because the surface consists of shifting sands or sterile salt flats or hard pan soil.

Dominant vegetation is composed of grasses and shrubs, pinon (*Pinus cembroides*) and juniper (*Juniperus deppeana*), mesquite (*Prosopis glandulosa*), creosote bush (*Larrea tridentata*), and various cactus varieties, such as *Echinocereus* and *Opuntia*. Overall, it is mainly a grassland community disturbed to some extent by overgrazing. The area sustains a variety of grasses, shrubs, and forbs, including alkali sacaton (*Sporobolus wrightii*), black grama (*Bouteloua eriopoda*), fourwing saltbush (*Atriplex canescens*), Mormon tea (*Ephedra viridis*), narrow leaf yucca (*Yucca angustissima*), and some agave species, including *Agave lechuguilla*.

The native vegetation in the local area is of scientific value because it represents a transition between semidesert and desert vegetation, highly vulnerable to human induced changes. It can serve as a valuable indicator of human perturbation, besides offering a valuable site with plant materials for drought-tolerant research. In recent times, overgrazing and trampling by livestock have caused semidesert shrub vegetation to expand widely into this area of the western United States that used to be grasslands.

4.3.3 Current land use

Land resources in the area near the sampling location are used for livestock grazing, water production, agricultural production, and camping, hiking, and other recreational activities. At the local scale, the sampling area is primarily used as impact areas for research and experimental testing of different types of energetic materials, with dedicated areas as rangeland for grazing cattle. Desert bighorn sheep (*Ovis canadensis nelsonii*), Rocky Mountain elk (*Cervus elaphus nelsonii*), and mule deer (*Odocoileus hemionus*) frequent stock tanks in the area that serve as supplemental sources of water for wildlife. Additional supplemental feeding for cattle is required, as rangeland productivity is low. Much of the surrounding land is undeveloped. Because the sampling location is undeveloped and barren, the effects of erosion, weathering, and mass movement of materials is pronounced in the surrounding area.

Figure 12: Typical terrain of surrounding landscape near sampling location.

Figure 13: Evidence of erosion and mass movement of materials near sampling location.

4.3.4 Geological background

The surrounding terrain near the sampling location for each testing range is comprised of giant calderas, rift-associated volcanism, uplift of fault blocks, along with alluvial basins near valley floors. Geologic uplift, historical seismicity, and thermal springs all characterize the surrounding subsurface environment. Precambrian igneous rock overlaid by sedimentary formations, later covered by volcanic deposits are the principal strata located under the sampling site (Julyan, 2006). Elevations range from 1494 to 2133 meters (4900 to 7000 feet). The area was historically mined for both silver and lead and is currently mined for gypsum.

4.3.5 Geomorphic background

The existing site conditions include soils composed of mainly gravelly loamy sand, with 1-5% slopes (NRCS Web Soil Survey, 2022). The hydrological soil group is Type B soil, a granular cohesive soil with an unconfined compressive strength between 48 kPa (0.5 tons (U.S.) per square foot) and 144 kPa (1.5 tons (U.S.) per square foot). The average depth to the water table is more than 2 meters (80 in). The area is comprised mainly of Aridisols, calcareous (calcium-rich) desert soils derived from limestone. Aridisols typically are soils found in dry climates with some development of the B horizon, often as precipitated compounds of calcium or other salts. Soil pH ranges from 6 to 8.

4.4 Site characterization of impacted areas on active explosive testing ranges

Site characterization in the sampling location was used to investigate the type and concentration of energetic compounds and explosives residues in soil. Sampling protocol focused on identifying the presence or absence of explosives on impacted areas in an explosive testing facility. The investigation included sampling at the point of detonation, along with randomized sampling from several locations on testing ranges to identify explosives and other compounds. For this study, soil sampling was performed at an outdoor testing facility in the American desert where development, research, testing, and munitions firing all serve to introduce energetic compounds, explosives residues, and metals to the surrounding desert terrain. The explosive testing facility used as a sampling location in this study has been in continuous use since the early 1940s. The purpose of the testing facility is to evaluate the effectiveness and proper functioning of energetic materials and to investigate stress loads, blast damage effects, and fragmentation patterns of explosive materials.

Figure 14: Representative explosive testing range used for soil sampling in this study. (Note 9 m (30 ft.) utility pole on right for scale)

4.4.1 Profiling energetic compounds and their residues

The analysis of soil samples in other sampling studies have found that energetic compounds vary in concentration even in the same general location due to variations in climate and activity densities (Pichtel, 2012). Soil sampling at military sites and at other explosive testing ranges has demonstrated that it is difficult to pinpoint the exact concentration of explosive residues due to spatial heterogeneity, resulting from an uneven distribution of explosives upon detonation, explosives that can bind to soil particles, and to the formation of discrete explosive particulate material. The relatively few similar studies available provide limited guidance on sampling and estimating explosives concentrations in soils where material is distributed over a large spatial area, like conditions at the sample site. Prior studies estimating chemical concentrations in desert soils recommend that a tight sample grid spacing be used for analyzing spatial heterogeneity. (Huenneke, Clason, & Muldavin, 2001) To avoid the costly high sample numbers created from grid sampling programs, sampling for this project consisted of small-scale, grab samples to determine the presence or absence of energetic compounds, to identify the type of explosive present, and to estimate explosive concentrations typically encountered in testing range soils.

For this field screening, representative topsoil samples at a depth of 15.2 cm (6 inches) were collected per site and analyzed as the initial site assessment of the testing ranges. Soil samples were collected from different locations on the same outdoor facility, and background samples from areas where no testing activity had occurred were also collected for analysis.

4.4.2 Geoenvironmental conditions at the sampling site

The testing facility used as the sampling location appears physically disturbed in areas with ongoing testing activities, but localized areas in remote locations where activity has ceased show observable plant regrowth and increased plant diversity.

Small fragments of metallic, glass, and plastic material are clearly visible and widespread on soil surfaces. Displacement and disturbance of soil in the sampling area show significant alteration in regional topography. Soil compaction from explosive events is also evident by the presence of fine-particle dust that adheres to all surface materials when the area experiences high winds.

Numerous craters, burned areas, range-related debris, such the end of blasting caps, shells, and sabot parts, are all clearly visible throughout the testing facility and sampling areas. Vibrant, lush, and abundant vegetation is observed in areas that are no longer currently used as active testing ranges, and the vegetation is often quite dense on test ranges where ammonium nitrate fuel oil (ANFO) was regularly used in testing operations.

High amounts of metals can be observed in areas where large amounts of fragmented and warped spent ammunition are found lying on the soil. These include both significant and localized amounts.

4.5 Sampling locations

The sampling locations at the explosive testing ranges used in this study were identified as follows:

Sampling Location Designation	Site Sample Date
300N	4/19/2022
3KW	4/19/2022
BE	4/19/2022
WV	4/19/2022
Background A	4/19/2022
MBTF	5/10/2022
ES	5/10/2022
HPM	5/10/2022
NSTF	5/10/2022
Background B	5/10/2022

Table 1: Explosive testing range designations and sample dates.

Each sampling location has been used continuously as an explosive test range, where research activities ranged from explosives development testing to ammunition and gun firing. In addition to the samples listed in Table 1, eight background samples were collected at locations where explosives use had never occurred.

4.6 Sampling collection strategy and data collection method

For this study, soil samples were collected and analyzed to investigate the type and concentration of energetic compounds and explosives residues in soil. Sampling was performed in outdoor locations on an active explosive testing facility, located in an arid region of the United States. These explosive testing ranges are used for development and testing operations of various explosive materials, all of which can introduce energetic compounds, explosives residues, and metals into soil in the surrounding desert terrain. The general location used for sampling has been used for explosive testing since the early 1940s. For analysis of compounds occurring in this soil, samples were retrieved from the point of explosive detonation on different testing ranges and from nearby locations around the detonation, but still located inside the testing range.

To characterize explosive testing ranges for explosive content in soil, soil samples from each range were taken to measure site variability from site to site. The sampling design involved the collection of surface soil samples at a depth range of 10 to 20 cm. Blank samples were obtained from nearby similar locations where explosives had never been used. Four samples per site were collected from 10 different sites, for a total of 40 samples.

The blank samples were collected to serve as control samples. These background samples were used as a baseline against which the studied locations were compared to determine the presence or absence of explosive compounds. The background samples were collected from locations well away from the explosive testing ranges, had similar soil and landscape conditions, and were not affected by site effluents or storm water run-off.

Sample collection consisted of insertion of a T-handle soil sampler probe composed of stainless steel. The sampler was cleaned with ethanol after each sample collection and allowed to air dry. Each soil sample was added to individual clean glass containers. Latex gloves and eye protection were worn during sampling to minimize contamination of the samples. The glass containers were laboratory-style short wide-mouth close top jars with screw-on lids, specifically for use in soil, sediment, and sludge sampling. The capacity of each jar was 500 mL for liquids and 16 ounces for solids. After collection, all sample containers were sealed to minimize headspace. The samples were sealed, labeled, and added to ice for transport to the analytical laboratory. Samples were transferred to the analytical laboratory within 24 hours of collection.

4.7 Determination of specific gravity, grain size distribution, and water content of soil from active explosive testing ranges

Representative soil samples were also collected from an undisturbed and uncontaminated area near the explosive testing ranges to determine the specific gravity, grain size distribution, and water content of soil in the localized area soil. The specific gravity of uncontaminated soil samples was calculated by comparing the ratio of the soil unit weight γ to the unit weight of water, γ_o at 4°C, according to Equation 3.

$$G = \frac{\gamma}{\gamma_o} \quad \text{[Equation 3]}$$

The standard method for measuring the specific gravity of solids is provided in American Society for Testing and Materials (ASTM) Technical Standard D854, using a calibrated glass flask known as a pycnometer. The pycnometer is first filled with water and set on a balance to find its mass. Then it is refilled with a known mass of dry soil plus water so that the total volume is the same as before. Again, its mass is determined. From this data, G_s of the soil can be computed.

Grain size distribution analysis was performed on uncontaminated soil samples to characterize and classify the soil used in this study. ASTM D422 was used as the guidance in performing sieve analysis to determine the percentage of different grain sizes contained within the soil. This method was used to determine the grain size distribution of soil particles that are greater than 0.075 mm in diameter.

The water content of the soil used in this study was determined by identifying how much water is present in the voids between soil particles relative to the amount of solids in the soil, defined by Equation 4.

$$w = \frac{M_w}{M_s} \times 100\% \quad \text{[Equation 4]}$$

where M_w = mass of water, and

M_s = mass of soil solids.

4.8 HPLC analyses of soil samples from active explosive testing ranges

All samples were analyzed for the presence of explosives and for ammonium nitrate fuel oil (ANFO). ANFO was indicated by the identification of ammonia-nitrogen and nitrate in each sample.

For the sample analysis, samples were analyzed for nitrite nitrogen and for nitrate nitrogen used EPA Method 300.0 for anions in soil. This method is designed to extract water soluble anions from soil for analysis via ion chromatography. EPA Method 8330 was used for the trace analysis and detection of explosives residues in the soil samples by high performance liquid chromatography (HPLC) using a UV detector. This method is used to determine the concentration of the following compounds in a water, soil, or sediment matrix.

HPLC analysis is vital in providing key data necessary to better identify trace explosive constituents in samples and to distinguish between different explosive isomers and transformation products (Schachel, Stork, Schulte-Ladbeck, Vielhaber, & Karst, 2020).

HPLC analysis using a UV detector is the most common type of analytical method for identifying the presence of explosives in a soil matrix (Yinon & Zitrin, 1993). A widely used HPLC method for the analysis of explosives in soil uses the UV detector wavelength of 254 nanometers (nm), because nitroaromatic compounds will absorb strongly at this wavelength (Jenkins, et al., 1989). In studies using a flow rate of 2 mL/min, HMX will be eluted first, followed closely by RDX. TNB, DNB, and nitrobenzene will be detected next. TNT will be eluted last, followed by 2,6-DNT and 2,4-DNT. These results are based upon using 10 gram soil samples, 20 mL of methanol-water (50:50) solvent, and a 25 µL injection into the instrument (Jenkins, et al., 1989).

CHAPTER 5 RESULTS

5.1 Introduction

The detection of explosive compounds in soil at explosive testing ranges was performed to determine if explosives testing and use can impact the surrounding environment after continued use. Samples were collected from active explosive testing ranges for the detection and identification of different compounds in the soil. Various laboratory analyses were performed on an uncontaminated, background soil sample from a location near the explosive testing ranges. The soil's composition was identified to develop additional data for this study. Using standard laboratory tests provided in American Society for Testing and Materials (ASTM) technical standards, the specific gravity (G_s), the grain size distribution, and the water content (w%) were calculated for the local soil. The analytical technique used to analyze the testing rang soil samples for explosive content was high performance liquid chromatography (HPLC) analysis. This method was used to identify and characterize the various types of explosive compounds in the soil. HPLC analysis detected the presence of nitrate and ammonia in the soil, along with the explosive compounds HMX, RDX, and TNT. The TNT transformation products 2-amino-4,6-DNT and 1,3,5-TNB were also identified in the soil.

5.2 Soil classification: specific gravity, grain size distribution, and water content of soil from active explosive testing ranges

From appearance, the uncontaminated background soil appeared to have a variety of soil particles ranging from coarse to fine. The soil was brown according to the Munsell Color Charts and the particles appeared to be round with various sizes. The general appearance of the testing range soil used in this study is provided in Figure 14.

Figure 15: Uncontaminated background soil appearance.

The specific gravity of the soil was determined by laboratory analysis, performed according to ASTM D854. The specific gravity, Gs, was calculated according to the following equations:

$$M_w = (M_1 + M_s) - M_2 \quad \text{[Equation 5]}$$

$$G_s = M_s/M_w \quad \text{[Equation 6]}$$

The results of the specific gravity analysis are provided in Table 2.

Mass of volumetric flask + water (M_1)	Mass of flask, water, & soil (M_2)	Mass of solids (g) (M_s)	**Calculated G_s**
662 grams	707 grams	77 grams	**2.41**

Table 2: Specific gravity analytical results

For this study, specific gravity is defined as the ratio of the density of the soil sample to the density of water at 20°C. For this soil sample, the specific gravity was determined to be 2.41. Typically, the specific gravity of soil is in the range 2.60 to 2.80. The specific gravity of many organic soils to sandy soils has been found to range from 2.41to 2.54, with most values between 2.48 and 2.50. The variation in the values is possibly due to the presence of debris or organic matter in the soil sample (Bowles, 2001). The small value of specific gravity for the soil analyzed in this study indicates that this soil will likely swell and expand with the addition of water, and it will have a low load bearing capacity (Das, 2016). This could cause issues if a heavy foundation is applied on the site. It could also indicate that the testing ranges probably will not allow for proper drainage due to the soil conditions.

To determine the grain size distribution (sieve analysis only), ASTM D422 was used to prepare the soil for analysis. The results are provided in Table 3 and Figure 16. The sieve analysis experimental design is shown in Figure 15.

Figure 16: Sieve shaker with a stack of various sieve sizes containing testing range soil.

US Sieve No.	Sieve Opening (mm)	Mass soil retained (g)	% Soil Retained	% Soil Passing
4	4.75	59	12.6	87.4
10	2.00	55	11.7	75.7
20	0.85	64	13.6	62.1
40	0.425	62	13.2	48.9
60	0.25	61	13.0	36.0
140	0.106	88	18.7	17.2
200	0.075	29	6.2	11.1
Pan	-	52	11.1	-
Total	-	470	-	-

Table 3: Soil grain size distribution analytical results.

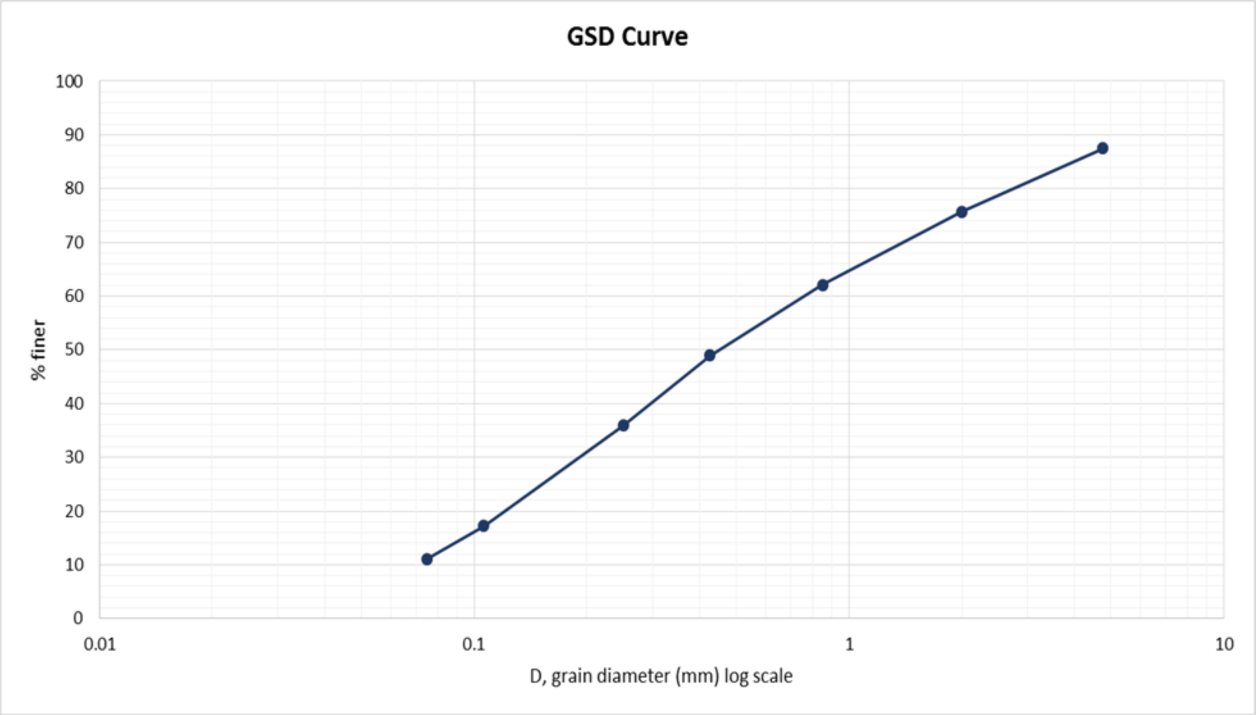


Figure 17: Grain size distribution curve of testing range soil.

The graph provided in Figure 16 indicates a somewhat flat curve that is steep and has a short range of particle sizes. Therefore, the soil commonly found in the explosive testing ranges in this study appears to be a uniformly graded soil with distribution of soil particles in the sand-sized range.

The coefficient of uniformity C_u, a measure of uniformity of grain size in the soil, is calculated according to the equation:

$$C_u = \frac{D_{60}}{D_{10}} = \frac{0.85}{0.075} = 11 \quad \text{[Equation 7]}$$

The coefficient of curvature C_c, which describes the general shape of the gradation curve, is calculated according to the equation:

$$C_c = \frac{(D_{30})^2}{(D_{10} \times D_{60})} = \frac{(0.25)^2}{(0.075 \times 0.85)} = 1 \quad \text{[Equation 8]}$$

This study used the soil classification guidelines recognized by the Unified Soil Classification System in the United States (ASTM D2487-10). Since 50% or more of the coarse fraction passes the No. 4 sieve, the soil is classified as coarse-grained soil. Since $C_u \geq 6$ and $1 \leq C_c \leq 3$, the soil is classified as a well-graded sand (SW). Therefore, the soil obtained from the explosive testing ranges analyzed in this study can be classified as coarse-grained soil composed of well-graded sand (SW).

To determine the water content of the soil, the procedures outlined in ASTM D2216 were used to prepare the soil sample. Small portions of the soil were added to moisture cans and weighed before and after drying in an oven at 110°C for 24 hours. The water content was calculated according to the equation:

$$w(\%) = (M_2 - M_3)/(M_3 - M_1) \quad \text{[Equation 9]}$$

The analytical results are provided in Table 4.

Sample Number	#1	#2	#3
Mass of empty can (M_1)	14.05 grams	14.34 grams	14.15 grams
Mass of can + soil (M_2)	29.91 grams	31.23 grams	29.78 grams
Mass of can + soil after drying (M_3)	26.73 grams	29.20 grams	28.07 grams
Water Content (%)	25.08%	13.66%	12.28%
Average Water Content (%)	**17.0%**		

Table 4: Testing range soil water content.

The moisture content was determined to be 17.0%. A small value for w indicates dry soil, while a large value for w indicates wet soil. Values in soil obtained under normal field conditions are usually between 3% and 70%, but values greater than 100% are sometimes calculated in soft soils collected from below the ground water table (Das, 2016). This indicates that these soils contain more water than solids.

The low moisture content of 17.0% in the explosive testing range soil is likely due to the high percentage of sand, as indicated from the grain size analysis. Previous studies have revealed that drier soils are generally more vulnerable to wind and water erosion than wet soils (Andreassian, Panabrokke, & Quirk, 2004). Hence the testing range soil, based on moisture content results, can be considered dry soil and may be vulnerable to erosion by running water and wind.

The results of the geotechnical laboratory analysis of the explosive testing range soil are presented in Table 5.

Specific Gravity (G_s)	Water Content (%)	Unified Soil Classification
2.41	17.0%	Coarse-grained soil composed of well-graded sand (SW)

Table 5: Geotechnical properties of testing range soil.

5.3 Detection and identification of analytes of interest in soil from active explosive testing ranges

Soil samples from various locations in active explosive testing ranges were analyzed by HPLC analysis for explosive analytes of interest. The soil samples were collected from different detonation areas at each explosive testing range to characterize areas of continuous explosives use. These values will then be available for comparison to similar locations where explosive and detonation activities commonly occur.

The presence of residual compounds remaining in soil from prior use of ammonium nitrate fuel oil (ANFO) was determined by identifying the presence of nitrite nitrogen, nitrate nitrogen, and ammonia. Explosives residues and their degradation products were also identified by HPLC analysis of the soil samples. Two similar sites where explosives use had never occurred were sampled to provide soil samples as background.

5.3.1. Comparison of nitrate and ammonia analytical results for different sites on active explosive testing ranges

The chemical compound ammonium nitrate, the nitrate of ammonia, is a white crystalline solid at room temperature and standard pressure. It is commonly used in agriculture as a high-nitrogen fertilizer, and it has also been used as an oxidizing agent in explosives, including improvised explosive devices. The commercial grade contains about 33.5% nitrogen, which is in the form utilizable by plants. It is the main component of ANFO, a very popular explosive. Ammonium nitrate is a Department of Homeland Security-regulated chemical in the United States.

Based upon the results from HPLC analysis, nitrate nitrogen and ammonia were detected in testing range soil samples, while nitrite nitrogen was either not present in the soil samples or was below the detection limit of the analytical instrument.

Figure 17 shows the average concentration of nitrate found in soil collected from different explosive testing ranges. Soil analyzed from one testing range, BE, contained an average concentration of 731.9 mg nitrate per kg of soil. Soil from another testing range, HPM, contained an average concentration of nitrate at 127.6 mg/kg soil. One testing range, WV, contained 58.5 mg nitrate/kg soil. Two testing ranges, 300N and NSTF, both contained average nitrate concentration in soil from those locations of 21.5 mg/kg soil. The background locations Background B contained an average concentration of 32.5 mg nitrate/kg soil, while Background B contained only trace amounts of nitrate, which were below the detection limit of the HPLC instrument used for the analysis.

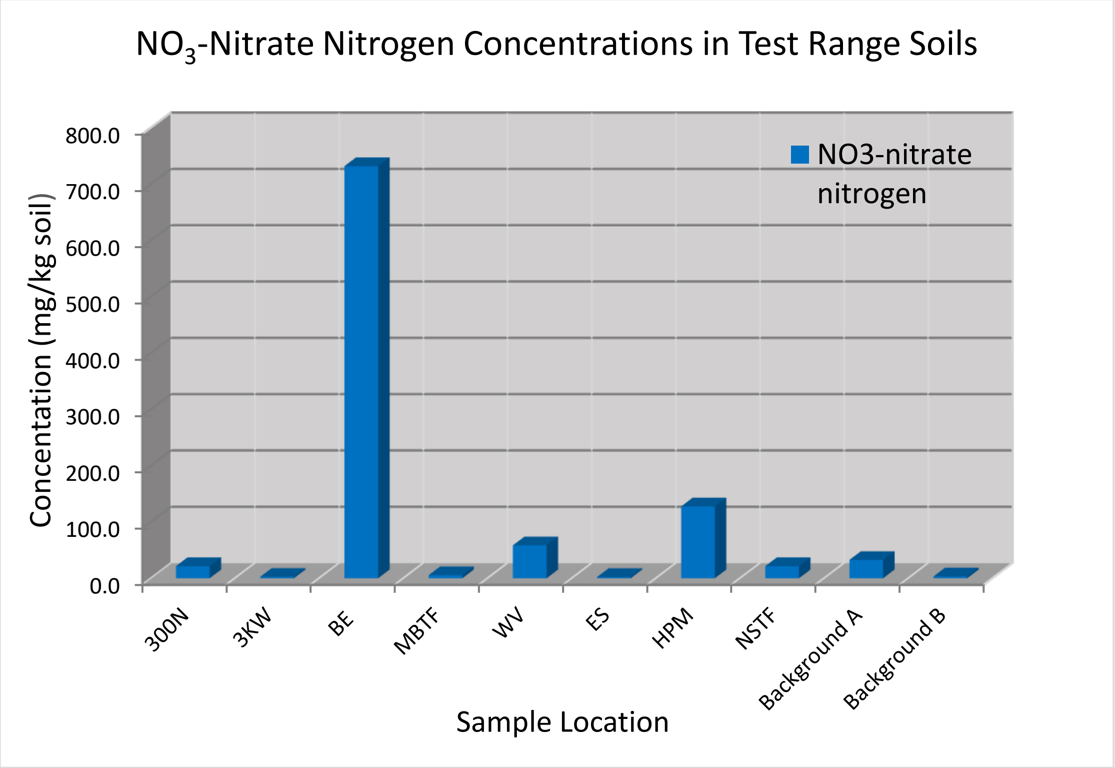


Figure 18: Nitrate concentrations in testing range soils.

Ammonia was found in soil at many locations in this study. Figure 18 shows the average concentration of ammonia in explosive testing range soil. Soil samples from one testing range, 300N, contained on average 52.5 mg ammonia per kg of soil. Four other testing ranges, HPM, MBTF, ES, and WV, contained average ammonia concentrations of 28.0 mg/kg, 29.8 mg/kg soil, 31.5 38.5 mg/kg soil of ammonia. One background location, Background B, contained an average concentration of 38.5 mg ammonia per kg of soil.

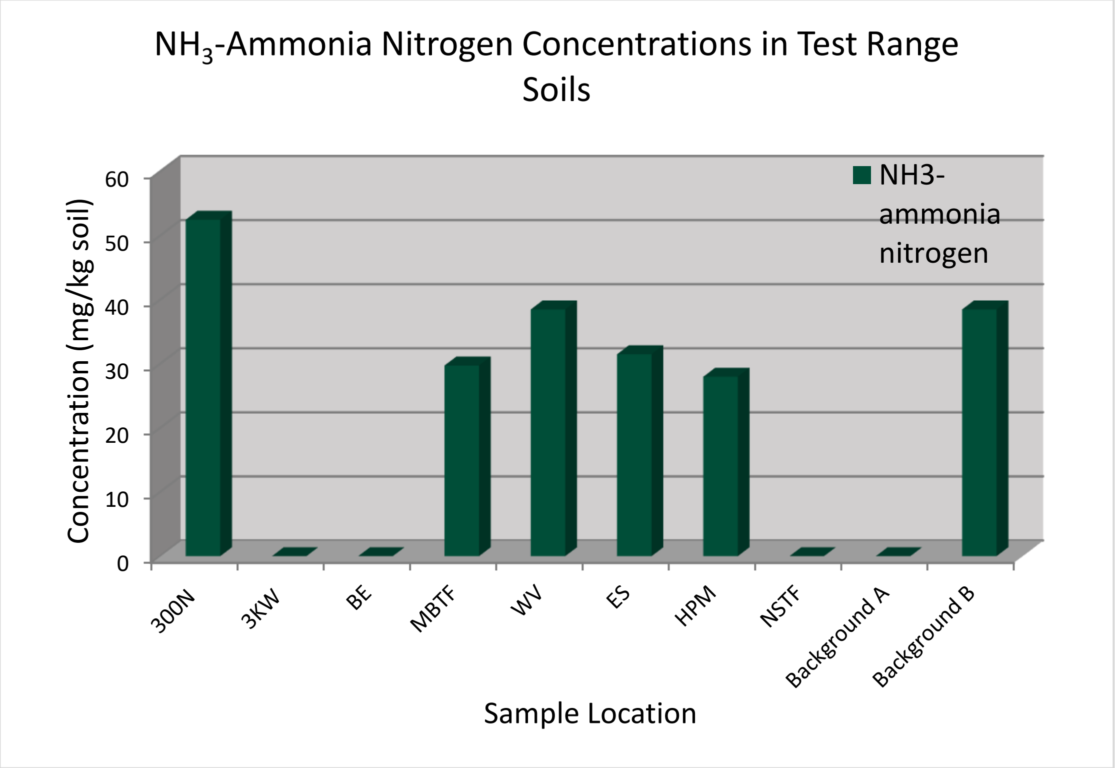


Figure 19: Ammonia concentrations in testing range soils.

5.4 Determination of explosives and energetic residues in soil from active explosive testing ranges by HPLC analysis

Based upon the HPLC analytical results, the explosive compounds HMX, RDX, 2,4,6-TNT, and the TNT transformation products 1,3,5-TNB and 2-amino-4,6-DNT were identified in the testing range soil samples analyzed in this study.

5.4.1 Comparison of explosive compound analytical results for different sites on active explosive testing ranges

The explosive compound HMX was detected in the analyzed testing range soils. HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), also known as octogen, is used as a booster charge, in rocket propellant, and in plastic explosives. It was identified in soil samples collected from all testing range soils analyzed in this study.

The HMX molecule is of low volatility, has a water solubility of 4.5 mg/L, and a K_{ow} of 0.16. Dissolved HMX does not readily sorb to soil and therefore may be mobile in the biosphere.

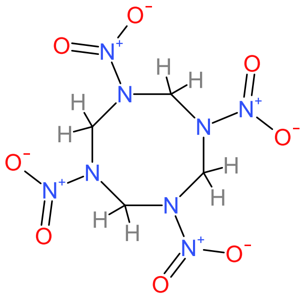


Figure 20: HMX molecule

HMX concentrations in explosive testing range soil varied in each location, as shown in Figure 20. Two testing ranges, BE and 3KW, contained an average HMX concentration of 2.27 mg HMX/kg soil and 2.54 mg HMX/kg soil, respectively. NSTF range contained 0.98 mg HMX/kg soil and MBTF contained 0.81 mg HMX/kg soil. For the soil samples collected from 300N, the average concentration of HMX was 0.29 mg/kg soil. For soil from HPM, the average concentration was determined to be 0.19 mg/kg. Soil analyzed from both background locations either did not contain any appreciable amount of HMX or the concentration was below the detection limit of the HPLC instrument.

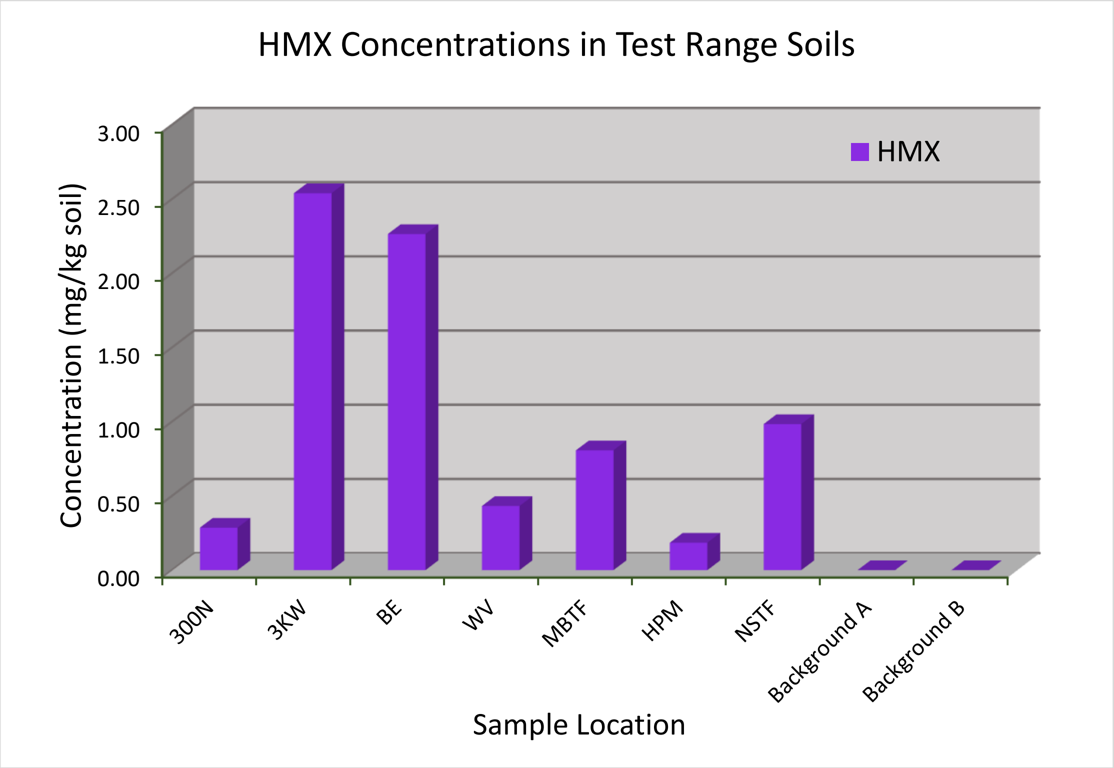


Figure 21: HMX concentrations in testing range soils.

The presence of the explosive compound RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) was also identified in the testing range soils. RDX is a highly stable nitramine compound. It is typically used in mixtures with other explosives. RDX is slightly soluble in water (56.4 mg/L at 25°C) and has a low vapor pressure. RDX will not readily volatilize from aqueous solution (Henry's law constant = 6.3 x 10^{-8} atm-m^3/mol) and will not sorb strongly to soil (K_{ow} = 0.90).

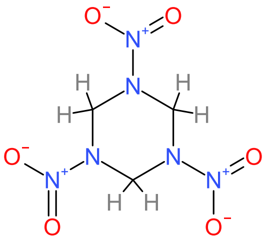


Figure 22: RDX molecule.

The maximum amount of RDX in soil analyzed for this study was found at WV, at an average concentration of 1.55 mg RDX per kg soil, as shown in Figure 22. RDX was also found in soil collected from BE, at an average concentration of 0.85 mg/kg soil, and at 3KW, at an average concentration of 0.76 mg/kg soil. Two other testing ranges, NSTF and HPM, were determined to contain average RDX concentrations of 0.33 mg/kg soil and 0.19 mg/kg soil, respectively. Soil analyzed from both background locations either did not contain any appreciable amount of RDX or the concentration was below the detection limit of the HPLC instrument.

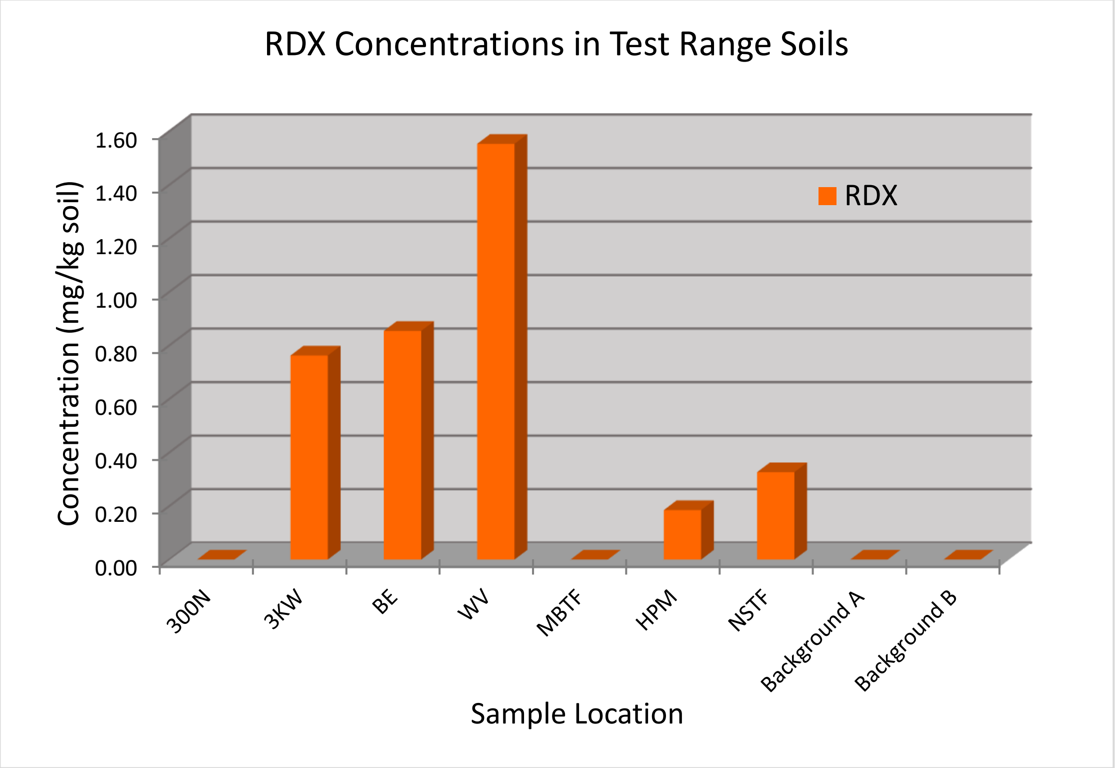


Figure 23: RDX concentrations in testing range soils.

TNT (2,4,6-trinitrotoluene) was identified in some soil samples collected from areas continuously used as explosive testing ranges. TNT is one of the most common bulk explosives in use today for both military ordnance and in mining and demolition operations. TNT is also used as a booster for high explosive munitions. It is used alone and in mixtures with other energetic compounds in various explosive formulations.

TNT is chemically and thermally stable and has a low melting point. TNT is slightly soluble in water and has a low vapor pressure (130 mg/L) and Henry's law constant. The low K_{ow} [log K_{ow} = 1.86] indicates that dissolved TNT will not sorb strongly to soils and therefore may be mobile in the biosphere.

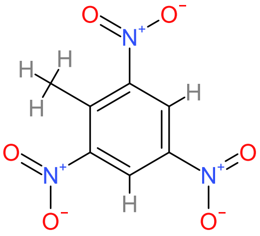


Figure 24: TNT molecule.

Figure 26 shows the amount of TNT identified in soil samples collected and analyzed with HPLC analysis from various explosive testing ranges. Only two sites, BE, with an average concentration of 0.32 mg TNT/kg soil, and WV, with an average concentration of 0.27 mg TNT/kg soil, were identified as containing the presence of TNT in testing range soil.

2-amino-4,6-dinitrotoluene (2-amino-4,6-DNT) was identified in one location from the soil sample analysis. 2-amino-4,6-DNT is generated in the biosphere from biotic transformation of TNT nitro groups to amino groups. The amino dinitrotoluene isomer is relatively nonvolatile and has a solubility of 17 mg/L. Amino dinitrotoluene has a low K_{ow} coefficient of 2.8; however, it can bind covalently to soil organic and mineral components, so it has the potential to remain in the soil environment.

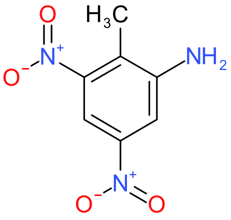


Figure 25: 2-Amino-4,6-DNT molecule.

The compound 2-amino-4,6-DNT is a primary reduction and microbial degradation product of the explosive TNT. Amino dinitrotoluene is formed relatively rapidly when TNT is released to the soil and can persist in the environment.

2-amino-4,6-DNT is found in the environment as a yellow solid with a slight odor and is one of the six forms of the chemical called dinitrotoluene (DNT). DNT is not a natural substance, but rather is usually made by reacting toluene, a solvent, with mixed nitric and sulfuric acids, both strong acids. DNT is used to produce flexible polyurethane foams used in the bedding and furniture industry. DNT is also used to produce ammunition and explosives, to make dyes, and is used in the air bags of automobiles.

2-amino-4,6-DNT has been found in the soil, surface water, and groundwater of at least 122 hazardous waste sites that contain buried ammunition wastes and wastes from manufacturing facilities that release DNT (Ware, 2003). DNT does not easily evaporate. DNT can be degraded in the environment by sunlight and bacteria into substances such as carbon dioxide, water, and nitric acid.

Figure 26 shows that soil from one explosive testing range, MBTF, was found to contain the TNT transformation product 2-amino-4,6-DNT, at an average concentration of 0.55 mg/kg soil.

The TNT transformation product 1,3,5-trinitrobenzene (1,3,5-TNB) was also identified in soil collected from one explosive testing range.

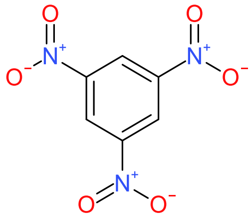


Figure 26: 1,3,5-TNB molecule.

1,3,5-TNB is a synthetic substance that is used in explosives and is a by-product of TNT. 1,3,5-TNB is also used in making rubber. Other names for 1,3,5-TNB include benzite, strinitrobenzene, sym-trinitrobenzene, symmetric trinitrobenzene, and syn-trinitrobenzene (Ware, 2003). 1,3,5-TNB is a yellow, crystal-like solid at room temperature. It can exist in air in very small amounts as a dust or a vapor and can dissolve in certain liquids. If the compound is put under very high heat, it will explode. It has no odor or taste.

1,3,5-TNB does not evaporate from water and does not adhere strongly to soil; therefore, it can move through soil into groundwater. Little information is available on the persistence of 1,3,5-TNB in water and soil.

The explosive compound 1,3,5-TNB is used as a high explosive for commercial mining and military use and as an agent to vulcanize natural rubber. The compound is a manufacturing by-product of TNT and can be released to the environment in discharged wastewater from ammunition plants. Additionally, any TNT that is present in the waste stream may be degraded to 1,3,5-TNB by photolysis under certain conditions of pH and organic matter content.

Figure 26 shows that the soil from the testing range BE contained, on average, 0.19 mg 1,3,5-TNB per kg of soil.

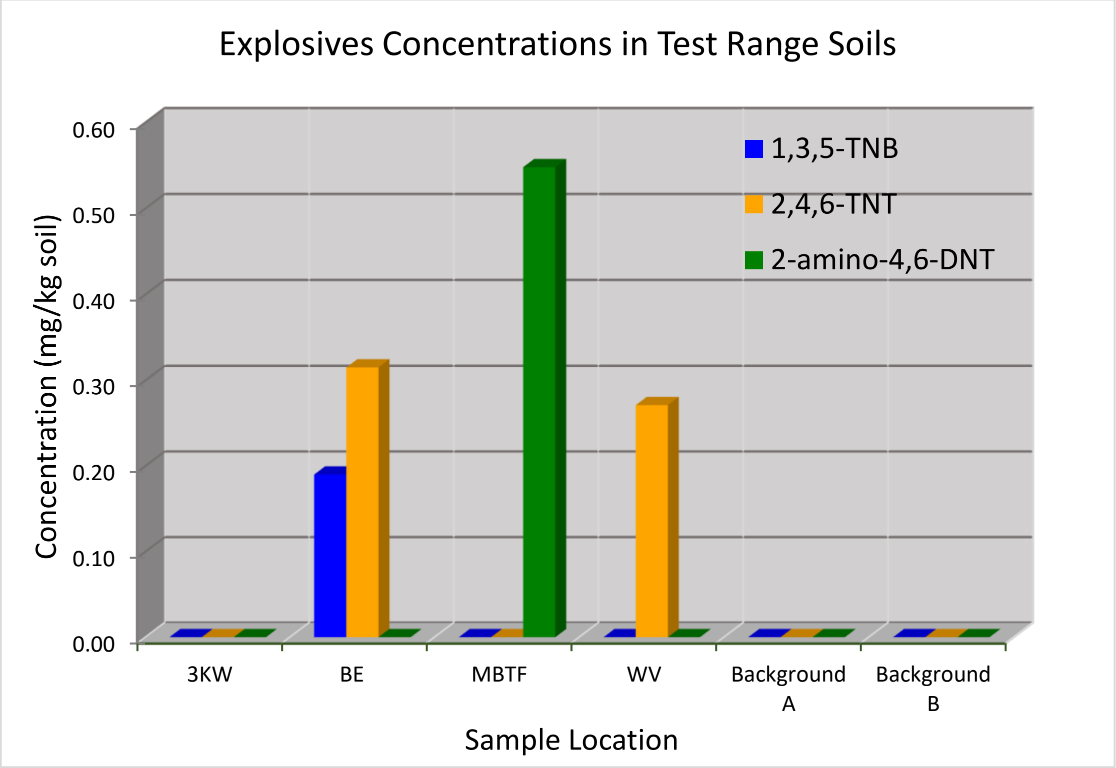


Figure 27: Explosive compounds and degradation products in testing range soils.

Table 6 provides concentrations of explosives identified in military-impacted soils (Broomandi, Guney, Kim, & Karaca, 2020). These values can be used to compare with the explosive concentrations identified in soil samples used in this study.

Country	HMX	RDX	TNT	2-amino-4,6-DNT	Comment
United States (military base area)	ND	ND	ND	ND	A
United States (demolition ranges)	0.04-4.63	0.06-28.61	0.05-234.05	ND	B
Canada (military base area)	20-1470	1.4-6000	40-500,000	ND	
Korea (military base area)	ND	51.2	53.1	ND	

*ND (Not Detected)

Table 6: Concentrations of common explosives compounds (mg/kg) in surface and subsurface soils in military-impacted soils in reviewed studies.

Comments:

(A) Clausen, et. al. Fate of Nitroglycerin and Dinitrotoluene in Soil at Small Arms Training Ranges. *Soil Sediment Cont.* 2001, 20, 649-671.

(B) Jenkins, et. al. Identity and Distribution of Residues of Energetic Compounds at Army Live-Fire Training Ranges. *Chemosphere* 2006, 63, 1280-1290.

(C) Bordeleau, et. al. Environmental Impacts of Training Activities at an Air Weapons Range. *J. Environ. Qual*. 2008, 37, 308-317.

(D) Oh, et. al. Evaluation of remediation processes for explosives-contaminated soils: kinetics and microtox bioassay. J. Chem. Technol. Biotechnol. 2016, 91, 928-937.

Table 7 provides reference values for various explosive concentrations in soil (Broomandi, Guney, Kim, & Karaca, 2020). These values can be used to compare with the explosive concentrations identified in soil samples used in this study.

Country	HMX	RDX	TNT	2-amino-4,6-DNT	Comment
United States	51,000	26	95	2000	A
United States	3900	5.8	21	160	B
Canada	32	4.7	3.7	11	C
Canada	4100	250	41	0.14	D
Canada	13	7.6	31	130	E
France	-	-	-	100	F

*Not available

Table 7: Reference/limit values (mg/kg) used for evaluating concentrations of energetic compounds in soil samples in reviewed studies.

Comments:

(A) Risk-based concentrations in soil (industrial) by U.S. EPA Region 3 [from U.S. EPA Contaminated Site Clean-up Information-Explosives (https://clu-in.org/characterization/technologies/exp.cfm)]

(B) Risk-based concentrations in soil (residential) by U.S. EPA Region 3. [from U.S. EPA Contaminated Site Clean-up Information-Explosives (https://clu-in.org/characterization/technologies/exp.cfm)]

(C) Preliminary soil quality guideline for the environment. [from Development of Ecological and Human Health Preliminary Soil Quality Guidelines for Energetic Materials to Ensure Training Sustainability of Canadian Forces; Report No. 45936, National Research Council of Canada: Ottawa, ON, Canada, 2006.]

(D) Preliminary soil quality guideline for human health. [from Development of Ecological and Human Health Preliminary Soil Quality Guidelines for Energetic Materials to Ensure Training Sustainability of Canadian Forces; Report No. 45936, National Research Council of Canada: Ottawa, ON, Canada, 2006.]

(E) Preliminary soil quality guideline to protect aquatic life in case of groundwater discharge. [from Development of Ecological and Human Health Preliminary Soil Quality Guidelines for Energetic Materials to Ensure Training Sustainability of Canadian Forces; Report No. 45936, National Research Council of Canada: Ottawa, ON, Canada, 2006.]

(F) German soil investigation values proposed for parks and recreational areas.

Overall, the results show that explosives residues and their transformation products were identified in testing range soils that have been continuously used and these concentrations remain in soil over time. The explosive compound most commonly identified in this study is HMX. The findings will be discussed in greater detail as they apply to this study in Chapter 6.

CHAPTER 6 DISCUSSION

6.1 Introduction

This experimental study serves to demonstrate how explosive testing activities and explosive use can impact soil and the surrounding physical landscape. A location in the Southwestern U.S. was analyzed in this study because desert regions in this region have been used extensively in explosive and weapons research, development, and testing activities. These areas have limited accessibility, isolated locations, and somewhat stable climatic conditions, and provide large, open spaces for explosive testing. These desert regions in the U.S. have been continuously used for explosive research and development since the 1940's and 1950's and so will provide good reference data for similar arid regions around the world.

Overall, the goal of this investigation is to increase understanding of how explosives and energetic residues behave in the soil environment and how their long-term use can affect the surrounding landscape. These influences can be contributed through the production of harmful compounds, physical debris and contamination, alteration of natural landscape equilibrium, and reduced environmental quality due to site activities. This study also examines how explosives influence soil quality, which soil determinants are most greatly impacted by explosives testing and use, and which explosive substances are most commonly found in soils at explosive testing ranges. This research used field screening for site characterization to gain an understanding of typical explosive concentrations in testing range soil. The three research questions proposed for this study include:

1. How does explosives testing and use affect soils and the physical landscape?
2. How can explosives use accelerate land degradation and contribute to desertification? In what ways does explosives use contribute to anthropogenic disturbance of the environment?
3. What technical measures and management strategies can be implemented to reduce impacts from explosives testing and use? How can these concepts be easily implemented for suitable management in arid locations around the globe?

6.2 Geotechnical analysis of explosive testing range soil

The specific gravity (G_s) for the explosive testing range soil analyzed in this study was determined to be 2.41. Typically, the specific gravity of most soils is in the range 2.60 to 2.80. The specific gravity of many organic sandy soils ranges from 2.41 to 2.54, with most values between 2.48 and 2.50, indicating the presence of organic matter (Bowles, 2001). Therefore, it is likely that the explosive testing range soil in this study can be characterized as a sandy soil containing organic matter.

For the grain size distribution using sieve analysis, the explosive testing range soil was classified as coarse-grained soil composed of well-graded sand (SW), according to U.S. Unified Soil Classification System. Coarse-grained soils are less affected by moisture than fine-grained soils (Verma & Kumar, 2019). Coarse grained soils contain larger soil void openings and will generally drain water rapidly. These soils are relatively good for use as subgrade materials, for instance, in installation on the top of an engineered embankment. However, coarse grained soils of the SW group of classification, like the soil investigated in this study, are not suitable for use as base course materials, such as those installed under roadways (Boudreaux, 1997).

The moisture content analysis showed that the explosive testing range soil had a moisture content value (w) of 17.0%. A small value for w indicates dry soil, while a large value for w indicates wet soil. Moisture content values in soil obtained under normal field conditions are usually between 3% and 70%, but values greater than 100% are sometimes calculated in soft soils collected from below the ground water table (Das, 2016). Because these soils are saturated, a high w for the soil indicates that they contain more water than solids and all void spaces are filled. The low moisture content in the explosive testing range soil is likely due to the presence of a high percentage of sand, as indicated from the grain size analysis. The variation in sand grain shape leads to large amounts of void space between soil particles in this soil. Previous studies have revealed that drier soils are generally more vulnerable to wind and water erosion than wet soils (Andreassian, Panabrokke, & Quirk, 2004). Hence the testing range soil, based on moisture content results, can be considered dry soil and may be vulnerable to erosion by running water from rainstorms and wing erosion due to aeolian transport.

6.3 Nitrite, nitrate, and ammonia soil concentrations identified in active explosive testing ranges in an arid region.

For the purposes of this study, nitrite, nitrate, and ammonia analysis using HPLC was performed on soil samples to detect ANFO, which is commonly used as an explosive compound. Based upon the soil sample analysis, nitrite nitrogen was not detected in the samples. This was probably attributable to the fact that denitrification had occurred in the soil, and nitrite was no longer present in significant amounts for detection by the analytical instrument.

The study results indicate that nitrate concentrations in explosive testing range soils were near levels found in similar uncontaminated, background soils. The active testing ranges did contain nitrate, with average concentrations ranging from 731.9 mg nitrate per kg of soil, 127.6 mg/kg, 58.5 mg/kg, to 21.5 mg/kg of soil. One background site contained 32.5 mg nitrate per kg of soil. Of the three analytes, ammonia was commonly found in the testing range soils and in the background samples. The analytical results show that one testing range contained the largest concentration found in this study at 52.5 mg ammonia per kg of soil. One background location was found to contain 38.5 mg ammonia per kg soil, which was comparable to concentrations found at other similar explosives testing ranges, from 38.5 mg/kg soil, 31.5 mg/kg soil, 29.8 mg/kg soil, to 28.0 mg/kg soil.

The analytical results strongly indicate that when ANFO is used as an explosive, for example in tests on active ranges or in military operations in arid regions, the principal compounds found in similar soils will be nitrate and ammonia. Since nitrate can readily be transported through soil horizons, it can move down through the soil profile towards underlying aquifers and possibly will be transported off site through ground water flow. Ammonia can move easily in coarse-textured soils and soils low in moisture, like the soil analyzed in this study. If the soil is saturated, then ammonia concentrations will be elevated in locations near sources of water (Bohn, 2001). Movement of ammonia toward the soil surface can be expected if the soil dries because less soil moisture means less retention of ammonia in solution with the drying soil. Ammonia can also move towards the soil surface if the soil breaks apart, due to mechanical activities from heavy equipment or from the blasting effects of explosives. These conditions can lead to greater ammonia concentration toward the soil surface, where both humans and animals can be exposed to elevated levels of ammonia.

Overall, the results indicate that both nitrate and ammonia residues in soil after ANFO use have the potential for long term, lingering impacts on both the soil environment and underlying aquifers, especially in arid regions. Arid regions are significant because much of modern explosive research, development, testing, and use occurs in dry remote regions. Dry arid regions in the American Southwest also received the additional impact of radioactive contamination from weapons testing in the 1940's, which can also introduce long-lived contaminants into soil.

6.3.1 How nitrogen behaves in typical soil

The common forms of nitrogen found in soil include organic nitrogen, ammonia, nitrate, nitrite, and gaseous nitrogen. In the soil environment, decomposition of nitrogenous organic matter releases ammonia to solution:

$$organic\ nitrogen\ compounds\ \longrightarrow NH_3\ (ammonia) \quad \text{[Equation 10]}$$

Under aerobic conditions, nitrifying bacteria oxidize ammonia to nitrite and nitrate:

$$NH_3 +\ O_2\ \longrightarrow NO_3^-\ (nitrate) \quad \text{[Equation 11]}$$

Bacterial denitrification occurs under anaerobic or anoxic conditions when organic matter (AH_2) is oxidized and nitrate is used as a hydrogen acceptor, releasing nitrogen gas:

$$NO_3^- + AH_2 \longrightarrow A + H_2O + N_2 \uparrow \quad \text{[Equation 12]}$$

6.3.2 How nitrate behaves in typical soil

The nitrate concentration in soil can provide an indication of the fraction of total soil nitrogen, the rate of nitrogen turnover in the soil, and plant availability of nitrogen. Fertilization can temporarily change this concentration until denitrification, leaching, and nitrogen uptake by plants and microbes restore the nitrogen balance.

Nitrate is actively taken up and reduced by soil organisms but is typically inert in the soil. If nitrate is leached below surface soil and plant root zones, it will move unhindered and unchanged through the subsoil. Overuse of fertilizers and organic waste disposal practices can increase the NO_3^- concentration in ground water and eventually in drainage water. In arid regions, similar to the location where soil was analyzed in this study, the downward water flow through soil is very slow. Usually, the ground water table is deep, and nitrate will slowly disappear by microbial transformations. Nearby surface water can be polluted by nitrate from both discharge of wastewater, movement of eroded soil off site, and drainage from agricultural land. Nitrate is a major anion of pollution concern because of its effects on the ecology of surface water. The current upper limit of NO_3^- in drinking water in the United States is 10 mg/L nitrate as nitrogen (45 mg/L as NO_3) or 7×10^{-5} M.

6.3.3 How ammonia behaves in typical soil

Several physical and chemical reactions take place when ammonia is introduced into soil. They include dissolution in water, reaction with soil organic matter and with clay, and the attachment of ammonium ions on soil particles through cation exchange. These reactions limit the movement of ammonia. The highest concentration of ammonia is found around 25-50 mm (1-2 inches) at the point of water introduction, with a tapering of ammonia concentrations toward the outer edge of the water retention zone, usually 76-102 mm (3-4 inches) radius in most soils. The specific size and shape of the ammonia retention zone varies depending upon the initial concentration, the soil type, and soil conditions, such as soil texture, soil structure, organic matter, and moisture status.

Soil moisture is important in limiting the movement of ammonia. Ammonia moves farther in coarse-textured soils and in soils low in moisture, like the soil analyzed in this study. If the soil is saturated, then ammonia may preferentially move back to the site of introduction. Movement toward the soil surface can occur if the soil dries due to less available water to retain free ammonia in solution. A similar movement within soil can occur if soil breaks into clods and there are large air voids between soil particles. These conditions can result in greater ammonia concentration toward the soil surface and greater potential for loss to the atmosphere.

Ammonia reacts and binds with various soil particles including organic matter and clay. It reacts with soil water to form ammonium (NH_4^+). After conversion to NH_4^+, it is retained on soil and does not move with the addition of water. Only after conversion to nitrate (NO_3^-), through nitrification, can it be lost from soil by leaching with water.

When ammonia reacts with water in soil, it causes an initial alkaline pH, according to the reaction:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad \text{[Equation 13]}$$

Free ammonia (NH_3) can be lost from soil and can be damaging to microorganisms and plant roots and seedlings (Sawyer, 2019). As pH rises, the equilibrium between ammonium and ammonia results in increased ammonia, where the percentage as ammonia can be 1% at pH 7.3, 10% at pH 8.3, and 50% at pH 9.3.

The biological nitrification process that occurs with ammonium in soil and ultimately results in a lowering of soil pH back to the original pH or lower occurs according to the reactions:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \quad \text{[Equation 14]}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad \text{[Equation 15]}$$

Common bacteria in extreme and arid soil environments and their influence on altering soil constituents

Once explosives have been used in an extreme environment like arid desert regions, common soil bacteria may transform explosives into other compounds. These transformations include the breaking of the aromatic ring components of explosives to create organic compounds, along with other compounds. These compounds can include other material that can then easily precipitate out of the soil solution and become attached to clay or soil particles, which could then serve to transport these materials off site. Common bacterial genera found in arid soil include *Acinetobacter, Agrobacterium, Alcaligenes, Arthrobacter, Bacillis, Brevibacterium, Caulobacter, Cellulomonas, Clostridium, Cornebacterium, Flavobacterium, Micrococcus, Mycobacterium, Pseudomonas, Staphylococcus, Streptococcus,* and *Xanthomonas* (Atlas, 1993). At neutral to alkaline pH, metals in desert soils will be immobilized by lack of water and will be adsorbed on cation exchange sites on clay minerals. Microbial production of acids and chelating agents can reverse this adsorption and then mobilize metals in soil. Microbial metabolic products that can chelate metals include dicarboxylic and tricarboxylic acids, pyrocatechol, aromatic hydroxy acids, polyols, and some specific chelators such as the enterochelins and ferrioxamines (Atlas, 1993). This can cause the movement of metals introduced from explosive testing casings and projectiles through the soil profile, towards underlying aquifers.

Environmental factors that control microbial growth in desert soil include extreme environmental conditions that microorganisms must tolerate. These include high temperatures, high alkaline soil pH in arid regions, high salt concentrations, low water availability, high irradiation levels, low concentrations of usable nutrients, and high concentrations of toxic compounds from explosive testing and use. Many microorganisms that inhabit extreme environments, including hot springs, salt lakes, and desert soils, possess specialized adaptive physiological features that permit them to survive and function within the physicochemical constraints of these ecosystems. Because relatively few microbes possess these adaptations, diversity in extreme environments, like the location used in this study, will be generally low. Therefore, it is probable that transformation of both ANFO and explosives into other compounds will be curbed for arid regions due to limited microbial activity. It is likely that the original compounds will remain unaltered in soil for some time, as indicated by the lack of significant amounts of explosive transformation products in soil from this study.

6.4 Explosives and energetic residues identified in active explosives testing ranges in an arid region.

The analytical results demonstrate that both explosives and some explosives residues can be readily detected in active testing range soils in an arid desert region. Explosives compounds identified in this study include HMX, RDX, TNT, and the TNT transformation products 2ADNT and 1,3,5-TNB.

6.4.1 HMX

HMX was detected in all soil samples collected from an active testing range, except for those samples collected as background. The concentrations identified fluctuated from values of 0.19 to 0.29 mg HMX per kg soil up to maximum concentrations of 2.3 to 2.5 mg HMX/kg soil.

The presence of HMX in all soil samples obtained from this study indicates that HMX is a commonly used explosive compound in testing activities and can be detected in similar regions where explosives are used. Since it was identified in all soil samples collected from an arid region, it appears that HMX will remain in the soil in dry environments and will not be easily transformed by native soil microorganisms.

The amount of HMX detected in the samples correlates with those levels commonly found in United States active demolition ranges, on the order of 0.04 to 4.63 mg HMX per kg of soil. The recommended environmental soil concentration for HMX to ensure military range sustainability in the U.S. is 89 mg HMX per kg soil. The results of this study show that the levels identified are well below the recommended values.

6.4.2 RDX

RDX concentrations in active testing range soils varied in concentration from the lowest value of 0.19 mg RDX per kg of soil up to high values of 0.76 to 0.85 mg/kg soil. The highest concentration of RDX in soil at an active explosive testing range was determined to be 1.55 mg RDX/kg soil.

The presence of RDX in most of the soil samples analyzed in this study indicates that RDX is another commonly used explosive that will be readily identified in similar soils in dry desert regions.

The concentrations of RDX detected in soil samples for this study are well below those commonly found in demolition ranges in the U.S., on the order of 0.06 to 28.61 mg RDX per kg of soil. In the U. S., the recommended RDX soil concentration to maintain range sustainability is 7.7 mg/kg.

6.4.3 TNT, 2ADNT, and 1,3,5-TNB

TNT was identified in only very small amounts in limited locations. The transformation products 2ADNT and 1,3,5-TNB were also only identified in trace amounts in a few locations. TNT (2,4,6-trinitrotoluene) was found in only two explosive testing range soils of all the samples analyzed, with concentrations ranging from 0.27 to 0.32 mg TNT per kg soil.

The TNT transformation product 2ADNT (2-amino-4,6-dinitrotoluene) was found in soil at one explosive testing range, at a concentration of 0.55 mg 2ADNT per kg soil. This explosive compound was not found on any other site analyzed in this study.

1,3,5-TNB (1,3,5-trinitrobenzene), another TNT transformation product, was found at a different active testing range, at a concentration of 0.19 mg 1,3,5-TNB per kg soil. No other site was found to contain this explosive residue.

The level of TNT detected in soil samples are well below those commonly found in demolition ranges in the U.S., which are on the order of 0.05 to 234.05 mg TNT per kg of soil. The recommended soil concentration for TNT to protect range sustainability in the U. S. is 9.6 mg TNT per kg of soil.

There is no readily available data for 2ADNT and 1,3,5-TNB identified on active explosive testing ranges. This indicates that further research and analysis into common concentrations of these compounds at active testing ranges is necessary. This will help develop a better understanding of TNT’s impact on soil and the transport and fate of its transformation products through soil and in the environment.

6.4.4 Typical compounds commonly found in testing range soil in an extreme, arid environment

The contaminants typically identified in explosive testing range soil include energetic compounds, energetic residues, and metals. The explosive compounds used in most conventional munitions are TNT, Composition B (a TNT/RDX mix), and octol (a TNT/HMX mix). In this study, the explosive analytes that were most commonly identified in active testing range soils in an arid environment include RDX, HMX, TNT and its degradation products 2ADNT and 4ADNT.

Explosives testing can also lead to the accumulation of inorganic contaminants, deposited by a variety of processes. These include metals, in fragments and in fine particles, which can be spread over the localized soil after detonation. When metals are introduced from the detonation of explosives, they can be transformed into other compounds not originally present in the munition. This transformation occurs during the detonation process and during the weathering of metallic fragments deposited on testing ranges. During detonation, the temperature and pressure reach extremely high values, which might exceed the melting point of some metallic compounds. These molten species are free to interact with other compounds to form new alloys, metallic complexes, and salts, which all may have a different environmental impact. After dispersion in surface soil, both chemical and physical weathering of metallic fragments will take place. Metals usually encountered in explosive testing range soil include lead (Pb), copper

(Cu), zinc (Zn), and aluminum (Al), although many different metal analytes can also be identified.

6.5 Research questions and discussion

6.5.1 Research question #1

How does explosives testing and use affect soils and the physical landscape?

Explosive use in testing activities, and to a larger extent, on large arid regions involved in conflict, can affect soil in various ways. This study showed that the most obvious sign is the visual impact that the detonation event has on the local environment. In areas analyzed in this study, there are obvious depressions and craters on the explosive testing ranges that indicate repeated use in the same location. These depressions are devoid of vegetation and contain soil that has effectively been "pulverized" from the blast effects of explosives. These soil particles bind as a fine dust on everything that it comes in contact with, from leather boots to plastic to glass. Plants surrounding the site at some distance from the point of detonation show a growth response to continued blasts from explosives, indicated as a bending of the entire plant in a direction away from repeated blasts. There are also older depressions and craters with no vegetative growth. If vegetation does colonize these craters, they have little to no foliage.

The results of this study demonstrate that explosive testing and use does impact and change both soil and the surrounding physical environment. There were various explosive residues that were identified in testing range soil in this study. Physical effects that were observed included a change in natural landforms and their equilibrium with the environment, such as erosion processes on surrounding hillslopes, increased sediment transport from overland flow on and channel cutting near testing ranges, and increased sediment transport by wind, leading to scouring effects and removal of topsoil.

The main explosive compounds identified in this study include HMX, RDX, and TNT. HMX has a water solubility of 4 mg/L and has a high residence time in surface soils. HMX represents a lower risk to off site transport to surface water or ground water, while it does have a high risk to surface soil ecosystems. RDX appears to remain in the localized area near the point of detonation for some time. It is not easily transformed by microorganisms. RDX is highly mobile in the environment and has a high water solubility of 42 mg/L, which indicates that it presents a high risk to contamination of both surface water and ground water when transported off site. TNT is retarded in the soil profile, where it can be transformed into various metabolites. Because TNT is retained in soil, it presents a lower risk to transport to water bodies.

Therefore, this study demonstrates that arid locations that experience explosive testing and use can be expected to contain explosives, explosive residues, and their transformation products, especially after long-term and continuous use. These compounds will remain in the localized area for an extended time and can be easily identified upon soil analysis. In arid regions, some explosives compounds may remain adhered to soil particles, but upon exposure to wind and water, especially during excessive rainfall events, will be transported off site to nearby waterways and sensitive environmental areas such as wetlands. Upon transport, explosive compounds that contain inorganic constituents may be present in natural water sources used for drinking and irrigation. Certain inorganic and cyclic compounds present in ground water used for drinking and irrigation purposes can cause a variety of health concerns. Some cyclic compounds are also known or suspected carcinogens. This demonstrates that continued monitoring of areas that contain or are suspected of containing explosive compounds should be continually monitored and managed to slow migration of materials off site.

Fate and distribution of an explosive compound in soil

The fate and distribution of an explosive compound released into soil are governed by various factors. These include the physicochemical properties of the compound, the prevailing environmental conditions at the point of release, and the degradation and transformation of the explosive (Leszczynski, 2017). Thus, determination of physicochemical properties for explosives is critical in developing valid environmental predictions and remediation approaches. Physicochemical properties such as melting point, boiling point, and vapor pressure are important in understanding an explosive's dispersion and fate.

Aqueous solubility, vapor pressure, chemical partitioning coefficients, degradation rates, and Henry's Law Constants provide information that can be used to evaluate explosive mobility in soil. High aqueous solubility and low degradation and transformation rates are an indication that the explosive can be easily transported through the soil and to surface and ground water. The boiling point of an explosive is the temperature at which the vapor pressure of the liquid equals the environmental pressure surrounding the liquid. The higher the vapor pressure of a liquid at a given temperature, the lower the normal boiling point of the liquid. Partitioning coefficients can be used to assess the relative affinities of the explosive compound's absorption to soil particles.

Chemical and physical properties of explosives

Molecular mass

The molecular mass of an explosive can be used to estimate the dermal flux across a pathway such as skin, to understand an organism's excretion rates, and any potential pathways of exposure. In general, a high lipophilicity as well as a high hydrophilicity limit skin penetration (McDougal & Boeniger, 2002). Substances that cross the skin barrier must have a low molecular weight. With increasing size, the chemical structure becomes more complex, and penetration is reduced. Since explosive compounds are usually aromatic ring compounds, they have a relatively high molecular mass.

Solubility in water

One of the most important physical properties related to the environmental behavior of an explosive compound is its aqueous solubility. Solubility is an equilibrium property defined as the maximum solute concentration possible at equilibrium. The water solubility is the maximum (saturated) concentration of the explosive in water at a given temperature and pressure. The aqueous solubility of an explosive compound also indicates its hydrophilic or hydrophobic nature. The solubility may vary due to the presence of salts, pH, and other constituents of the water source and its temperature. The tendency for an explosive compound to be transported by ground water is directly related to its solubility and inversely related to both its tendencies to adsorb to soil and volatilize from water. Explosive compounds with high water solubilities tend to desorb from soils and sediments and are more likely to reside in water. The solubility of an explosive in water can help in understanding the environmental fate and transport of the compound.

The octanol-water partition coefficient (K_{ow})

The octanol/water partition coefficient, log K_{ow}, can be used to identify the fat solubility of an explosive and its tendency to bioaccumulate and magnify between trophic levels. Explosive compounds with high partition coefficients tend to accumulate in the fatty tissues of organisms.

The water/organic carbon partition coefficient (K_{oc})

The water/organic carbon partition coefficient (K_{oc}) is a measure of the tendency of an explosive compound to partition between soil and water. The K_{oc} is defined as the ratio of the absorbed compound per unit weight of organic carbon to the aqueous solute concentration. This coefficient can be used to estimate the degree to which an explosive compound will adsorb to soil. The higher the K_{oc} value, the greater the tendency of the explosive compound to partition into soil. The K_{oc} value depends on temperature, pH, particle size distribution, concentration, ratio between solids and solution, volatility of the compound, degradation of the compound, and contact time.

The soil sorption coefficient (K_d)

The soil sorption coefficient (K_d) of an explosive is calculated from the K_{oc} coefficient by multiplying the K_{oc} value by the fraction of organic carbon in the soil, according to the formula:

$$K_d = K_{oc} \times organic\ fraction. \quad \text{[Equation 16]}$$

Vapor pressure

Vapor pressure is the pressure at which an explosive compound and its vapor are in equilibrium. The value can be used to determine the extent to which an explosive compound would travel in air, as well as the rate of volatilization from soils. In general, explosive compounds with vapor pressures much lower than 10^{-7} mm (about 0.28 in) mercury will not be present in the atmosphere or soil in significant amounts, while compounds with vapor pressures higher than 10^{-2} mm (about 0.08 in) mercury will exist in the air.

The vapor pressure of an explosive can be used to provide an estimation of its environmental half-life. Explosives with a low vapor pressure will be less likely to vaporize and enter the atmosphere.

Another important explosive property that can be used to determine its impact on the environment is its affinity to organic carbon, log $K_{oc.}$ This property can be used to understand the explosive's fate and transport, its soil sorption potential, and thus its potential to reach ground water upon release into the environment. A K_{oc} high value indicates that the explosive compounds it strongly sorbed onto soil and organic matter and does not move easily through the soil horizon. A very low value means it is highly mobile in soil.

Henry's Law Constant (K_H)

The Henry's Law Constant (K_H) is a measure of the ratio of the explosive compound's vapor pressure to its aqueous solubility. The K_H value can be used to make general predictions about the explosive compound's tendency to volatilize from water and to be an air pollutant.

Substances with K_H values less than 10^{-7} atm-m^3/mol will volatilize slowly, while compounds with a K_H greater than 10^{-3} atm-m^3/mol will volatilize rapidly.

Henry’s law constant values can be used to identify the environmental persistence of explosives in water. Henry’s law states that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid. Explosive compounds with high Henry’s law constants will volatilize from water into air, and compounds with low values will tend to remain dissolved in water.

Melting point and boiling point

Prediction of melting points and boiling points are important in finding thermal behavior of an explosive compound. The melting point and boiling point indicate the relative purity and physical state of the material. The boiling point also indicates the volatility of an explosive compound.

The boiling point of an explosive can be used as an indication of its environmental persistence. The boiling point is the temperature at which the vapor pressure of the explosive compound equals atmospheric pressure. This parameter can also be used to characterize the environmental phase partitioning between gas and liquid phases. An explosive’s melting point can be used to demonstrate environmental fate and transport.

The behavior of explosives in soil

The behavior of explosives of soil is another important consideration concerning explosive fate and transport. Soil is defined as the uncemented aggregate of mineral grains and decayed organic matter (solid particles) along with the liquid and gas that occupy the empty spaces between the solid particles. Important engineering properties of soil include its grain-size distribution, ability to drain water, compressibility, shear strength, and loadbearing capacity (Das B. M., 2016).

Soil horizons form within unconsolidated materials on stable surfaces that have been exposed for a length of time, as material is added or removed from parent material. Soil can also form as material is translocated, upward, downward, or laterally, within a soil profile, or as it is transformed in place. These processes form distinct layers of soil within the upper portion of unconsolidated materials.

Soil horizons are divided into a few types of master horizons: O, A, E, B, C, D, and R (hard continuous bedrock). O horizons are layers dominated by organic material, litter, and humus, in various stages of decomposition. A horizons are mineral horizons that formed at the surface or below an O horizon and are characterized by an accumulation of organic matter mixed with the mineral fraction, or have properties resulting from cultivation, pasturing, or similar kinds of disturbance. B horizons are subsurface mineral horizons dominated by accumulations of clay, iron, aluminum, and humus. C horizons are mineral horizons, excluding hard bedrock, that have hardly been affected by pedogenic processes. D horizons are deep horizons that show no evidence of pedogenic alteration.

Soil formation in landscapes is characterized by a deficiency of soil water most of the year in desert regions, regions like the location chosen for this study. The process of soil formation involves weathering and translocation of soluble materials through the soil profile. After each rainstorm, soluble compounds are brought into solution and translocated downward through the soil profile. At some depth these compounds are deposited. Continued movement of compounds through the soil horizon can eventually result in plugging of soil pores and the formation of an aquiclude, nearly impermeable to water. These soils are typically identified as Aridosols, often found in arid locations. This is the type of soil analyzed in this study.

The type of soluble materials that are translocated in Aridosols is a function of availability. Salts and soluble compounds have different mobilities and solubilities in soils, with carbonates being the most least soluble in desert soil:

$$Cl^- > SO_4^{2-} > HCO_3^- > CaSO_4 \cdot 2H_2O > CaCO_3$$

(chlorides > sulfates > bicarbonate > gypsum > carbonates)

In general, as the climate gets drier, salts in desert soils become more common and closer to the surface. In the American Southwest desert, the location used in this study, soils accumulate solid calcium carbonates and are characterized by layers of thick and massive soil horizons that resemble limestone, commonly called caliche. The correct scientific description of this soil type is a cemented $CaCO_3$ layer, called the petrocalcic horizon, K horizon, or Bk horizon. (Bohn, 2001).

Physical impacts of explosives on soil

Geomorphological effects in this study show that changes and impacts to the surrounding landscape can influence the mobility of explosives and other materials. Fragments of metal and other debris, such as plastic and wood, can be observed in various locations in and around the active testing ranges. The materials can change the natural drainage patterns in the area by clogging ephemeral channels, changing erosion processes on nearby hillslopes and on downgradient areas. Changes in landscape equilibrium can also accelerate the movement of explosives and other compounds, especially those that are attached to soil particles, through erosion of large quantities of soil during intense thunderstorms in this arid region.

Obvious signs and impacts of explosive use include the presence of large particles such as metal fragments and plastics, wood, and other debris, along with anthropogenic materials and refuse, such as aluminum cans and plastic grocery bags, which can also be transported off site in storm water runoff and testing range drainage water. High winds and the resulting dust storms in the area can move small particulate material and other lightweight material off site.

Maintaining geomorphological equilibrium at a site can help prevent severe environmental alteration and impacts. The blast and pressure effects from explosive testing and use can obviously alter landscape equilibrium. In this study location, these effects include hillslope alteration and mass wasting of rock from explosives detonation, rock fracturing from blast effects, channel sedimentation from soil movement, and the physical alteration of soil from large grained and small pebble sized particles to fine grained particles after explosive pulverization. All of these explosive impacts serve to alter site geomorphology in the surrounding landscape at the study location.

To better determine how explosive testing and use affect the physical landscape, the current geomorphology of the site must be considered to identify landscape change over time. Geomorphological knowledge has a valuable role to play in the management of testing ranges located in arid environments. Using this concept of applied geomorphology in arid regions will be primarily concerned with the evaluation of local landforms, superficial materials and processes, and with managing, monitoring, and predicting landform and process changes after explosive use.

Because many explosive testing ranges are on arid lands that are in remote locations, a survey and evaluation of the existing characteristics of the site and its surroundings must be performed.

Landforms provide an obvious landscape characteristic to use as a basis for initial site conditions. Water flows and flooding events on explosive testing ranges used in this study tend to not occur very frequently but can be intense. Sediment concentrations in these desert fluvial flows tend to be high and to increase downstream. The processes associated with wind and wetting and drying cycles that lead to increased salt content in the local soil are widespread and evident throughout the testing ranges. These processes can all have major influences on both soil contaminant concentrations and on the surrounding landscape, especially in similar arid locations.

Therefore, major geomorphological issues that must be monitored in the environmental management of explosive testing ranges include erosion, transportation, and deposition of sediment and other materials by water and wind, soil stability, and desiccation. Soil erosion by rilling, sheet erosion, which is erosion of soil along a wide area, and gullying are all serious problems observed in the explosive testing ranges analyzed in this study. The wind transport of fine dust from the testing ranges is evident as it can bury, abrade, and clog many important components of infrastructure such as local roads, pipelines, agricultural land, and industrial facilities and equipment.

General geomorphological indicators of explosive use on the testing ranges in this study include the formation of craters produced from “bombturbation” (Hupy, 2012), which can disrupt the sequence of soil horizons and alter the original site topography. Compacted soil both from repeated explosives testing in the same area and from vehicle traffic over the testing ranges increases surface erosion and promotes transport of materials off site through stormwater and aeolian transport. The temporary lack of vegetative cover increases wind erosion on each testing range. Sites impacted by explosive testing and use also contain visible signs of rubble, consisting of excess materials remaining after the detonation event, including steel panels, concrete, wood, and plastics. Metallic items can include metal fragments, bullets, metal casings, and sabot parts. Anthropogenic waste materials, such as soda cans, water bottles, and plastic shopping bags are also evident, and cause an eyesore in the natural surrounding landscape. Reactive materials, such as finely powdered metals and powerful oxidizers such as Teflon or other fluoropolymers, along with UXO (unexploded ordnance) are found at the study location where explosives have been tested.

The impacts that explosives have on soil and the surrounding landscape have certain characteristics that can be recognized in different arid locations. One current study in an arid region demonstrates that explosive testing and use can disrupt and severely damage the surrounding physical landscape, impacting soil, native vegetation, and wildlife habitats (Omar, 2017). The damage can include the physical disturbance to the soil due to construction of test structures to study explosive effects, the laying of mines and other buried munitions, and the increased movement of heavy equipment and vehicles. The detonation of munitions results in large depressions in the soil and the off-road movement of heavy machinery during testing operations can cause lasting damage. Preliminary observations indicate that these activities can disturb soil horizons, disrupt ongoing pedogenic processes, result in severe soil compaction, and adversely affect vegetation structure, species composition, and plant production.

With extreme temperatures, low and erratic rainfall and high evaporation rates, soil and plant recovery in arid environments is fundamentally slow. Previous studies have indicated that natural recovery of severely disturbed and compacted desert soil is extremely slow, and that due to surface compaction, the soil may not recover at all. The establishment of desert plants may be significantly retarded in compacted soils. It is estimated that it requires 8 to 112 years for vegetation to recover to pre-disturbance conditions on moderately compacted desert sites, and 100 to 3000 years on heavily compacted sites (Omar, 2017). In desert regions impacted by explosives testing and use, the loss of biological diversity and desertification are the most serious ecological problems. The main causes of desertification are harsh climatic conditions, increased human activities and pressure, overgrazing, and war activities. The importance and fragility of topsoil and loss of native vegetation cover accelerate land degradation further. Several plant and animal communities can become either rare or endangered due to human activities in desert regions. Under these circumstances, establishment of site monitoring and protection measures and restoration of floral and faunal diversity to their original status will assume great importance to assure continued use of explosive testing ranges in arid regions.

Another study clearly demonstrates the consequences of explosive effects on the physical landscape (Alaba, 2018). This study in an arid environment shows that detonated explosives are stable in soil due to their chemical structures and will easily bind to soil organic matter, which makes soil remediation difficult. High concentrations of explosives residues can result in the decrease of terrestrial plant biomass, abnormal growth in plants, and can cause a decrease in biomass and fertility of earthworms. Therefore, the contamination from explosives residues can go beyond physical impacts. Contamination from explosives use can also include the presence of explosives residues, carbon monoxide, and nitrogen oxides as airborne particulate matter, dust, smoke, and undetonated explosives in the environment. The effects of explosives therefore can have a direct influence on the growth and development of ecosystems and the geomorphic and topographic deformations that affect areas where explosives have been used.

Ultimately, the results of this study indicate that explosives testing and use result in contamination of the soil environment with explosives, along with alteration of the natural surrounding landscape. Developing an understanding of how explosives accelerate land degradation and cause environmental disturbance will help to create remediation and ongoing site management strategies for similar sites to continue the sustainable use of active testing ranges.

6.5.2 Research question #2

How can explosives use accelerate land degradation and contribute to desertification?
In what ways does explosives use contribute to anthropogenic disturbance of the environment?

The findings from this study indicate that explosives use does contaminate and degrade the land upon which it is detonated, both through the introduction of explosive compounds that remain in soil for long periods of time and from the deposition of various materials, such as metal fragments and plastics. This can degrade the surrounding landscape by causing an unsightly debris problem. It can also contribute to disturbance of the environment by changing and altering the landscape equilibrium of the surrounding environment from blast pressure, leading to rock fracturing, from mass rock movement, and the alteration of natural drainage patterns. All these consequences of explosive use can contribute to increased erosion and sediment transport, desiccation and aeolian transport by wind, along with long-term landscape alteration from continued use.

The scientific evidence that humans are causing unprecedented anthropogenic disturbance is well documented. Among human activities, warfare is almost constant and can be far-reaching in its ecological impact. There have been over 122 armed conflicts around the world in the past 20 years, and 163 of 192 countries currently maintain regular armed forces, along with explosives and weapons testing and training activities associated with defense (Machlis, 2008). There is also significant research and resulting evidence that explosives use does accelerate land degradation. Land degradation can be caused by multiple natural forces, including extreme weather conditions, particularly drought. It can also be caused by human activities and land use patterns that pollute or degrade the quality of soils. It negatively affects food production, livelihoods, and the production and provision of other ecosystem goods and services. Desertification is a form of land degradation by which fertile land becomes desert.

One particular area of concern for increasing areas of desertification is in Africa. Climate change predictions for Africa show rising temperatures with potentially serious impacts on already stressed resources, including water and food (IPCC, 2007). The rate of land degradation and possible desertification may be further aggravated by global climate change (United Nations Environment Programme, 2005). Urbanization, loss of fertile topsoil, overexploitation of water resources, overgrazing, destruction of natural vegetation, and rapid land use change are all causes for desertification.

Climate change is characterized by shifts in temperatures and weather patterns on a planet-wide scale. These shifts can be natural, such as normal variations in the solar cycle. However, since the 1800s, human activities have been a major contributor to climate change, primarily due to burning fossil fuels like coal, oil, and gas. Greenhouse gas concentrations are at their highest levels in 2 million years, with carbon dioxide levels at 420 ppm (CO2, 2023). As a result, the Earth is now about 1.1°C warmer than it was in the late 1800s. The last decade, 2011-2020, was the warmest in human-recorded history on Earth. Various impacts from both a warming planet and from climate change will be encountered. The most significant of which is glacial ice melt, leading to not only a rise in sea levels, but changes in regular precipitation on land masses, also contributing to increased desertification.

According to current analysis, environmental damage from war, like that currently happening in Ukraine, is growing, with the possibility of long-term consequences (Mednick, 2022). Because of this war alone, more than 280,000 hectares (692,000 acres) of forests have been impacted, with an estimated $37 billion in environmental damage. Identified impacts include fuel oil in drinking water supplies and massive fires that destroy both forests and food supplies. Any impact of explosives on the local environment identified from sampling performed in May 2022 has not yet been released by the Kyiv Food Safety and Consumer Protection Agency. Toxic military scrap material and unexploded ordnance (UXO) remain spread across the land.

Soil compaction, surface sediment disruption, and land degradation

As indicated in this soil study from explosive testing ranges, the activities associated with explosives testing and use can also potentially lead to desertification of surrounding areas. The results of this study show that there are various categories of land degradation that can be traced to explosive testing and use. One example demonstrated from this study is cratering of the soil surface and mixing of the soil by explosive effects. This is termed bombturbation and is indicative of the presence and use of explosives (Hupy, 2012). After detonation, an excavated pit of mixed soil layers, with an accompanying rim of debris along the immediate edge of the crater is apparent. Deposition beyond the immediate rim is dispersed, so soil, debris, and explosive compounds can be scattered around the surrounding landscape. Because the explosive event can be considered both a vegetative denuding and depositional geomorphic process, it can be considered a cause of land degradation.

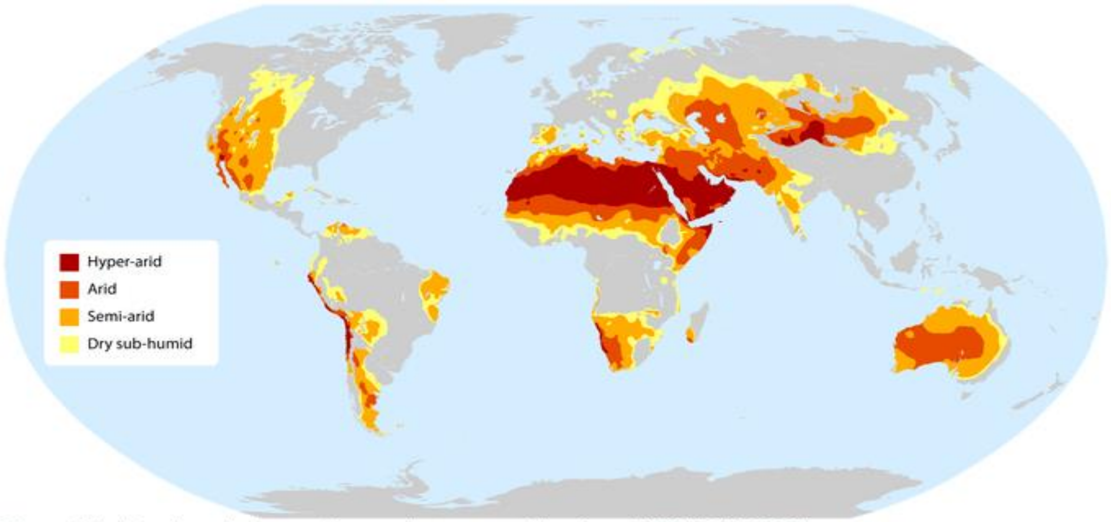
This study also demonstrates that explosive testing activities can disrupt the important relationship between native vegetation and soil. Explosive use causes severe soil compaction. Depending on the soil type, the degree of compaction, and status of natural vegetation, soil compaction can reduce the infiltration capacity of soils by 20-100% (Gregory, 2006). Consequently, runoff, erosion, and surrounding terrain deformation can increase. Soil compaction reduces the ability of the soil to hold water and decreases pore space. The infiltration rate will decrease while the penetration resistance will increase in compacted soils impacted by explosive testing and use. Plant roots in compacted soils will encounter considerable difficulty in penetrating the soil layers with noticeable effects on seedling establishment and plant growth. This study clearly demonstrates that vegetation has difficulty recolonizing denuded explosive ranges. The lack of diverse vegetation can also degrade landscapes by accelerating the loss of topsoil from wind erosion.

Wind erosion in arid areas, like the study region, is very active due to scarce, irregular rainfall, the prevalence of strong westerly winds, and extremely hot, dry weather during summer months. All of these issues can increase the mobility of soil particles. The severity of wind erosion depends on climatic conditions, vegetative cover, both type and density, soil erodibility, and land use. Prior to disruption from explosive testing activities, the original landscape in the study area had a protective desert soil surface, known as desert pavement, that served to stabilize the underlying soil with native vegetation covering and stabilizing the soil. Testing range structures, such as bunkers, berms, and trenches, when constructed for testing activities, are built over a large area with heavy equipment, exposing soil materials to wind erosion, affecting desert biodiversity, soil and water relationships, and long-term soil productivity. Vehicles travel from location to location for testing operations, which also disrupts surface soil. Environmentally, the entire process of explosive testing operations causes a wide variety of damage including soil pollution by residual explosives, loss of natural vegetation, surface soil deformation, and topsoil loss. Displacement and disturbance of soil can also be observed as a significant alteration in regional topography in the study area. Grading test ranges and clearing debris from testing activities contribute to the continued removal of topsoil, changing the topography of the testing ranges when compared to the rest of the local landscape.

From the results of this study, the landscape degradation issues that are associated with explosives testing and use can be grouped into four categories: (1) soil compaction due to explosives detonation; (2) surface sediment disruption due to physical infrastructure-related activities; (3) disruption of vegetative and ultimately wildlife habitat; and (4) soil contamination with explosives residues, metal fragments, and other anthropogenic materials.

At a time when climatic and environmental change is the subject of much debate, this research into explosive testing and use focuses on locations in arid regions for two reasons. First, under many scenarios of global warming it is predicted that substantial portions of the earth’s land area, including the polar ice caps, will become hotter and drier. Second, human-induced environmental changes are inevitable in the earth’s arid regions because they contain 1/6 of the world’s population, of which are directly affected by the natural environment (Millington, 1994).

Arid regions of Earth are provided in Figure 27. The United Nations Environment Program (UNEP) defines an arid region according to an aridity index (AI), which is the ratio between average annual precipitation and potential evapotranspiration. Arid regions are lands with an AI of less than 0.65. Arid regions are found in most of the world’s biomes and climatic zones and thus constitute 41% of the global land area.



The world's drylands and subtypes. Prepared using spatial data from UNEP-WCMC (2007).

Figure 28: The world's arid regions.
(Source: https://www.fao.org/dryland-forestry/background/what-are-drylands/en/, accessed 5/23/2022)

Desertification appears to be an ongoing process across the globe, especially in the arid Southwestern region of the U.S, where this study is located, indicated in Figures 28 and 29. The results of this study show that desert-like conditions first develop in localized areas impacted by testing activities and nearby locations in the surrounding landscape, away from areas of geomorphological landscape equilibrium and areas with dense cover of diverse native vegetation. These localized areas then enlarge, spread, and merge, increasing the area of desert and degraded land in the local landscape. In the study region, the fragile ecosystem can be further disturbed by the continued removal of shrubs and other vegetation through continued testing of explosives and testing range site construction for the addition of new testing-related infrastructure, such as large buildings used as test structures, personnel bunkers, and roads. The removal of vegetation leads to the creation of deep incisions in the surrounding landscape for drainage water, resulting in increased sediment transport off site. Large-scale military movements can disrupt desert surfaces, especially in arid regions. The U.S. National Training Center in the Mojave Desert is a good example of a testing facility where soil compaction and increased soil erosion, large-scale denuded landscapes, and changes in the structure of native successive plant communities are all evident (Caldwell, McDonald, & Young, 2006). At this location, there is evidence that testing and training activities are impacting the continued growth and succession of the native Joshua tree. Regions that are currently undergoing desertification are now experiencing temperatures rising 3 times faster than the global average (Hostile Planet, 2019).

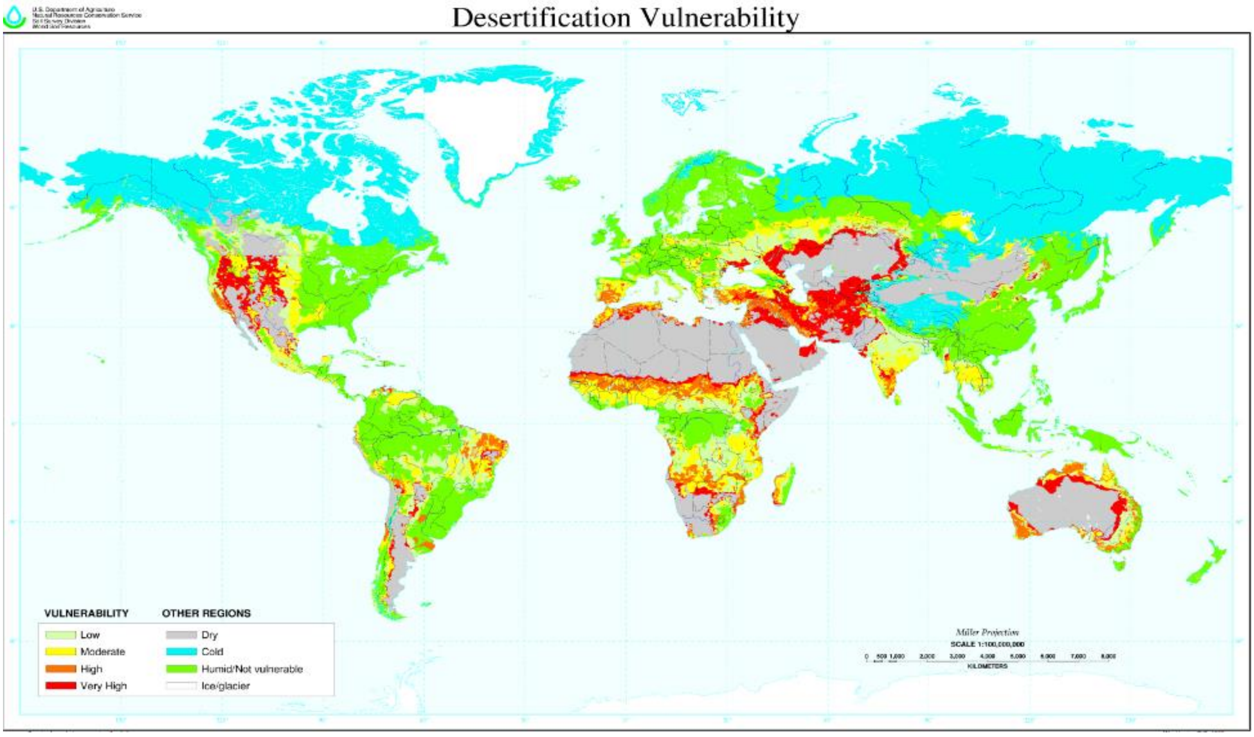


Figure 29: World map of desertification vulnerability.
(Source: U.S. Department of Agriculture, 1998)

This study demonstrates that explosive testing and use can impact soil and surrounding landscapes in various ways. Site activities related to explosive use can also impact local environmental conditions, contributing to the increase in arid, and often unusable, land. But there are geotechnical approaches that can be used to stabilize testing ranges against surficial erosion and mass movement.

6.5.3 Research question #3

What technical measures and management strategies can be implemented to reduce impacts from explosives testing and use? How can these concepts be easily implemented for suitable management in arid locations around the globe?

Impacted landscape recovery rates can take extensive time to recover without human intervention. Research shows that in an average natural ecosystem, approximately 22 years is required to recover from an impact (Jones, 2009). The period required for a location's recovery can range from 10 years for grassland communities to 42 years for more complex communities such as forests. If multiple disturbance events occur or an impact occurs in a complex or old growth ecosystem, then the recovery period can be hundreds of years. Studies have also shown that the minimum interval between military training activities to allow for natural recovery needs to be at least 10 years if environmental degradation is to be avoided (Jones, 2009). This period can be significantly longer, ranging between 50 and 200 years in some locations, for example, in those containing old trees, which can have a lengthy growing period. If landscape-scale environmental degradation is to be avoided, then solutions are required which explicitly recognize and manage environmental disturbance associated with explosives training and use.

Arid land, like the location used in this study, can be successfully managed using stabilizing methods. Careful management, using man-made or natural materials to promote colonization and manage successions of native plants and xerophytes, can stabilize arid locations. Such stabilization methods can halt further desert encroachment and reduce the environmental damage from explosive use on sensitive areas downgradient. Based upon this study, the main problems encountered from explosive testing and use appear to be increased wind and water erosion, with both on site and off site effects, loss of vegetative biodiversity, and the negative effects of vegetation change and soil erosion on the local hydrological cycle, leading to increased runoff and channel creation during rainstorms. These mechanisms can promote the movement of materials off site, leading to the spread of contamination.

There are various technical measures and management strategies that can be implemented to both combat desertification and to reduce impacts from explosive testing and use. These include various techniques to use as appropriate strategies for reclamation programs. Stabilization of a site uses structures in combination with biological elements to arrest and prevent slope failures and erosion (Gray & Sotir, 1996). Effective stabilization measures and techniques include:

Windbreaks. Areas with aeolian transport can implement extensive planting of trees and shrubs as windbreaks. Windbreaks can provide valuable wildlife habitat and timber, erosion protection for stream and riverbanks, and act as filter strips for runoff, protecting water quality and fish habitat. Professionally designed windbreaks can provide additional income from wood products, tree crops, and wood for fuel while enhancing wildlife populations. Finally, windbreaks add beauty to the landscape and increase the value of the land.

Irrigation. Irrigation not only adds water to desert soils and, when silt-laden river water is used, can improve the physical, chemical, and biological properties of reclaimed soils. Horizontal layers of sediment will build up as deposits over time from irrigation, creating a new soil horizon of various particle sizes and crossbedding, slowing erosion and deep channel cutting from intense rainstorm events.

Straw and clay checkerboards. To provide an environment for native and xerophytic vegetation to colonize and survive on impacted soils, localized surface stabilization is essential. Artificial checkerboards comprised of straw and clay can be used to increase surface roughness and reduce wind erosion, thereby encouraging plant colonization.

Use of native plants. To accelerate the process of plant recolonization, areas stabilized using artificial means should be planted with native and xerophytic plant species. The morphology and physiology of xerophytes are adapted to conserve water and have the capability to store large quantities of water, especially during long dry periods.

Land enclosure. The combined effects of overgrazing by livestock animals, the impact of off-road vehicles, along with explosives testing and use can all severely degrade arid regions. Proper management of explosive testing ranges is essential for both successful site recovery after testing events and for continued use. Plant communities will respond positively to fenced enclosures to prevent both human and animal impacts in terms of vegetation coverage, height, above and below ground biomass.

Chemical treatment. Various chemical agents can be used on impacted sites for the stabilization of deserts and to prevent movement of sand and surface materials. However, material and application costs, along with the added problem of inaccessibility and distance to most active testing ranges, make these treatments prohibitively expensive in many regions.

Many other applicable techniques can be employed to reduce the harmful effects of explosive use. These include continued testing range oversight and monitoring and land use management strategies such as rotating site activities to different testing ranges from areas currently in active use. This is based on agricultural approaches to land management where land is rested from either grazing or harvesting pressure, allowing for recovery to occur. For sites that have continued drainage water runoff, explosively contaminated areas can be treated with the construction of downgradient wetlands or lagoons, with the realization that these sites will eventually require sediment removal. The added benefit is that explosive contamination will be contained in smaller areas and off site transport can be controlled. Other potential treatment techniques for explosively contaminated sites are wide ranging. They include transitioning these locations to other uses, including transfer to other government agencies for rangeland leases and the establishment of protected areas or conservation areas to serve as nature reserves and wildlife sanctuaries (Havlick, 2011).

Management strategies for explosive testing range continued use

There are various effective management approaches for explosive testing ranges include retention, rotation, mixed use, and intensive use (Zentelis, 2017). The management approach to be applied at a specific location is based upon the level of environmental disturbance, the training type and frequency, and the local ecosystem recovery rate. For example, training that results in high levels of local explosive impacts and is conducted in ecosystems with slow recovery rates, should occur on a dedicated sacrificial range that is regularly monitored and sampled for contaminate concentrations, along with the addition of soil stabilization measures to prevent movement of materials.

Retention is a land management strategy that has its origin in forestry, promoting retention of stands of undisturbed forest within logging areas (Zentelis, 2017). Explosives testing areas generally contain significant areas of undisturbed land, including safety buffer areas near homes and highways, and sites near environmentally sensitive areas such as ponds and other water bodies, that can be used as retention areas. These areas can then be designated and protected as critical habitats for wildlife.

Rotation management traditionally has been used to rest land from agricultural production to allow soil nutrient replenishment (Zentelis, 2017). This management strategy can be applied at site conducting training and testing activities to different sites which can serve to provide different challenges and scenarios. Rotation management can also be used to remove a range from testing activities to allow the environment of a site to recover, however, this will not result in recovery of the environment to its pre-testing conditions.

Land sharing or mixed use can be implemented to integrate conservation and production across a landscape, spreading a lower level of impact throughout a greater area of the environment (Zentelis, 2017). An example is mixing farming and forestry activities where they sustainably co-exist. A common mixed-use strategy is land sharing and wildlife friendly farming. An applicable application for explosive testing ranges is to dedicate specific areas for training activities such as 4-wheel drive training purposes or for patrol training of personnel.

Land sparing/TRIAD (intensive use) is used to maximize crop yields through intensive farming or logging in an area, and separate areas are created for biodiversity conservation (Zentelis, 2017). For example, farming and logging areas can become production zones that are managed to both maximize resource output and yield. Two common intensive land use strategies are

Land Sparing in agricultural production and TRIAD harvesting in forestry. Explosive testing activities that occur repeatedly in one location can be analogous to intensive use agricultural and forestry production, with the explosive research and testing activities being the “yield” derived from the land. Unlike agriculture and forestry yields resulting from intensive use land management strategies, the training yield of the testing range will never be exhausted.

Due to the nature of explosive testing activities, where different testing scenarios can have various impacts, combining rotation and intensive use is probably the most desirable technique to implement. This management strategy minimizes large scale landscape impacts by limiting the disturbance to intensively used ranges and reduces management costs by minimizing the area of land that requires future remediation.

Treatment strategies for explosive contamination in soil

Remediation strategies for explosive contamination in soil must be considered on a site-by-site basis. For example, the toxicity of nitroaromatics may limit the applicability of some biological methods when concentrations are high or the treatment process may produce recalcitrant reaction by-products. Conversely, energy-intensive treatments such as soil incineration may be too expensive or may cause other environmental problems such as NOx emissions.

Phytoremediation, although not as widely used as other methods, has the potential to become an important strategy for the remediation of soil contaminated with explosives. It is best suited where contaminant levels are low, such as at explosive testing ranges where pollution is diffuse and where large, contaminated areas require treatment. This *in situ* treatment method has the advantage of low treatment costs, but the disadvantage is a considerably longer treatment time.

A recent study demonstrates that phytoremediation is a viable method of treatment for explosively contaminated soil. The remediation of contaminated areas near an ammunition plant applied geotechnical engineering approaches to efficiently treat the site (Gerth, 2005). Explosively contaminated runoff water from the site was seeping into the soil. The surrounding soil was contaminated with TNT, at levels of 1 gram TNT/kg soil up to 50 grams TNT/kg soil. Crystalline TNT was also observed on surface soils. The area of contamination was estimated to be about 2000 m^2.

Highly contaminated hot spots at levels above 1 g TNT/kg soil were first excavated. Next *in situ* bioremediation was initiated using natural microbes in the soil that were stimulated by the addition of a carbon source, molasses. Iron particles were also tilled into the top surface layers of the soil. The TNT concentration was reduced to 0.1 mg TNT/kg soil after 2 years of this biological treatment technique. To reduce continued seepage into groundwater under the site, a geotechnical liner along with a clay layer were installed. Finally, a vegetative cover over the area was established to visually restore the site and to help achieve long term protection of the underlying aquifer. The cover was comprised of treated soil. Grass and poplar and willow trees were planted over the site to minimize the formation of leachate by encouraging evapotransporation and to activate phytoremediation and removal of remaining explosive compounds. The cost of the initial materials was less than those to fully excavate and remove all soil in and around the site. Excavation and off site transport of only a small amount of contaminated soil was necessary.

Wetland treatment units are one of the best options to remediate extensive areas of land contaminated by explosive compounds. Wetlands are defined as land in which the water table is at or above the ground surface long enough each year to maintain saturated soil conditions and the growth of related vegetation (Rittman, et al., 1994). Wetlands used in this manner include natural marshes, swamps, bogs, peat lands, and systems specially constructed for wastewater treatment and site runoff. A major constraint on the use of many natural wetlands is the fact that they are considered part of the receiving water by most regulatory authorities. As a result, the water discharged to the wetland has to meet discharge standards prior to application to the wetland.

Constructed wetland units avoid the special requirement on influent quality. Constructed wetlands containing rush plants (*Juncus effusus*), reed plants (*Phragmites australis*), or water hyacinth (*Eichhornia crassipes*) be used for discharge water treatment with gravel- and sand-filled bottoms supporting stands of vegetation. Typically, a constructed wetland will perform better than a natural wetland of equal area since the bottom is usually graded and the hydraulic regime in the system is controlled. Constructed wetlands have exposed free water surface, as well as a vegetated submerged bed (VSB), utilizing subsurface flow through a permeable medium. For optimum performance, all wetlands require at least the equivalent of primary treatment as the preliminary treatment level. This can be obtained using the application of screened or degritted wastewater to the inlet zone of the treatment bed. Artificial wetlands can be easily built on contaminated sites to treat explosives contamination. Bentonite clay layers or geosynthetic materials such as geomembranes can be used to line the wetland and prevent infiltration of contaminated water into underlying aquifers. Gravel drains can be added to act as filtration units, trapping large particulates. These treatment units are relatively inexpensive to operate and maintain and are good for remote locations requiring minimal oversight.

The treatment of sites impacted by explosives should always include a program of geotechnical stabilization of the area, construction of water drainage collection systems, and implementing passive treatment systems such as constructed wetlands to treat intermittent runoff water from intense rainstorms, especially in arid regions. Chemical and climatic constraints, including pH variations and elevated metals content in both the soil and in runoff water, along with the seasonal variability of runoff water discharge can make any explosive testing range management activity difficult, so ongoing monitoring and sampling is essential to track the effectiveness and progress of the program.

Most importantly, in regard to ongoing global explosive development and testing, ecological science should be incorporated into military policymaking and planning. These applications can provide better policies to mitigate warfare preparation impacts, such as those resulting from explosives development and testing activities and from explosives manufacture. International regulations protecting the environment should be enforced, while new regulations covering military and war remnants and postwar restoration should be established. An example of this is the Convention on the Prohibition of Military or Any Other Hostile Use of Environmental Modification Techniques (ENMOD), prohibiting environmental modification tactics such as weather manipulation, defoliation, and crop destruction as tools of war (United Nations General Assembly, 1978). ENMOD has been ratified by 70 countries yet remains largely unknown and unenforced.

Military sites and explosive testing ranges that are no longer actively used can serve as prime candidates for restoration, rehabilitation, and conversion for study into applicability into conservation sites. Examples include closed or decommissioned bombing ranges, training facilities, munitions plants, weapons storage facilities, ports, and airfields. War-impacted landscapes such as defoliated forests, battle sites, and land mine regions can serve also as study areas for restoration and rehabilitation.

CHAPTER 7 CONCLUSIONS

7.1 Summary of the findings

This study investigates the effects and impacts that explosive testing and use has on soil and surrounding physical environment. There are several aims of this study, first and foremost, to determine if explosives use leads to persistence of explosives residues remaining in soil over time.

Another important consideration of this study is to determine how explosive testing and use can alter and change landscape equilibrium and how this can affect the movement of contamination to other locations.

This research helps to answer important questions relating to explosives testing and use. The study is guided by three research questions:

1. How does explosive testing and use affect soil and the physical landscape?
2. How can explosive use accelerate land degradation and contribute to desertification? In what ways does explosive use contribute to anthropogenic disturbance of the environment?
3. What technical measures and management strategies can be implemented to reduce impacts from explosive testing and use? How can these concepts be easily implemented for suitable management in arid locations around the globe?

To provide solutions to these questions, site characterization through soil sample analysis was performed to better quantify how explosives testing and use impact soils and the physical landscape. Soil samples from active explosive testing ranges were analyzed in this study to determine explosive content commonly found in similar locations. This research also identified how explosives use can accelerate land degradation and how it contributes to desertification of local regions. This was accomplished by studying active testing ranges in an area with limited rainfall in an arid location. This study also demonstrated how explosives use can be considered a contributor to anthropogenic disturbance of the environment by studying how similar activities can impact other locations. Finally, this work intended to provide technical measures and management strategies that can be easily implemented at other sites to reduce explosive impacts, especially in arid regions around the world.

This chapter will provide a brief overview of the study findings and their significance, including the explosive compounds found in soil samples from the study location. Geotechnical effects of explosives testing and use observed in and around the explosive testing ranges will also be examined. Finally, an evaluation of this study and applications of this research will be discussed.

7.2 Explosives and other compounds found in soil in active explosive testing ranges

Currently, the explosive formulations most commonly used in conventional explosives include 2,4,6-trinitrotoluene (TNT), Composition B, which is composed of a mixture of TNT and RDX, and octol, composed of TNT and HMX (Chatterjee, 2017). These compounds should be expected to be identified in soil in explosive testing ranges, near explosives manufacturing plants, and near sites that load, assemble, and package explosives into munitions items, as they all experience the continued presence and long-term use of explosives. TNT and its photodegradation products are among the most commonly identified contaminants in soils and groundwater near sites that manufacture and test explosives (Anderson, 1999).

Based upon geotechnical soil analysis of uncontaminated soil that was collected from background locations in the study area, the testing range soil was classified as coarse-grained soil composed of well-graded sand (SW), according to the U.S. Unified Soil Classification System. The specific gravity of the local soil was determined to be 2.41, indicating that the local soil is a sandy soil containing organic matter. The moisture content calculated from soil sample analysis was 17.0%. This value indicates that it is normally quite dry and contains many soil voids.

The explosive compounds identified through HPLC analysis of active testing range soil in this study included HMX, RDX, TNT, and the TNT transformation products 2ADNT and 1,3,5-TNB. The highest concentration of HMX identified in this study was 2.3 to 2.5 mg HMX/kg soil. For RDX, the high concentration identified in soil was 0.76 to 0.85 mg/kg soil.

TNT was identified in only very small amounts in soil at two locations, at maximum concentrations of 0.27 to 0.32 mg TNT per kg soil. The transformation products 2ADNT and 1,3,5-TNB were also only identified in trace amounts in soil samples from a few testing ranges. The TNT transformation product 2ADNT was found in soil from only one location, at a concentration of 0.55 mg 2ADNT per kg soil. 1,3,5-TNB, another TNT transformation product, was found in soil from a different active testing range, at a concentration of 0.19 mg 1,3,5-TNB per kg soil.

A significant conclusion based upon this study shows that explosive compounds encountered at sites with continuous explosives testing and use will include TNT, RDX, and HMX. The levels identified in this study are comparable to explosives concentrations found in similar locations, including testing ranges and areas that experience long term explosives use.

Ammonium nitrate fuel oil (ANFO) is another explosive compound that can be encountered in soil in active testing ranges. Soil samples from this study also found the residual presence of nitrate and ammonia from the long term and continuous use of ANFO. ANFO is a simple fuel-oxidizer mixture of ammonium nitrate and fuel oil that is widely used as an explosive in mining and construction industries. ANFO is used extensively as the main charge in large improvised explosive devices (IEDs) around the world (Texas University at Austin for Advanced Technology, 2008). It is a reasonably powerful explosive, easy to manufacture, and requires little to no specialized skills or equipment to handle. It is generally characterized as having a large heaving force and low rock shattering capability. Other materials can be added to ANFO before initiation, such as aluminum powder, to increase the energy output and shattering capability.

The analytical results strongly indicate that when ANFO is in explosive compounds, the principal components found in similar soils will be nitrate and ammonia. The highest concentration of nitrate identified in this study from HPLC soil sample analysis was 731.9 mg nitrate per kg of soil. Most soil samples collected from explosive testing ranges had much lower concentrations, from 58.5 mg/kg to 21.5 mg/kg of soil. A soil sample collected from an uncontaminated background site contained 32.5 mg nitrate per kg of soil. Ammonia was commonly found in many of the testing range soils and in the background samples analyzed in this study. The results show the largest concentration found in this study at 52.5 mg ammonia per kg of soil. A soil sample from a background location was found to contain 38.5 mg ammonia per kg soil, which was comparable to concentrations found at other similar explosives testing ranges, from 38.5 mg/kg soil to 28.0 mg/kg soil.

A significant conclusion from this study indicates that nitrate and ammonia will be among the most prevalent compounds identified in areas where continued explosives use occurs, especially in arid regions. Nitrite will likely not be readily detected in soil in these areas due to denitrification.

The range in explosive compound concentrations measured in this study in surface soil samples suggests that detonation of explosive materials does load soils with explosive compounds. All soil samples in this study were collected from areas where explosive materials were detonated. However, bulk soil samples at each location were not collected. Therefore, it is difficult to draw conclusions from the results on how sample proximity to a detonation event controls the loading and resulting soil concentration of explosive compounds in active testing range soil. At an explosive detonation site, the heterogeneous nature of the detonation event along with soil biogeochemical conditions will play a major role in the deposition and overall fate and transformation of explosive compounds.

Other sources of soil impacts identified in this study include metals and other cartridge casing materials used to enclose the explosive. Metals can be transformed into various compounds once introduced into soil, especially from weathering processes. During detonation events, temperatures can exceed the melting point of some metallic compounds, which in turn can create alloys, metallic complexes, which have their own environmental impact. The metals most commonly encountered in explosives testing ranges and in areas where explosives are used include lead, copper, zinc, and aluminum (Walsh, 2003). Corrosion of metal fragments, the movement of materials, and biotransformation in the soil environment is a complex phenomenon, depending on the explosive type, the cartridge material, biogeochemical soil conditions, and on water availability in different locations (Brannon & Pennington, 2002).

The results of this study indicate that arid regions that have continued testing of explosives can be expected to retain explosive residues and their transformation products in surface soil. These compounds can remain in the localized environment for some time. In arid regions, some explosive compounds may remain adhered to soil particles, but upon exposure to wind and water, especially during excessive periods of rainfall, be transported off site to nearby waterways. Explosive compounds and their residues contain inorganic constituents that can become mobile in water bodies used for drinking water and irrigation. Some inorganic compounds found in both surface and groundwater used for drinking water supplies can cause health concerns upon continued use by both humans and animals.

7.3 Evaluation of this study

Based on the study results, explosives will typically degrade slowly in soil. Mineralization to very simple compounds such as methane, carbon dioxide and nitrates will occur under anaerobic rather than under aerobic conditions in soil (Fuller, 2009). This study demonstrates that TNT will be retained on surface soil and may also transform into various metabolites. An important result of this study is that TNT compounds can be expected in soil surrounding areas exposed to explosives testing and use. In other studies evaluating soils containing high clay content, TNT will remain absorbed and trapped between clay layers (Pennington & Patrick, 1990). This mechanism could possibly prevent the movement of TNT off site. TNT transformation products commonly found in soil include the formation of two mono-amino transformation products, 2ADNT and 4ADNT (Brannon & Pennington, 2002). These were also observed in testing range soil analyzed for this study.

According to the literature, the primary release mechanisms of RDX into the environment are from process wastewater during explosives manufacture, testing and training activities involving explosives, and open burning/open detonation (Sheremata, et al., 2001). Transformation products of RDX are not frequently observed in soil from similar studies. Although RDX is sorbed less than TNT by soils, RDX has been observed to move into groundwater, impacting areas away from the point of entry (Williams, Reddy, Quinn, & Johnson, 2015). RDX has also been identified in various species of aquatic plants grown in explosively contaminated water. In general, RDX is not easily retarded in soil and is highly mobile in water, as it has a water solubility of 42 mg/L. RDX then tends to accumulate in water, especially in groundwater. An important conclusion from this evaluation will be that continued monitoring of water resources near explosives testing ranges and sites where explosives have been used is necessary for the protection of nearby drinking water sources.

Little is known regarding the transformation of HMX. In laboratory studies, HMX has been found to be stable under a broad range of redox and pH conditions. Transformation products of HMX have rarely been detected in environmental samples, suggesting that HMX transformation in soil does not easily occur. HMX has a low log K_{oc} of 0.54, which indicates that it has a potential for mobility in soil. The results obtained from this study indicate that further investigation into HMX soil concentrations in active explosive testing ranges is necessary to better characterize the impact that HMX can have in the environment.

Commonly used fuel oils in ANFO include kerosene, diesel fuel, jet fuel, and home heating oil. These fuel oils differ from one another by their hydrocarbon compositions, boiling point ranges, chemical additives and uses. Some chemicals found in fuel oils may evaporate easily, while others may easily dissolve in water. Other research studies recommend that dry, soft, and porous soils may wick away significant amount of fuel oil from ANFO during long intervals between explosive loading and firing (Brochu, 2010). The soil classification determined for the testing range soils analyzed in this study are very similar to these soils and therefore additional study of ANFO and its impact on the soil and surrounding environment is necessary to better evaluate the research results. Another conclusion derived from this study is that surface water and ground water near areas of explosives use should be monitored for the presence and concentration of nitrate and ammonia, especially in locations that use ANFO. These water bodies should also be monitored for the presence and level of fuel organics from leaking fuel oil from stored ANFO. This monitoring and management of water resources should be of the utmost importance in environmental sustainability in areas that test and use explosives.

7.4 Geotechnical effects of explosives testing and use

Landforms that comprise the earth’s landscapes will be in dynamic equilibrium if it is assumed that they have developed during a long and continuous period. Variability of landscape features is controlled by rock and soil type, vegetation, climate, and geologic structure. If the surface is disturbed by human activity, vegetation is destroyed, soil properties are altered, and erosion will be greatly accelerated. The geomorphic effect of explosives use is another important focus of this study. Explosives use can lead to permanent changes in topography and increased site runoff and sedimentation downstream. Nearby land is disturbed by explosives through the removal of surface soil covers and alteration soil profiles at explosive testing ranges through bombturbation and blast effects. New topographies and drainage basins can be generated by explosive effects. The balance between force and resistance is altered, destroying the equilibrium locally. This effect can, in turn, change the geomorphic system off site as well, due to the increased runoff water and sediment transport to locations nearby. Exposed, unconsolidated materials, such as loose rocks, on sloping surfaces are also exposed, leading to more off site impacts when moved downgradient through mass wasting.

An important conclusion observed from this study is that a site impacted by explosives use should be managed to ensure that the location has similar functions to that of the natural, pre-existing geomorphic system. This is engineering the site so that it geomorphically fitted, given the new post-explosive event conditions. This requires that the new landscape has hillslope lengths, gradients, and shapes like those of a natural system, with both hillslopes and channels having nonlinear curvatures. The design and construction of testing range drainage channels should be based on geomorphic principles, so that naturally functioning channels and stream beds can be used for excess runoff from storms. This is essential to ensure that water and sediment flows from the new landscape are improved in geotechnical design and that they integrate easily into the surrounding landscape. To reach this new equilibrium state, the geoengineered landscape should have a soil growth medium that allows flora and fauna to germinate, grow, and achieve vegetative succession as well as seamlessly blend with the natural surroundings. The ultimate goal of testing range management identified in this study is the creation of an engineered landscape that is ecologically similar to natural unaltered sites and indistinguishable from its disturbed surroundings. In this way, the site can be effectively managed for continued use, either as explosive testing areas or for some other use, such as a protected space or a wildlife refuge.

Another conclusion from this research is that areas where explosives testing activities occur should seek to disturb the smallest footprint possible. Increasing a site footprint is something that should be avoided, as the cleanup cost incurred at an explosive testing site is based on the amount of area disturbed. Another line of reasoning is that if there is less disturbed area, then there will be fewer site problems that require remediation. Implementing a geomorphic-based rehabilitation plan can provide functional landforms that work naturally with little to no human intervention. If slopes are too steep and space is limited at a testing range, such as those located in mountainous areas, extending the footprint to accommodate geomorphically stable landforms after site rehabilitation for continued use may not be possible.

7.5 Applications of this research

A common practice for explosive testing landscapes is to create and use flat test pads to detonate the explosive in a controlled location away from the public. They are constructed in different physiographic locations to simple linear designs to maximum test and evaluation efficiency. These sites are usually located in remote regions, so that the travel time and distance to the nearest population center is maximized. To manage runoff, control structures such as graded banks and engineered channels are constructed. There is usually little consideration as to how these landscapes will mature over time. Landform design in explosives test range management, using linear or terraced landforms, with revegetation programs, is usually not implemented at many sites due to continued use for explosive testing. However, rotating testing range use can provide sound environmental management in the long term.

There is a need at each explosive testing range or similar site to have a formal process of record keeping, including firing logs, historical documentation such as sampling data, and records of environmental management and rehabilitation programs. This will benefit the site by providing a robust database. Knowledge of both what works and, even more importantly, what does not work, is vital. This record keeping is important not just for each site, but for the entire explosives testing industry. Communication of this knowledge will greatly improve site management and rehabilitation at other sites impacted by explosives. Given the importance of developing sustainable landscape systems there may also be a need for diverse management and rehabilitation approaches, with their successes and failures to be collected in a central database. This would allow for important information to be available locally, nationally, and internationally and would enhance management at many areas impacted by explosive use.

This study can also add to the knowledge of classification of emerging pollutants. Emerging pollutants are released into the environment from a wide range of sources, including pharmaceutical residues, personal care products, synthetic colorants, pesticides, surfactants, polycyclic aromatic hydrocarbons (PAHs), explosives, and polychlorinated biphenyls and dioxins. These types of pollutants are widely dispersed as organic contaminants in the environment. They often have a low solubility in water and are not easily degradable.

Different organic pollutants exhibit different properties in the environment. They can be classified as natural or synthetic compounds, including volatile organic compounds, pesticides, antibiotics, herbicides, industrial byproducts, and residues from the incomplete combustion of fossil fuels. Organic pollutants are persistent in nature and can remain in the environment up to numerous decades or even centuries before their degradation occurs (Tomar, 2019). Organic compounds can exhibit unique characteristics, as they can be adsorbed on various soil particles or persist in a vapor phase, both of which can lead to transport in the environment. Organic pollutants have been found in ice and snow at the North Pole. This indicates that organic pollutants can travel long distances and reach the far distant regions of the world (Kumar K. , 2005). Persistent organic compounds in the environment can cause stresses in both plants and soil microbes, by affecting cell division, respiration, and other metabolic processes inside cells. However, remediation of soil and water contaminated with organic compounds requires a high cost.

This research can provide important approaches for characterizing active explosive testing ranges by using field screening and soil sampling to develop a plan for remediating contaminated areas, while managing and maintaining ranges for continued use and, at the same time, protecting the surrounding environment. This research is especially applicable to lands subjected to explosives use in arid regions of the world. As current conflicts and weapons use clearly indicate, significant portions of both arable and arid locations will require management and remediation when conflict ceases and populations return. In arid regions, research indicates that soil formation is a slow process and ecosystem recovery can take extremely long periods of time (Belnap, 1995). As human population increases and farmable land space decreases due to increasing global temperatures, the geotechnical engineering approaches recommended in this study can be implemented to improve land in regions impacted by explosives use.

This research may be practically useful in real world situations by contributing to a number of key issues in the field of explosives development, testing, and use. Among the important considerations are explosives testing site management and rehabilitation, where highly disturbed areas can be engineered to become sustainable landscapes. Commonly used conventional explosives, such as HMX, RDX, and TNT, can be found in soil from arid regions of the world that experience explosives use, weapons testing, and repeated warfare and conflicts. There is also an indication that natural attenuation processes by native microorganisms and local soil and atmospheric interactions will lead to the transformation of explosive compounds into other residual compounds.

Many of the risks faced by the world today are products of certain processes of modern technology that have led to effects beyond what could have been imagined (Beck, 1996).

In conclusion, this study contributes to the literature by demonstrating that explosive use can generate various environmental impacts, often leading to significant anthropogenic disturbance of the surrounding environment. Active and continuous use of explosives often leads to residual unexploded ordnance (UXO) in the landscape, chemical contamination with both organic compounds and explosive residues, landscape alteration, vegetation removal, and increased soil erosion. Often, continued explosives use, especially in warfare, can lead to intense pollution of ecosystems, unsightly metal scrap material along with UXO, damaged and destroyed infrastructure, degraded landscapes and ecosystems, and repeated soil compaction.

CHAPTER 8 RECOMMENDATIONS

8.1 Introduction

This study serves to identify the impacts that explosives can have on the environment and applicable corrective actions that can be implemented for site remediation in similar arid regions. The results of this study demonstrate that explosive testing and use can leave various explosive compounds and their transformation products in soil after continuous use. Explosive testing and use can also affect and alter the geomorphological equilibrium of the surrounding landscape, leading to increased soil erosion and movement of materials off site. The results of this study demonstrate that in an arid location where explosive testing is performed, the major explosive contaminants detected in soil can include HMX, RDX, and TNT, along with its transformation products 1,3,5-TNB and 2-amino-4,6-DNT. In testing ranges where ANFO is continuously used, nitrate and ammonia can also be detected in soil from those locations. There are various geomorphological impacts that can be identified based upon the results of this study, including blast and pressure effects on soil, vegetation, and impacts to the surrounding landscape, including hillslope alteration and mass wasting of rock slopes. Various cost-effective treatment techniques and geotechnical engineering measures can be applied to both contain the contamination from explosive use and to prevent further environmental deterioration, especially in areas located in arid regions of the world.

This chapter will suggest different ways of treating similar sites in arid regions that contain explosives and their residues to prevent contamination of locations off site, while at the same time, managing and protecting the area for future use. The recommendations presented in this chapter will be organized as follows. An overview of recommended treatment techniques for similar sites will be presented. Geotechnical approaches to remediation of explosives on impacted locations will be discussed. Recommendations for continuing site management for explosive testing ranges will be presented. Applications of this research to similar contaminated sites in arid regions will also be recommended.

8.2 Recommended treatment techniques for areas impacted by explosive testing and use

Approaches to prevent the contamination of surface soils, water bodies, and groundwater with nitrite, nitrate, ammonia, and organic compounds as well as the reduction of the production of toxic transformation products, should be proactively planned and implemented at explosive testing ranges. Many treatment techniques are applicable for soil in arid locations contaminated with explosives and their residues. The long term benefit of such treatments will most likely benefit sites that are closed to public access, sites pending final decommissioning, or to areas that are in inaccessible locations. For sites pending decommissioning, the time period between the start of site characterization and site closure can be long and can depend on the availability of adequate financial assurance and funding sources. On these sites, the wait time to establish access to adequate funding can be used to initiate treatment techniques that require little to no human intervention. For regions located nearby urban areas or city centers or in areas experiencing continued military actions, the applicable treatment will depend on current climate conditions, local soil conditions, and on accessibility to the site.

Explosive contamination, no matter the age of the site, will eventually enter groundwater and can impact the quality of drinking water and other water resources (Albright, 2012). Even explosives considered insoluble will eventually be found in groundwater given enough time to migrate through soil profiles. Explosives may also break down or be transformed by soil microbes into equally toxic transformation compounds.

Explosive testing facilities, weapons manufacturing facilities, and military research projects using explosives can leave residual contamination from a variety of processes. Currently, these sources of contamination are disposed of by various methods including incinerating soil and related waste materials with final disposal of residual materials in a licensed facility, opening burning in pits or open detonation on the ground (OB/OD), and underwater disposal. Prior to modern environmental regulation, these wastes were often buried or disposed of untreated in the ocean or in underground in soil (NATO, 2010). In addition, many explosive materials detonated on testing ranges have left chunks of material, including metal fragments, plastics, inorganic compounds, and undetonated explosive (UXO) on the ground and deep in soil.

Many of the explosive compounds used decades ago can still be detected in soil using numerous laboratory analytical techniques. As of 2021, the U.S. EPA identified over 37 sites with RDX contamination from explosives manufacture and use (U.S. Environmental Protection Agency, 2021). Dinitrotoluene (DNT), trinitrotoluene (TNT), HMX, and RDX are typically found in military ranges throughout the U.S., along with various transformation products and isomers (Miller & Barrall, 2005).

Many explosives also produce toxic vapors when detonated. This is a frequent problem for miners and other explosive users working in confined spaces. Adequate time must be allowed before reentry into a mine to allow toxic vapors to clear after using many common explosives. The scope of vapor contamination near closed explosive testing ranges, explosive burial sites, and nearby mines is largely unmonitored. In addition to explosives, lead, mercury, cadmium, and other toxic metals from shell casings and explosive components may also be present in soil.

Many types of mitigation measures can be implemented to remediate or control explosive contamination. Remediation measures can be readily implemented on closed testing ranges or in areas that were previously impacted by explosive use. Mitigation measures can be used on sites such as active testing ranges to ensure continued use without disruption, while at the same time, minimizing the impacts as they cannot be fully eliminated while testing is ongoing.

8.2.1 Physical treatment options

The most common type of physical treatment for soil contaminated from explosives is by using thermal treatment. Thermal treatment of explosively contaminated soil involves using indirect infrared heat emitted by a hot steel plate. Good results have been obtained when using this type of thermal treatment when surface soil temperatures are brought up to 460°C so the heat successfully penetrates the soil profile down to at least 15 cm, reaching a temperature high enough to decompose energetic ring compounds. The best results are obtained when the soil is allowed to cool after one hour of treatment, followed by another heating cycle. After thermal treatment, explosive concentrations will range from around 1000 mg explosive residue per kg soil to non-detectable amounts after treatment (Downe & Ampleman, 2015). Cost estimates for this technology are between €90 to €272 per cubic meter ($100 to $300 per cubic yard).

8.2.2 Chemical treatment options

There are different types of chemical treatment options. The most effective type includes abiotic treatment of explosives, including iron dependent depletion, oxidation technology, and degradation through electrolytic transformation (Johnson, Tratnyek, & Miehr, 2005). In iron dependent depletion, iron can be used in the decontamination of explosives in soil. Research demonstrates that 1% Fe^0 (w/v) can remove TNT and RDX from an aqueous soil solution within 8 to 96 hours (Kalderis, 2011). Zero valent iron has also been reported to treat highly contaminated soil, resulting in reduced TNT and RDX concentrations below USEPA remediation limits. When the process is modified using nanoscale zero valent iron particles in contaminated water and soil samples, the reaction time decreases significantly. This method can also be combined with other processes to remove intermediate products during TNT degradation in soil. Another chemical treatment option for explosive removal is degradation through electrolytic transformation. Various oxidants, such as potassium permanganate, and iron minerals like hematite and pyrite can be used to degrade TNT in soil slurries (Siegrist, Crimi, & Simpkin, 2011).

8.2.3 Biological treatment options

A cost-effective and efficient method of removing explosives from soil soils is to do so *in situ*. Phytoremediation, growing plants at contaminated sites or introducing specific plants to alter, and, eventually, reduce contamination of the soil environment, is a useful remediation method to implement on explosive testing ranges that are no longer active or on explosively-contaminate sites that are closed to public access. For example, some plants indigenous to areas with high soil metal content have been found to uptake and transform explosives and to concentrate such metals as lead, nickel, and copper into roots and aboveground shoots and leaves (McCutcheon, 2003). After soil concentrations are reduced to a regulatory limit, the plants can then be removed from the site and disposed of or used to recover the metal of interest. Explosive contaminants can be degraded to the point of mineralization using plants. Explosives will thus be effectively immobilized in natural plant parts and in the natural environment and their impact to the surrounding areas is greatly reduced. One method using the concept of phytoremediation that can be applied to explosive testing ranges is phytorestoration, essentially stabilizing the contaminants in a site through the direct use of green plants (Prasad & Frietas, 2003).

The plants chosen for phytorestoration should be those that establish easily, grow quickly, produce dense vegetation, strong root systems, and tolerate adverse environmental conditions. Phytostabilization is most useful for contaminated sites with sandy soils and high organic matter, like the soil analyzed in this study. Phytostabilization is especially practical in locations where a contaminated area is too large for decontamination for removal of the soil or as an interim strategy for site stabilization until a long-term solution to the contamination problem is selected. Recommended plants that are effective for phytostabilization in arid regions include Goldenrod (*Solidago hispida*), Willow trees (*Salix* spp.), Indian mustard (*Brassica juncea*), sunflower (*Helianthus annuus*), alfalfa (*Medicago sativa*), creosote bush (*Larrea tridentata*), tall fescue (*Festuca arundinacea*), and ragweed (*Ambrosia artemisiifolia*) (McCutcheon, 2003).

8.3 Geomorphic analysis of land disturbance in areas impacted by explosive use

Environmental impacts from explosive testing and use can also be observed in the change from natural site geomorphic processes to new geological operations at increasingly accelerated rates. Increased forces from explosive testing and use leads to decreased resistance from the surrounding landscape, and both occurring together, such as from explosive blast pressure effects on surrounding loose rocks and shear wall faces, can increase the rate and cumulative amount of geomorphic change. Consequently, explosive impacts lead to increases in hillslope gradient, which in turn, leads to increases in downslope gradients, creating more movement of materials, such as rock, soil, and testing debris to locations off site. The resulting changes in the characteristics of surface materials can also increase the rate and volume of runoff generation and sediment transport, resulting in more overland flow and channel cutting during intense rainstorms. Increases in hillslope gradient and length due to explosive effects can accelerate this process. More runoff moving faster downgradient can cut great channel depths and generate greater forces on surface materials, leading to even more sediment transport. Increases in hillslope gradient and length due to continued explosive use can accelerate this process. Surface resistance is also reduced due to explosive impacts. The vegetative cover which can slow erosion is changed or removed altogether. Soil properties, including permeability, soil moisture holding capacity, and grain size distribution, can be modified in such a way as to increase the susceptibility of surface materials by impinging forces. Resistance provided by geological structures and lithology can be reduced through continued rock fragmentation from blast pressure and explosive use.

8.4 Geotechnical approaches to control damage in areas impacted by explosive use

Geomorphologic principles should be used in the management of disturbed land, especially areas impacted by explosive testing and use (Toy & Hadley, 1987). To begin testing range site modification and remediation to prevent further damage, geomorphology and disturbed landscape design can be used to create a management plan with the best chance of success. To protect the surrounding environment from impacts related to the release of explosive compounds, the management of explosives during testing and detonation activities, along with management of surface water runoff and the prevention of soil and sediment moving off site from testing ranges is necessary. Explosive use can take its toll on the surrounding environment over time, but there are physical measures that can be implemented to slow geomorphic change. Identifying the impacts of disturbance on the soil profile can be provided by the observation of lack of vegetation or change in vegetation types. The replacement of surface soils with concrete or buildings on testing ranges will change underlying and surrounding soil properties, often altering the functioning of normal hydrological and geomorphic processes. Surface soil disturbance can alter its infiltration capacity and generate increased site drainage. The resistance provided by vegetation to rain and overland flow is altered. Fragmentation of the underlying rock foundation and of nearby hillslopes can also change the equilibrium state of geomorphological processes on sites impacted by explosives use.

There are various abatement and remedial actions that can be applied on testing ranges to decrease the severity of problems that explosive use can cause. Certain geotechnical improvements including the installation of geotechnical liners under newly planned testing ranges before construction can be used to control migration of water-borne materials to underlying aquifers. The installation of erosion control structures and implementing site specific preventative maintenance measures such as hillslope improvement design, can be used to minimize the impacts that explosive testing and use have on the surrounding landscape. In arid regions like the Southwestern U.S., the area is characterized by long periods of drought with intermittent storms, usually coinciding with flash floods. Many geotechnical approaches to controlling erosion can be used to control excess water runoff. These include the installation of erosion control measures to increase channel resistance to scour by suspended sediment. Some of these measures can also be applied to areas in similar arid regions that are impacted by explosive use from military conflict. Design considerations include explosive compound compositions and the volume of material moved, the flow rate of the water, which will fluctuate based on site specific temperature cycles, rainfall patterns, and humidity.

A specific geotechnical measure that can be easily implemented at sites that have current explosive testing or prior explosive use is applying the concept of storm water management, the use and application of structural and engineered control devices (Barbosa, Fernandes, & David, 2012). The goal of storm water management is to increase storm water runoff efficiency as water moves from higher elevations to surrounding lower elevations. This can be accomplished by dissipating storm water energy using engineered devices to reduce scour and erosion and preventing channel cutting and deepening around testing ranges. Storm water velocity can be reduced by reducing the range's gradient with grade control structures. Detention devices such as riprap can slow down surface flows as they move away from the site. Geoengineered structures such as hard armor can be installed at sites to increase the conveyance's resistance to erosion using channel lining.

Figure 30: Hard armor erosion control system.

The best management practices for erosion control will reduce or eliminate negative effects of erosion and sediment deposition from land downstream of the geoengineered structure. Some examples of how to apply this to storm water management practices include erosion protection at structures, rock outlet protection, and the application of erosion control matting. However, even the best design cannot manage extreme storm events. The engineered design must be created and installed to account for climate and expected flows, with the realization that the design will only work for the design flows. Unexpected storm events can often overwhelm the system design.

Figure 31: Geoengineered erosion control system to reduce stormwater flow velocity.

There are many geoengineered structures that can be installed on active explosive testing ranges to prevent transport of excess water, sediment, and other debris to surrounding areas. One such structure is an engineered conveyance system using riprap. They are comprised of large angular stones of varying sizes and layers that can serve as channel liners. Hydraulic design considerations include the expected flow velocity, channel depth, channel bedding material, and side slope orientation. This system will flex with freeze and thaw cycles to eliminate cracking.
Another geoengineered structure that can be installed in areas near structures, such as personnel bunkers and ordnance storage magazines, includes the installation of erosion control at structures. Using erosion protection measures at structures prevent building settlement, shifting of foundations due to water infiltration, and reduce the kinetic scouring effect of storm water. Large rocks or stones can be placed along the soil interface of structures and be used to reduce erosion at roof corners, drains, or natural drainage channels where water flows could undercut the structure. For long-term stabilization, wire-tied riprap can be used to minimize maintenance. Requirements include using angular-shaped rocks of adequate sizing, based upon the maximum design flow velocity. Some disadvantages to these systems will be the need for inspection at sites with deep conveyance channels, as accumulated debris can become deposited on the rocks. There are also soil retaining measures utilizing structural or vegetative stabilization practices to hold soil firmly in place and confine it to the boundary of the testing range. Some examples to implement include reinforced soil retaining systems and vegetative protection by planting and establishing vegetation along a channel. Reinforced structural measures used to hold soil in place can include continuous sheeting consisting of fibrous mats, steel, or concrete, covering the slope face in a continuous manner.

Erosion control matting consists of natural or synthetic mats that can be installed on slopes to reduce soil erosion on testing ranges. The matting reduces storm water impact by holding the soil firmly in place and holds moisture near the soil surface to help establish vegetation. It also will prevent scouring during intense rainstorms in arid regions. Erosion control matting can consist of an interlocking matrix of concrete blocks, placed over a geotextile fabric base. The voids present between the blocks allow vegetation to fully establish, decreasing storm water flow velocity and preventing future site erosion.

Installing a hard armor erosion control system can also provide testing range soil stability in channels and prevent movement of materials off site. The hydraulic conditions and flow velocities on the site will determine the block size and the layout design. This erosion control system provides flexibility and permeability as the open area of the hard armor mat allows for relief of hydrostatic pressure without permitting migration of fine grain size soil particles. Site specific native grasses and shrubs will colonize open areas of the hard armor mat and plant roots will enhance the stability of the channel slopes by creating binding networks of roots to increase soil shear strength.

Figure 32: Engineered conveyance system using riprap.

Hillslope design can also be used to reduce the impacts from explosive testing and use. Hillslope profile shape influences the magnitude of forces. A convex hillslope is more erodible than a uniform or straight hillslope. A convex hillslope is steepest where runoff is greatest, and a concave hillslope is steepest where flow is the least. Creating a concave hillslope profile is the most desirable design shape, relatively gentle in gradient and short in length (Stokes, et al., 2014). Surface mechanical site management, such as terracing, dozering, or plowing, can be used to reduce the force of flowing water by improving the site's infiltration capacity and shortening the hillslope length. The reduction of hillslope gradient in this way will help reduce mass movement and soil erosion. Mechanical grading can be implemented to reduce hillslope gradients for geotechnical stability.

Surface amendments of geomorphic significance include mulches and soil tackifiers. Mulches act like permanent vegetative cover. Tackifiers increase surface resistance by binding soil particles together into larger and less transportable aggregates. The addition of seeds with mulch or tackifier application for establishment of a vegetative cover is the best way to increase surface resistance to the forces of sediment transport. Vegetation will function to intercept, absorb, and reduce the kinetic energy of falling rocks or other materials and flowing water. Barren spots in soil on testing ranges can be regarded as indicators of hillslope erosion in arid regions because it often begins as rilling in barren patches of soil. These principles could also be incorporated into testing range management and hillslope design to reduce the probability of mass movement or wind erosion. The reduction of hillslope gradients and heights increases mass stability. The establishment of a vegetative cover will also greatly reduce wind erosion.

8.5 Management of areas impacted by explosive testing and use

Managing sites impacted by explosive testing and use involves monitoring the impacts, implementing activities to reduce future impacts, and using remedial actions to repair existing impacts. Monitoring the impacts involves measurements of impact caused by geomorphic processes and erosion by water. This work is an expression of the relationship between force and resistance. Usually, there is observational evidence of existing or potential problems. Deterioration of vegetative cover indicates the likelihood of increased sheet erosion on a site. The presence of rills or gullies indicates accelerated erosion by channelized flow. Tension cracks across hillslopes suggest mass instability.

Phased reclamation can be used to manage, repair, and reclaim areas of testing ranges that are not currently being used while other ranges are still active. This allows site managers to reduce management and treatment costs by minimizing areas of disturbance, while optimizing equipment and personnel use during the range closure. Specific areas of testing ranges in these projects can be used as large-scale treatment areas, and the effectiveness of the chosen procedures can be evaluated under local climate conditions. During phased reclamation, documentation of test protocols and results is necessary to maintain continuity, as the reclamation manager who initiated the project may not be working on the site when the project if finally complete (Gusek & Figueroa, 2009).

8.6 Limitations and suggestions for future research

This current study is not without limitations. General limitations of quasi-experimental studies involve the lack of random assignment and lack of control of other confounding variables. This study only involved soil sampling from different explosive testing ranges in one region in an arid location; therefore, generalization of results to other arid locations or other sites impacted by explosive use may not be appropriate. Lastly, causality is not clearly established in this quasi-experimental study because of the lack of randomization and control of all variables. In other words, it cannot be directly inferred that certain elements or explosive testing strategies contribute to soil contamination in the surrounding environment.

This study adds to the literature regarding explosive testing and use and its related effects, but further research on the impacts of ongoing explosive use on soil and the surrounding environment in arid locations is still necessary. This study demonstrates that explosive testing and use can introduce explosive compounds into soil which can be identified in soil some time after use. Further research into explosive fate and transport in the environment is necessary to determine how off site transport of materials can impact distant locations from the point of detonation. As a recent study provided evidence that explosives can be identified in sediment and seawater from a Baltic Sea munitions dump (Nawala, et al., 2020), future research could involve soil and sediment analysis of deltas, rivers, stream, and wetlands and indicate how far explosively contaminated material can be transported from the site of detonation. This could provide an indication of how explosive use impacts both distant locations and their valuable water resources.

8.7 Recommended approaches for continuing explosive testing and use in a responsible manner

Several key issues regarding continuing explosives testing and use while also maintaining a sustainable environment are evident from the results of this study. They include having a better understanding of the fate and transport of various components used in explosives, especially how an arid climate can influence those components. Identification of the main combustion, detonation, and degradation products for each explosive used are necessary to better understand potential ecological system exposure routes. A record of the manufacturing process for each explosive, historical use records and firing logs for each testing range, and cradle to grave documentation including ongoing site sampling and monitoring results, are all necessary to gain an insight into environmental impacts based on the type and age of explosive compounds detected in soil. New methods for treating explosive contamination will need to be developed, including enhancing natural microbial attenuation and at each specific site. New range management methods to avoid and correct damage and remove old explosive waste and other waste materials must be developed. Continued range management including the maintenance and preservation of testing ranges, removal of excess debris, and ongoing fire control measures to prevent wildfires, usually easily caused from hot metal fragments produced from explosive detonation, should be implemented.

This study shows that explosive use can generate ecological consequences, leading to significant anthropogenic disturbance of the environment. Active use of explosives often leads to metal and plastic material in soil, chemical contamination with organic compounds, landscape alteration, vegetation removal, and increased soil erosion. Often, continued explosives use, especially in areas impacted by warfare, can lead to intense pollution, UXO, damaged and destroyed infrastructure, degraded landscapes and ecosystems, and soil compaction, along with soil sterilization. Building erosion control structures for site containment and to prevent the movement of materials off site, along with storm water management and control, can be implemented at locations where explosives have been used to help decrease the amount of land impacted.

The results of this study are significant because it will add to the research regarding explosives use and their fate after detonation on testing ranges and in arid regions involved in military conflicts. Furthermore, this research and the suggested mitigation measures provided based upon the results can be used to protect animal, plant, and human health and could benefit countless individuals and the overall environment. The results from this study could be beneficial for the public, researchers, and policy makers. For instance, the public can benefit from safer land, soil, and water and from the protection of ecosystems. Researchers will also benefit from this study since they will have a better understanding of how explosives and their residues behave in arid environments and will have various treatment practices to address the environmental damage their use creates, including physical impacts to the surrounding habitat and landscape change over time. Policy makers could be informed of better explosive testing practices and of harmful research and development practices using explosives that should be avoided. Additionally, this study could ultimately help create a safer environment for future generations on an increasingly drier and more densely populated planet. This study may help to better understand the composition of the suite of explosives to be encountered in regions where military activities have occurred, which can further increase understanding of predicted impacts on the environment. This will allow for a better assessment of treatment processes that would be best implemented to protect valuable land resources.

In conclusion, opening new explosive testing ranges is almost impossible with the encroachment of urban populations in desert areas of the U.S., not to mention the opposition to continued human conflict and weapons use. Therefore, site specific preventative management, ongoing site maintenance, and historical sampling will support the continued use of explosive testing ranges for research, training, and conflict preparation activities. It is therefore evident that continued ecological stewardship and a focus on environmental protection along with ongoing testing range monitoring, treatment, and site restoration should be a part of every explosive testing facility's operating process.

References

Abd-Elghany, M., Klapotke, T., & Elbeih, A. (2018). Environmentally safe (chlorine-free): new green propellant formulation based on 2, 2, 2-trinitroethyl-formate and HTPB. *RSC Advances, 8*(21), 11771-11777.

Agrawal, J. (2010). *High Energy Materials: Propellants, Explosives, and Pyrotechnics.* Weinheim, Germany: Wiley VCH Verlag GmbH and Co. KGaA.

Ahmad, M., Lee, S. S., Moon, D. H., Yang, J. E., & Ok, Y. S. (2012). A review of environmental contamination and remediation strategies for heavy metals at shooting range soils. In *Environmental Protection Strategies for Sustainable Development* (pp. 437-451).

Akhavan, J. (2004). *The Chemistry of Explosives.* London, England: RSC Paperbacks.

Akinyemi, M. L., Emetere, M., & Usikalu, M. R. (2016). Virtual assessment of air pollution dispersion from anthropogenic sudden explosion. *American Journal of Environmental Sciences, 12*(2), 95-101.

Alaba, O. (2018). Assessment of Environmental Effects of Post-Blasted Explosive on the Ecosystem of Old Netim Village in Akamkpa Local Government Area of Cross River State, Nigeria. *Journal of Applied Sciences and Environmental Management, 22*(5).

Albright, R. D. (2012). *Cleanup of Chemical and Explosive Munitions.* Waltham, Massachusetts: William Andrew , Elsevier.

Alothman, Z. A., Bahkali, A. H., Elgorban, A. M., Al-Otaibi, M. S., Ghfar, A. A., Gabr, S. A., . . . Ahmed, A. Y. (2020). Bioremediation of explosive TNT by Trichoderma viride. *Molecules, 25*(6), 1393.

Anderson, W. C. (1999). *Environmental Availability in Soils.* Annapolis, Maryland: American Academy of Environmental Engineers .

Andreassian, C., Panabrokke, C., & Quirk, J. (2004). Effect of initial water content on stability on soil aggregates in water. *Soil Science Society of America, 83*, 185-195.

Arbeli, Z., Garcia-Bonilla, E., Pardo, C., Hidalgo, K., Velasquez, T., & Pena, L. (2016). Persistence of pentolite (PETN and TNT) in soil microcosms and microbial enrichment cultures. *Environ. Sci. Pollut. Res., 23*, 9144-9155.

Atlas, R. M. (1993). *Microbial Ecology.* Redwood City, CA: Benjamin Cummings Publishing Company .

Balakrishnan, V., Pradhan, M., & Dhekne, P. (2019). Field investigation in the detonation behavior of emulsion explosive column induced with air gaps. *Mining Science, 26*, 55-68.

Barbosa, A., Fernandes, J., & David, L. (2012). Key issues for sustainable urban stormwater management. *Water Research, 46*(20), 6787-6798.

Batnagar, N., Kamath, G., & Potoff, J. (2013). Prediction of 1-octanol-water and air-water coefficients for nitroaromatic compounds from molecular dynamics simulations. *Physical Chemistry Chemical Physics, 15*, 6467-6474.

Beck, U. (1996). World risk society as cosmpolitan society? Ecological questions in a framework of manufactured uncertainties. *Theory, Culture and Society, 13*(4), 1-32.

Belden, J., Ownby, D., Lotufo, G., & Lydy, M. (2005). Accumulation of TNT in aquatic organisms part 2-bioconcentration in aquatic invertebrates and potential for trophic transfer to channel catfish (Ictalurus punctatus). *Chemosphere, 58*, 1161-1168.

Belnap, J. (1995). Surface disturbances: Their role in accelerating desertification. *Environmental Monitoring and Assessment, 37*, 39-57.

Ben-Jaber, S., Peveler, W. J., Quesada-Cabrera, R., Coreés, E., Sotelo-Vazquez, C., Abdul-Karim, N., . . . Parkin, I. P. (2016). Photo-induced enhanced Raman spectroscopy for universal ultra-trace detection of explosives, pollutants and biomolecules. *Nature Communications, 7*(1), 1-6.

Biessikirski, A., Czerwonka, D., Biegnska, J., Kuterasinski, L., Z. M., Dworzak, M., & Twardosz, M. (2021). Research on the possible application of polyolefin waste-derived pyrolysis oils for ANFO manufacturing. *Energies, 14*(1), 172.

Biessikirski, A., Kuterasinski, L., Dworzak, M., Pyra, J., & Twardosz, M. (2019). Comparison of structure, morphology, and topography of fertilizer-based explosives applied in the mining industry. *Microchemical Journal, 144,* 39-44.

Bohn, H. (2001). *Soil Chemistry.* Wiley.

Bolter, M. (2018). *Synthesis and characterization of new environmentally benign secondary explosives based on azoles.* Doctoral dissertation, Ludwig Maximillian University.

Bordeleau, G., Martel, R., Ampleman, G., & Thiboutot, S. (2008). Environmental Impacts of Training Activities at an Air Weapons Range. *Journal of Environmental Quality, 37*(2), 308-317.

Boudreaux, L. (1997). *Military Soils Engineering.* Washington, D.C.: U.S. Department of the Army.

Bowles, J. (2001). *Engineering Properties of Soils and their Measurement.* McGraw-Hill Science.

Brannon, J. M., & Pennington, J. C. (2002). *Environmental Fate and Transport Process.* Strategic Environmental Research and Development Program, US Army Corp of Engineers.

Brochu, A. (2010). *Assessment of ANFO on the Environment Technical Investigation 09-01.* Defence R&D Canada Valcartier TM 2009-195.

Brochu, S., Diaz, E., Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., . . . Taylor, S. (2005). *Assessment of 100 years of military training in Canada: the case of Canadian Force Base Petawawa.* Quebec: Defense Research Development Canada (DRDC-Valcartier) .

Broomandi, P., Guney, M., Kim, J., & Karaca, F. (2020). Soil contamination in areas impacted by military activities. *Sustainability, 12*(21), 9002.

Brown, G. (1998). *The Big Bang: A History of Explosives.* Gloucestershire, United Kingdom: The History Press.

Bunning, T. H., Strehse, J. S., Hollmann, A. C., Botticher, T., & Maser, E. (2021). A toolbox for the determination of nitroaromatic explosives in marine water, sediment, and biota samples on femtogram levels by GC-MS/MS. *Toxics, 9*(3), 60.

Caldwell, T., McDonald, E., & Young, M. (2006). Soil disturbance and hydrologic response at the National Training Center, Fort Irwin, California. *Journal of Arid Environments, 67,* 456-472.

Campbell, D., & Stanley, J. (2001). *Experimental and Quasi-Experimental Designs for Research.* Cengage Learning.

Carton, G., DuVal, C., Trembanis, A., Edwards, M., Rognstad, M., Briggs, C., & Shjegstad, S. (2017). *Munitions and Explosives of Concern Survey Methodology and In-field Testing for Wind Energy Areas on the Atlantic Outer Continental Shelf.* US Department of the Interior, Bureau of Ocean Energy Management.

Cary, T. J., Rylott, E. L., Zhang, L., Routsong, R. M., Palazzo, A. J., Strand, S. E., & Bruce, N. C. (2021). Field trial demonstrating phytoremediation of the military explosive RDX by XplA/XplB-expressing switchgrass. *Nature Biotechnology*, 1-4.

Certini, G., Scalenghe, R., & Woods, W. (2013). The impact of warfare on the soil environment. *Earth-Science Reviews, 127,* 1-15.

Chatterjee, S., Deb, U., Datta, S., Walther, C., & Gupta, D. (2017). Common explosives (TNT, RDX, HMX) and their fate in the environment: emphasizing bioremediation. *Chemosphere, 184* , 438-451.

Chaturvedi, S., & Dave, P. (2019). Solid propellants: AP/HTPB composite propellants. *Arabian Journal of Chemistry, 12*(8), 2061-2068.

Chen, J., Qiu, W., Rai, P., & Ai, X. (2021). Emission characteristics of CO and NOx from tunnel blast design models: a comparative study. *Polish Journal of Environmental Studies, 30*(6), 5503-5517.

Chen, L., Cao, X., Gao, J., He, W., Liu, J., Wang, Y., . . . Tan, D. (2021). Nitrated bacterial cellulose-based energetic nanocomposites as propellants and explosive for military applications. *Applied Nano Materials, 4*(2), 1906-1915.

CO2. (2023, January 31). *Daily CO2*. Retrieved from CO2 Earth: https://www.co2.earth/daily

Cooper, P. W. (1996). *Explosives Engineering.* New York: Wiley-VCH.

Cross, K., Dullum, O., Jenzen-Jones, N. R., & Garlasco, M. (2016, June 3). *Explosive weapons in populated areas: technical considerations relevant to their use and effects*. Retrieved from International Committee of the Red Cross (ICRC): https://www.icrc.org/en/document/explosive-weapons-populated-areas-use-effects

Das, B. M. (2016). *Principles of Foundation Engineering.* Boston, MA.: Cengage Learning.

Dinake, P., Maphane, O., Sebogisi, K., & Kamwi, O. (2018). Pollution status of shooting range soils from Cd, Cu, Mn, Ni and Zn found in ammunition. *Cogent Environmental Science, 4*(1), 1528701.

Domozhirov, D. V., Pytalev, I. A., Nosov, I. I., Nosov, V. I., & Gaponova, I. V. (2019). Substantiation of choice of method of manufacturing and delivery of emulsion explosives in modern conditions of functioning of mining enterprises. *IOP Conference Series: Earth and Environmental Science* (p. 0022178). IOP Publishing.

Downe, S., & Ampleman, G. T.-C. (2015). Remediation of contaminated surface soil at firing positions by open burning. *Global Demilitarization Symposium, NDIA Conference.* Parsnippy, New Jersey.

Evenari, M., Noy-Meir, I., & and Goodall, D. W. (1985). *Hot Deserts and Shrublands.* New York: Elsevier Science Publishing Company.

Fawcett-Hirst, W., Temple, T., Ladyman, M., & Coulon, F. (2021). A review of treatment methods for insensitive high explosive contaminated wastewater. *Heliyon*, e07438.

Fayiga, A. (2019). Remediation of inorganic and organic contaminants in military ranges. *Environ. Chem., 16*(2), 81-91.

Fayiga, A., & Saha, U. (2016). Soil pollution at outdoor shooting ranges: health effects, bioavailability and best management practices. *Environmental Pollution, 216*, 135-145.

Ferreira, C., Ribeiro, J., Clift, R., & Freire, F. (2019). A circular economy approach to military munitions: valorization of energetic material from ammunition disposal through incorporation in civil explosives. *Sustainability, 11*(1), 255.

Figuli, L., Kavicky, V., Jangl, S., & Zvakova, Z. (2018). Comparison of the efficacy of homemade and industrially made ANFO explosives as an improvised explosive device. *Communications, 20,* 23-27.

Forbes, T., Krauss, S., & Gillen, G. (2020). Trace detection and chemical analysis of homemade fuel-oxidizer mixture explosives: emerging challenges and perspectives. *TrAC Trends in Analytical Chemistry*, 116023.

Fuller, M. E. (2009). Transformation of RDX and other energetic compounds by xenobiotic reductases XenA and XenB. *Applied Microbiology and Cell Physiology, 84,* 535-544.

Gerth, A. (2005). Biological in situ remediation of TNT contaminated soil. *TerraTech, 1-2*(TT), 21-23.

Gray, D. H., & Sotir, R. B. (1996). *Biotechnical and Soil Bioengineering Slope Stabilization.* New York: John Wiley and Sons, Inc.

Gregory, J. (2006). Effect of urban soil compaction on infiltration rate. *Journal of Soil and Water Conservation, 61*(3), 117-124.

Gusek, J., & Figueroa, L. (2009). *Mitigation of Metal Mining Influenced Water.* Society for Mining, Metallurgy, and Exploration, Inc.

Hargather, M. (2013). Background-oriented Schlieren diagnostics for large-scale explosive testing. *Shock Waves, 23*(5), 529-536.

Hasanuzzaman, M., & Prasad, M. N. (2021). *Handbook of Bioremediation: Physiological, Molecular, and Biotechnological Interventions.* Elsevier Academic Press.

Havlick, D. G. (2011). Disarming Nature: Converting Military Lands to Wildlife Reguges. *The Geographical Review*, *101*(2), 183-200.

Henry, J. G., & Heinke, G. W. (1989). *Environmental Science and Engineering.* London, England: Prentice-Hall, Inc.

Hostile Planet (2019). [Motion Picture]. United States: National Geographic.

Hudson, J., & Harrison, J. (1997). *Engineering Rock Mechanics.* Amsterdam: Pergamon.

Huenneke, L. F., Clason, D., & Muldavin, E. (2001). Spatial heterogeneity in Chihuahuan Desert vegetation: implications for sampling methods in semi-arid ecosystems. *Journal of Arid Environments, 47*(3), 257-270.

Hupy, J. P. (2012). Modern warfare as a significant form of zoogeomorphic disturbance upon the landscape. *Geomorphology, 157-158*, 169-182.

IPCC. (2007). *Climate Change IPCC Fourth Assessment Report* . New York: Cambridge University Press.

Irlam, R. C., Parkin, M. C., Brabazon, D. P., Beardah, M. S., O'Donnell, M., & Barron, L. P. (2019). Improved determination of femtogram-level organic explosives in multiple matrices using dual-sorbent solid phase extraction and liquid chromatography-high resolution accurate mass spectrometry. *Talanta, 203*, 65-76.

Jagtap, D. (2018). Air pollution controller-fabric filter. *International Research Journal of Engineering and Technology, 5*(2), 1830-1833.

Jenkins, T., Walsh, M., Schumacher, P., Miyares, P., Bauer, C., & Grant, C. (1989). Liquid chromatographic method for determination of extractable nitroaromatic and nitramine residues in soil. *J. Assoc. Off. Anal. Chem.*, *72*, 890-899.

Johnson, R., Tratnyek, P., & Miehr, R. (2005). Reduction of hydraulic conductivity and reactivity in zero-valent iron columns by oxygen and TNT. *Ground Water Monitoring Review, 25*, 129-136.

Jones, H. (2009). Rapid Recovery of Damaged Ecosystems. *PLOS One*. Retrieved from https://doi.org/10.1371/journal.pone.0005653

Julyan, R. (2006). *The Mountains of New Mexico.* Albuquerque: University of New Mexico Press.

Kalderis, D. (2011). Soils contaminated with explosives: environmental fate and evaluation of state of the art remediation processes. *Pure and Applied Chemistry, 83*(7), 1407-1484.

Khomenko, O., Kononenko, M., Myronova, I., & Savchenko, M. (2019). Application of the emulsion explosives in the tunnels construction. *E3S Web of Conferences. 123*, p. 01039. EDP Sciences.

Kielmann, M., Prior, C., & Senge, M. (2018). Porphyrins in troubled times: a spotlight on porphyrins and their metal complexes for explosives testing and CBRN defense. *New Journal of Chemistry, 42*(10), 7529-7550.

Klapec, D., Czarnopys, G., & Pannuto, J. (2020). Interpol review of detection and characterization of explosives and explosives residues. *Forensic Science International: Synergy, 2*, 670-700.

Konovalov, A., Yudin, N., Kolesov, V., & Ul'yanov, V. (2019). Increasing the heating efficiency and ignition rate of certain secondary explosives with absorbing particles under continuous infrared laser radiation. *Combustion and Flame, 414*, 407-414.

Koske, D. (2020). *Dumped munitions: Effects, metabolism and detection of explosive compounds and chemical warfare agent-related chemicals in fish from the Baltic Sea.* Doctoral dissertation.

Koske, D., Straumer, K., Goldenstein, N. I., Hanel, R., Lang, T., & Kammann, U. (2020). First evidence of explosives and their degradation products in dab (Limanda limanda L.) from a munition dumpsite in the Baltic Sea. *Marine Pollution Bulletin, 155*, 111131.

Kovacs, A., Vasilescu, G. D., Gheorghiosu, E., Rus, D., & Jitea, C. (2017). Improvement of security measures during the use of explosives in firedamp hazardoud mines. *Environmental Engineering and Management Journal, 16*(6), 1295-1299.

Krauss, S., Forbes, T., & Jobes, D. (2021). Inorganic oxidizer detection from propellants, pyrotechnics, and homemade explosive powders using gradient elution moving boundary electrophoresis. *Electrophoresis, 42*(3), 279-288.

Kubli, L., Pinto, R., Burrows, H., Littlefiedl, P., & Brungart, D. (2017). The effects of repeated low-level blast exposure on hearing in Marines. *Noise and Health, 19*(90), 227.

Kumar, K. (2005). Analysis of UNEP priority POPs using HRGC-HRMS and their contamination profiles in livers and eggs of great cormorants (Phalacrocorax carbo) from Japan. *Archives of Environmental Contamination and Toxicology, 48*, 538-551.

Ladyman, M. K., Temple, T. J., Piperakis, M. M., Fawcett-Hirst, W., Gutierrez-Carazo, E., & Coulon, F. (2019). Decision framework for the environmental management of explosive contaminated land. *Science of the Total Environment, 690*, 730-738.

Lease, N., Holmes, M. D., Englert-Erickson, M. A., Kay, L. M., Francois, E. G., & Manner, V. W. (2021). Analysis of ignition sites for the explosives 3, 3′-Diamino-4, 4′-azoxyfurazan (DAAF) and 1, 3, 5, 7-Tetranitro-1, 3, 5, 7-tetrazoctane (HMX) using crush gun impact testing. *ACS Materials Au, 1*(2), 116-129.

Leszczynski, J. (2017). *Energetic Materials From Cradle to Grave.* Cham, Switzerland: Springer International Publishing.

Li, K., Li, X., Yan, H., Wang, X., & Wang, Y. (2018). Study of continuous velocity probe method for the determination of the detonation pressure of commercial explosives. *Journal of Energetic Materials, 36*(4), 377-385.

Li, Y., Huang, H., Shi, Y., Yang, J., Pan, R., & Lin, X. (2017). Potassium nitraminofurazan derivatives: potential green primary explosives with high energy and comparable low friction sensitivies. *Chemistry-A European Journal, 23*(30), 7353-7360.

Lundgaard, S., Ng, S., Cahill, D., Dahlberg, J., Ruan, D., Cole, N., . . . Juodkazis, S. (2019). Towards safer primers: a review. *Technologies, 7*(4), 75.

Luo, J., Xia, H., Zhang, W., Song, S., & Zhang, Q. (2020). A promising hydrogen peroxide adduct of ammonium cyclopentazolate as a green propellant component. *Journal of Materials Chemistry, 8*(25), 12334-12338.

Machlis, G. E. (2008). Warfare Ecology. *Bioscience, 58*(8), 729-736.

Manley, P., Sagan, V., Fritschi, F., & Burken, J. (2019). Remote sensing of explosives-induced stress in plants: hyperspectral imaging analysis for remote detection of unexploded threats. *Remote Sensing, 11*(15), 1827.

Manner, V. W., Tiemann, C. G., Yeager, J. D., Kay, L. M., Lease, N., Cawkwell, M. J., . . . Montanari, D. (2020). Examining explosives handling sensitivity of trinitrotoluene (TNT) with different particle sizes. *AIP Conference Proceedings.* AIP Publishing LLC.

Manzoor, S., Cao, W., & Zhang, J. (2021). Recent advances in the synthesis and energetic properties of potassium-based potential green primary explosives. *Defence Technology*.

Marrs, F. W., Manner, V. W., Burch, A. C., Yeager, J. D., Brown, G. W., Kay, L. M., . . . Cawkwell, M. J. (2021). Sources of variation in drop-weight impact sensitivity testing of the explosive pentaerythitol tetranitrate. *Industrial and Engineering Chemistry Research, 60*(13), 5024-5033.

Masoumi, S., Hajghassem, H., Erfanian, A., & Rad, A. M. (2018). Design and manufacture of TNT explosives detector sensors based on GFET. *Sensor Review, 38*(2), 181-193.

Matyas, R., & Pachman, J. (2013). *Primary Explosives.* Heidelberg: Springer-Verlag .

McCutcheon, S. C. (2003). *Phytoremediation: Transformation and Control of Contaminants.* Hoboken, New Jersey: John Wiley & Sons, Inc.

McDougal, J. N., & Boeniger, M. F. (2002). Methods for Assessing Risks of Dermal Exposures in the Workplace. *Critical Reviews in Toxicology, 32*(4), 291-327.

Mednick, S. (2022, November 11). *AP News*. Retrieved from Ukraine war's environmental toll to take years to clean up: https://apnews.com/article/russia-ukraine-kyiv-pollution-europe-business-d2282edd65a0caad45472f2524e5a9be

Mehta, N., Oyler, K., Cheng, G., Shah, A., Marin, J., & Yee, K. (2014). Primary explosives. *Zeitschrift für anorganische und allgemeine Chemie, 640*(7), 1309-1313.

Mertuszka, P., Fuławka, K., Pytlik, M., & Szastok, M. (2020). The influence of temperature on the detonation velocity of selected emulsion explosives. *Journal of Energetic Materials, 38*(3), 336-347.

Meyer, R., Kohler, J., & Homburg, A. (2016). *Explosives* (7th ed.). Wiley-VCH.

Michalske, T., Edelstein, N., Sigman, M., & Trewhella, J. (2007). *Basic Research Needs for Countering Terrorism.* Retrieved from http:;//www.er.doe.gov/bes/reports/files/NCT_rpt_screen.pdf

Miller, J. B., & Barrall, G. A. (2005). Explosives detection with Nuclear Quadrupole Resonance: an emerging technology will help to uncover land mines and terrorist bombs. *American Scientist, 93*(1), 50-57.

Millington, A. (1994). *Environmental Change in Drylands: Biogeographical and Geomorphological Perspectives by A. Millington.*

Muter, O. (2014). ssessment of bioremediation strategies for explosives-contaminated sites. In *Biological Remediation of Explosive Residues* (pp. 113-148). Springer.

NATO. (2010). *Environmental Impact of Munition and Propllant Disposal.* North Atlantic Treaty Organization Research and Technology Organization.

Nawala, J., Szala, M., Dziedzic, D., Gordon, D. D., Fabisiak, J., & Popiel, S. (2020). Analysis of samples of explosives excavated from the Baltic Sea floor. *Science of the Total Environment, 708*, 135198.

NRCS Web Soil Survey. (2022, January 7). Retrieved from https://websoilsurvey.nrcs.usda.gov

O'Grady, C., Marquez, M. P., Rupper, S., Vasiliauskas, J., Knepper, R., S. S., & Tappan, A. (2020). Investigating typical additive manufaturing defect geometries using physical vapor deposition explosives as a model system. *AIP Conference Proceedings* . AIP Publishing LLC.

Oluwoye, I., Dlugogorski, B., Gore, J., Oskierski, H., & Altarawneh, M. (2017). Atmospheric emission of NOx from mining explosives: a critical review. *Atmospheric Environment, 167*, 81-96.

Omar, S. (2017). Land and vegetation degradation in war-affected areas in the Sabah Al-Ahmad Nature Reserve of Kuwait. *Restoration Ecology, 25*(6), 982-993.

Oxley, J. C., Smith, J. L., Bowden, P. R., & Rettinger, R. C. (2013). Factors influencing triacetone triperoxide (TATP) and diacetone diperoxide (DADP) formation: part I. *Propellants, Explosives, and Pyrotechnics*, *38*(2), 244-254.

Oyler, K. (2014). Green Primary Explosives. In *Green Energetic Materials* (pp. 103-132). Wiley and Sons.

Panja, S., Sarkar, D., & Datta, R. (2018). Vetiver grass (Chrysopogon zizanioides) is capable of removing insensitive high explosives from munition industry wastewater. *Chemosphere, 209*, 920-927.

Panz, K., Miksch, K., & Sojka, T. (2013). Synergetic toxic effect of an explosive material mixture in soil. *Bulletin of Environmental Contamination and Toxicology, 91*(5), 555-559.

Pennington, J. C., & Patrick, W. H. (1990). Adsorption and Desorption of 2,4,6-Trinitrotoluene by Soils. *Journal of Environmental Quality, 19*(3), 559-567.

Pichtel, J. (2012). Distribution and fate of military explosives and propellants in soil: a review. *Applied and Environmental Soil Science*, 1-33.

Prasad, M., & Frietas, H. (2003). Metal hyperaccumulation in plants: biodiversity prospecting for phytoremediation technology. *Nature Biotechnology, 6*, 1-27.

Rai, P. K., Kim, K. H., Lee, S. S., & Lee, J. H. (2020). Molecular mechanisms in phytoremediation of environmental contaminants and prospects of engineered transgenic plants/microbes. *Science of the Total Environment, 705*, 135858.

Remediation Technologies Screening Matrix and Reference Guide. (2023). Retrieved from Excavation, Retrieval, and Off site (Other Soil Remediation Technology): https://www.frtr.gov/matrix2/section4/4-29.html

Rittman, B., Seagren, E., Wrenn, B., Valocchi, A., Ray, C., & Raskin, L. (1994). *In Situ Bioremediation.* Park Ridge, New Jersey: Noyes Publications.

Robinson, J. (1979). *The Effects of Weapons on Ecosystems.* New York: Pergamon Press.

Sanderson, P., Qi, F., Seshadri, B., Wijayawardena, A., & Naidu, R. (2018). Contamination, fate, and management of metals in shooting ranges-a review. *Curr. Pollut. Rep., 4*(2), 175-187.

Sandham, L. A., Van der Vyver, F., & Retief, F. P. (2013). The performance of environmental impact assessment in the explosives manufacturing industry in South Africa. *Journal of Environmental Assessment Policy and Management, 15*(3), 1350013.

Sawyer, J. (2019). *Integrated crop management: understanding anhydrous ammonia in soil.* Iowa State University Extension and Outreach.

Schachel, T. D., S. A., Schulte-Ladbeck, R., V. T., & Karst, U. (2020). Identification and differentiation of commercial and military explosives via high performance liquid chromatography–high resolution mass spectrometry (HPLC-HRMS), X-ray diffractometry (XRD) and X-ray fluorescence spectroscopy (XRF): towards a forensic sub. *Forensic Science International, 308*, 110180.

Scharsack, J. P., Koske, D., Straumer, K., & Kammann, U. (2021). Effects of climate change on marine dumped munitions and possible consequence for inhabiting biota. *Environmental Sciences Europe, 33*(1), 1-10.

Serrano-Gonzalez, M. Y., Chandra, R., Castillo-Zacarias, C., Robledo-Padilla, F., de J. Rostro-Alanis, M., & Parra-Saldivar, R. (2018). Biotransformation and degradation of 2,4,6-trinitrotoluene by microbial metabolism and their interaction. *Defence Technology, 14*(2), 151-164.

Shanmugaraju, S., Umadevi, D., Savyasachi, A., Byrne, K., Ruether, M., Schmitt, W., . . . Gunnlaugsson, T. (2017). Reversible adsorption and storage of secondary explosives in water using Troger's base-functionalized polymer. *Journal of Materials Chemistry, 5*(47), 25014-25024.

Sheremata, T., Halasz, A., Paquet, I., Thiboutot, S., Ampleman, G., & Hawari, J. (2001). The fate of cyclic nitramine explosive RDX in natural soil. *Environmental Science and Technology, 35*(6), 1037-1040.

Siegrist, R., Crimi, M., & Simpkin, T. (2011). *In Situ Chemical Oxidation for Groundwater Remediation.* Germany: Springer.

Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System) (2011).

Stokes, A., Douglas, G., Fourcaus, G. F., Gillies, C., Hubble, T., Kim, J., . . . McIvor, I. (2014). Ecological mitigation of hillslope instability: ten key issues facing researchers and practitioners. *Plant and Soil, 377,* 1-23.

Strehse, J., & Maser, E. (2020). Marine bivalves as bioindicators for environmental pollutants with focus on dumped munitions in the sea: a review. *Marine Environmental Research, 158*, 105006.

Tauqeer, H., Karczewska, A., Lweinsha, K., Fatima, M., Khan, S., Farhad, M., . . . Iqbal, M. (2021). Environmental concerns assoicated with explosives, heavy metals, and metalloids from shooting ranges. In M. Hasanuzzaman, & M. N. Prasad, *Handbook of Bioremediation* (pp. 569-590). Elsevier Academic Press.

Temple, T., Ladyman, M., Mai, N., Galante, E., Ricamora, M., Shirazi, R., & Coulon, F. (2018). Investigation into the environmental fate of the combined insensitive high explosive constituents 2, 4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil. *Science of the Total Environment, 625*, 1264-1271.

Texas University at Austin for Advanced Technology. (2008). *Development of Nanothermite Projectile for Improvised Explosive Device (IED) and Vehicle-Borne Improvised Explosive Device (VBIED) Neutralization.* Austin: National Institute of Justice Final Report ADA502140.

Thomas, D. S. (2011). *Arid Zone Geomorphology.* New York : John Wiley & Sons, Inc. .

Tomar, R. S. (2019). *Photosynthesis Productivity and Environmental Stress.* John Wiley and Sons, Inc.

Toy, T. J., & Hadley, R. F. (1987). *Geomorphology and Reclamation of Disturbed Lands.* Orlando, Florida: Academic Press, Inc.

Trifunovic, V., & Antonijevic, M. (2019). Impact of TNT explosive and its degradation products on the environment. *Zastita materijala, 60*(2), 162-173.

U.S. Army Corps of Engineers. (2006). *Distribution and fate of energetic materials on DoD test and training ranges.* ERDC-TR-06-13, Strategic Environmental Research and Development.

U.S. Environmental Protection Agency. (1988). *Health Advisory for HMX.* Washington, D.C.: U.S. EPA.

U.S. Environmental Protection Agency. (2021). *Explosives manufactering effluent guidelines.*

U.S. Environmental Protection Agency. (2021, August). *Fact Sheet-RDX*. Retrieved from The Environmental Challenge of Military Munitions and Federal Facilities:

https://www.epa.gov/sites/default/files/2017-10/documents/ffrro_ecfactsheet_rdx_9-15-17_508.pdf

United Nations Environment Programme. (2005). *Ecosystems and Human Well-Being: Desertification.* Washington, D.C.: World Resources Institute.

United Nations General Assembly. (1978). ENMOD. *Convention on the Prohibition of Military or Any Other Hostile Use of Environmental Modification Techniques, Bureau of International Security and Nonproliferation.* Geneva, Switzerland.

Verma, G., & Kumar, B. (2019). Prediction of compaction parameters for fine-grained and coarse-grained soils: a review. *International Journal of Geotechnical Engineering, 14*(8), 970-977.

Via, S. (2020). Phytoremediation of explosives. In B. Shmaefsky, *Phytoremediation: In-situ Applications* (pp. 261-284). Springer.

Walsh, M. E. (2003). Sampling for Explosives-Residues at Fort Greely, Alaska. *Soil and Sediment Contamination, 12*(5), 631-645.

Ware, G. W. (2003). *Reviews of Environmental Contamination and Toxicology.* New York, NY: Springer.

Williams, M. A., Reddy, G., Quinn, M. J., & Johnson, M. S. (2015). *Wildlife Toxicity Assessments for Chemicals of Military Concern.* Amsterdam: Elsevier .

Wyllie, D. C., & Mah, C. W. (2004). *Rock Slope Engineering.* New York: Spon Press.

Xiao, Y., Sun, Y., Zhen, Y., Guo, L., & Yao, L. (2017). Characterization, modeling, and simulation of the impact damage for polymer bonded explosives. *International Journal of Impact Engineering, 103,* 149-158.

Yadav, N., Srivastava, P., & Varma, M. (2021). Recent advances in catalytic combustion of AP-based composite solid propellants. *Defence Technology, 17*(3), 1013-1031.

Yao, Y. L., Cheng, Y. F., Zhang, Q. W., Xia, Y., Hu, F. F., Wang, Q., & & Chen, Y. (2021). Explosion temperature mapping of emulsion explosives containing TiH2 powders with the two-color pyrometer technique. *Defence Technology, 18*(10), 1834-1841.

Yinon, J., & Zitrin, S. (1993). *Modern Methods and Applications in Analysis of Explosives.* New York: John Wiley & Sons.

Zapata, Q., & Garcia-Ruiz, C. (2020). Chemical classification of explosives. *Critical Reviews in Analytical Chemistry, 51*(7), 656-673.

Zentelis, R. (2017). Managing military training-related environmental disturbance. *Journal of Environmental Management, 204*(1), 486-493.

Zhang, Q., Chen, D., Jing, D., Fan, G., He, L., Li, H., . . . Nie, F. (2019). Access to green primary explosives via constructing coordination polymers based on bis-tetrazole oxide and non-lead metals. *Green Chemistry, 21*(8), 1947-1955.

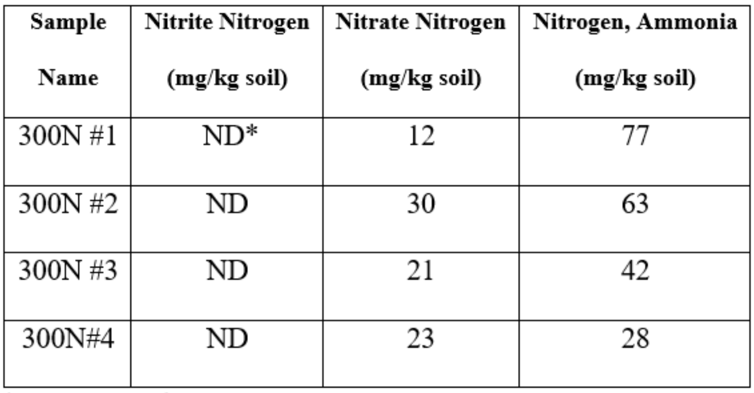
Zhao, X., Wang, G., Fang, H., Fan, Y., & Du, X. (2021). Shock wave propogation characteristics of a cylindrical charge and its aspect ratio effects on the damage of RC slabs. *Advances in Materials Science and Engineering*, 1-20.

Zou, D. (2016). Explosives. In *Theory and Technology of Rock Excavation for Civil Engineering* (pp. 105-170). Springer.

Zukas, J., & Waters, W. (1985). *Explosive Effects and Applications.* Springer Publishing.

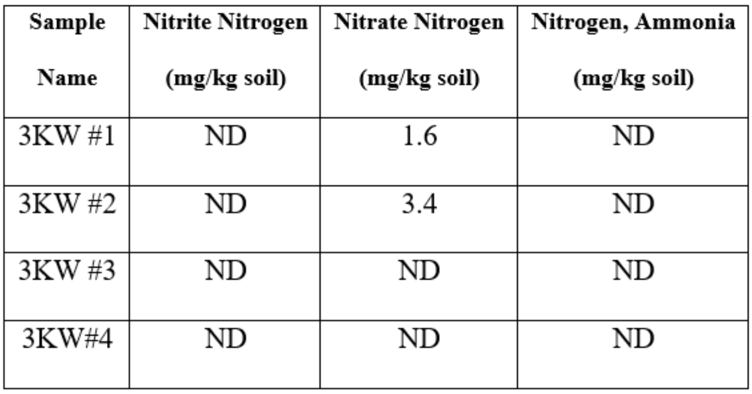
Appendix
Analytical Results

A. Nitrite, Nitrate, and Ammonia as Nitrogen

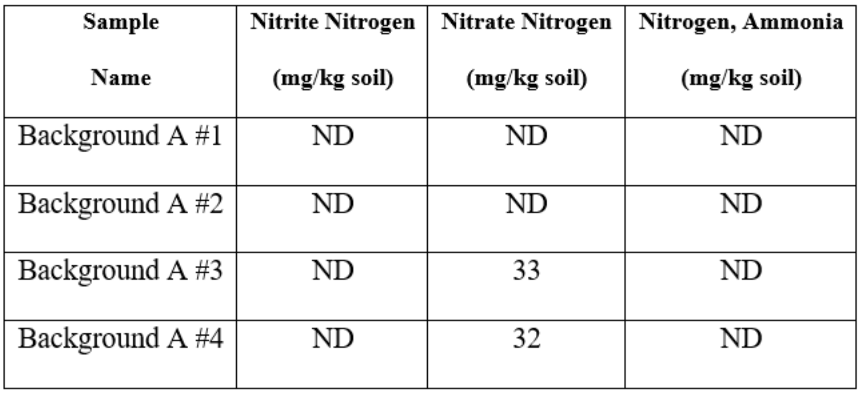


Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
300N #1	ND*	12	77
300N #2	ND	30	63
300N #3	ND	21	42
300N#4	ND	23	28

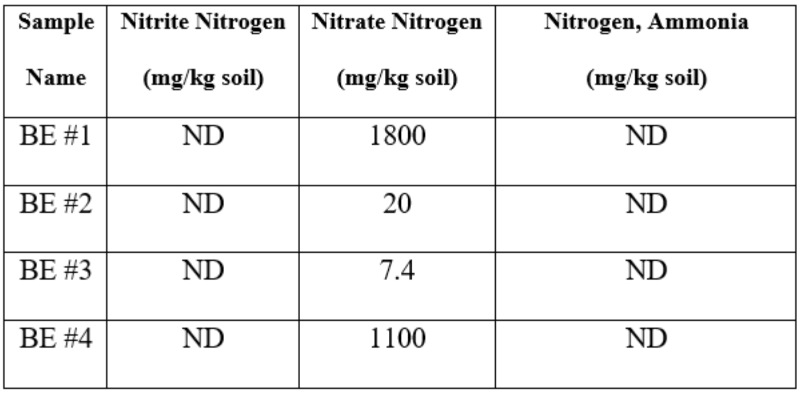
*Not Detected



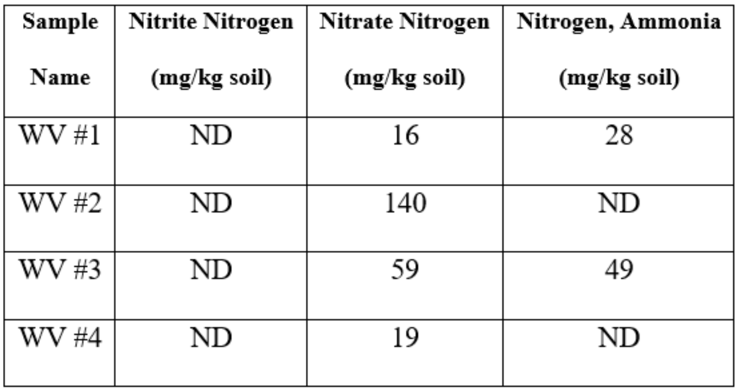
Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
3KW #1	ND	1.6	ND
3KW #2	ND	3.4	ND
3KW #3	ND	ND	ND
3KW#4	ND	ND	ND



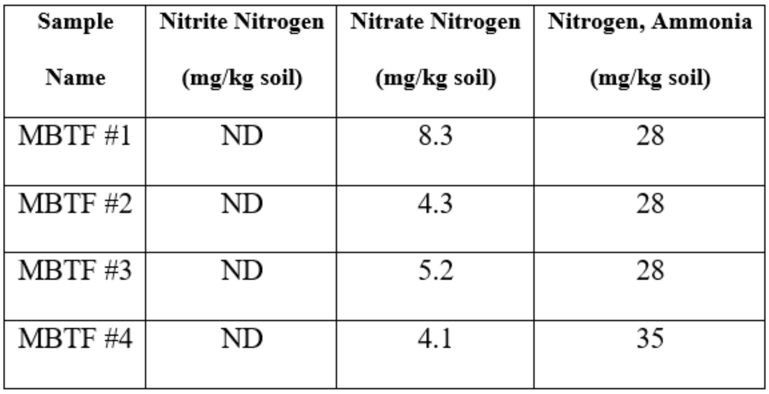
Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
Background A #1	ND	ND	ND
Background A #2	ND	ND	ND
Background A #3	ND	33	ND
Background A #4	ND	32	ND



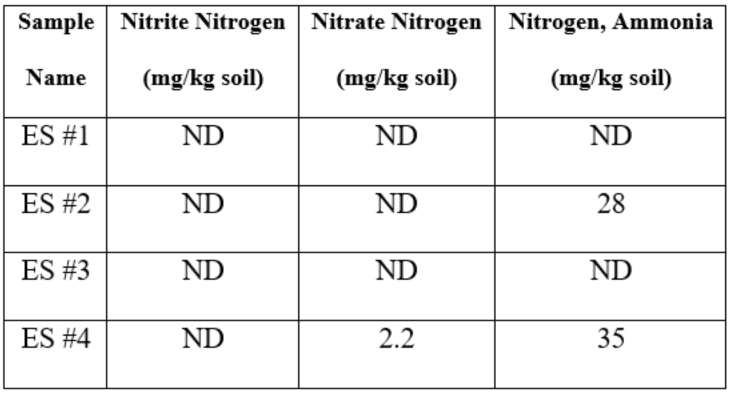
Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
BE #1	ND	1800	ND
BE #2	ND	20	ND
BE #3	ND	7.4	ND
BE #4	ND	1100	ND



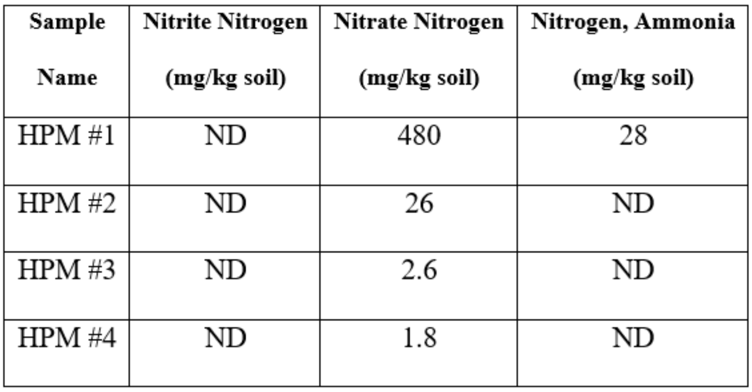
Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
WV #1	ND	16	28
WV #2	ND	140	ND
WV #3	ND	59	49
WV #4	ND	19	ND



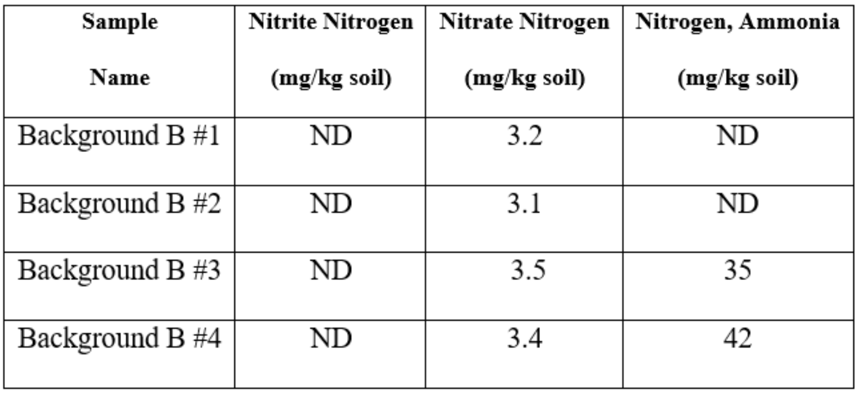
Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
MBTF #1	ND	8.3	28
MBTF #2	ND	4.3	28
MBTF #3	ND	5.2	28
MBTF #4	ND	4.1	35



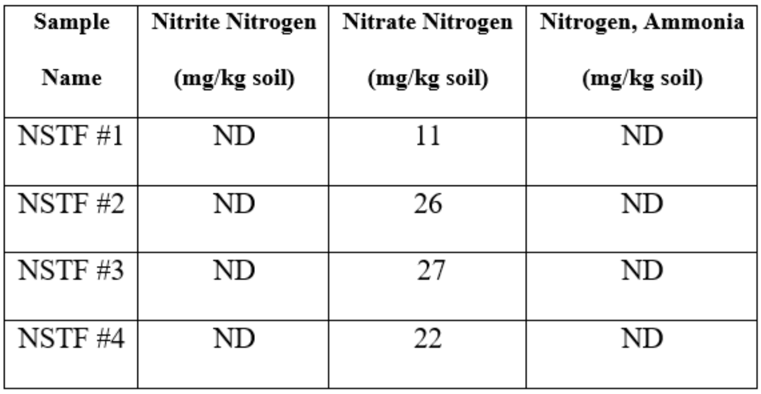
Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
ES #1	ND	ND	ND
ES #2	ND	ND	28
ES #3	ND	ND	ND
ES #4	ND	2.2	35



Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
HPM #1	ND	480	28
HPM #2	ND	26	ND
HPM #3	ND	2.6	ND
HPM #4	ND	1.8	ND



Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
Background B #1	ND	3.2	ND
Background B #2	ND	3.1	ND
Background B #3	ND	3.5	35
Background B #4	ND	3.4	42



Sample Name	Nitrite Nitrogen (mg/kg soil)	Nitrate Nitrogen (mg/kg soil)	Nitrogen, Ammonia (mg/kg soil)
NSTF #1	ND	11	ND
NSTF #2	ND	26	ND
NSTF #3	ND	27	ND
NSTF #4	ND	22	ND

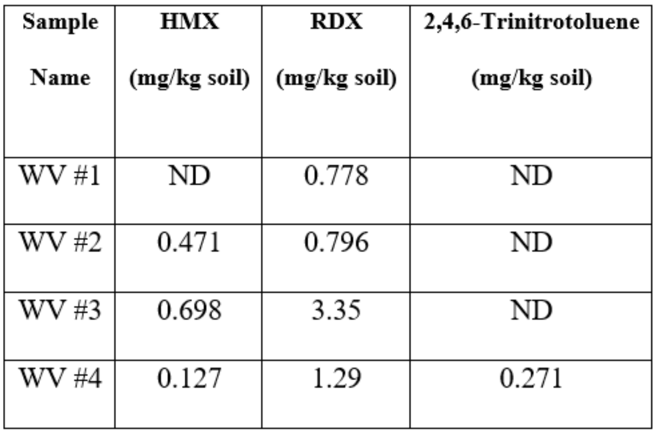
B. Explosives and Energetic Residues

Sample Name	HMX (mg/kg soil)
300N #1	ND
300N #2	0.286
300N #3	ND
300N #4	ND

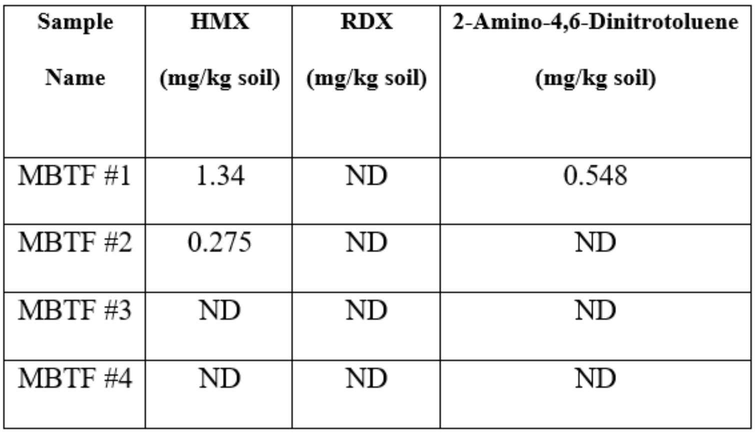
*Not Detected

Sample Name	HMX (mg/kg soil)	2,4-Dinitrotoluene (mg/kg soil)	RDX (mg/kg soil)
3KW #1	ND	1.22	ND
3KW #2	ND	ND	ND
3KW #3	3.46	ND	0.915
3KW #4	ND	ND	0.610

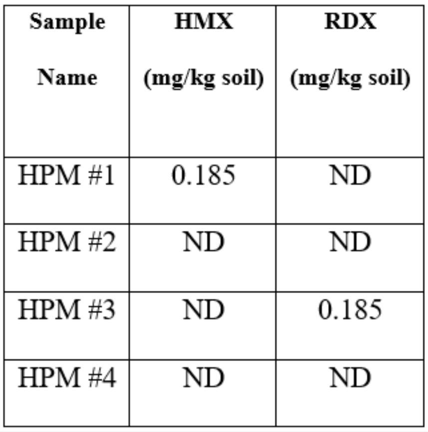
Sample Name	HMX (mg/kg soil)	RDX (mg/kg soil)	1,3,5-TNB (mg/kg soil)	2,4,6-Trinitrotoluene (mg/kg soil)	2-amino-4,6-dinitrotoluene (mg/kg soil)
BE #1	6.26	0.384	0.181	0.462	0.157
BE #2	0.462	0.159	0.198	0.205	ND
BE #3	0.238	ND	ND	ND	ND
BE #4	2.10	2.02	ND	0.277	0.177



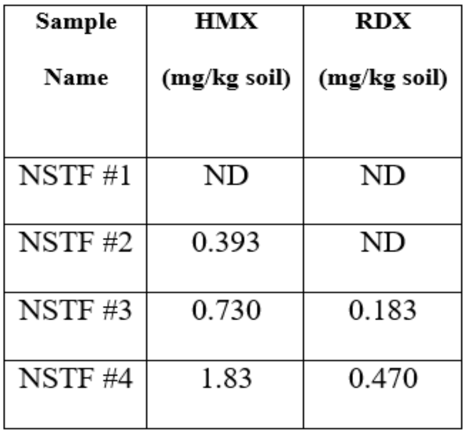
Sample Name	HMX (mg/kg soil)	RDX (mg/kg soil)	2,4,6-Trinitrotoluene (mg/kg soil)
WV #1	ND	0.778	ND
WV #2	0.471	0.796	ND
WV #3	0.698	3.35	ND
WV #4	0.127	1.29	0.271



Sample Name	HMX (mg/kg soil)	RDX (mg/kg soil)	2-Amino-4,6-Dinitrotoluene (mg/kg soil)
MBTF #1	1.34	ND	0.548
MBTF #2	0.275	ND	ND
MBTF #3	ND	ND	ND
MBTF #4	ND	ND	ND



Sample Name	HMX (mg/kg soil)	RDX (mg/kg soil)
HPM #1	0.185	ND
HPM #2	ND	ND
HPM #3	ND	0.185
HPM #4	ND	ND



Sample Name	**HMX (mg/kg soil)**	**RDX (mg/kg soil)**
NSTF #1	ND	ND
NSTF #2	0.393	ND
NSTF #3	0.730	0.183
NSTF #4	1.83	0.470