Environmental impact of military explosive munitions at General De La Rey Training Area, Potchefstroom

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Declaration

I, Captain L.K. Mokalapa (Student Number 34484507), hereby declare that the work contained in this dissertation titled "The Environmental Impact of Military Explosive Munitions at General De La Rey Training Area in Potchefstroom" handed in at the Unit of Environmental Sciences and Management at North West University, has been carried out by me, that all literary sources used have been duly acknowledged in the list of references and that no part of this dissertation has been previously presented in whole or in part before any institution for the purpose of obtaining any qualification.

Capt L.K. Mokalapa **Date**

Preface

The Defence Review of 2015 identifies spillages, remnants of munitions, explosive residues, and Unexploded Ordnance (UXO) as problematic in Military Training Areas (MTAs). A review of literature revealed that this is a military pandemic and has been reported in several countries. Range sweeps for dangerous munitions constituents have not been sufficiently effective. The Defence Review (2015) proposed a Military Range Clearance (MRC) capability to combat the above environmental threats. This study is motivated by the need for capacitating the MRC by providing the starting point to solving the above-mentioned problems in the military context. Characterisation and impact studies are important for developing methodologies and technologies for solving the above environmental problems globally. This study is intended to support the vision of the Defence Review and to galvanise the interest of environmental scholars to focus on unique aspects of the environment such as the impact of explosive munitions in MTAs. As such, the current study investigated the impact of explosive munitions at a military munitions testing range. Much of the data collection and analysis techniques were drawn from United States Environmental Protection Agency (US EPA), particularly from the work of the US Army Engineer Research and Development Canter's Cold Regions Research and Engineering Laboratory (CRREL).

This study was funded by an SANDF Bursary and the FNAS Bursary Scheme of the North-West University. Collectively, both bursaries made the study possible by providing the critical funds required including the acquisition of explosive analysis columns for high-performance liquid chromatography (HPLC) and the necessary reagents. A large volume of soil and water samples were collected and analysed for explosives and heavy metals. The MTA findings were compared to control samples from neighbouring farms. High Explosives were detectable in all sectors in both soil and water samples. Most detections were metabolites of 2,4,6-TNT and its co-contaminant 1,3,5-TNB, suggesting the residues were present in the environment for a long period. Interestingly, explosive detections were also observed in control and in underground water sources. Heavy metal concentrations in MTA samples were higher than control concentrations. Mn was detected at UXO disposal sites in extremely high concentrations. UXO sites were located, categorised, and quantified. A significant amount of UXO was also found at various collection and OB/OD sites within the MTA. 81 mm and 60 mm Mortar bombs were dominant with over two orders of magnitudes than other UXO. 127 mm MRL duds were the dominant random UXO. Further studies are required to characterise better these military unique environmental problems and remediation methods must be developed to limit possible future environmental catastrophes.

Acknowledgements

First and foremost Glory be to God for providing me with the will, resilience and the energy to complete the project. Special thanks to my lovely wife and our unborn child, my two sons and my family for believing in me, ever encouraging me not to give up during difficult times. This work was completed under severe circumstances in the middle of a global pandemic that affected everyone and everything in different ways. This research was carried out under the dedicated and capable supervision of Prof Oriel Thekisoe of the Unit for Environmental Sciences and Management at the University of the North West, Potchefstroom. The assistance rendered by Mr Johan Hendricks with sample analysis at ECO Analytica laboratory at the North-West University cannot go unnoticed. This goes for all the staff at the institution who contributed positively to the achievement of the project. Special thanks to Professor Carlos Bezuidenhout for exceptional leadership in overseeing the completion of this study. The study was made possible by financial assistance from the SANDF Bursary Fund and the NWU's Faculty of Natural and Agricultural Science's Bursary Scheme.

The local farmers at Sweet Cinnamon and Aadill Farms have contributed immensely to the success of the study by allowing us access for sampling in their properties. Not to forget my professional supervisor and esteemed colleague, Lieutenant Colonel J.L. Van Rensburg for rendering mentoring support and advice throughout the period of the study, nor forget the selfless service rendered by of Lieutenant L. Mulugisi by lending a helping hand during sample collection. I further thank the SANDF and colleagues for giving us access to the military training area during live training exercises for sample collection.

Abstract

Explosives are manufactured in the industry using energetic chemicals such as 2,4,6-Trinitrotoluene (TNT), Hexahydro-1,3,5-Trinitro-1,3,5-Triazinanane (RDX), Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine (HMX), Composition B and Tetryl, 1,3,5-Trinitrobenzene (TNB). Propellants generally contain Nitrocellulose (NC) combined with other energetic compounds. Published literature has shown that explosives are not completely consumed by detonation or deflagration during a firing event and this results in deposition of some of the explosive residues onto the ground, thereby causing contamination. Heavy metal contamination also occurs in training areas due to metal fragments from munitions castings and explosive additives. This study was conducted at General De La Rey Training Area to investigate the environmental impacts of explosive munitions. The unexploded explosive ordnance (UXO) locations were investigated by foot and vehicle reconnaissance, recorded and quantified. Soil and water samples were collected within the training area and two control areas adjacent to the study area and analysed for explosive residues using HPLC and for heavy metals using Microwave Assisted Acid Digestion and ICP MS. Nine areas used as UXO disposal and Open Burning/Open Detonation (OB/OD) sites were located and the amount and diversity of UXO determined.

A total of 181 samples were collected of which 133 were soil samples and 48 water samples. Contamination from RDX and HMX contamination were dominant in control water samples from in orders of 100 µg/kg. Soil samples from all sectors of the military training areas (MTA) contained low concentrations of High Explosives (HE) in the order of 10 µg/kg. TNT transformation products were the most frequent detections. The study area was also contaminated with various concentrations of heavy metals. Most of the contamination was in soil samples from UXO sites and explosion craters. MTA soil samples exhibited higher metal concentrations, particularly Mn, Cu and Cr, than control samples. Hg and Cd exhibited the lowest concentrations in control soil samples. Contamination in water samples was minimal. Little overall variability existed between MTA and control water samples. The MTA exhibited slightly higher concentrations of heavy metals than control environments. More than 1000 UXO items from various types of explosive munitions were counted within the MTA. A total of nine UXO sites were found in the study area. The UXO consisted of mortars, 155 mm shells, antitank rockets, hand grenades, etc. UXO was only counted from the surface due to safety considerations. The overwhelming majority of UXO were 60 mm and 81 mm mortar bombs, which accounted for 38 % and 31 % of the total UXO.

The study concluded that contamination from both explosive compounds and heavy metals was detectable but not severe enough to warrant urgent clean-up operations. Although no indices were found for determining intervention level contamination for explosive compounds, toxicity data indicated that the detected concentrations were much lower than reported toxic levels. This was also the case with heavy metals. Individual samples exhibited hot-spots of high concentration where remediation may be required, such as the OB/OD sites at Sector B. The study further concluded that mere existence of UXO is an explosive hazard and recommended that all UXO must be rendered safe and cleared from the MTA. The SANDF needs urgent development of characterisation, monitoring and remediation strategies for controlling these impact of explosive munitions before contamination reaches costly toxic levels.

Key Words: Explosives, Energetic Compounds, Munitions, Unexploded Ordnance, Heavy Metals, Environmental contamination, Military Training Area.

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List of Abbreviations

BIP	Blow In Place
DANT	Di-amino Nitrotoluene
DNBA	Diaminobenzoic Acid
DNT	Dinitrotoluene
DNX	1,3-nitroso-notro-1,3,5-triazine
EF	Enrichment Factor
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-trizocine
HOD	High Order Detonation
LOD	Low Order Detonation
MTA	Military Training Area
MNX	1-nitroso-3,5-dinitro-1,3,5-triazine
NB	n-Nitrobenzene
NC	Nitrocellulose
NG	Nitroglycerin
NQ	Nitroguanidine
NEMA	National Environmental Management Act
OB/OD	Open Burning/Open Detonation
RDX	Royal Demolition Explosive (Hexahydro-1,3,5-trinitro-1,3,5-triazine)
RWU NW	Regional Works Unit North West
SANDF	South African National Defence Force
TNB	2,4,6-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
TNX	1,3,5-trinitroso-1,3,5-triazine
US EPA	Unites States Environmental Protection Agency
UXO	Unexploded Ordnance

List of Acronyms

ASB Potch	Army Support Base Potchefstroom
Demo Area	Demonstration Area
I*geo*	Geo-accumulation Index
PETN	Pentaerythriol-Tetranitrate
SA Army	South African Army
Tetryl	Trinitrophenyl N-methylnitramine
4 Arty Regt	4 Artillery Regiment
5 SF Regt	5 Special Forces Regiment

Chapter 1 Introduction

1.1 Introduction

The concept of “Environment” covers both the biotic and abiotic elements including but not limited to the surroundings that sustain the lives of organisms and naturally occurring physical phenomena (Singh, 2006). Definitions of environment must cover a multitude of external factors to an organism (H.A.P. Smit, 2017) and its interaction with the phenomena cohabiting a particular location (Singh, 2006). The Constitution of South Africa (South Africa, 1996) defines ‘environment’ in terms of how it should promote a democratic society. This definition has a strong human focus in it and is enshrined in the National Environmental Management Act 108 of 1998 (NEMA, 1998).

The South African National Defence Force (SANDF) is one of the major beneficiaries and users of South Africa’s diverse and rich environment. The NEMA governs environmental management across all sectors of government through Cooperative Governance. This concept places the shared environmental management responsibility to the government departments, including the Department of Defence and the SANDF (NEMA, 1998). The SANDF has a long history of environmental management (Marx, 2014; Ncubukezi, 2019; H.A.P. Smit, 2017). Three important pieces of legislation have been developed that compels the SANDF to involve environmental management as part of military strategy; (1) The White Paper on Defence of 1972, (2) The Defence Review of 1998, with its second issue in 2015, and (3) The Environmental Implementation Plan (EIP) of 2008 (Department of Defence, 2008). These legal constructs guide the SANDF environmental management practices and attitudes through the concept of Military Integrated Environmental Management (MIEM).

In the past few decades, the military industry worldwide has realised its share of environmental degradation. According to Hilbert, (2012) and Magagula, (2014) the industry is taking steps to improve legislation that limits or reduces military impacts on the environment. In the SANDF, Environmental Services is the custodian of the environmental management capability of the SANDF Logistics Division, commonly known as Military Integrated Environmental Management [MIEM] (Defence Review, 2015; Magagula, 2014; Ncubukezi, 2019). The MIEM is applied throughout the structure of SANDF by deployment of Environmental Officers in each of 5 regions exquisitely highlighted by Ncubukezi, (2019).

Several studies emerged in the last decade reporting the environmental performance of the SANDF (Magagula, 2014; Marx, 2014; Ncubukezi, 2019; Smit & Mokiri, 2016; Smit & Magagula, 2016; H.A.P. Smit, 2017). A range of environmental issues were addressed, such as (1) structural and financial challenges experienced in the implementation of MIEM (Magagula, 2014); (2) the impact of military activities at military training areas [MTAs] (Magagula, 2016; Marx, 2014) and (3) environmental awareness, education and training (Smit & Magagula, 2016; Smit & Mokiri, 2016; H.A.P. Smit, 2017). Both Defence Reviews (1998 & 2015) have reported other major health risks and environmental concerns that need to be addressed. These include MTA contamination with explosive residues, heavy metals leached from munitions, and the accumulation of Unexploded Ordnance (UXO) in MTAs. The latter environmental problems are the focus of this study.

1.2 Background

The MTAs host a variety of ecosystems, habitats, as well as numerous species of flora and fauna, that are constantly at risk of exposure to military action (Defence Review, 2015; Department of Defence, 2008; Ellwanger & Reiter, 2019; Marx, 2014). Heavy vehicles, equipment, and military ordnance compact the soil, rendering it impenetrable by precipitation while grasses and other plants are destroyed (Magagula, 2016). Loss of vegetation cover exposes soil to erosion and vice versa. Scarcity in vegetation affects the carrying capacity of the biome for herbivorous animals. All these risks negatively affect the species composition along food chains, therefore the biodiversity, of that particular ecosystem and consequently changing the landscape.

This study takes the epistemological position that the environmental degradation of MTAs by toxic chemical compounds is a function of the use of military explosive munitions. These compounds directly affect vegetation, soil and water systems that sustain the ecological integrity of the MTAs. Explosive munitions are categorically isolated as major polluters of soils and water resources in MTAs by posing as the main contamination pathway for (1) energetic compounds, (2) heavy metals fragments and (3) Unexploded Ordnance (UXO). These contaminants were reported as a major concern common to MTAs in South Africa (Department of Defence, 2008; Defence Review, 2015; H.A.P. Smit, 2017) and around the world (Jenkins et al., 2001; Kalderis et al., 2011; Pichtel, 2012; Walsh et al., 2009).

Target engagement systems using heavy and long range weapons provide a generic model of contamination (Figure 1.1) Explosive residues and heavy metals are introduced into the environments in one or more contamination pathways. (1) Explosives can be dissolved in wastewater during production of explosives at manufacturing industries. (2) Explosives can be dispersed as gases and residues during deflagration at firing sites. (3) Explosives can be dispersed as gases and residues during detonation on target. (4) Explosives can be dispersed as gases and residues during burning or detonation of excess propellant charges and (5) explosives can leach from Unexploded Ordnance (UXO) and heavy metals after firing events.

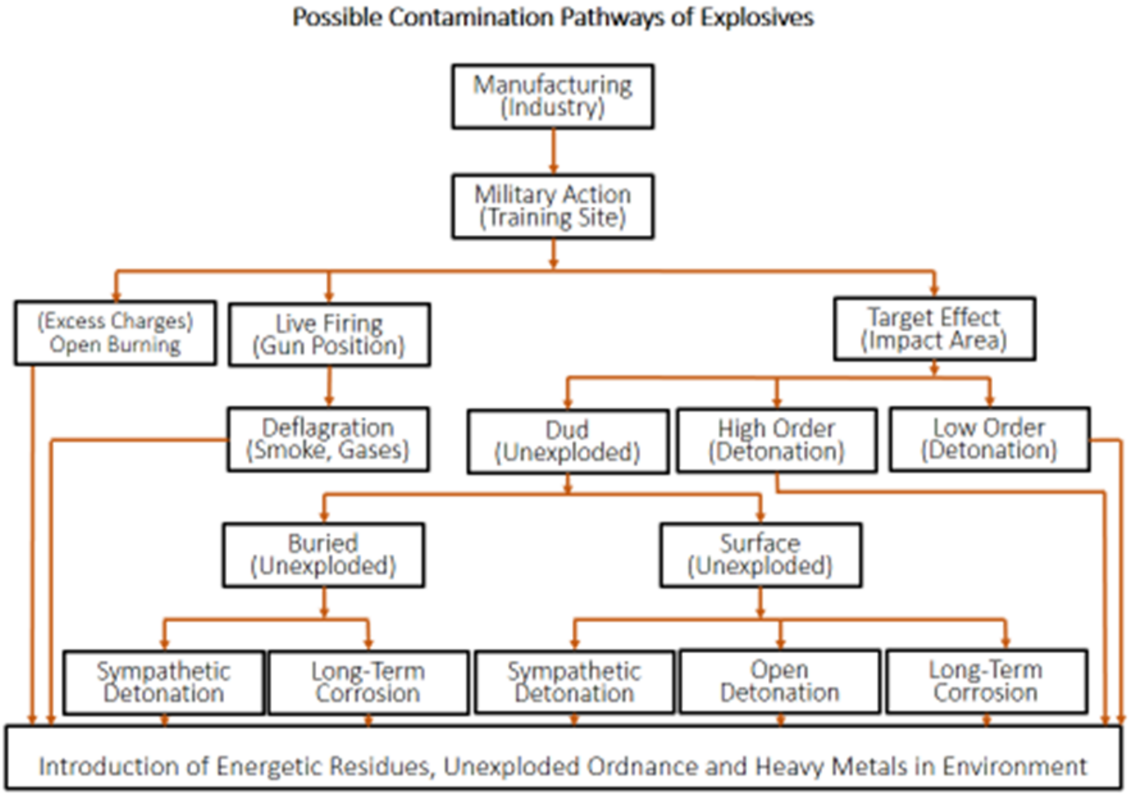


Figure 1.1.Contamination pathways of energetic compounds (Kalderis et al., 2011; Pichtel, 2012)

1.3 Modelling the introduction of munitions to training environments

At gun positions during live firing exercises involving long-range weapons, ammunition is launched against a target by igniting propellant charges. Propellants generally contain one or a combination of nitrous chemical compounds such as Nitrocellulose (NC), Nitroglycerine (NG) and Nitroguanidine (NQ) (Jenkins, et al., 2001; Pichtel, 2012; Walsh, et al., 2009). Propellants deflagrate on ignition, generating large volumes of gasses and pressure in the launcher bore. This results in exponential acceleration of a projectile in the gun muzzle, which attains great terminal velocities towards a target. The exodus of a projectile is followed by a plume of gases containing unburnt propellant residues and metabolites of propellants (mainly sub-classes of nitrous chemicals). These residues contaminate the environment around gun positions at MTAs as shown in Figure 1.2. (Pichtel, 2012; Walsh, et al. 2009)

Figure 1.2.Smoke dispersion from live firing of large calibre weapons; SANDF120mm M5 Mortar (left) firing at high angle releases gases above the position and SANDF 155mm GV5 Howitzer (right) has long muzzle and releases gases forward of its position (Defence Review, 2015)

At target areas, explosive munitions use High Explosives (HE) such as 2,4,6 – Trinitrotoluene (TNT), Hexahydro – 1,3,5 – Trinitro – 1,3,5 – Triazinane (RDX) and Octahydro – 1,3,5,7 – Tetrenitro – 1,3,5,7 – Tetrazocine (HMX), or Composition B (60% TNT, 11% RDX and 1% wax) cast in steel shells. Launched ammunition (including Hand Grenades) arrive at the intended target with a certain terminal velocity and angle of arrival (Cross et al., 2016; GICHD, 2017) and is detonated according to engagement parameters set by the user (above, on or below ground). Detonation causes acceleration of chemicals, metal and debris (Cross et al., 2016; GICHD, 2017) which are dispersed into the environment. Detonations are divided into high order detonations (HOD) and low order detonations (LOD). The LODs scatter residues closer to the impact area while the HODs scatter residues farther from impact areas. As a result, HODs are expected to deposit lower concentrations of explosive residues as compared to HODs.

Debris resulting from detonation of munitions follow different fates (Pichtel, 2012). Energetic residues can be transported through the environment in pure form, as metabolites in solution due to precipitation or in solid form by wind. Explosive residues transported by runoff may reach surface water sources, where it may dissolve and follow any of the various transformation pathways detailed in Kalderis (2011). Dissolved energetics can reach underground wells by leaching through soil pores. Energetics can also undergo biotic and abiotic transformation into various forms of transformation products. Transformation pathways include volatilisation, adsorption, dissolution, biodegradation, phytoremediation and microbial degradation (Kalderis et al., 2011; Pichtel, 2012; Singh et al., 2015). Part of the debris scattered by detonation of munitions are heavy metals. Heavy metals in this context refer to the fragments of ruptured ammunition shells deposited by detonation (GICHD, 2017). Heavy metals such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb) are introduced to soils in two or both forms; (1) as solid metals in the form of fragments of various sizes which remain polluting range soils unless removed (Bricka et al., 1994), or (2) as a heavy metal leachate that can be transported to groundwater or remote environments in solution (Gautam et al., 2016).

Furthermore, destruction of UXO and excess propellant charges after firing events typically involves detonating the rdnance with a donor charge or by burning as described by Dontsova et al. (2006) and Walsh et al. (2009). Dontsova (2006), Pennington et al. (2008), Pichtel (2012) and Walsh et al. (2009), provide in-depth analysis of the characterisation and fate of energetics at MTAs. UXO have become a major problem at MTAs since explosive munitions are utilised continuously during training at MTAs in peace time. Left over ordnance is gathered for destruction in open pits. Open Detonation (OD) and Open Burning (OB) of UXO has been criticised for failing to subdue the explosives (Dontsova et al., 2006). OB/OD disposal techniques exacerbate the problem by scattering the contamination, making characterisation and remediation a complicated endeavour (Jenkins et al., 2001; Pennington, 2008; Walsh et al., 2009).

1.4 Environmental impacts beyond explosion

Environmental impacts of military activities are mainly affect the physical environment. These impacts can be direct and indirect in nature. Physical impacts include the compaction of the ground due to heavy vehicle manoeuvring, detonation of large calibre explosive munitions and troop traffic during exercises. According to Magagula (2016), these exercises denude the ground of vegetation and exposes the soil to erosion. They can further be short term or long term, may be spatially extensive or local, depending on the intensity of the activities. Magagula (2016) suggested that these physical impacts create heterogeneous landscapes within MTAs. According to the Environmental Impact Assessment (EIA) guidelines, assessment of potential impacts provide important information for in depth understanding of potential environmental impacts of activities prior to considering remediation and mitigation strategies that are necessary to alleviate the problems (NEMA, 1998).

Apart from contamination of MTAs with energetics, UXO and heavy metals, environmental impacts of explosive munitions reach further than the MTAs through a number of scenarios. (1) Protection of training areas determines the level of access by civilians to contaminated areas. (2) Vegetation quality and the presence of wild game in the training area may be jeopardised by the employment of explosive munitions. (3) Neighbouring land users may develop negative attitudes towards the SANDF depending on the nature of the impact of military activities on their properties, such as veld fires, munitions constituents and other contaminants originating from the MTA.

It was argued herein that failure of range management to prevent civilians entering training sites would result in a number of problems such as the above-mentioned scenarios. Civilians have no training or relevant information regarding the nature of activities and dangers they could be exposed to when entering MTAs. By entering these sites, they could become exposed to UXO and explosive contaminated soils and water sources. Additionally, they may unknowingly enter areas of active live firing, leading to unintended fatalities. This points to physical security of MTAs as an integral part of Integrated Training Area Management (ITAM). Preventing civilian casualties by appropriately fencing and marking MTA borders can prevent costly claims against the SANDF. A historical study of the relationship between the MTA and local land users will enhance understanding of the environmental performance of the MTA from a security point of view. This information is expected to be available in range management archives and police records. Where this is not possible, primary data can be collected through interviews with military and civilian personnel who are in one-way or another affected by activities in the MTA.

Vegetation is an important casualty of live fire exercises with explosive munitions. Shells affecting targets cause craters (GICHD, 2017) and compact soils, causing destruction of vegetation and affecting plant growth patterns. Toxic explosive residues are also scattered on plants, water sources or absorbed by plant roots. Absorbed energetics may reside in terminal shoots of plants or precipitated in water ponds and become available for passive consumption by animals. Due to varying different health tolerances among species to energetic toxicities, some vegetation and animal species genomes may be affected by chronic exposure to the contaminated environment. Consequently, a variation in plants and animal species composition, and genome integrity, between the MTA and surrounding environmental ecotones may occur. Knowledge of the impact of munitions constituents on biota and chemical toxicity margins is important for environmental monitoring when management decisions are required for mitigating and preventing these adverse effects.

Training areas do not exist in isolation from surrounding land uses (Defence Review, 2015; Ellwanger & Reiter, 2019). The future land use of MTAs has a bearing on current land uses of the neighbouring farming community. Local land users like farmers may have interest in the nature of activities within SANDF properties adjacent to theirs. MTAs are expected to be returned to civilian authorities upon expiration of their current use. This may expose some military unique environmental problems previously not observed. Ellwanger & Reiter (2019) indicated that decommissioned military land has often failed to meet the socioeconomic requirements intended at the time of transfer. This is due to contamination and the presence of UXO and military debris in many former conflict zones, particularly in Europe. Rehabilitation of these lands has to date not been possible. Furthermore, contamination may have a spill over effect to adjacent properties. Ground and surface water from MTAs can reach remote water systems, or explosive gases and residues could contaminate agricultural land (Broomandi, et al., 2020). Where future land use is expected to be agricultural in nature, explosive residues may affect the agricultural potential of a farmer’s land, which has been identified as one of the problems during decommissioning of military training areas worldwide (Ellwanger & Reiter, 2019). Pichtel, et al., (2012) indicated that clean-up of contaminated military ranges is costly and require specific technical capabilities. This calls for frequent or continuous assessment of MTAs for environmental impact of military activities (Defence Review, 2015).

1.5 Description of the study area

1.5.1 Geographical location

General De La Rey Training Area is located northwest of the town of Potchefstroom as indicated on the 1: 50 000 Topographical Map of Potchefstroom (Figure 1.3). The Training Area is located between Latitudes 26˚55’30’’S and 27˚05’00’’S and between Longitudes 26˚33’30’E’ and 26˚40’55’’E as determined from the WGS 84 1: 50 000 Potch Eleaser map obtained from Joint Tactical Head Quarters North West (Le Roux, 2020). General De La Rey Training Area is under the administrative control of Army Support Base (ASB) Potchefstroom. The ASB is responsible for range safety, facility and environmental management functions with the assistance of the North West Regional Works Unit. The ASB Range Management Office enforces a rigorous set of range standing orders that regulate range use (Van Tonder, 2020).

The training area has the shape of a severed triangle cut a quarter of the way from the northern limit. According to oral sources (Van Rensburg, 2020; Van Tonder, 2020) the R53 Ventersdorp arterial route is the eastern boundary, the unpaved Welgegund road forms the northern boundary, the electrical power line bordered the length of the western boundary and Eleazar secondary road forms the southern boundary. All sides are fenced off with a 1.5 m high barbed wire fence except the entire length of the southern side along Eleazar Road where encroachment of informal settlements is suspected to have contributed to theft of the boundary fence and illegal hunting (Van Rensburg, 2020).

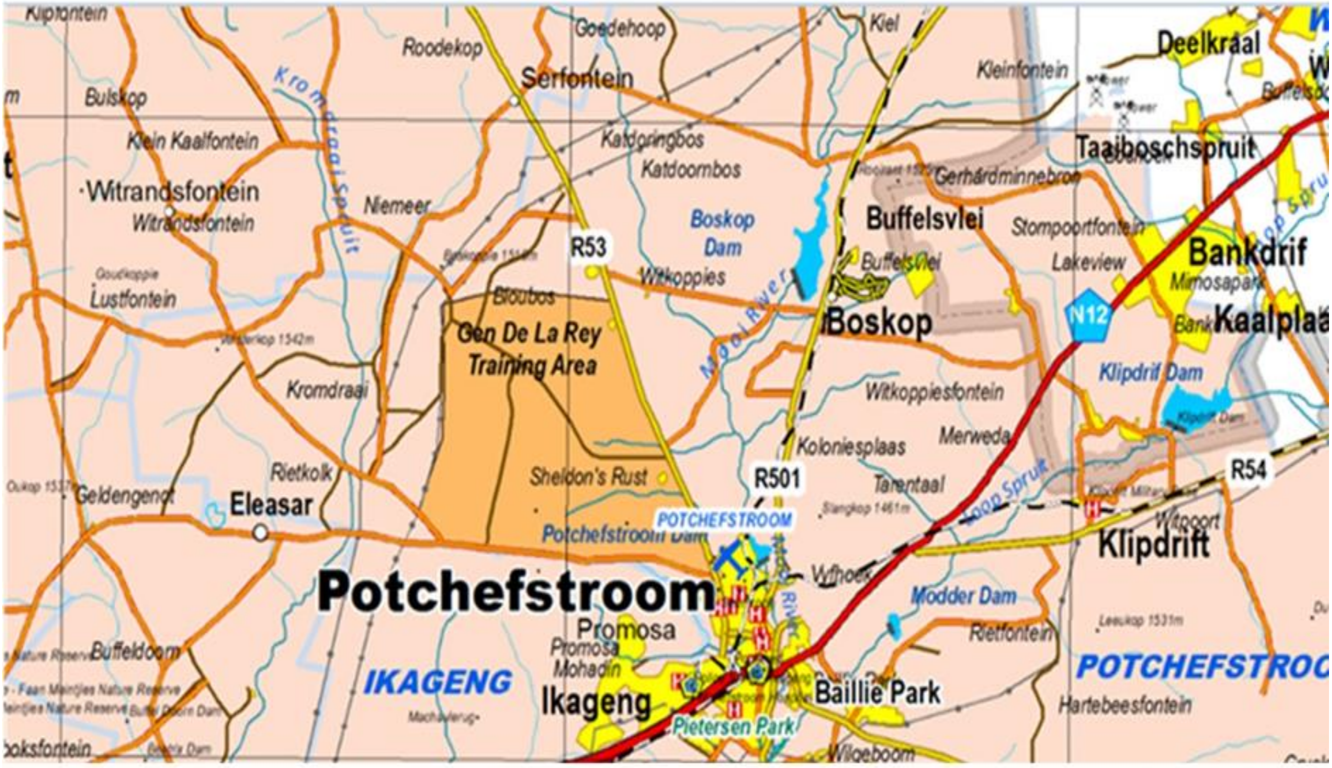


Figure 1.3:Map of Potchefstroom illustrating the study area scaled 1:50 000 (Le Roux, 2020)

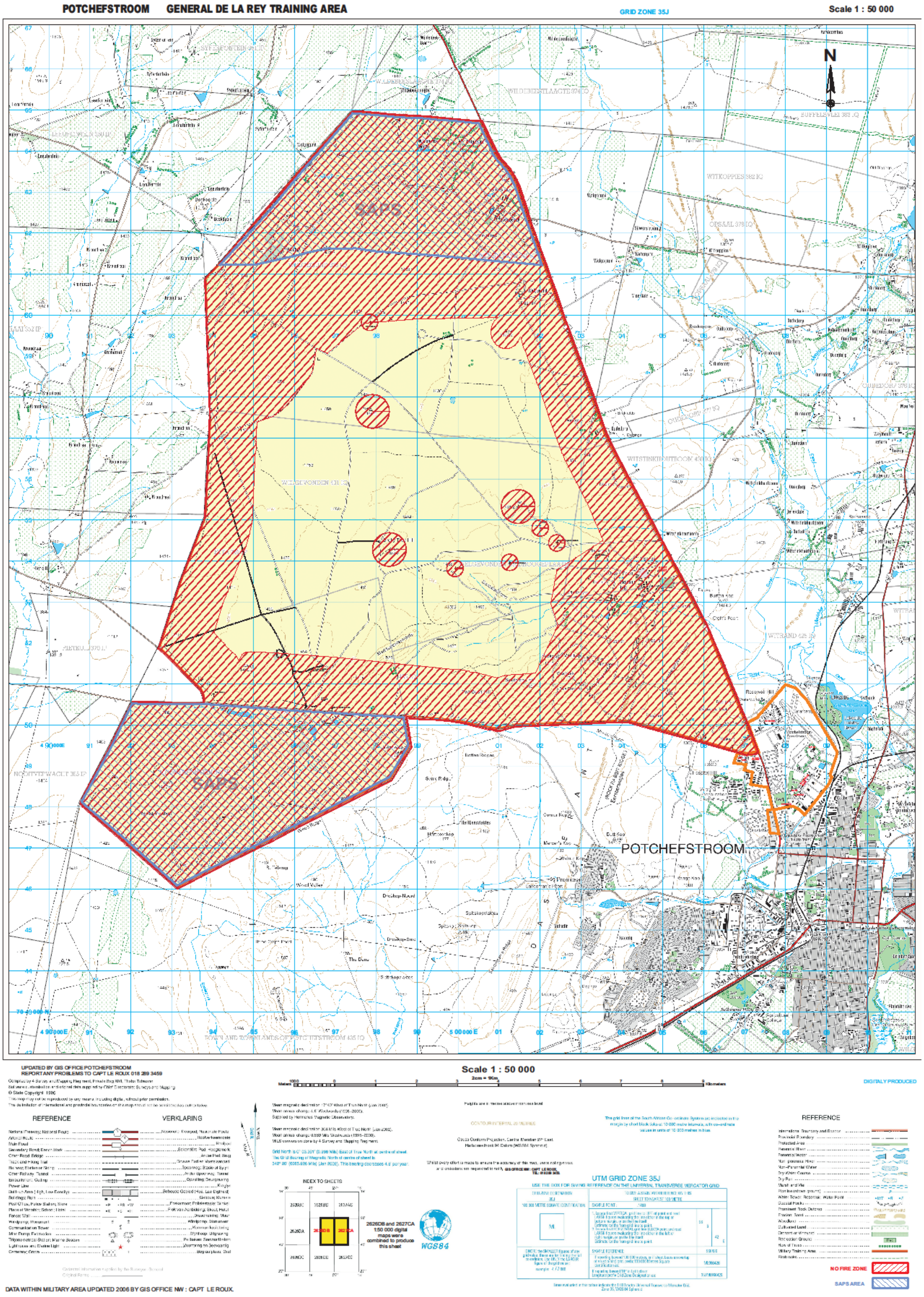


Figure 1.4:Topographic map of Gen De La Rey Training Area scaled 1: 50 000 (Le Roux, 2020)

A No Fire Zone (NFZ) is an approximately 1km buffer on the inside of the range border, red-shaded area on Figure 1.4, is used in fire planning to prevent munitions impacting external limits of the training area. Gun positions can be located in the NFZ when firing toward target areas in the Central Sector but not targets are acquired in this zone. The topography, climate, vegetation and geology of the area is described in later sections.

1.5.2 Geology, topography and drainage

General De La Rey Training Area is located on the edge of a Dolomitic Landscape, which is described by geologists as the Karst terrain (J.J. Smit, 2017). The area under study lies at a geological region influenced by the underlying Ventersdorp Supergroup and the Transvaal Supergroup (Celliers, et al., 1999; Van Rensburg, 2020; Nel, et al., 1939). The area dominating the southern quarter of the MTA, including Modderfonteinrante and Gonzalespoort, extending east to Valkop, is dominated by rocky outcrops, hills and ridges characteristic of the Pretoria Series of the Transvaal Supergroup (Van Rensburg, 2020). Three main rock types in this area are shale, slate, chert and quartzite of the Pretoria Series (Celliers, et al., 1999; Nel, et al., 1939). The tops of the hills at Valkop, Modderfonteinrante and Gonzalespoort for example, have visible rocky ridges but their slopes are covered in shallow soils mixed with fragmented rocks.

The northern and western part of the MTA landscape is dominated by plains with some scattered, slightly irregular, undulating steppe and low hills characteristic of the Ventersdorp Supergroup as evidenced by loamy to sandy soils supporting the Vaal-Sandy Grassland biome. The largest part of the MTA, most of the eastern half, is dominated by a plane plateau with a few hills with disserted rocky ridges. It supports the largest variety of grassland species and is underlain with dolomites and cherts from the Malmani Sequence of the Transvaal Supergroup (Van Rensburg, 2020; J.J. Smit 2017).

The 1: 50 000 map of General De La Rey Training Area indicates that average height above sea level of the training area ranges from about 1300 m in the north-west and about 1500 m in the south east at Valkop and South End Hill. The large portion of the land, however, slopes eastwards where two non-perennial streams flow from the MTA into Mooi River some 10 km east of the training area. The land also falls westwards outside the western limits of the MTA towards Kromdraai. This places the training area at a miniature watershed and therefore the highest terrain in the locality.

1.5.3 Climatic conditions

The study area is situated in a summer rainfall region with rainfall averages of around 600 to 900 mm per annum (Celliers et al., 1999; Daemane et al., 2012). Rainfall is in mostly in the form of brief but intense showers and the rainfall averages are highly variable (J.J. Smit, 2017). J.J. Smit, (2017) recorded an average 629 mm over 98 year period. This places Potchefstroom area at above average rainfall conditions compared to most areas of the country. The abundance of grasses and successful stock farming activity in the province is possibly related to these auspicious and reliable rainfall conditions.

Celliers et al. (1999) reported mean maximum temperature of 32˚C and mean minimum temperature is -1˚C around the Potchefstroom area. J.J. Smit (2017) provided 98-year temperature averages and recorded highest average maximum temperatures of just below 30˚C in December/January and lowest maximum temperature averages of nearly 20˚C in June. Highest minimum temperature average of around 15˚C was recorded in December/January and the lowest minimum of around 0˚C in June. Summers are generally very warm and the cold winters are characterised by frosty conditions.

1.5.4 Flora and fauna

The biodiversity in General De La Rey Training Area is expected to reflect the species composition of the local ecosystem owing to its location in Potchefstroom (North West Province). Celliers et al., (1999) found that the vegetation status around Potchefstroom is influenced by anthropogenic interaction with natural environment through urbanisation, which altered the phyto-sociological composition of the area and resulted in fragmented distribution of plant species. According to Van Rensburg (2020) ecological compartments and transitionary ecotones between them provide a range of habitats for a wide range of species diversity of vegetation and wildlife at General De La Rey Training Area. Van Rensburg (2020) reported 185 species recorded in the Regional Works Unit North West Biodiversity Register found in the training area. Ninety-three of these are Plantae and 92 are Animalia. Three main vegetation units at these ecological compartments and transitionary ecotones; namely (1) the Vaal-Vet Sandy Grassland, (2) the Carletonville Dolomitic Grassland and (3) the Andesite Mountain Bushveld. Some of the most common vegetation types listed in the biodiversity register at the Environmental Office at RWU NW are listed on Table 1.1 below.

Table 1.1: Vegetation types in General De La Rey Training Area (Van Rensburg, 2020)

Scientific Name	Common Name	Tops Classification	Population Status
Senegalia hebeclada	Candlepod thorn	Not Listed	Increasing
Eragrostis obtusa	Dew grass	Not Listed	Stable
Aristida congesta	Tassel Three awn	Not Listed	Stable
Eucalyptus grandis	Saligna Bloekom	Invasive species	Decreasing
Eragrostis superba	Saw tooth love grass	Not Listed	Stable
Melinis repens	Natal red top	Not Listed	Stable
Cymbopogon caesius	Broad leafed turpentine grass	Not Listed	Stable
Cynodon dactylon	Couch grass	Not Listed	Increasing
Eragrostis lehmanniana	Lehmanns love grass	Not Listed	Stable
Themeda triandra	Red grass	Not Listed	Stable
Acacia mearnsii	Black wattle	Invasive species	Increasing
Solanum elaeagnifolium	Silver-leaf nightshade	Invasive species	Stable
Heteropogon contortus	Spear Grass	Not Listed	Stable

Vaal-Vet Sandy Grassland is limited to the northwestern part of the range due to its characteristic habitat of sandy soils overlying the andesite and gneiss basement rocks of the Ventersdorp Supergroup (Van Rensburg, 2020). Vegetation in this area largely consist of low grasses mixed with a large shrub component. This grassland type is classified as endangered and about 24% of it is expected to be conserved throughout the range of species. Agricultural activity was identified as responsible for over 60% of its transformation. This area is avoided when executing training.

Carletonville Dolomitic Grassland is the largest grassland type in the range and is located to the west of the Modderfontein Ridges, extending east to the range border and north to Welgegund. Part of this vegetation type is found in the vicinity of ASB’s ammunition magazine at the south eastern corner of the range. It also supports the largest variety of grass species in mosaic pattern in the MTA. Agriculture, urban sprawl, mining activity and building of the Boskop and Klerkskraal have transformed more than 25% of this vegetation unit throughout its range. Carletonville Dolomitic Grassland is listed as "vulnerable" and 24% of this vegetation earmarked for conservation. Andesite Mountain Bushveld occurs on the plateau formed by the triangle of elevated terrain between the Modderfontein and Valkop ridges extending eastwards. Andesite Mountain Bushveld is a Savannah grassland of dense, medium-tall Thorn-Bushveld with a well-developed grass layer on the hilly and undulating landscape. A large part of the grass type is under conservation throughout its range and was allocated conservation status of "least threatened" (Van Rensburg, 2020).

A range of animal species are part of the General De La Rey Training Area ecosystem. These include the entire range from microbes, burrowing animals, birds and numerous types of Mammalia. There is a number of known large animal species found although most are not actively managed. Tops species managed incudes the *Connochaetes gnou* (Black Wildebeest). These animals freely roam the plains of the training area. The Black Wildebeest was identified as the only tops listed animal monitored in the MTA. A small herd of Zebra was also spotted in the MTA. However, the nature of military activities are expected to have significant impact on the survival of the animals located in the area. A combination of poaching activity, military live fire exercises, occurrence of UXO and contaminated soils and water resources are a recognisable constant threats to the survival of these animals. The most prominent large animal species monitored by the MIEM Office are listed in Table 1.2.

Table 1.2: Large animal species in General De La Rey Training Area (Van Rensburg, 2020)

Scientific Name	**Common Name**	**Tops Classification**	**Population Status**
Connochaetes gnou	Black Wildebeest	Threatened	Stable
Raphicerus campestris	Steenbok	Not Listed	Decreasing
Antidorcas marsupialis	Springbok antelope	Not Listed	Decreasing
Damaliscus pygarus phillipsi	Blesbok	Not Listed	Increasing

1.5.5 Brief history of General De La Rey Training Area

Literature on the history of the study area is scarce and information was derived from the author's knowledge and oral sources. The size and shape of the training area was determined by the nature of the forces supported and the safety trace and parameters of the weapons employed during training (Defence Review, 2015). Van Rensburg (2020) and Van Tonder (2020) provided most of the information relating to the history of the area. General De La Rey Training Area covers a total area of 12 275 ha (of which 11 200 ha is reserved for Military Field Training Exercises). The Union of South Africa first acquired the land in 1962 when adjoining clusters of farmland were expropriated for military use. It was previously for small-scale mixed agriculture based on livestock and crop farming. Military live firing exercises commenced in 1965. The training area was renamed two years later to General De La Rey Training Area after Jacobus Herclaas de la Rey, a Boer general during the Second Anglo-Boer War.

Welgegund, the blue shaded area to the north of the training area (Figure 1.4), situated north of range covering 2,000 ha, was once part of the main training area of the Army's mounted infantry, 12 South African Infantry Battalion. It is now in use by the mounted wing of the South African Police Service (SAPS) fwing disbandment of the Army's unit in 2005 (Van Rensburg, 2020). Modderfontein, a land parcel of 2,000 ha, shaded in blue (Figure 1.4) to the south-western boundary to the south of the Eleazar road, originally formed part of the greater training area but was recently returned to the Department of Public Works. Modderfontein was then entrusted to the local municipality whence it is administered with the intent of conserving the vulnerable Carletonville Dolomitic Grassland ecosystem prevalent at the site.

1.6 Problem formulation

The International Peace Bureau (2002) lists some of the serious environmental threats that the world faces to-date, which increase dramatically and continue to threaten the wellbeing of future generations. These include deforestation, various types of pollution, desertification, loss of biodiversity, etc. The Military Industry is one of the major degraders of the environment while not being strictly held to account by governments for the protection of the environment within their delegation (Hilbert, 2012; Marx, 2014). This resulted due to belligerent states recognising the military as an industry participating in environmental degradation but left to make decisions regarding its environmental responsibilities with minimal accountability. Marx (2014) supported this observation, citing that the environmental management function in the SANDF was simply placed under the Commanding Officer’s list of obligations, whose primary function was force preparation, and therefore could not impose on his forces measures that limit his ability to achieve the military objective. Under these pretexts, the military has been responsible for adding more than half the chlorofluorocarbons (CFC) 113 to the Ozone Layer (International Peace Bureau, 2002), releasing enormous amounts of military waste into the environment post the Cold War Arms Race, including Nuclear Wastes, which are uneconomically costly to clean and have long term impacts on the environment.

The SANDF currently considers management of the environment a serious endeavour. According to Defence Review (2015) the SANDF is one of the biggest users of property in South Africa holding land and infrastructure in all of the nine provinces. Eventually it is defence strategy to hand back surplus usable land to public (Defence Review, 2015). Marx (2014) reported that this process has already started as far back as 2002. It is therefore required that the SANDF must use the land under is control sustainably in view of its future use and to maintain a realistic environment for its force preparation activities. This prompts regular assessment and rehabilitation of degraded environments, as South African land is an important national asset and may have future agricultural or domestic use. According Defence Review (2015) disposal of Unexploded Ordnance (UXO) and Range Sweeps after firing exercises is often not enough (Magagula, 2019) as there are explosive chemicals and UXO left in the ground and remain a threat to human and environmental health (Defence Review, 2015). Lack of the implementation of remediation strategies is attributable to the Defence Review’s (2015) notion that the SANDF has limited capacity and skills base to characterise and quantify environmental problems in MTAs emanating from explosive munitions constituents and other military debris. The result, in addition to a lack of budget for environmental management, is a slow and diminishing implementation of a robust Environmental Management System (EMS) and MIEM strategy to ensure sustainable use of SANDF training facilities (Defence Review, 2015; Magagula, 2019; H.A.P. Smit, 2017).

A review of the literature reveals a lack of investigation into the degree of contamination of training grounds due to energetic chemicals deposited by explosive munitions in South Africa. Magagula (2019) reported on the impact of military exercises on vegetation cover at an MTA and Magagula (2014) further provided an in-depth review of the Military Integrated Environmental Management system of the SANDF at two SANDF bases. Peter et al., (2019) provided valuable information about the fate and transport of explosive compounds but not as a characteristic problem of MTAs. Marx (2014) reported on the impact of military activities at one of SANDF training bases, citing some of the environmental changes due military debris left after training exercises. Studies abroad have covered sufficient ground in characterising munitions contamination of military training grounds in recent decades (Jenkins et al., 2001; Pennington, 2006; Pichtel, 2012; Singh et al., 2015; 2014; Walsh et al., 2009). Jenkins et al. (2001), Pennington (2008) and Walsh et al. (2009) and hypothesized that, not all of the explosive is consumed by the detonation or deflagration during a firing event and this results in deposition of some of the explosion onto the ground, thereby causing contamination. This is also the case with burning of excess propellant charges and UXOs remaining after live firing exercises. Walsh et al. (2009) observed that open burning (OB) and open detonation (OD) of charges under controlled conditions in various climatic and terrain conditions revealed in all cases that energetic residues were deposited by both the propellants charges and UXO in similar fashions. A conclusion can be drawn that these methods, currently used at SANDF sites, simply disperse the contaminants at disposal sites. Significant contamination of soil and groundwater was found to be problematic in several US Army training areas (Jenkins et al., 2001). The distribution and levels of contamination were found to be a function of the fate and transport of energetics in soil and water media (Dontsova et al., 2006), thus there is a relationship between the persistence of energetics in the environment, climatic conditions and soil characteristics.

Reporting from the African continent is plagued with severe cases of environmental problems such as deforestation, various types of pollution, land degradation as well as an inherent lack of environmental management strategy and poor agricultural practices (Macharia, 2016). Masindi & Muedi, (2018) and Sehube et al. (2017) are some of the few publications that focused on contamination at military sites. South Africa, situated at the southern tip of the continent, covers about 121.9 million hectares of land. The SANDF holds an excess of 4.2 million hectares of land (Defence Review, 2015; Helfrich, 2013; H.A.P. Smit, 2017) of which over 335 144 hectares has been designated for training purposes, that is excluding a further 56 000 hectares used as weapon ranges. In view of the South African Department of Defence (SA DoD) strategy on land redistribution the SANDF has a duty to use the land in its possession sustainably so that it can be useful to future generations when no longer in use by the military (Defence Review, 2015; Department of Defence, 2008). This can be achieved by continuous environmental assessment and reporting in order to address environmental problems before they reach a state of crisis.

Defence Review (2015) was clear in citing that the SA DoD was aware of numerous training sites contaminated with heavy metals, UXOs and explosive contaminated soils that posed a threat to personnel and the environment. Numerous existing fate studies have shown how this problem area has attracted attention of researchers for many decades and prompts a need to establish sustainable training area management strategies by identifying, characterising and quantifying the problem in order that appropriate management strategies can be developed.

1.7 Problem statement

General De La Rey Training Area covers approximately 120 km² (12 000 ha) of land, which classified it as the largest training areas in the North West Province. Situated in Potchefstroom, it provides training ground for over 14 Military Units within the North West region. Numerous training methods with weapons ranging from 9 mm pistols, 5.5 mm Semi-Automatic Rifles, direct Antitank Weapons to large calibre weapons such as 60 mm, 81 mm and 120 mm Mortars and 155 mm Artillery Howitzers, respectively. The use of explosive munitions in this training area has potential of inflicting severe environmental impacts by contaminating soil medium and water resources in and around the study area with energetic chemicals, unexploded ordnance (UXO) and heavy metals, which either may directly or indirectly, have negative impacts on agriculture, human wellbeing, biodiversity and neighbouring land users.

1.8 Research aim

The aim of this research project was to investigate the impact of explosive munitions within and around General De La Rey Training Area.

1.9 Objectives of the study

- To investigate the impact of explosive munitions on soil by collecting and analysing soil samples for energetic chemical residues deposited during firing exercises.

- To investigate the impact of explosive munitions on water by collecting and analysing water samples for energetic chemical residues deposited during firing exercises.

- To investigate related impacts of explosive munitions through deposition of heavy metals and UXO.

- To determine how the results compare with samples from surrounding lands (non-military) for the level of contamination.

1.10 Research hypotheses

- Residues from propellant charges are deposited around firing positions contaminating the soil around the affected areas. Explosive residues from High Explosive (HE) ammunition will also be detected at impact areas in varying quantities depending on the intensity and frequency of use of the training range.

- Residues of the explosive compounds are expected to be detected in water points within the training area near firing positions and munitions impact areas. Watercourses leading away from the training area may have carried some residues into neighbouring farms.

- Exploded and Unexploded Ordnance cause contamination of soils and water with Heavy Metals and leaching of energetic chemicals. The UXO remaining on the training area may be harmful to animals and humans.

1.11 Significance and impact of the study

Since the 1970s, South African Military received a series on instructions for the armed forces to assume responsibility and accountability for the environment. These include the Defence Instruction on Environment (1972), White Paper on Defence (1996), Defence Review (1998, 2015) and the Environmental Implementation Plan (EIP) of 2008. These legal constructs are enshrined in Section 2 of the National Environmental Management Act No. 108 of 1998 (NEMA, 1998) which instructs National Departments to ensure protection of the environment within their respective control. All state departments are instructed to conduct impact studies where listed activities were conducted and provide environmental impact reports to guide remediation of potentially adverse impacts. Chapter 1 of the EIP for Defence is clear in stating that “contamination of surface and sub-surface substrates by armament debris and unexploded ordnance is the major focus in impact management.” of military activities (Department of Defence, 2008).

According to Department of Defence (2008), the SANDF has established formal relationships with other government departments such as the Department of Environmental Affairs and Tourism where it participates in cooperative government committees for coordinated environmental management at national level. The Chief of SANDF or his delegate is the coordinating officer in Ad hoc committees to ensure coordinated and harmonised application of environmental legislation and formalisation of Environmental Management Plans (EMPs) and Environmental Implementation Plans (EIPs). This arrangement ensures that environmental issues are made known and management decisions are coordinated across all spheres of government. It is therefore important that the SANDF report its unique environmental impacts on the environment under its custody for public benefit. The SANDF also has a bilateral agreement with the United States Military on environmental management strategy. The focus of the arrangement is to establish a solid coordinated Military Integrated Environmental Management (MIEM) strategy that allows for the sharing of important environmental information at international level. Due to a unique set of potential impacts of military activities, the two forces devised a guide for conducting environmental impact assessments (Department of Defence, 2008). The US Military has covered significant ground in characterising environmental impacts of explosives in their training areas (Jenkins et al., 2001; Pichtel, 2012; Walsh et al., 2008). According to Defence Review (2015), the SANDF is behind with characterisation and remediation of environmental impacts of munitions residues in training sites due to lack of skilled personnel.

This study will provide a baseline for future research of this type in the SANDF and spark more interest into characterisation and impact remediation studies. Results from this study are expected to inventories important information for future studies and assist SANDF Environmental Services with valuable information in carrying out its MIEM function in planning of MTA clean-up operations. Training and operational methods can be improved by instituting informed Ecological Considerations in Operations (ECOPS) and Integrated Training Area Management (ITAM). Sharing onsite information with the broader environmental management community, such as the Department of Environmental Affairs and Forestry can improve cooperation with other Government Departments, local communities and provide basis for successful implementation of the Military Integrated Environmental Management (MIEM).

1.12 Organisation of this study

Chapter 1: Introduction

Provides a broad definition of the concept of the environment and introduces the SANDF as an important and unique participant in environmental issues. The multifaceted nature of environment is explored in broad and the land resource along with its soil and water media is isolated as a vital environmental resource for all ecosystems. Military live fire exercises are exposed as the vehicle introducing explosive contaminants to the environment. The study area is presented in this section in terms of its topography, ecology, location and history. This problem statement, aim and hypotheses of the study are also presented in this chapter.

Chapter 2: Literature Review

It explores a variety of literature sources aimed at (1) providing the background and understanding of explosives, (2) characterisation of explosives and fate of explosives in the environment and (3) the introduction of heavy metals and unexploded ordnances (UXOs) in the environment. The review of literature is expected to provide the most suitable methodologies and techniques for conducting fieldwork and analysing results.

Chapter 3: Materials and Methods

This section provides detailed methods and techniques employed during field investigations by the researcher to collect, analyse and interpret field data. Information in this section includes sampling methods, information collected from interviews, methods and technology used in analysis. Information is organised and presented in primary format to warrant understanding of the data prior to interpretation.

Chapter 4: Results and Analysis

In this section, information collected is interpreted and generalisations are made about the interrelationships between the data. Information in this section form the basis for answering research objectives and assessing if hypotheses are satisfied.

Chapter 5: Conclusions and Recommendations

This section makes connections among the results. It provides in-depth discussion of the results generated in the previous section. In this section, environmental management strategies are evaluated against the results and recommendations for possible solutions to identified problem areas are presented. This chapter concludes by indicating whether environmental impacts under investigation are significant and whether methodologies used were effective for the investigation.

Chapter 2 Literature Review

2.1 Introduction

Various environmental hazards have been identified in Military Training Areas (MTAs) and former battlefields across the globe in the past few decades (Craig et al., 1995; Pichtel, 2012; Martin et al. 2019). These can be classified into a number of categories including, but not limited to, (1) contamination of MTA environments with energetic compounds from explosive munitions (Defence Review, 2015; Ellwanger & Reiter, 2019), (2) Unexploded Ordnance that continue to pose danger in MTAs and former conflict sites (Martin et al., 2019) and (3) Heavy metal contamination of the soil in MTAs from remnants of explosive munitions and explosive additives (Defence Review, 2015; Cross et al., 2016). Contamination of ambient environments with the mentioned materials may lead to environmental problems when military facilities are handed over to civilian users (Defence Review, 2015).

Although explosives are widely thought to be consumed completely during explosions, previous studies (Jenkins et al., 2001; Pennington et al., 2008; Pichtel, 2012) established that substantial concentrations of High Explosives (HE) and propellants were present at MTAs and former battlefields and this has become a global problem as land reform programs face off with the huge responsibility for clean-up operations to rehabilitate the contaminated environment. According to Ellwanger & Reiter, (2019) over 730 000 ha of land was handed back to civilian authorities in Central Europe and Eastern Europe alone and over 1.5 million ha of former military land was abandoned due to post-war disarmament drives. Many of these sites near cities were successfully converted to industrial, conservation or domestic use but land reform programs could not execute reform projects due to existence of UXO, explosive contaminated sites and other military debris.

Characterisation studies of MTAs are important for risk assessment and environmental impact of military activities in order to establish viable remediation of the adverse impacts. An in-depth understanding of the military activities at MTAs is essential for determining the cause and effect of environmental impacts. Employment of explosive munitions during training and conflict is largely responsible for the aforementioned environmental issues. Explosive weapon systems use propellants and high explosives (HE), which have been the subject of extensive study in recent decades (Jenkins et al, 2001; Jenkins et al., 2004; Pennington et al., 2008; Pichtel, 2012; Walsh et al., 2008). Explosive residues have been detected at various concentrations at firing positions and target areas of artillery and antitank ranges across the globe. Literature studies indicate these are environmentally toxic due to their carcinogenic and mutagenic attributes, therefore hazardous to the environment and biotic health (; Kiiskila et al., 2015; US EPA, 2014a; US EPA, 2014b).

Shell fragments distributed by exploding detonations litter MTAs and have the potential of enriching the environment with heavy metals. Clausen and Korte (2009) outlined how metal compositions of Artillery shells have been influenced by environmental considerations due to toxicity of certain alloys employed in the manufacturing Artillery shells. Heavy metals are not biodegradable and their toxicity is related to their bioaccumulation in environmental compartments and subsequently in living organisms, becoming harmful to their health (Gautam et al., 2016; Masindi & Muedi, 2018; Vasarevicius, & Greiciute, 2004). Characterisation of heavy metal contamination in MTAs has not received significant attention in studies. Bricka et al. (1994), Macharia (2016) and Sehube et al. (2017) are some of the few publications that focused on heavy metal contamination at military sites. Most studies on heavy metal contamination focused on characterisation of farmland, urban and rural environments and largely mining industries.

2.2 Properties of explosive munitions

Weaponisation of explosive compounds and nomenclature defining these weapons has changed with time and the distinction between munition classes has become ambiguous. According to Brehm (2012), weaponisation of explosives changed the nature of warfare by changing mechanisms through which munitions can interact with targets. Centuries of innovation brought an increase in the destructive power of munitions, complexity of munitions and numerous methods of delivery. Brehm (2012) noted that defining ‘explosive weapon’ in literature is becoming ambiguous and may soon require revision to accommodate the spectrum of explosive weapons. These are classified into Artillery Shells, Aircraft Bombs, Mines, Torpedoes, Mortars, Rocket Warheads, Missiles and similar items depending on the nature of their employment. Chemical constituents of these weapons and their use has also diversified. Propellants and high explosives share many characteristics. An example is Nitroglycerin, which has a detonation velocity greater than TNT, but it is designed and used as a propellant. Brehm (2012) suggests that it is possible to employ some propellants in HE munitions using their detonating properties or HEs as in propellant formulations using their deflagrating properties. Thus, the words ‘explosives’ and ‘energetics’ in this work may be used interchangeably but with clear context.

According to Brehm (2012) and Cross et al. (2015), two important properties provide a unique identity to explosive weapons. (1) They can be launched from a system, airdropped, emplaced or thrown against a target. (2) They contain energetic material that explode/deflagrate and have a shattering and fragmentation effect. In addition, explosive weapons are part of a system, which determines their deployment. Explosive weapons such as Artillery projectiles are launched from a platform where propellants are used to deploy a warhead. This process results in contamination of both launch areas and target areas with energetic compounds. Later sections probe the nature of interactions between these characteristics and the environment.

2.2.1 Physical properties of explosive munitions

In Artillery terminology, the projectile and propellant charge are collectively termed “munition” or “ammunition” (Brehm, 2012). The latter is used in language to denote the plural form of munitions. In rifle bullets, the propellant is cast in a metal casing propped with a metal projectile. In Artillery, the projectile is called a warhead and contains the payload. Propellant charge is loaded behind the warhead in the chamber, at which point they both form a complete munition. Artillery projectiles, particularly HE projectiles, which are the focus of this study, are typically a combination of (1) a metal shell filled with (2) energetic material (explosives) and (3) plugged with a fuse. Although the propellant is consumed at launch, it is considered part of the munition. However, it is generally accepted that the warhead alone is called the munition. This is just the opposite with rifle bullets, in which case the fired slug alone cannot be classified as a munition. Several publications (Brehm, 2012; Cross et al., 2015; GICHD, 2017) highlighted that explosive munitions cause damage to targets through a combination of blast and fragmentation. This target-munition interaction was designed to offer belligerents tactical advantages in conflict by covering larger target areas with fewer projectiles. This concept favours military objectives but neglects the lasting environmental problems emanating from contaminants left on targets. The three components of munitions that result in environmental contamination are explained below.

The Ammunition Shell. The purpose of a shell is threefold. Firstly, it is a metal frame containing explosive chemicals (payload) in storage, on site and in flight to engaged targets. Secondly, it serves as containment for the explosive fill to accumulate potential energy to accelerate fragments and blast shock waves during detonation. Thirdly, the shell interacts with a target as determined by the user, disintegrating into hundreds or thousands of varying sizes of fragments at velocities of around 1500 m/s (Baskin & Holcomb, 2005; Cross et al., 2015; GICHD, 2017). The thickness of the shell wall depends on the target effects required and the brisance of the explosive fill. Cross et al. (2015) indicates that less than 20% of the warhead is filled with explosive. This translates to about 33.6 kg out of 42 kg of a typical 155 mm Artillery shell splintered into fragments on impact.

The shape of the shell is aerodynamically designed for inflight trajectory. Long range, high velocity shells such as 155mm shells tend to be pointed and tubular, while low velocity shells, such as 120mm Mortar shells, tend to have elongated elliptical shapes (see Figure 2.1).

Figure 2.1:Shape difference between the 155mm shell (left) and 120mm Mortar shell (right). (Images: Mokalapa, 2020)

The Explosive Fill. The explosive fill is explained in this section as a physical part of the projectile in as far as it has mass, occupies space and is configured to detonate, overcome the confining strength of the shell and cause physical damage to the target. This is achieved through conversion of chemical potential energy into kinetic energy in metal fragments, there by inflicting damage through a combination of blast waves, heat and sound (Cross et al., 2015; GICHD, 2017). Illumination rounds, leaflets, cluster bombs and smoke shells are called carrier projectiles and are filled with a payload of any of the said constituents depending of the requirements of the user, instead of explosive fill. Cluster munitions contain bomblets that are dispersed as mines or as tactical bombs on targets. Illumination rounds are deployed to illuminate targets at night and smoke projectiles can be used for covering troop withdrawals or spotting landing zones.

The Fuse. A fuse is a mechanical or electronic device usually attached to the nose of the projectile, which is responsible for arming and activating the weapon according to the user’s requirement (Cross et al., 2015; GICHD, 2017). It contains a primary explosive, which provides the necessary shock for initiating the main explosive charge (secondary explosives). A fuse is designed to arm the weapon when it has reached some distance and time in flight (GICHD, 2017). It can be set to point detonate (PD), delay action (DA) or Proximity (Prox). These settings allow the fuse to detonate the warhead below (DA), on contact with (PD) or above (Prox) the target. Electronic Time fuses can be set to detonate sometime after launch or before impact.

2.2.2 Chemical properties of explosive munitions

The energetic compounds used in explosive munitions must be understood according to (1) type as detonating (HE) or deflagrating (low explosive), (2) according to their sensitivity to initiation and (3) according to their molecular structure, which places them into distinct chemical groups. Explosive compounds are defined as energetic compounds (Monteil-Rivera et al., 2009; Pichtel, 2012), or mixtures of energetic compounds (US Army, 1990), that react rapidly and violently, releasing a large volume of gaseous products and energy upon initiation (Lotufo, 2013). According to Baskin and Holcomb (2005) the volume of gases generated during explosions is much higher than the original chemical volume and initiation of the explosion can be achieved through heat, shock, friction, impulse or a combination of these factors. Kalderis et al. (2011) adds that a common condition for an explosion is "local accumulation of energy" which is then suddenly released. This is achieved by containing the reaction in a sealed environment, such as a gun breech or a metal projectile with a specified tolerance to rapid expansion. Collectively the redox exothermic reactions of energetic compounds are termed "explosion". Various compositions of explosive chemicals are employed by military and civilian industries for respective purposes.

Chemical Structure of Explosives. As shown in Table 2.1 and Table 2.2, common explosive compounds used by the military include 2,4,6- Trinitrotoluene (TNT), 1,3,5- Hexahydo-1,3,5-trinitro-1,3,5-triazine (RDX), Octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine (HMX), Nitrocellulose (NC), Nitroglycerin (NG), Nitroguanidine (NQ), 2,4-Dinitrotoluene (DNT), 2,6-Dinitrotoluene (DNT, 2,4,6-Trinitrophenylmethylnitramine (Tetryl), and Pentaerythriol Tetranitrate (PETN). (Baskin & Holcomb, 2005, Pichtel, 2012; US Army, 1990). Explosives are inorganic Nitrogen containing compounds capable of self-oxidation into N_2, H_20 and (CO_2) (Kalderis et al., 2011). According to Kumar & Elias (2019) the most basic structure of an explosive is a Carbon-rich backbone ring attached with Nitrous Oxygen-rich compounds such as -NO_2 at the functional groups. This arrangement of fuel and oxidiser in a molecule provide conditions for self-oxidation and rapid decomposition in the molecule, releasing high volume gases (Kumar & Elias, 2019). TNT is based on a Benzene ring and RDX on a Triazacyclohexane ring. Explosive potential is a function of the ratio and arrangement of the elements on the molecular structure. Most explosives are synthesized by the nitration of organic compounds using strong acids such as Nitric Acid and Sulphuric Acid.

Table 2.1: Commonly used military explosive compounds (Pichtel, 2012; De la Ossa 2012)

Chemical Compound	Abbreviation	Chemical Formula/Composition
High Explosives		
Trinitrotoluene	TNT	$C_7H_5N_3O_6$
Hexogen	RDX	$C_3H_6N_6O_6$
Octogen	HMX	$C_4H_8N_8O_8$
Propellants		
Nitro-glycerine	NG	$C_3H_5N_3O_9$
Nitrocellulose	NC	$[C_6H_7O_2(OH)_{3-x}(ONO_2)_x]_n$
Nitro-guanidine	NQ	$CH_4N_4O_2$
Dinitrotoluene	DNT	$C_7H_6N_2O_4$

Reactive Potential of Explosives. US Army (1990) elaborates extensively on explosive potential of weaponised explosive compounds. Explosive reactions can be initiated by heat and shock. Different explosive compounds possess different sensitivities due to varying chemical/molecular structures. Sensitive explosives require minimal friction or heat to activate them. Sensitivity and detonation velocity determines which compounds are likely to deflagrate or detonate. According to US Army (1990), deflagrating compounds are low explosives owing to their slower reaction rate. Jenkins et al. (2012) classified deflagration as explosions that occur at subsonic speeds (less than 6000m/s), while detonations occur at supersonic speeds (more than 6000m/s). Baskin & Holcomb (2005: 46) specified explosion velocity of ≤2000 m/s for low explosives and around 9000m/s for high explosive. By controlling reaction potential, explosive experts can optimise explosives as “propellants” and “high explosives” for munitions or as blasting agents in industries such as mining (Kumar & Elias, 2019). Low explosive materials are typically targeted for propellant formulations as they burn longer and produces large volumes of gases for thrusting projectiles during firing of guns. Nitroglycerin is the most powerful and most sensitive propellant with detonating ability. Explosive power and sensitivity can be regulated by composition with different high explosive compounds such as RDX, Nitrocellulose and aluminium to improve or delay the brisance of the propellant formulation, which is the concept behind Double- and Triple Base Propellants (Pichtel, 2012). Table 2.2 summarizes some propellant formulations.

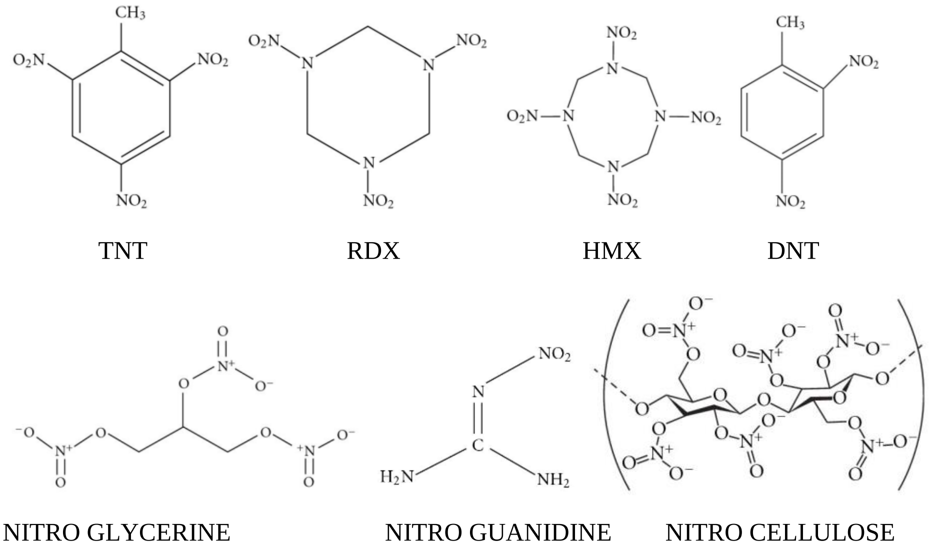
High Explosive compounds are classified as primary, secondary and tertiary explosives (Pichtel, 2012: 2; US Army, 1990). Primary explosives such as Silver Azide and Mercury Fulminate are highly sensitive to initiation and have the lowest stability. They are used in fuses of warhead munitions in small quantities to provide the initiating shock for the secondary charge. Secondary explosives are the main charge in HE munitions and are listed in Table 2.1 and Table 2.2. These explosive compounds are more stable and can withstand a reasonable amount of heat, shock or impulse without detonation. They have the ability to deflagrate when exposed to fire without detonating (Kumar & Elias, 2019). Commonly used secondary explosives include TNT, RDX and HMX. Tertiary explosives, such as Ammonium Nitrate (NH_4NO_3), are highly inert and require a secondary high explosive to initiate them (Pichtel, 2012).

Classification of Explosives. Explosives are classified into Nitroaromatics, Cyclic Nitramines and Nitrate Esters (Jenkins et al., 2012; Pichtel, 2012; US Army, 1990). This classification is based more on arrangement of atoms in compound molecules than their classification as high or low explosives. Some Nitramines such as RDX and HMX are high explosive while others such as NG are propellants (SA Army, 1990). Figure 2.2 illustrates basic molecular structures of some commonly used explosive compounds. Nitroaromatics consist of at least one nitro group ($-NO_2$) attached to an aromatic ring (Ju & Parales, 2010; Singh et al., 2015). This group of chemicals is used widely in industry for the production of dyes, pesticides and explosives. According to US Army (1990) preparation of nitro aromatics involves the C-type nitration, in which a nitro group is attached to a Carbon atom on the aromatic ring. The aromatic ring can be benzene, phenol or toluene. Electrophilic substitution of the H-atom with a nitro group in a nitrous acid results in the formation of Nitrobenzene, Nitrophenol or Nitrotoluene (Ju & Parales, 2010).

Table 2.2: Common military explosive compositions (Pichtel, 2012)

Composition Name	Chemical Composition
	High Explosives
Amatex	TNT, RDX, Ammonium Nitrate
Anatols	TNT, Ammonium Nitrate
C4	RDX 91%, Plasticiser 9%
Composition A	RDX 91%, Wax 9%
Composition B	RDX 60%, TNT 39% and Wax 1%
Cyclotols	TNT, RDX
Octols	HMX (70%-75%) and TNT (25%-30%)
Pentolite	TNT, Ammonium Picrate
Tetrytols	Tetryl, TNT
Torpex	RDX, TNT, Aluminium
Tritonal	TNT 80%, Aluminium 20%
	Propellants (Single Base Smokeless Powders)
M1	Nitrocellulose (NC), 2,4-DNT
M6	Nitrocellulose (NC), 2,4-DNT
M10	Nitrocellulose (NC), Diphenylamine
	Propellants (Double Base Smokeless Powders)
M2	Nitrocellulose (NC), 2,4-DNT
M5	Nitrocellulose (NC), 2,4-DNT
M8	Nitrocellulose (NC), Diphenylamine
	Propellants (Triple Base Smokeless Powders)
M30	Nitrocellulose (NC), Nitroglycerin (NG), Nitroguanidine (NQ), Ethyl Centralite
M31	Nitrocellulose (NC), Nitroglycerin (NG), Nitroguanidine (NQ), Ethyl Centralite

The geometry of the aromatic ring and the position of the nitro group gives a Nitroaromatic compound its distinct name. 2,4,6-Trinitrotoluene means that three nitro groups are located at position 2,4 and 6 of a toluene ring. The electron deficiency resulting from the oxidation state of the nitro groups is responsible for the self-oxidation ability of explosives and the electron-withdrawing tendency renders the molecules recalcitrant to biodegradation and persistence in the environment (Ju & Parales, 2010). Table 2.3 lists known Nitroaromatics. TNT is the most prominent compound in HE warheads. The nitro group of TNT draws electrons by resonance from the aromatic ring, enhancing the planar TNT molecule to form chemical complexations with non-bonding (n) electrons of Oxygen containing co-planar media such as soil particles and making it less soluble and less mobile in the environment (Qasim et al., 2007). The larger the reactive surface, the greater the adsorption potential. This suggests that finer soils have greater potential of retaining TNT than sandy soils.

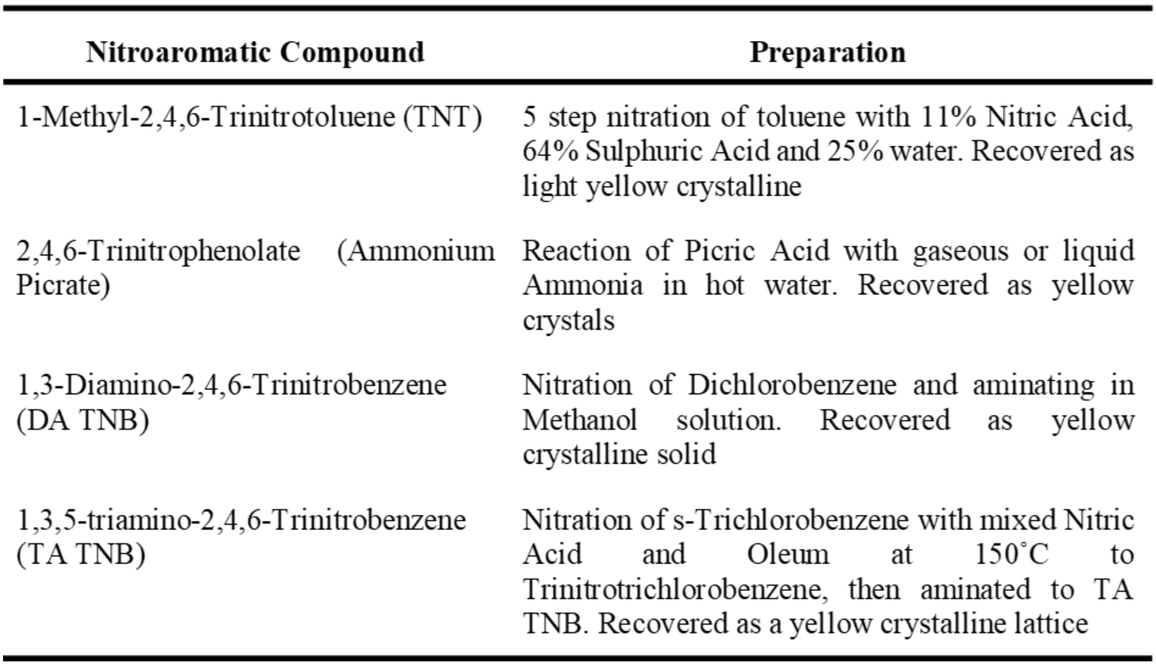


TNT RDX HMX DNT

NITRO GLYCERINE NITRO GUANIDINE NITRO CELLULOSE

Figure 2.2:Molecular structure of explosive compounds used in munitions (Kalderis et al., 2011; Pichtel, 2012)

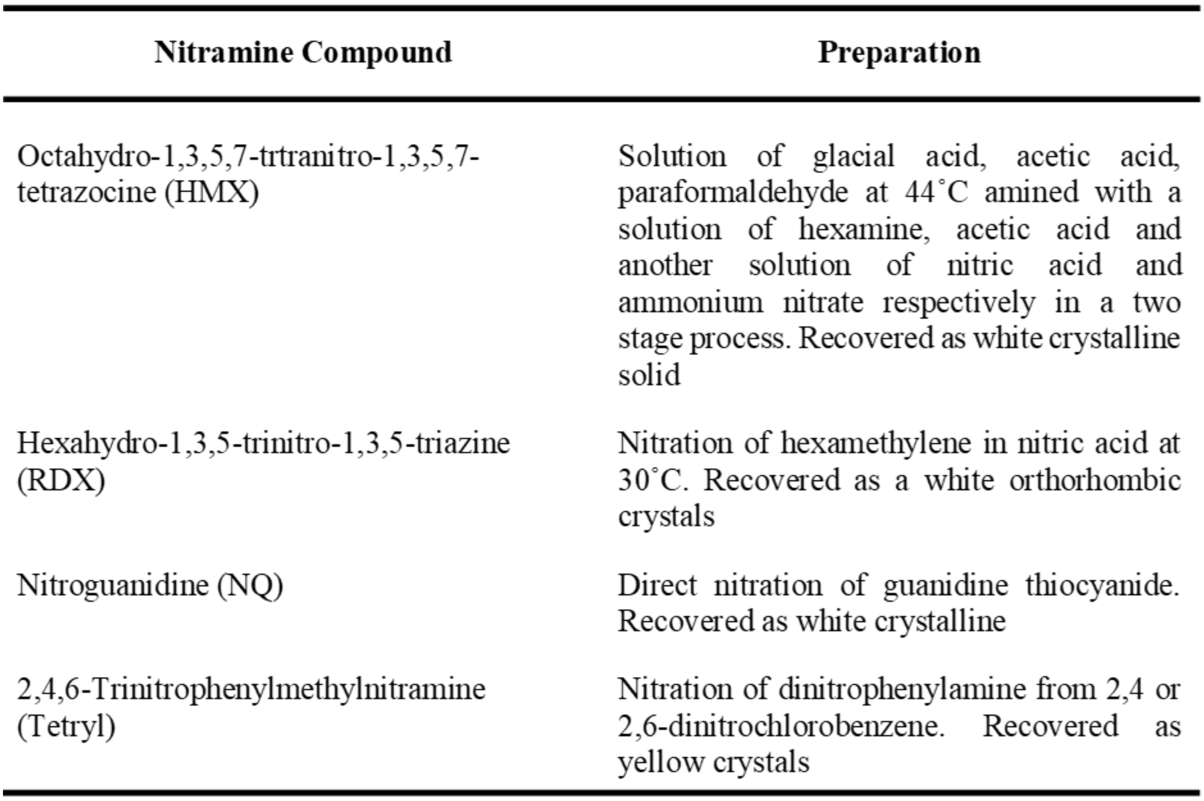
Table 2.3: Nitroaromatic compounds and their preparation (US Army, 1990)



Nitroaromatic Compound	Preparation
1-Methyl-2,4,6-Trinitrotoluene (TNT)	5 step nitration of toluene with 11% Nitric Acid, 64% Sulphuric Acid and 25% water. Recovered as light yellow crystalline
2,4,6-Trinitrophenolate (Ammonium Picrate)	Reaction of Picric Acid with gaseous or liquid Ammonia in hot water. Recovered as yellow crystals
1,3-Diamino-2,4,6-Trinitrobenzene (DA TNB)	Nitration of Dichlorobenzene and aminating in Methanol solution. Recovered as yellow crystalline solid
1,3,5-triamino-2,4,6-Trinitrobenzene (TA TNB)	Nitration of s-Trichlorobenzene with mixed Nitric Acid and Oleum at 150˚C to Trinitrotrichlorobenzene, then aminated to TA TNB. Recovered as a yellow crystalline lattice

According to US Army (1990) Nitramines are a group of explosive compounds produced by N-type nitration in which at least one nitro group is attached a Nitrogen atom in an aromatic ring. The geometry of the aromatic ring is similar to Nitroaromatics except that Nitramines have an N-N bond between the nitro group and the aromatic ring. Examples are Cyclotrimethylenetrinitramine (RDX) and Octatetramethylenetetranitramine (HMX). Table 2.4 lists common Nitramine compounds used in munitions and preparation method.

Table 2.4: Nitramine compounds and their preparation (US Army, 1990)



Nitramine Compound	Preparation
Octahydro-1,3,5,7-trtranitro-1,3,5,7-tetrazocine (HMX)	Solution of glacial acid, acetic acid, paraformaldehyde at 44˚C amined with a solution of hexamine, acetic acid and another solution of nitric acid and ammonium nitrate respectively in a two stage process. Recovered as white crystalline solid
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	Nitration of hexamethylene in nitric acid at 30˚C. Recovered as a white orthorhombic crystals
Nitroguanidine (NQ)	Direct nitration of guanidine thiocyanide. Recovered as white crystalline
2,4,6-Trinitrophenylmethylnitramine (Tetryl)	Nitration of dinitrophenylamine from 2,4 or 2,6-dinitrochlorobenzene. Recovered as yellow crystals

Aliphatic Nitrate Esters are a group explosive compounds formed by O-type nitration. At least one nitro group is attached to an Oxygen atom of an aliphatic compound (US Army, 1990). Two fundamental differences between nitrate esters and other groups is the chainlike geometry of the aliphatic molecule and the O-N bond between the nitro groups and the aliphatic chain. An example of an aliphatic nitrate ester is Nitrocellulose (NC) on Figure 2.2. Nitro groups (US Army, 1990) replace the three hydroxyl groups (OH) of the anhydroglucose long chain polymer of cellulose in a substitution reaction. Common aliphatic nitrate esters are listed on Table 2.5.

Table 2.5: Aliphatic Nitrate Esters and their preparation (US Army, 1990)

Aliphatic Nitrate Ester Compound	Preparation
Nitrocellulose (NC)	Nitration of cellulose fibre by mechanical dipping in mixed nitric and sulphuric acids (Gun cotton).
Nitroglycerin (NG)	Nitration of glycerine with mixture of 45-50% nitric acid and 50-55% sulphuric acid. Recovered as clear oily liquid which crystallise at 33.2˚C
Nitrostarch (NS)	Dissolving starch in excess nitric acid and adding the solution to excess sulphuric acid. Nitrostarch precipitates as an amorphous powder.
Pentaerythriol Tetranitrate (PETN)	Treating pentaerythriol with nitric acid and adding concentrated sulphuric acid. Recovered as a white crystalline solid

2.3 Functioning of explosives in munitions

Explosive compounds are arranged according to sensitivity in a firing system. In warheads, the initiation sequence is called the “explosive train” (Jenkins et al., 2012; Pichtel, 2012; US Army, 1990). Detonation of the fuse propagates shock waves through the secondary explosive and the detonation of the secondary explosive initiates the tertiary explosive. In propellants this process is similar to the explosion train but reversed. While projectile fuses are forward located, ignition of the propellant is from the rear and the process is termed the “firing train” (US Army, 1990; Jenkins et al., 2012). A sensitive primer is mechanically ignited by a firing pin to ignite the propellant charges (Figure 2.3). While a primary explosive in fuses detonates, propellants primers deflagrates to burn the secondary charges (Jenkins et al., 2012; US Army, 1990). Mechanisms of explosion are covered in technical detail by Borde & Enstrom (1969).

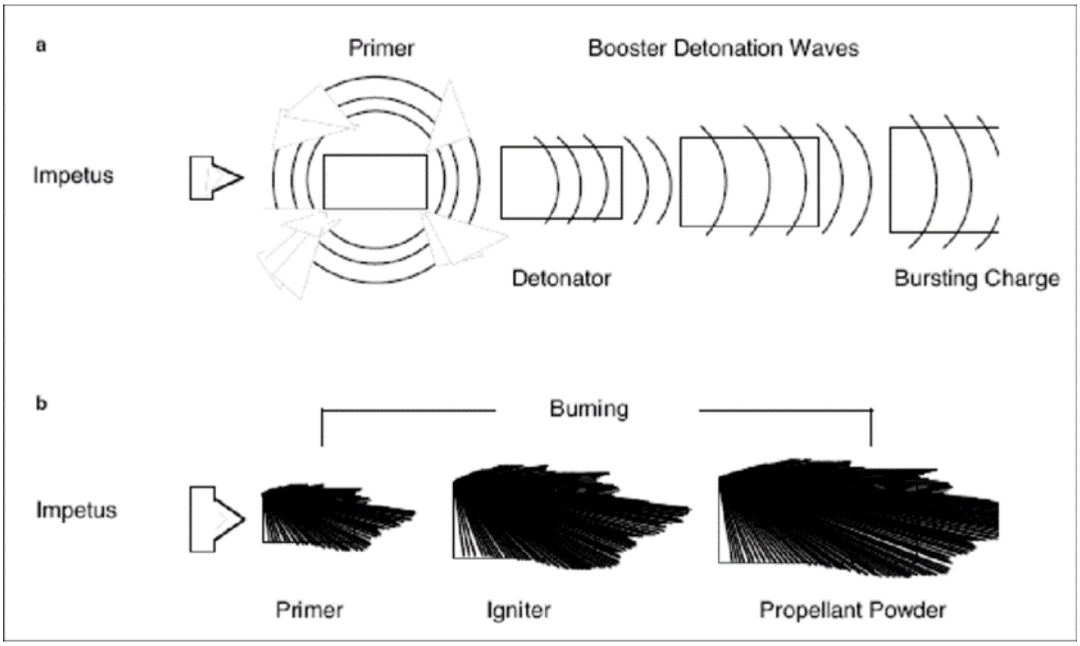


Figure 2.3:Illustration of (a) the "explosive train" and (b) the "firing train" (Jenkins et al., 2012)

2.4 Effects of explosive munitions

Literature reporting explosive weapon effects provide information on various degrees of physical damage to a hypothetical target (Baskin & Holcomb, 2005; Brehm, 2012; Cross et al., 2012; GICHD, 2017). These are classified as primary, secondary and tertiary target effects (GICHD, 2017). Primary effects are damages inflicted directly on a target such as by high velocity fragments from the shell case and the shock or blast wave radiating outwards from the point of detonation (Brehm, 2012; GICHD, 2017). These include physical injury to organisms from shell fragments (shrapnel), damage to vehicles from the combination of fragments and blast waves and destruction of buildings in the lethal zone of the detonation. Specially designed Fragmentation munitions use specially designed pre-fragmented shell casings that produce moderate blast but disintegrate into thousands of perforated shell fragments that cause primary damage to personnel, vehicles and buildings (Cross et al., 2012).

Secondary effects include damage caused by debris or secondary fragments such as natural ground, stones and pieces of the target accelerated by the combination of blast waves and shell fragments (Cross et al. (2015). Explosive munitions can be optimized for blasting effects. Blasting munitions produce less fragmentation but a powerful blast wave that generate large quantities of secondary fragments from the environment (Cross et al., 2015; GICHD, 2017). Collapsing structures due to explosion shockwave cause secondary injuries. Powerful shockwaves have a shattering effect and can destroy buildings and other structures, accompanied by intense thermal radiation which can set fire to vegetation and other installations (Baskin & Holcomb, 2005).

Tertiary effects involve lasting effects of munition explosion such as environmental pollution from metal fragments, Unexploded Ordnance (UXO) and contamination of soil with energetic residues (Ellwanger & Reiter, 2019; Jenkins et al., 2001; Pichtel, 2012). Tertiary effects also involve human and health effects such as energetics reaching food chains and explosion fires that burns vegetation, which are not directly related to intended employment of explosive weapons (Cross et al., 2015; GICHD, 2017). Sources reporting explosive munition effects have focused on primary and secondary effects in terms of their impact on human lives and infrastructure in urban environments (Brehm, 2012; Cross et al., 2016; GICHD, 2017) but have not made connections between these effects to the lasting tertiary impacts described above. Tertiary effects on the environment have been a major discourse of environmental investigations such as contamination, fate and transport of explosives in MTAs (Dontsova et al., 2006; Pennington et al., 2001; Pichtel, 2012; Walsh et al., 2009) and vegetation (Via, 2016). Contamination, fate and transport of heavy metals in MTAs (Clausen & Korte, 2009), phyto- and bio- remediation of explosives contamination (Claus et al., 2007; Kalderis et al. 2011) has also been studied.

2.5 Environmental impacts of explosive munitions

Explosive weapon systems are the main pathway for contamination of the environment at (MTAs) and conflict sites by (1) contamination of soils and water sources with energetic materials and (2) introducing heavy metals from remnants of exploded munitions and UXO. The separation between the launch systems and the targets create a unique pattern of environmental impacts as illustrated on Figure 2.4 (Cross et al., 2015). Different types of launch systems have different ranges and accuracy, but the environmental impacts are generally similar. Knowledge of employment of these systems provide a starting point for characterising environmental impacts (Dullum et al., 2017). Characterisation studies indicated that most contamination of soils at firing positions is from propellant residues while HE residues were detected at target areas (Pichtel, 2012). MTA environments are typically littered with metal fragments, thus potentially have enriched heavy metals in soil and water sources.

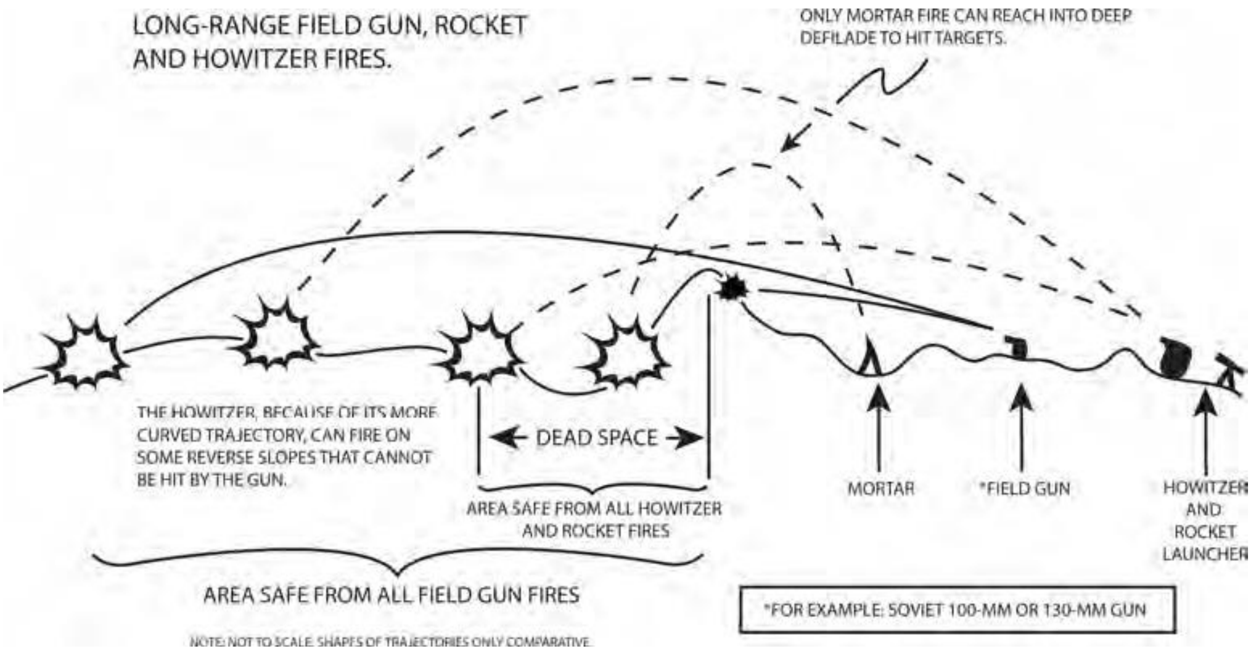


Figure 2.4: Assortment of military explosive weapon systems (Cross et al., 2015)

2.5.1 Contamination with heavy metals

Soils contain metals from natural pedological processes in trace concentrations of less than 1000 mg/kg (Wuana & Okieimen, 2011; Addis & Abebaw, 2016; Gautam et al, 2016). Naturally occurring metals in soil include Iron (Fe), Zinc (Zn), Manganese (Mn), Copper (Cu), Cobalt (Co) and Nickel (Ni) (Addis & Abebaw, 2016). Herselman et al. (2005) and NEMA (2017) listed metals of environmental interest in South Africa as Cobalt (Co), Copper (Cu), Nickel (Ni), Cadmium (Cd), Chromium (Cr), Lead (Pb), Zinc (Zn), Vanadium (V), Manganese (Mn), Mercury (Hg) and Arsenium (As). Most metals are essential for growth and normal functioning of living organisms but toxic in elevated concentrations (Kwaya et al., 2019). Ambient soils in the environment contain adequate concentrations and compositions of metals, which are essential for sustaining local ecological processes. According to Addis & Abebaw (2016) and Masindi & Muedi (2018), metal contamination relates to enrichment of metal contents in soil and water sources above background concentrations. This can occur naturally or through anthropogenic activity. Pollution occurs when concentration of heavy metals become environmentally toxic or harmful.

Knowledge of background concentration is important for assessing contamination and pollution (Abrahim & Parker, 2008; Herselman et al., 2005; Su et al., 2014). The World Health Organisation (WHO, 2017) lists global background concentrations of heavy metals for drinking water but not for soils. Herselman et al. (2005) explained in support that universal indices are inadequate for assessing local soils due to different environmental characteristics and ecology in different parts of the world. NEMA (2008) provides Soil Screening Values for assessing soil metal content in South Africa. It specifies maximum enrichment values for Water Protection, Ecosystem Protection, Urban and Agricultural soils but not for drinking water. This suggest that the WHO (2017) indices remain globally accepted for assessing contamination of drinking water as all humans and animals are equally vulnerable to heavy metals with drinking as a common pathway.

Anthropogenic contamination is largely responsible for most of the global heavy metal contamination (Addis & Abebaw, 2016). A study by Su et al. (2014) revealed that global heavy metal contamination has reached disconcerting levels. In Table 2.6 Su et al. (2014) provide average annual global mass of metal enrichment in urban and agricultural soil. Global enrichment of heavy metals in urban soils were in the order Pb > Zn > Cr > Cu > Ni > Cd > As. Most of the metals were enriched above sustainable environmental capacity. All metals had average enriched masses above recommended background masses. Average enrichment masses in agricultural soils were in the order Zn > Pb > Cr > Cu > Ni > As > Cd. All heavy metals studied were enriched below recommended environmental capacity but were enriched above recommended background concentrations. The data suggests that global anthropogenic enrichment of heavy metals is severely exacerbated. Su et al. (2014) stressed that accumulation of heavy metals in the environment is odourless, colourless and almost irreversible. Once metal enrichment reaches elevated concentrations they may be activated and cause serious ecological problems (Masisndi & Muedi, 2019). Untreated contamination may remain in the environment for over 200 years (Su et al., 2014).

Sources reporting heavy metal contamination at MTAs is lacking but there is a growing body of literature focusing on the topic. Most of the literature studies focused on explosive contamination of MTAs (Jenkins et al., 2001; Pichtel, 2012, Walsh et al., 2008). Employment of explosive weapons at MTAs and conflict sites also introduces heavy metals through various pathways. Clausen et al. (2012) reported contamination of MTAs with heavy metals from pyrotechnic munitions. Sehube et al. (2017) also reported lead contamination at a rifle range. Bricka et al. (1994) and Clausen & Korte (2009) reported the extent of metal contamination at various US Army bases. This suggest that heavy metal contamination in MTAs has become a subject of inquiry in the past few decades.

Table 2.6: Annual global heavy metal enrichment in 1000 tons/year (Su et al., 2014)

Loading of Heavy Metals In Urban Environments							
Metal	**Cr**	**Cu**	**Pb**	**Zn**	**Ni**	**Cd**	**As**
Range	23.1-121	20.06-112.14	17-25380.55	60-1964.12	12.4-72.1	0.15-6.9	-
Average	66.08	49.6	1733.94	289.78	29.14	1.52	-
Background	61	22.6	26	100	26.9	0.1	-
Environmental Capacity	200	100	300	250	50	0.3	-
Loading of Heavy Metals in Agricultural Soil							
Range	1.23-87.73	1.20-107.65	0.95-213.93	4.65-427.8	0.14-57	0.05-13.50	0.78-92.7
Average	46.69	38.03	51.19	117.35	26.12	1.5	21.19
Background	61	22.6	26	74.2	26.9	0.097	11.2
Environmental Capacity	200	100	300	250	50	0.3	30

2.5.1.1 Sources of heavy metals

Anthropogenic contamination has been cited as the major contributor to heavy metal enrichment in the environment (Gautam et al., 2016; Kwaya et al., 2019; Masindi & Muedi, 2018). Prominent sources include industrial waste, fertilizers, sewage dumps, pesticides, mine tailings and industrial emissions (Addis & Abebaw, 2016; Wuana & Okieimen, 2011). A list of heavy metal sources and the extent of contamination was provided by Su et al. (2014) on Table 2.7. The composition may vary per country and region. The data indicates that annual enrichment per metal exceeds natural environmental background load for most of the metals assuming the sum of contributions from different sources. As a result, heavy metal contamination is receiving attention of many environmental investigations and research on remediation strategies has been intensifying in the last decade (Gautam, 2016; Su et al., 2014; Tangahu et al., 2017). Geoaccumulation Index and Enrichment factor calculations are instrumental in assessing the contamination and enrichment levels by classifying them in severity margins for determining remediation requirements (Abrahim & Parker, 2008; Gupta et al., 2014; Muzerengi, 2017).

Table 2.7: Sources of Heavy Metals in 1000 tons/year (Su et al., 2014)

Source	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Agriculture	0-0.6	0-0.3	4.5-90	3-38	0-1.5	6-45	1.5-27	12-150
Municipal Waste	0,09-0.7	0.88-7.5	6.6-33	13-40	0-0.26	2.2-10	18-62	22-97
Metal Processing	0.01-0.21	0-0.08	0.65-2.4	0.95-7.6	0-0.08	0.84-2.5	4.1-11	2.7-19
Coal Ash	6.7-37	1.5-13	149-446	93-335	0.37-4.8	56-297	45-242	112-484
Fertiliser	0-0.02	0.03-0.25	0.03-0.38	0.05-0.58	-	0.2-3.5	0.04-2.3	0.25-1.1
Commodity Impurities	36-41	0.78-1.6	305-610	395-790	0.55-0.82	6.50-32	195-390	310-620
Atmospheric Deposition	8.4-18	2.2	5.1-38	14-36	0.63-4.3	11-37	202-263	49-135
Organic Waste	0-0.25	0-0.01	0.1-0.48	0.04-0.61	-	0.17-3.2	0.02-1.6	0.13-2.1

Many studies consulted on the subject have not identified the military industry as a contributor to the global problem. Sporadic literature focusing on military sites did not specify the extent of the military contribution. A growing body of literature in the last few decades indicates that focus military sites is gaining momentum (Bricka et al., 1994; Clausen & Korte, 2009; Vasarevicius & Greiciute, 2004). Characterisation studies at MTAs indicate that the composition of heavy metals at military sites is similar to that of other industries. Heavy metals enter MTA environs as shell fragments, fuel burning, unexploded ordnance (UXO) and metal additives to explosive compositions. A typical 155mm round is around 40 kg of which about 20% is explosive fill. About 32 kg of metal is dispersed in the environment or buried for each 155 mm round fired. Cross et al. (2015) shows that 155mm fragments can reach 725m from the point of detonation. While explosions scatter multiple fragments, gun batteries deploy in groups of six at a time, suggesting that fragment concentration is likely to be high at target areas and overtime these will erode or leach into soil receptors.

About 800 tons of UXO fired by US forces were reported buried in ambient soils in Vietnam, Laos and Cambodia after the Vietnam War (Martin et al., 2019; Pichtel, 2012). These range from aircraft bombs to artillery shells and mines (Figure 2.5). UXO are more likely to be buried and result in acute point contamination by leaching heavy metals and explosives. OB/OD operations also provide pathways for heavy metals in MTAs. Craig et al. (1995) cited that UXO that can be safely removed are collected in prepared burn pits for destruction. Pennington et al. (2008) and others criticized this method as inefficient and only exacerbating the problem by scattering explosive residues. Blow in Place (BIP) operations for unsafe UXO using donor explosive devices (Sympathetic Detonation) were also reported to have similar effects (Pennington et al., 2008). These methods result in irrecoverable metal fragments and explosive residues buried in soil. Clausen et al. (2012) identified pyrotechnic munitions as another pathway. These munitions are designed for slow burning and typically used for producing illumination, smoke, sound or heat. Typical metals deposited by pyrotechnic munitions include Al, Sb, Ba, B, Cr, Ce, Cu, Fe, Pb, Mg, Mn, Ti, W, Zn and Zr. Different combinations of these are used to produce specific desired effects. Simulation tests revealed that these munitions contribute lower than background concentrations of heavy metals (Clausen et al., 2012). At worst ground burst munitions were reported to cause minimal point contamination.

Figure 2.5:Assortment of UXO recovered in Vietnam clean-up operations (Martin et al., 2019)

2.5.1.2 Toxicity of heavy metals

Heavy metals are inorganic minerals with atomic number > 20 (Tangahu et al. 2011). Most are naturally occurring in the environment but some have been altered by anthropogenic synthesis and are known to be environmentally toxic (Masindi & Muedi, 2018). Heavy metal contamination is an odourless, colourless and is a slow accumulation process which is difficult to remedy, which Su et al. (2014) assimilated with a chemical time bomb. They are also persistent (up to 1000 years soil residence) and recalcitrant to biodegradation (Tangahu et al., 2011). When the rate of deposition exceeds the rate of removal by natural systems, they accumulate in food chains and cause serious health and deleterious environmental problems (Masindi & Muedi, 2018; Wuana & Okieimen, 2011). Some of these metals are reported to be highly toxic even at trace concentrations (Addis & Abebaw, 2016).

Arsenic (As) is an odourless and tasteless silver-grey crystalline solid usually used as a pesticide in agriculture (Tangahu et al., 2011). Inorganic As is suspected to be carcinogenic in large doses. According to Tchounwou et al. (2012) chronic As exposure can cause clinic-pathological diseases such as neurobehavioral disorders, hearing loss, diabetes, cardiovascular, and peripheral vascular diseases. As was reported to cause gene amplification, arrest cells and impair DNA repair. Mercury (Hg) is a highly toxic heavy metal typically introduced by industrial waste (Pachana et al., 2010). It is easily transportable in water systems or remains sorbed to soil and can remain immobilized in the environment. It can bioaccumulate in phytoplankton, algae, fish, birds and even humans as it is not biodegradable. Jaishankar et al. (2014) explained that Hg attacks cell mitochondria and causes neurotoxic molecules to form in cell bodies. The brain and central nervous system are the main targets of Hg toxicity.

Cadmium (Cd) is a typical by-product of smelting processes of Zn, Pb, and Cu in mining industries (Pachana et al., 2010). It is not biodegradable and can bioaccumulate in plants and animals, reaching toxic levels in the body. According to Tchounwou et al. (2012) some foodstuffs, such as leafy vegetables, mushrooms, liver and some fish species contain trace amounts of Cd, resulting in slow bioaccumulation. Cd toxicity is associated with blood vessel circulatory disorders. Where inhalation is the pathway, it causes changes in pulmonary functions, leading to emphysema. Cd is also known to attack cells and cause mutations in DNA. Signs of Cd intoxication in humans include increased excretion of low-molecular weight proteins in urine from damaged cells or cancer related diseases in lungs (WHO, 2017). Lead (Pb) is a bluish grey metal mainly enriched in environments by fuels synthesized by humans (Wuana & Okieimen, 2011). It is mainly found at 30 mg/kg in ambient soils worldwide. According to Pachana et al. (2010) it is introduced to environment through fallout from exhaust smoke and fuel production. It enters aquatic environments through runoff and accumulates in water sources where it contaminates drinking water and aquatic plants and animals. According to Jaishankar et al. (2014) Pb gets taken up by plants but is not metabolized. Once it bio-accumulates in plants, it forms complexes with other compounds and attack photosynthetic processes, retarding plant growth and reducing plant biomass. Tchounwou et al. (2012: 12) indicated that Pb in animals might damage internal organs such as the kidney, liver and the central nervous system.

Copper (Cu) concentrations of 50 mg/kg are not toxic to citrus plants (Su et al., 2014), but may accumulate to toxic levels. According to Tchounwou et al. (2012) Cu is known to be useful in enzymatic processes both in oxidized and in reduced states. However, when the concentration is elevated, it results in cellular and tissue damage, a property shared with other heavy metals. Tchounwou et al. (2012) also observed that there is a very fine margin between beneficial and toxic concentrations of some of the heavy metals. Other heavy metals such as Cobalt (Co), Zinc (Zn), Manganese (Mn) and Vanadium (V) have been studied and their toxicities, environmental and biological effects are generally similar, particularly in attacking cellular structures and disrupting normal functioning of tissues and nervous systems in humans and retarding germination and growth in plants. This indicates that monitoring strategies must include guarding against accumulation of heavy metals in the environment and implementing remediation measures before heavy metals become an advanced environmental problem. Table 2.8 summarises some of the known heavy metals and how they affect human health.

Table 2.8: Summary of toxicities of heavy metals to human health (Su et al., 2014; Tangahu et al., 2011)

Heavy Metal	**Pathway**	**Human Health Effect**
Cadmium (Cd)	Inhalation of Cadmium	Kidney, bone and lung disease. Damages lungs in low doses.
Lead (Pb)	Digestion and inhalation	Damage to kidney, liver, nervous, urinary and immune systems.
Zinc (Zn)	Combustion exhaust, galvanized metal parts, cement processing	Liver damage, respiratory disorder and disturbs protein metabolism
Copper (Cu)	Essential to human body in trace dietary concentrations	Tumor promoting factor
Nickel (Ni)	Essential to human body in trace dietary concentrations	Respiratory cancer
Arsenic (As)	Agriculture (pesticide)	DNA breakdown, As poisoning and cancers
Mercury (Hg)	Fertilizer fungicide and household detergents	Brain damage, Hg poisoning, neurological disturbances

2.5.1.3 Environmental impacts of heavy metals

Primary recipients of heavy metal contamination are the soil and water sources of the environment (Bricka et al., 1994; Wuana & Okieimen, 2011). Soil acts as a sieve and adsorbent of heavy metals.

According to Bricka et al. (1994) a correlation between decreasing soil particle size and increasing retention of heavy metals held by soil exists. Su et al. (2014) reiterated that heavy metals accumulate in the top 10 cm of soils. Adsorption, chemical bonding and ion-exchange were identified as the main mechanism of retention and bioaccumulation. Soils have net-negative charge and metals project positive ions (Pachana et al., 2010). Clay soil has a larger reactive surface, therefore expected to have a lower pH and attracting more metal ions than silt and sand. Heavy metals retained in this way become bioavailable to ambient ecosystems. Retained metals are exposed to geochemical interactions such as precipitation, adsorption, organometallic bonding and chemical complexations with soil constituents (Wuana & Okieimen, 2011). These can enter food chains by direct consumption through drinking water and terminal parts of vegetation (Tangahu et al., 2011). Since metals are not biodegradable and not metabolised by plants and animals, they bioaccumulate in food chains (Masindi & Muedi, 2018). Some metals such as, Pb, Cd, Ni, Hg, Co and Zn are reported highly toxic even at trace amounts.

According to Bricka et al. (1994) heavy metals introduced to the environment by anthropogenic activities are usually present in higher concentrations than natural metal content. These become bioavailable to plant and microbial uptake. The rate of uptake is greater when quantity of metals sorbed to ambient soil constituents is lower than the quantity of desorbed metals. Other environmental factors affecting uptake are soil pH, chemical complexity, plant and microbial species and soil organic matter (Bricka et al., 1994; Tangahu et al., 2011). Depending on the vegetation species, some metals will be absorbed to higher plant sections due to the nature of their complexations with micronutrients while others will precipitate in soil around the plant roots. Metals remaining in soil continue to impact soil communities such as microbes and invertebrates. Due to carcinogenic tendency of many metals, microbial activity decreases, affecting the quality of vegetation. Tangahu et al. (2011) indicated that some plants have evolved mechanisms for selective uptake and translocation of micronutrients. Certain species have the ability to absorb heavy metals and store them in terminal shoots and can be used for phytoremediation of heavy metals (Gautam et al., 2016; Wuana & Okieimen, 2011). Excessive plant uptake of heavy metals may also result in toxic effects on the plants or may accumulate in terminal shoots where it becomes available for consumption by animals and humans (Su et al., 2014). In some plants heavy metals inhibit seedling germination and hamper plant growth, impacting other ecosystem activities (Via, 2016).

Metals not absorbed by plants remain in immobilized sorbed phase, transported to remote locations or form other chemical complexes, depending on external environment factors such as pH, acidity, temperature, soil content (Donelly et al. 1994). The bond between soil and sorbed metals can become weakened by interstitial flux changes, releasing metals for further dissolution and possible plant uptake following complexations with newly introduced chemicals (Bricka et al., 1994; Pachana et al., 2010). Desorbed metals may be transported by wind and surface runoff to remote environments where they react with different soil constituents or preferred by other plant species for absorption and possible bioaccumulation (Pachana et al., 2010). According to Bricka et al. (1994) most of the transportation by water is in dissolved ions in interstitial solution. This way heavy metals may migrate downstream to aquatic ecosystems, groundwater and even reach neighbouring properties.

2.5.2 Contamination with explosive residues

Explosive contamination at MTAs is directly related to employment of explosive weapon systems. Contamination pathways include deposition of propellant residues at firing positions by firing trains and deposition of HE residues at target areas by explosive trains (Jenkins et al., 2012). Not all explosive is consumed by the firing train or the explosive train (Pennington et al., 2008b ; Walsh et al., 2009). At target areas, HE concentrations and dispersion depend on the order of the detonation. In a study by Walsh et al. (2008) HE residues were not detected in samples from high order while residues were detected in LOD craters. Samples from OB/OD pans measured 2.3 g/kg of 2,4-DNT from within the pans immediately after detonation tests and 0.12 g/kg outside of the pan after propellant burning (Walsh et al., 2009). Pennington et al. (2008b) indicated that about 10^{-3} to 10^{-6} % of high explosive is deposited at the target during a high order detonation. Literature studies indicated that HE deposition is extremely heterogeneous at target areas while propellant deposition is consistent and predictable at firing positions (Pichtel, 2012). As a result, propellants are often detected at higher concentrations than HE detections. This trend is due to the fact that firing positions are often selected in predetermined localities and positions for training purposes. At target areas, heterogeneity may be due to the inherent inaccuracy of indirect fire, launcher dispersion, the size of the target, the level of training of the crews, etc. In the unlikely event that all fired munitions were perfectly accurate and consistent (GICHD, 2017), the deposition of HE residues per target would have been somewhat comparable with propellant deposition.

Propellant deposition is primarily in close proximity with the launcher system depending on prevailing weather conditions. Jenkins et al. (2012) reported that pistols, rifles and machine guns deposit residues within 5 m, 10 m and 50 m, respectively, in the direction of fire. Light rocket launchers deposit residues further than 50 m behind gun lines and within 20 m to the front. Large calibre launchers such as 105 mm anti-tank and 155 mm Artillery guns deposit residues further and knowledge of these technicalities is needed to predict possible contamination. Also, with knowledge of the round to round deposition, both at gun positions and at target areas, one can predict the possible amount of propellant and HE contamination resulting from certain exercises (Jenkins et al., 2001). Predictions can be even more accurate when the background contamination levels are known. Continuous measuring and recording of contamination levels will therefore be helpful when measuring contamination trends at MTAs and at-risk locations can be identified before adverse environmental effects occur.

2.5.2.1 Physicochemical characteristics of explosive compounds

Physicochemical characteristics of explosive compounds determine their fate and transport in the environment (Kalderis et al., 2011). These are chemical and physical characteristics of explosive compounds at atomic and molecular level that determine their interaction with environmental features such as soil, water and biota. These characteristics are summarized in Table 2.9. Explosive residues enter MTAs in solid particulate form, except NG which is a liquid at ambient temperatures (Jenkins et al., 2012). When the residues are exposed to ambient environment, various transformation pathways occur, such as biotic (microbial) and abiotic transformation (such as photolysis). Transformation changes the chemical composition of explosives, forming transformation products that may also transform further. This process is illustrated magnificently by Kalderis et al. (2011). Explosive residues are also exposed to fate and transport mechanisms, which determine the mobility and spread of the contamination, such as dissolution, volatilisation and adsorption (Monteil-Rivera et al., 2009; Pichtel, 2012). Understanding physicochemical characteristics of explosive compounds is key to understanding their potential environmental impacts. Figure 2.6 illustrates various fates and distribution of explosives in the environment.

Table 2.9: Physicochemical characteristics of explosive compounds (Jenkins et al., 2012)

Compound Name	**Molecular Weight (g/mol)**	**Melting Point (˚C)**	**Water Solubility (mg/L)**	**Octanol/Water Partition Coefficient (log Kow)**	**Henry's Law Constant at 25˚C (atm m^3/mol)**	**Vapor Pressure (mm/Hg)**
			High Explosives			
TNT	227.13	80.1	130	1.6	4.57 x 10^-7	1.99 x 10^-9
RDX	222.26	205	26.3	0.90	196 x 10^-11	4 x 10^-9
HMX	296.16	286	4.5	0.17	2.60 x 10^-15	3.3 x 10^-14
			Propellants			
NC	10^5-10^6	206	Insoluble	ND	ND	ND
NG	227.11	13.5	1800	1.62	3.4 x 10^-6	2 x 10^-4
NQ	104.07	249	4400	-0.89	4.67 x 10^-16	1.43 x 10^-11
2,4-DNT	182.15	71	270	1.98	182 x 10^-7	1.47 x 10^-4
2,6-DNT	182.17	64-66	206	2,02		5.7 x 10^-4

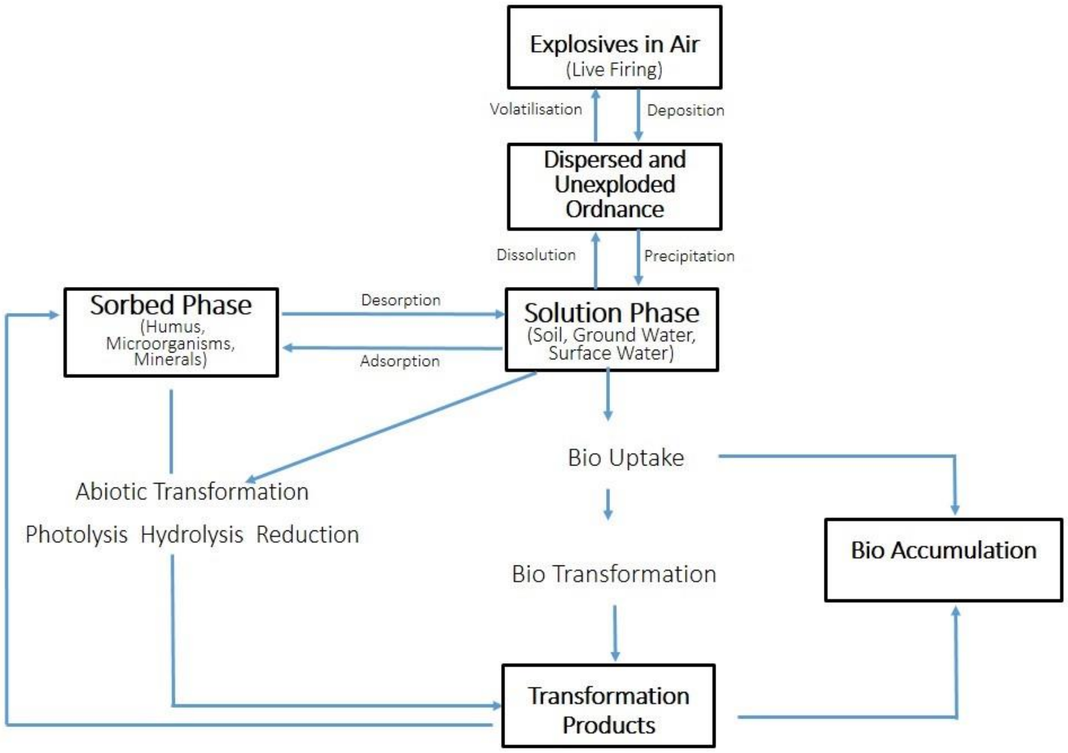


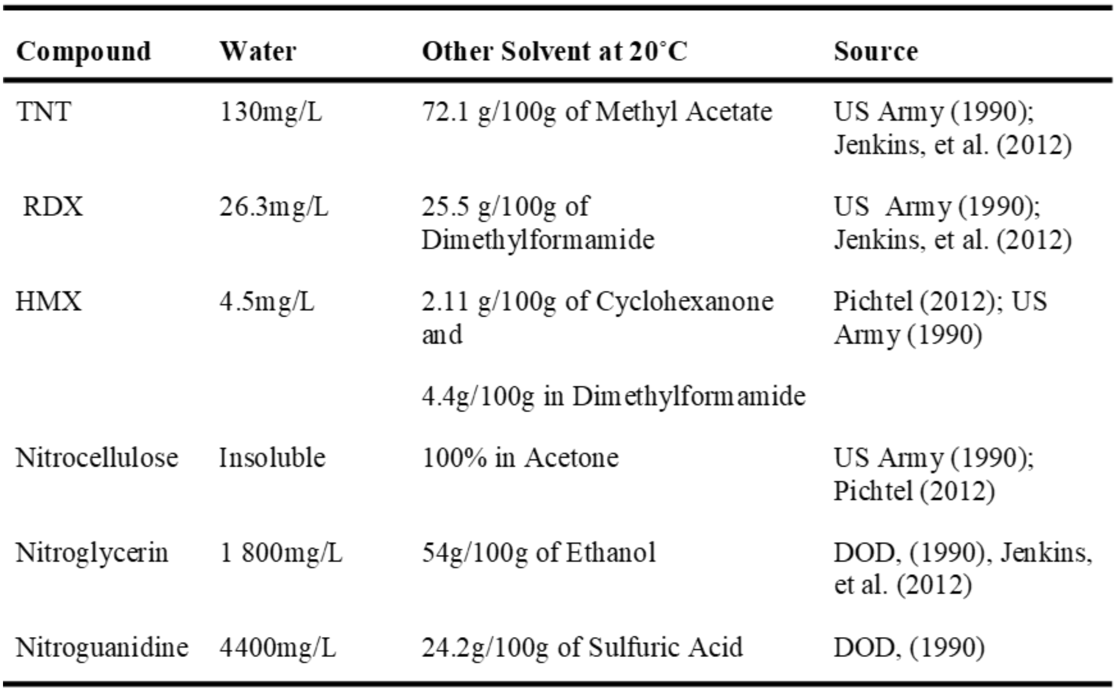
Figure 2.6:Fate and transport model for explosive chemical compounds (Kalderis et al., 2011; Pichtel, 2012)

Dissolution is the major pathway in explosive fate and transport studies because plants, microbes and animals become exposed to the chemicals in interstitial solution or drinking water. Craig et al.

(1995) observed that explosives have varying but typically low dissolution rates and are persistent in the environment due to low volatility and recalcitrance to biodegradation. Propellants are more soluble in water than high explosives, with solubility increasing with temperature between 3°C and 33°C (Kenyon, 1982). Jenkins et al. (2012) summarised dissolution rates and potentials of explosives (see Table 2.9). Explosive solubilities range from 4.5 mg/L for HMX to 4400 mg/L for NQ. Solubilities of Propellants are in the order NQ > NG > DNT > NC. Isomers of DNT, also impurities of Nitrocellulose (NC) and transformation products of TNT, dissolve slower when combined with propellant formulations than its normal rate due to binders in the formulations that slow down reactions between water and DNT. According to Pichtel (2012), although NG is highly soluble and mobile in the environment, its encapsulation in insoluble NC in double and triple base propellants makes NG seem unusually persistent in the environment due to a slow release of the compound into solution.

Jenkins et al. (2012) indicates that solubilities of HEs vary in the order TNT (130 mg/L) > RDX (26.3 mg/L) > HMX (4.5 mg/L). Deposited TNT dissolves more than RDX and HMX and also readily sorbs more to soil constituents than RDX and HMX, both of which have lower solubility and adsorption properties, thus readily migrate deeper into soil or transported to remote environments. The HMX has less adsorption potential than RDX, and easily migrate deeper through the vadose zone. Adsorption potential of a compound is determined by finding its log K_{ow} value. This value is an indication of the hydrophobicity or hydrophilicity of the compound (Dalrymple, 2005). Compounds with a high log K_{ow} are highly hydrophobic, have high adsorption characteristics and therefore less mobile in soil a soil medium. Impurities in explosives (plasticisers and binders) also influence dissolution and sorption rates (Pichtel, 2012). The degree to which explosive compounds dissolve depends also on the type solute involved. From Table 2.10 (adaptation of US Army, 1990), solubilities of explosives in water relative to other solvents are illustrated. Organic solvents are evidently more effective in dissolving explosives than aquatic solvents. Highly polar solvents such as acetone and acetonitrile are effective and popular for extracting explosives during laboratory analyses.

Table 2.10: Solubilities of explosive compounds



Compound	Water	Other Solvent at 20°C	Source
TNT	130mg/L	72.1 g/100g of Methyl Acetate	US Army (1990); Jenkins, et al. (2012)
RDX	26.3mg/L	25.5 g/100g of Dimethylformamide	US Army (1990); Jenkins, et al. (2012)
HMX	4.5mg/L	2.11 g/100g of Cyclohexanone and 4.4g/100g in Dimethylformamide	Pichtel (2012); US Army (1990)
Nitrocellulose	Insoluble	100% in Acetone	US Army (1990); Pichtel (2012)
Nitroglycerin	1 800mg/L	54g/100g of Ethanol	DOD, (1990), Jenkins, et al. (2012)
Nitroguanidine	4400mg/L	24.2g/100g of Sulfuric Acid	DOD, (1990)

Explosive compounds have low Henry's Law constants and Vapour Pressure, therefore insignificantly volatile (Kalderis et al., 2011). The Loss of explosives compounds from the environment is therefore not expected to be a result of sublimation. Adsorption is one of the mechanisms of explosive retention in soil. The soil partitioning coefficient (log K_d) indicate the potential of explosives to sorb to soil constituents (Pichtel, 2012). High log K_d indicate high adsorption potential. Explosives generally have low sorption values. Both DNT isomers are likely to be detected in surface soils due to higher log K_d values. RDX and HMX have considerably low sorption potential and have been reported to migrate to groundwater below MTAs (Jenkins et al., 2012; Pichtel, 2012). Adsorption mechanisms include hydrophobic partitioning, ion-exchange, hydrogen bonding and chemical adsorption (Kalderis et al., 2011). Clay soils retain higher concentrations of explosive residues due to large surface area than sandy soils. According to Pichtel (2012) TNT is reversibly sorbed to clay minerals while only small amounts RDX and HMX are semi-permanently sorbed to clay minerals. The rest precipitate and migrate easily in the environment. TNT sorption strength is due to the number of amino groups of the compound, which is significant in Nitroaromatics such as 2,4-DANT > 4-ADNT > TNT (Kalderis et al., 2011; Pichtel; 2012).

Deposited energetics undergo various transformation pathways which differ according to different physic-chemical characteristics and environmental conditions, therefore site specific. Abiotic transformation mechanisms include photolysis, hydrolysis and reduction (Pichtel, 2012). Biotic transformation pathways include biodegradation by enzymatic or bacterial activity under aerobic or anaerobic conditions (Kalderis et al., 2011; Monteil-Rivera et al., 2009; Pichtel, 2012). Transformation pathways of explosives have been sufficiently covered in literature and are illustrated on Figure 2.6 above. Transformation products of TNT include 2,4-Dinitrotoluene (DNT), 2,6-DNT, 2-A-4,6-Diaminobenzoic Acid (DNBA), 2-A-2,6 DNBA, 2-ADNT, 4-ADNT, 2,4-DANT and 2,6-DANT. Under strictly anaerobic conditions, the derivative Triaminotoluene (TAT) has been identified. Transformation products of RDX are the polyamines 1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), 1,3-nitroso-nitro-1,3,5-triazine (DNX) and 1,3,51-trinitroso-1,3,5-triazine (TNX). The HMX transformation products are not sufficiently documented and further research is required. Kalderis et al. (2011) proposed that HMX forms nitroso intermediates which may further metabolise into nitrous oxide and formaldehyde under both aerobic and anaerobic conditions.

Photolysis occurs when explosive compounds in soil and water are exposed to light. According to Monteil-Rivera et al. (2009) photolysis occurs through hemolysis of the $X\text{-}NO_2$ bond (Where X=C or N), resulting in transformation products similar to hydrolysis. Photolysis reaches deeper in aquatic environments and restricted to the surface in soils. According to Kalderis et al. (2011) exposed explosives have half-lives in the order of 0.5 h to 22 h (TNT) < 0.6 days to 2.3 days (NQ) < 9 hours to 14 days (RDX) < 1.4 days to 70 days (HMX). Information on other propellants was not found. TNT photolyses into Nitrobenzene (NB), benzaldehydes, azoxydicarboxylic acids and nitrophenols following oxidation of the methyl groups and reduction of the nitro groups. RDX and HMX are photolysed into azoxy compounds, ammonia, formaldehydes, nitrates, nitrites, nitrous oxides and n-nitroso-methhylenediamides. NQ photolyses into nitrite, which is intermediate to formation of hydroxyl-guanidine, which forms further unknown products (Spangord et al., 1987). Samples exposed to light are likely to contain more transformation products of the explosives depending on the temporal nature of exposure.

Hydrolysis involves the nucleophilic substitution of methyl and nitro groups in explosives with hydroxide ions (OH) under alkaline conditions (Kalderis et al., 2011). According to Monteil – Rivera et al. (2009) hydrolysis is enhanced by raising the pH and increasing temperature. About 95% of TNT was observed to transform into its amino products (2A-DNT and 4A-DNT) at pH 12. These transformation products require even higher pH than TNT to further transform (Monteil-Rivera et al., 2009). The hydrolysis of RDX and HMX require a pH higher than 10 to transform into NO_2, ammonia (NH_3), N_2O, N_2, HCHO and HCOO-. The HMX hydrolysis is 70 times slower than that of RDX under the same conditions. Denitration under these conditions led to ring cleavage and decomposition of the compounds. Reduction of the nitro groups into amino groups also occurs through alteration of pH and redox potential in the presence of a catalyst such as Iron (Fe), clay particles and soil organic matter (Kalderis et al., 2011). The Fe degrades RDX and HMX to form NH_4 ions (Monteil-Rivera et al., 2009).

Biotransformation refers to the degradation of explosives to their metabolites by microbial activity. Certain bacterial and fungal strains degrade explosive compounds (Pichtel, 2012). Biotransformation of Nitroaromatics follow sequential de-nitration under anaerobic conditions followed by ring cleavage. The nitro group of Nitroaromatics prevents initial reaction with oxygenases but favours reductase attacks in anaerobic conditions (Bernstein & Ronen, 2011; Monteil-Rivera et al., 2009). The formation of intermediate DNTs attract oxygenase attack under aerobic conditions, releasing the nitro groups and leading to ring cleavage and mineralization of the compound. According to Bernstein & Ronen (2011), TNT is degradable by strains from *Pseudomonas* sp., *Pseudomonas fluorescence* and *Enterobacter cloacae*. *Pseudomonas* sp. strain is the dominant species during the initial anaerobic step. Fungal strains such as *Phanerochaete chrysosporium* also mineralise TNT derivatives by denitration into nitroso-DNT (Bernstein & Ronen, 2011; Monteil-Rivera et al., 2009; Pichtel, 2012). Accumulation of TNT azoxy products suppress RDX and HMX degradation in the environment.

The denitration of RDX follows similar steps as TNT but catalyzed by reduced Iron (Fe) in soil. According to Bernstein and Ronen (2011), the denitration of RDX by *Rhodococcus* under aerobic conditions was reported as the most effective degradation of RDX as denitration step is immediately followed by ring cleavage. Other bacteria such as *P. chrysosporium*, *Pseudomonas fluorescens* (Xen A) and *Pseudomonas putida* (Xen B) form intermediate MNX, DNX, TNX and methylene dinitratramine (MEDINA) under anaerobic conditions, which must be degraded further. The HMX is recalcitrant to mineralization. It is transformed under aerobic conditions to N_2O and formaldehyde, then to CO_2. The *P. chrysosporium* was reported to degrade HMX under nitrogen-limiting environments to 97% removal after 52 days incubation, forming 1-NO-HMX. This strain was also reported to degrade azoxy products of TNT within two weeks (Bernstein & Ronen, 2011)

2.5.2.2 Sources of explosive compounds

Explosive compounds have been in use for over two centuries all over the world. The use of these compounds has civilian and military use (Kiiskila et al., 2015; Panz et al., 2013). The mining industry is one of the biggest users of explosives such as Dynamite for extraction of minerals underground. Construction industries also use explosives to clear routes of rock formations. The biggest user of explosives remains the military, where explosives are used in HE munitions and propellants. Munitions manufacturing sites have been identified as the most contaminated environments due to the high volume release of waste water from production (Bernstein & Ronen, 2011; Monteil-Rivera et al., 2009; Pichtel, 2012). Production of 100 000 tons of TNT, in one instance, produced 5 400 000 cm^3 contaminated of waste water (Kalderis et al., 2011). Concentrations of over 10 000 mg/kg of energetics were detected near a Louisiana Army Ammunition Plant in USA resulting from production operations. Contamination of soil and groundwater in training areas has become a point of major concerns in many countries worldwide (Bernstein & Ronen, 2011; Jenkins et al., 2012; Pennington et al., 2008b). Explosive compounds in MTAs and conflict sites are by-products of live firing of explosive weapon systems. Sources include; (1) detonation of munitions, (2) leaching of explosive residues from UXO and (3) destruction of munitions by OB/OD methods (Kiiskila et al., 2015).

High Order Detonation (HOD) of munitions spread less than detectable or as little as 0.0003% to 0.00017% of explosive in the environment (Jenkins et al., 2012; Pennington et al., 2008b; Walsh et al. 2008). Pichtel (2012) reported that as little as 140 g of explosive is deposited by high order detonations. Artillery barrages and frequent exposure may lead to elevated contamination. Explosives concentrations ranging between 460 mg/kg to over10 400 mg/kg were reported in surface soils within 0.5 cm of surface soils at numerous US MTAs. Jenkins et al. (2001) reported concentrations of Octols (60/40 HMX/TNT) ranging between 1 640 000 µg/kg and 3 700 000 µg/kg. Via (2016) and Jenkins et al. (2012) highlighted that the nature of contamination at impact sites was extremely heterogeneous and using improper sampling techniques may lead to false characterization of the sites. Jenkins et al. (2012) recommended then use of Multi Increment Sampling (MIS) to average out the error of heterogeneity. Low Order Detonations (LODs) deposit higher concentrations of explosives. As much as 3 kg of explosive residue is deposited when an artillery round undergoes LOD (Pichtel, 2012). Around 3% of fired explosive munitions experience LOD (Pennington et al., 2008b). Propellant formulations have also been reported as problematic contaminants at firing points. Characterisation studies indicate that not the entire volume of propellant is consumed by explosions (Jenkins et al., 2012; Walsh et al., 2009). The unburnt residues settle within 50 m of the firing point for large calibre weapons and around 10 m for small arms ordnance. The OB/OD sites are also a concern due to deposition of explosives during UXO destruction. These Blow in Place (BIP) operations also fail to consume all the explosive and propellant charges. Continuous use of burn pits result in elevated concentrations of explosives at these sites.

The United States Envirnmenta Prtectin Agency (US EPA, 2002) listed common UXO locations as training range impact areas, Open Burn (OB) and Open Detonation (OD) sites, ammunition disposal sites, proving grounds and ammo depots. UXO may lie on soil surface (Figure 2.7), partially covered with top soil or buried in the ground or surface water points. UXO may be whole munitions or partially detonated shells with explosive fill. Taylor et al. (2012) reported that corrosion of the shell resulted in leakage of explosive onto soil. Concentrations as high as 110 mg/kg have been reported next to a 155 mm round due to leaching of explosives from the shell and concentrations decreased away from the point of leak. A 1mg/kg concentration of dissolved energetic compounds was also discovered in soil pore water in the vicinity of the shell. Taylor et al. (2012) found that partially exploded shells leaked more explosive residues than corroded UXO.

Figure 2.7: Partially exploded 155 mm artillery shell (Image: Mokalapa, 2020)

2.5.2.3 Toxicity of explosive compounds

Toxicity of explosive compounds has been extensively studied. Explosive compounds can be toxic to soil invertebrates, vertebrates and plants (Kalderis et al., 2011). Exposure to explosive residues is mainly through inhalation, ingestion and dermal absorption. Toxicity of explosives is sufficiently documented. Most studies have focused on effects of the high explosives TNT, RDX and HMX. A large part of the studies were based in laboratory settings and many of the tests were conducted using samples spiked with raw explosives (Dontsova et al., 2006; Lotufo, 2013; Panz et al., 2011). Results indicate that energetic compounds are xenobiotic, toxic and are environmentally undesirable. According to Lotufo (2013) microorganisms including bacteria and fungi, both aquatic and terrestrial, are less vulnerable to RDX, HMX and CL-20 toxicity than TNT. Raw TNT was reported to be more toxic to microorganisms than its metabolites 2,6-DNT and 2,4-DNT. For TNT metabolites, toxicity to microorganisms varied according to the position of the nitro groups (2,6-DNT > 2,4-DNT) and toxicity decreased further with transformation products (Kalderis et al., 2011). Laboratory tests indicated that HMX was not significantly toxic to bacteria and algae in samples spiked with explosives (Dontsova et al., 2006; Panz et al., 2011). For invertebrates, explosive compounds affect fertilization, embryo development and juvenile survival (Kalderis et al., 2011). Concentrations of 12 to103 mg/kg of both TNT intermediates (2,4-DNT and 2,6-DNT) did not inhibit fertilization but 2,6-DNT was toxic to embryo development at around 36 mg/kg. The TNT retards juvenile survival of microorganisms more than its metabolites even at low concentrations of 0.8 to 11.9 mg/L, altering the species diversity of the microbial community, potentially altering local ecosystems.

Invertebrates such as earthworms presented various responses from exposure to explosive compounds (Lotufo, 2013). Panz et al. (2011) observed 70% earthworm mortality rate when a soil sample was spiked with 369 mg/kg TNT against a mortality of 60% for a 540 mg/kg RDX spike. HMX was the least toxic of the compounds where mortality of earthworms was the limit (60% mortality at 1000 mg/kg). A proportional combination of the explosives cause 100% earthworm mortality at 180 mg/kg. Vertebrates such as animals and humans also present varying responses to explosive toxicity. Burrowing animals such as the salamander showed no negative effects to skin contact with TNT contaminated soil, but their internal organs, such as the liver, were found severely affected and growth was limited during the treatment period (Kalderis et al., 2011). Most explosive compounds are suspected human carcinogens. Exposure to TNT is mainly through inhalation of explosives contaminated dust or through skin adsorption (dermal sorption) and enter the human blood stream, causing various diseases such as anaemia and severe liver damage (Bernstein & Ronen, 2011). About 17 000 poisoning cases and more that 470 fatalities were reported during the 20th Century (US EPA 2014a). RDX and HMX have similar health effects, such as nausea, vomiting, convulsions, etc. RDX targets the nervous system and if large doses are ingested, may result in seizures in both humans and animals (US EPA, 2014b). NQ was reported to be only slightly toxic to fish. Kenyon, (1982) observed a mortality rate of 30% of fish at NQ concentration of 3650 mg/L, the limit of NQ dissolution. The NQ was also reported to be much less toxic to mammalian vertebrates. Albino rats were fed 0.93 mg/kg doses ingested daily and 10 g/kg dermal exposure for 20 hours and showed no harmful effects.

According to Panz et al. (2011) explosive compounds are toxic to plants by inhibiting seed germination, plant biomass and root growth. These effects occur rapidly and vary with soil type, concentration, explosive composition, plant tissue and microorganism activity (Via, 2016). The TNT, RDX and HMX at concentration of 180 mg/kg individually resulted in biomass loss of red clover seedlings. Kenyon, (1982) observed growth stimulation in fresh water algae by 40 mg/kg NQ in test samples, while growth inhibition was observed in a 130 mg/kg NQ test sample.

However, RDX and HMX induced growth in wheat biomass while TNT produced opposite results with incremental observations (Panz et al., 2011). The TNT significantly inhibited seed germination of red clover seed by 70%. This aspect is reported to increase with TNT concentration in soil. According to Via (2016) TNT inhibits new root growth and root hairs in addition to destroying the root system. While TNT damages below ground parts of vegetation, RDX is known to be mobile within plant systems and damages above ground parts and causes leaf necrosis, curled leafs, irregular leaf margin, reduced shoot length, delayed emergence, bifurcated leaves and atypical bilateral symmetry (Via, 2016). Limited underground effects include decreased root length, underdeveloped roots and curled root tips. Explosives reach plants through soil solution and interstitial water and gets absorbed through meiotic processes. The TNT adsorbs to soil and plant roots and its absorption by plants is less that other energetics. Other explosives such as RDX are mobile within plants (Figure 2.8). Some plants have the ability to quarantine the compounds while other have limited ability to biodegrade them.

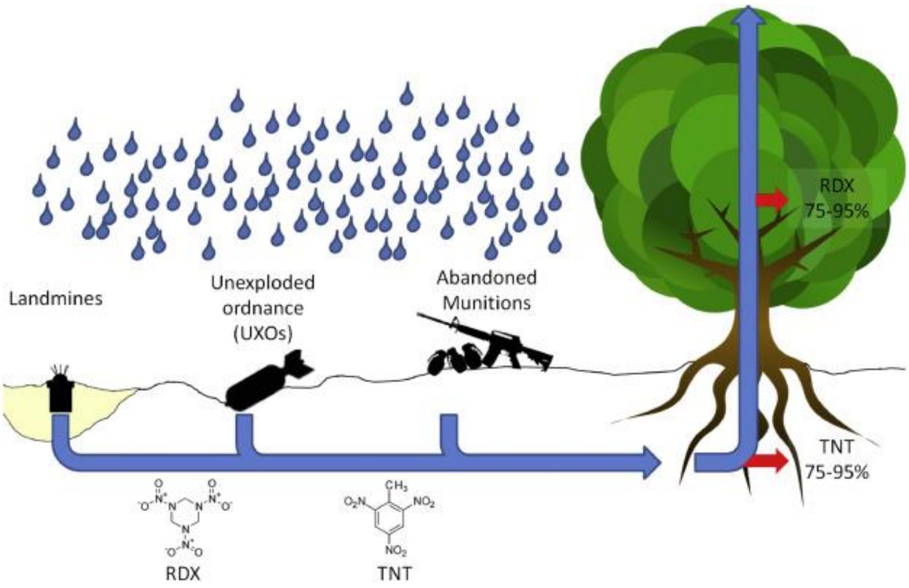


Figure 2.8: Pathways for explosive contamination of vegetation at MTAs (Via, 2016)

2.5.2.4 Environmental impact of explosive compounds

Training at MTAs using explosive weapon systems such as artillery and antitank weapons release explosive chemicals to the environment. The separation between the launcher and the target provide unique characteristic patterns of contamination. Launching areas are contaminated with propellant mixtures and target areas are contaminated with HE residues (Pichtel, 2012). According to Jenkins et al. (2012) the rest of the area is not affected by the explosive contamination. During live firing events, varying quantities of propellants are released to the environment depending on the weapon system in use, causing environmental hazards to soil, groundwater and other environmental receptors (Pennington et al., 2008b). Nitroglycerin is the most common contaminant of surface soils at antitank firing positions at above 100 mg/kg concentration due to the use of double base propellants in antitank weapons (Pichtel, 2012; Jenkins et al., 2004). At artillery firing positions, DNTs, NG, NQ and NC are the main contaminants (Walsh et al., 2009). The HMX at antitank targets was recorded at above 100 mg/kg concentrations (Pichtel, 2012). In contrast, artillery targets were reported to contain lower concentrations of explosives. LODs release around 3 kg of explosive while HODs release under 1 g/kg of explosive residues. Octols and Cyclotols are common contaminants at artillery ranges. Concentrations of 0.7 mg/kg to 74 000 mg/kg of RDX and 0.8 mg/kg and 87 000 mg/kg of HMX were reported in some USA bases. Different concentration trends were reported at various MTAs worldwide, probably as a result of different intensities of use or weapon systems in use.

Explosives released into the environment may be mobile or remain sorbed, depending on prevailing environmental and physicochemical conditions. These are introduced to food chains in similar pathways as heavy metals. For example, the mobility of RDX in soil pore water makes it more available to plant uptake and move to higher plant echelons (Via, 2016). Here it may either harm the plant or stored in terminal shoots and leaves where xenobiotic storage may proceed while it becomes available for animal consumption (Peter et al., 2019). The TNT sorbs to humic material in soil and is immobilized. However, with increased soil particle size and less humic content, or changing chemical content, it becomes less bound and available for plant-explosive reactions (Via, 2016) or further fate and transport mechanisms. The TNT can be metabolised by some plants as a nitrogen source (Peter et al., 2019). Most of the TNT remain sorbed to plant roots while its dissolved phase is available for plant uptake where it may enter the food chain. Most of the RDX is recovered in parent form from plant stems and leaves (Peter et al., 2019). Combinations of microbial and root activity degrade explosives in soil. Lack of explosive degrading strains will therefore have an impact on the rate of removal of explosives in soils. The reaction of plants to exposure is important for the species composition of the environment. Explosive resistant plants are expected to form larger communities while explosive sensitive species are expected to form smaller communities. This will result in alteration of species diversity of the vegetation communities at MTAs.

Explosives also have varying degrees of toxicity to vertebrates and humans (US EPA, 2014a; US EPA, 2014b). Toxicity of explosive compounds was discussed in section 2.5.2.3. Explosive sensitive animals are expected to have less communities than explosives resistant species (Peter et al., 2019). Animals and humans may also come into contact with explosives in soil through dermal contact, ingestion or inhalation. Another pathway is exposure to explosives in drinking water. Thus explosives in the environment potentially have a determining factor on bio-diversity (Via, 2016). According to Craig et al. (1995) explosives are persistent in the environment and reports showed detection of explosives in soil and groundwater 20-50 years after disposal of munitions was discontinued. Some of the most explored methods of remediating for explosive contaminated soil and water include phytoremediation, soil washing and bioremediation (Kalderis et al., 2011).

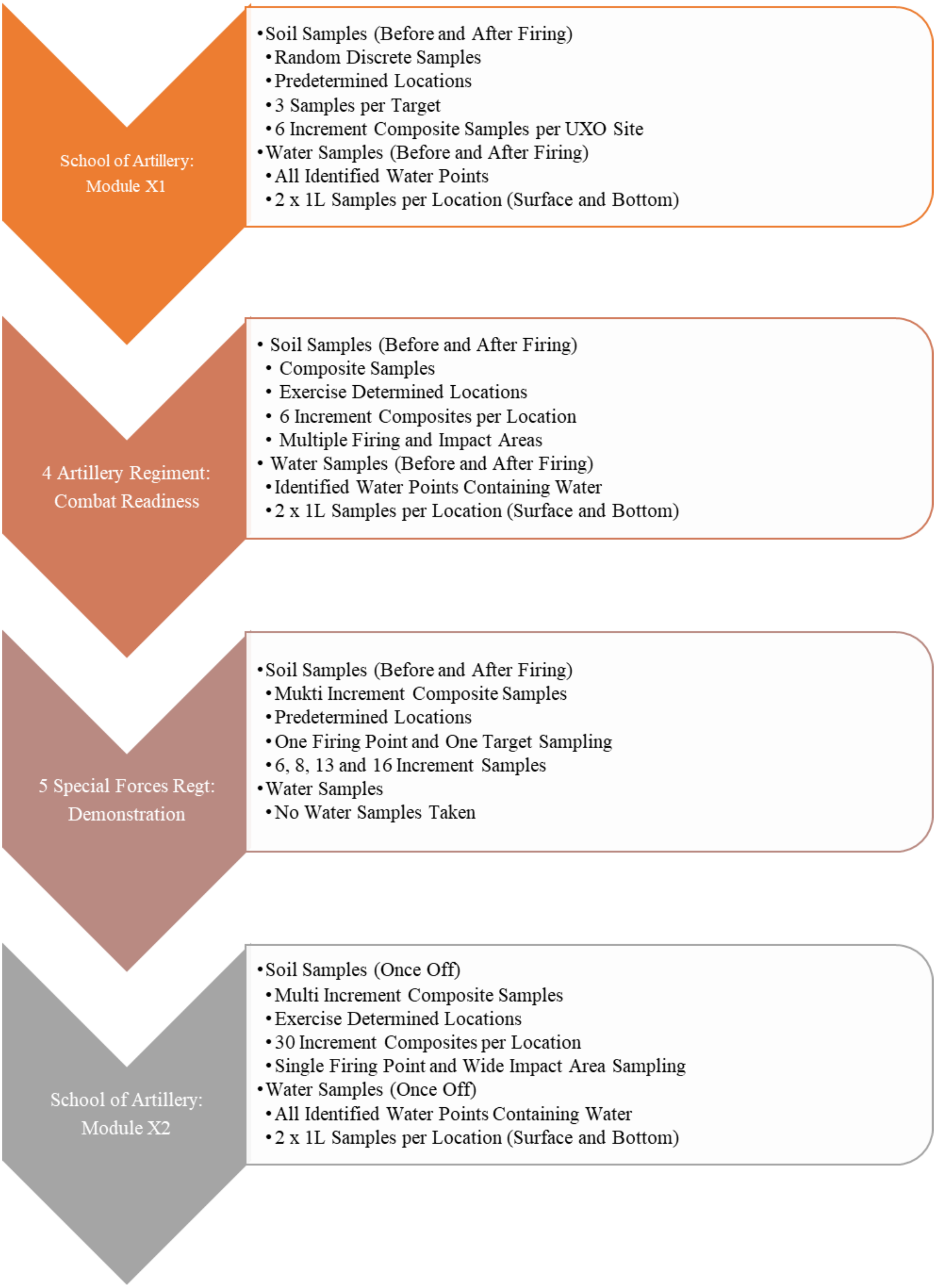
Chapter 3 Materials and Methods

3.1 Layout of the study

The sequence of data collection was guided by the frequency and nature of live firing exercises taking place in the study area over the period of study. Characterising the impact of explosive munitions under field conditions was climacteric for characterising environmental impacts on the Military Training Area (MTA). Training exercises involving live firing of explosive weapon systems were identified. Four environmental impacts were characterised; (1) the deposition of explosives at firing and target areas, (2) explosive contamination of OD/OB sites, (3) accumulation of UXO in the study area and (4) heavy-metals contamination in soil and water media in the study area.

Selected exercises were identified during weekly range meetings at ASB Potchefstroom Range Office. Four training exercises were identified; (1) the School of Artillery Module X1 of February 2020, (2) the 4 Artillery Regiment Combat Readiness exercise in October 2020, (3) the 5 Special Forces Regiment Demonstration in November 2020 and (4) the School of Artillery Module X2 of February 2021. Module X1 involved firing from a single point to multiple targets. The second exercise involved firing of multiple targets from multiple locations. The third exercise involved firing of a single target from a single position. Module X2 involved firing of multiple targets from a single position. 120 mm Mortars, and 60 mm Mortars, 81 mm Mortars and 105 mm Rockets were fired over a period of one year.

Environmental impact was assessed by collecting and analysing soil and water samples using Multi Stage Sampling of impacted areas before and after live firing. Background samples collected from the entire sampling frame before Module X1 were used to determine contamination levels before exposure events for comparative analysis. Thereafter, sampling was carried out only in affected areas. The UXO sites were identified during field observation and sampled. Water samples were collected at four monitoring points within the study area. Two control points were identified outside the MTA, where hypothetically uncontaminated (blank) samples were collected. Figure 3.1 summarises the flow of data collection during the study. Sampling methods were varied by sample size to assess variability in the results relative to methods used. Module X1 soil samples were all discreet samples while the rest of the exercises were composite sampled. Composite samples were also varied between exercises by increasing the number of increments composited.



School of Artillery: Module X1

- Soil Samples (Before and After Firing)
  - Random Discrete Samples
  - Predetermined Locations
  - 3 Samples per Target
  - 6 Increment Composite Samples per UXO Site
- Water Samples (Before and After Firing)
  - All Identified Water Points
  - 2 x 1L Samples per Location (Surface and Bottom)

4 Artillery Regiment: Combat Readiness

- Soil Samples (Before and After Firing)
  - Composite Samples
  - Exercise Determined Locations
  - 6 Increment Composites per Location
  - Multiple Firing and Impact Areas
- Water Samples (Before and After Firing)
  - Identified Water Points Containing Water
  - 2 x 1L Samples per Location (Surface and Bottom)

5 Special Forces Regt: Demonstration

- Soil Samples (Before and After Firing)
  - Mukti Increment Composite Samples
  - Predetermined Locations
  - One Firing Point and One Target Sampling
  - 6, 8, 13 and 16 Increment Samples
- Water Samples
  - No Water Samples Taken

School of Artillery: Module X2

- Soil Samples (Once Off)
  - Multi Increment Composite Samples
  - Exercise Determined Locations
  - 30 Increment Composites per Location
  - Single Firing Point and Wide Impact Area Sampling
- Water Samples (Once Off)
  - All Identified Water Points Containing Water
  - 2 x 1L Samples per Location (Surface and Bottom)

Figure 3.1:A modelled summary of the flow of data collection activities (Mokalapa, 2020)

3.2 Description the study area

The study area is introduced in Chapter 1. This section focuses on the unique characteristics of the study area that influenced formulation hypothesis and choice of methodology for this study. The use of weapon systems in a training area is greatly dictated by a set of safety parameters inherent in the weapon system. The greatest user of explosive weapons in General De La Rey Training Area is the SA Army Artillery Corps. Three Artillery units are present in the Potchefstroom area (4 Artillery Regiment, Light Artillery Regiment and School of Artillery). SA Artillery employs the 120mm Mortars, the 155mm GV5 towed system and the 155 mm GV6 Self Propelled Howitzer. One battery of 127 mm Multi Rocket Launchers (MRL) is also employed by 4 Arty Regt. Artillery systems are of particular interest for the current study due to the artillery's traditional employment of explosive munitions and indirect fire. A concoction of Infantry direct fire munitions such as the 90 mm High Explosive Anti-Tank (HEAT) are also commonly used in the study area.

3.2.1 Delineation of the study area

The unique topography of the study area has deterministic implications for long range indirect fire weapon systems. The area available for targeting and manoeuvring is reduced by a No-Firing Area (NFA) of 1.3 km all around (See Figure 3.2), restricting the available area for large calibre targeting. The central part of the MTA is preferred for targeting. Artillery systems are affected greatly by their long range application and it is often necessary to deploy launchers at the furthest range from the target area to allow for minimum range and where terrain features will not affect applicable safety parameters. Observation of fire also requires a forward observer to use key terrain features of specific characteristics to control indirect fire. These terrain features, mostly high grounds are limited to the central part of General De La Rey Training Area, orchestrating a somewhat biased habit of target acquisition towards the centre of the MTA.

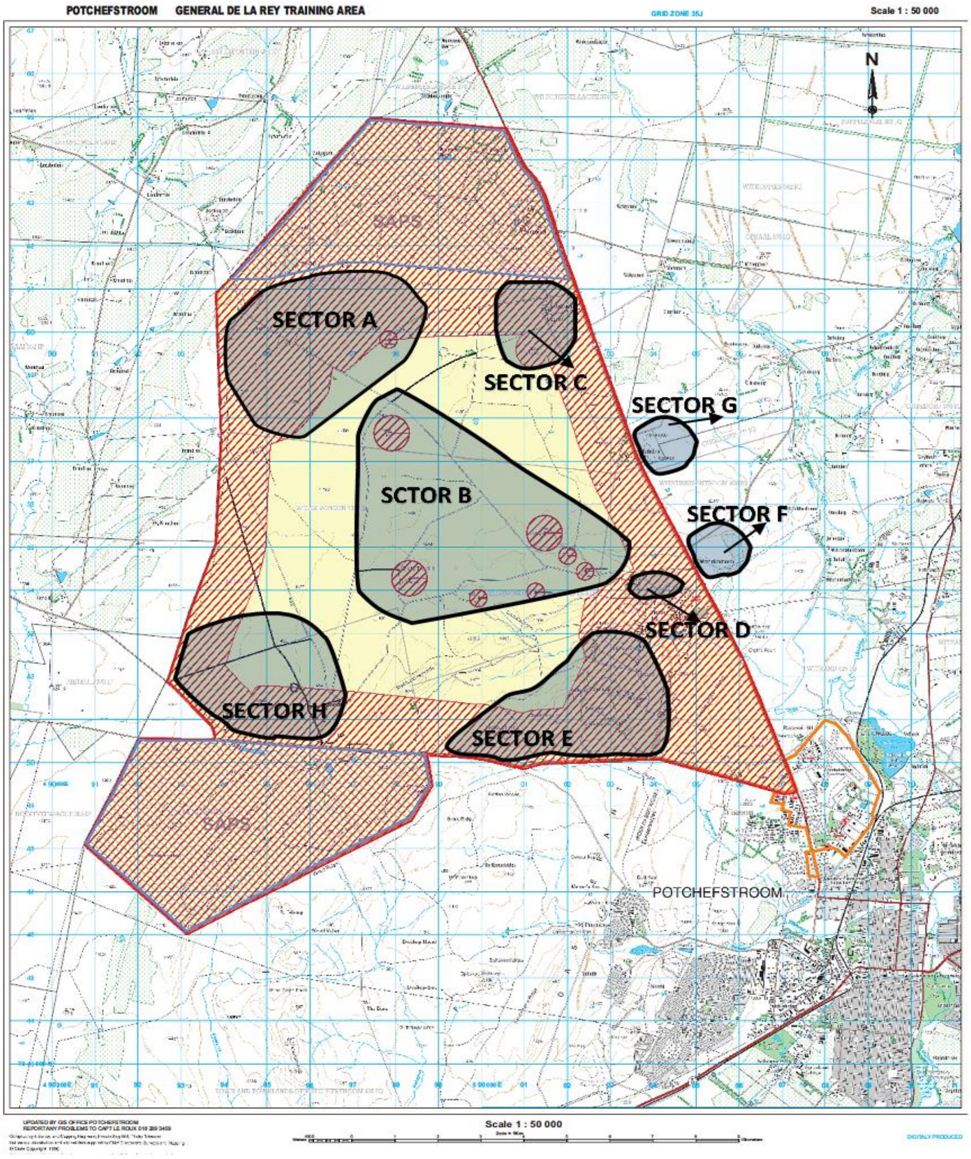


Figure 3.2: Deployment options for indirect fire systems (Mokalapa, 2020)

The result of this myriad of restrictions were explored for investigating possibly impacted areas. Figure 3.2 exhibit predicted and known artillery manoeuvre areas and impact areas on a 1: 50 000 Map of Potchefstroom showing General De La Rey Training Area. These areas were arbitrarily selected to correspond to locations where application of fire would be most feasible, then divided into zones of use or sections based on applicability of use as target or firing point (black polygons on Figure 3.2). The zones represent areas in which gun positions and targets are most likely to be located during training and were used to form the main sampling frame for the study.

3.2.2 Location of firing positions

Artillery firing positions are limited to the outer edges of the MTA and mostly in the NFA (shaded in red of Figure 3.3). The green and red arcs mimic safety arcs for a hypothetical firing exercise. The important aspect represented is the direction of fire relative to position of observers, firing positions and impact area. The narrow end of the arc represents a hypothetical gun position while the wide end represent the limit of the safe impact area. Red arcs represent unlikely or possibly unsafe position and/or direction, limiting feasibility of using that zone for live firing.

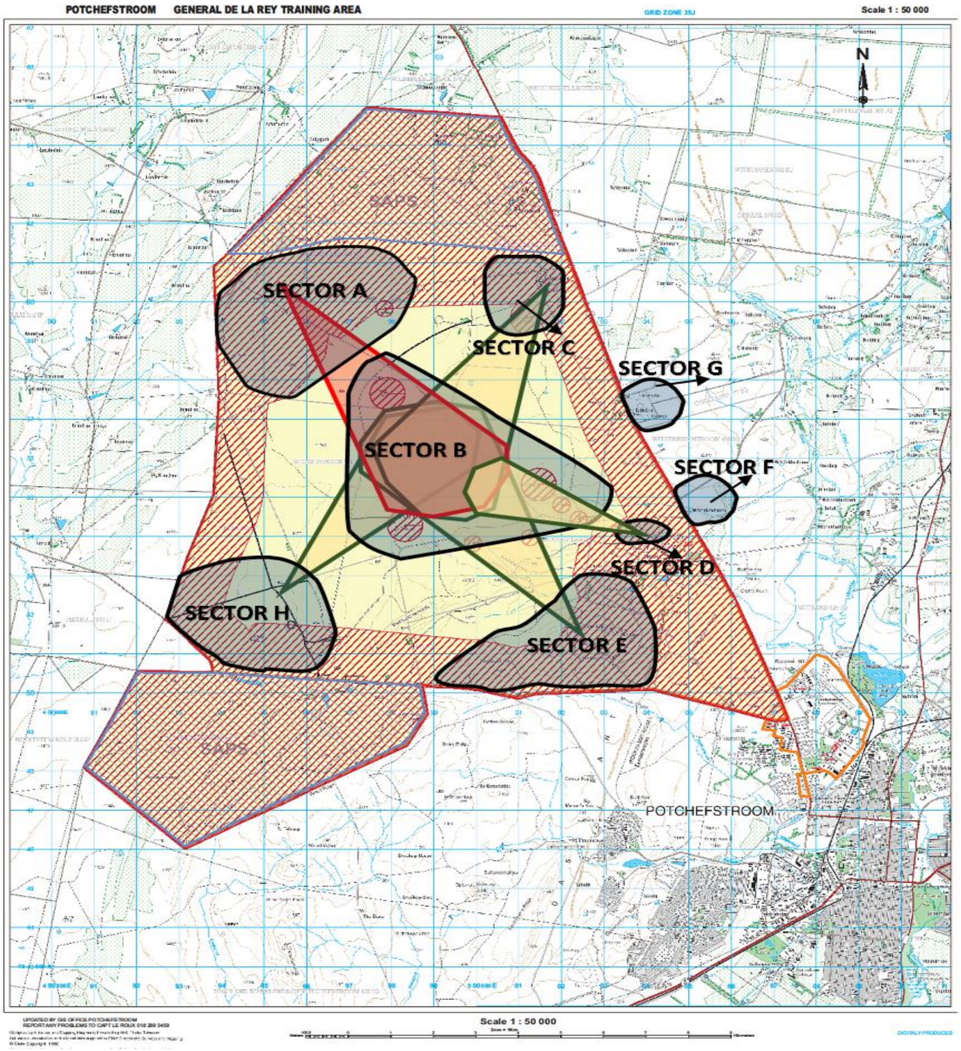


Figure 3.3: Possible firing and impact locations for Artillery weapon systems (Mokalapa, 2020)

Sectors A, C, D, E and H represent possible firing and manoeuvre areas. These areas were sampled for possible propellant contamination. Sector A is unlikely to be used for a live firing due to (1) the location of the firing position in an ecological compartment containing sensitive vegetation and (2) the direction towards 4 Artillery Regiment is potentially unsafe and require considerable safety measures. Sector A is therefore not expected to be significantly contaminated with propellants. It also contains one of the most prominent water sources for wild animals naturally occurring in the MTA. However, scattered shrapnel, discarded remnants of munitions and UXO found in this sector suggests that the area was previously used as a target area.

Sector C, D, E and H are known manoeuvre areas for indirect weapons and contamination with energetics was expected. Sector C is located on a large flat terrain almost without high grounds except for Trig Beacon 187 at the north eastern corner of the MTA. A large area is available for deployment of launchers. Exact launcher positions are not easily discernible during the off season. The red shaded circles on Figure 3.3 indicate NFAs. Large red circles protect Trig Beacons while small circles protect graves, UXO sites and boreholes. Sector D is located at Leerdagstelling, a demonstration area where exhibitions and weapon testing are performed. Launchers routinely occupy exact same positions during these events, thus the affected area is predictable. Sector E is located below Trig Beacon 80 (northern western slope of Valkop), a mountain peak located in the NFA south east of the MTA. This area is favoured for Mortar positions due to a small mountain range (Modderfonteinrante) which limits employment of Howitzers. Although Howitzers are fired from here, their lower trajectory limits their zones of fire as opposed to the high trajectory of Mortars. These parameters are illustrated on figure 2.4 in Chapter 2. Sector E is intensively used due to direction safety and allowance for longer range application. Launcher positions are predictable owing to the tightness of available space for deployments.

Sector H is located in a large open flat terrain of loamy soil underlain by shallow bedrock. This area is widely used by various units for infantry type manoeuvres. Explosive residues detected in this area would most likely be TNT and Composition B from 60mm Patrol Mortars and M26 Hand Grenades due to small scale platoon manoeuvers exercised routinely by other units. It also allows for multiple deployment areas for Artillery guns. Many possible deployment areas exist and determining exact launcher positions would be impractical. Other parts of the MTA are also usable but it is currently not known if they have been used, and to what extent, for engagements with explosive ordnance.

3.2.3 Location of impact areas

The most intensively used target area for explosive weapons is Sector B, centrally located in the MTA. Figure 3.3 illustrates general direction of safety arcs converging between three Trig Beacons (Trig Beacons 186, 116 and 131). These Trig Beacons are key terrain features for observation of fire due to their location on high grounds, allowing observers a wide area view of the impact area.

The significant impact of these features on observation of indirect fire is their central location and their triangular formation. Safety arcs are drawn through pairs of Trig Beacons to allow observer teams to deploy on the elevated terrains.

Observation is not always possible with Trig Beacon 116, the northern most Trig Beacon, due to its lack of height and field of view. The size of the impact area also greatly influences the range at which effective fire control is feasible. Knowledge of these parameters is vital for predicting deployments of fire units and therefore potentially contaminated areas. A number of targets are set up within Sector B for training purposes. These include an assortment of vehicle wreckages placed to present unique challenges during training. Figure 3.4 shows one of the Tank wreckage targets located at the low lying area of the impact zone. Further north of this target are two other vehicle wreckages on a slope. Sector B was further subdivided into four sub sections (BA (Trig Beacon 116), BB (Trig Beacon 131), BC (OP Tree), BD (Wreckages), and BE (Gonzalespoort Firebreak) to simplify the sample coding.

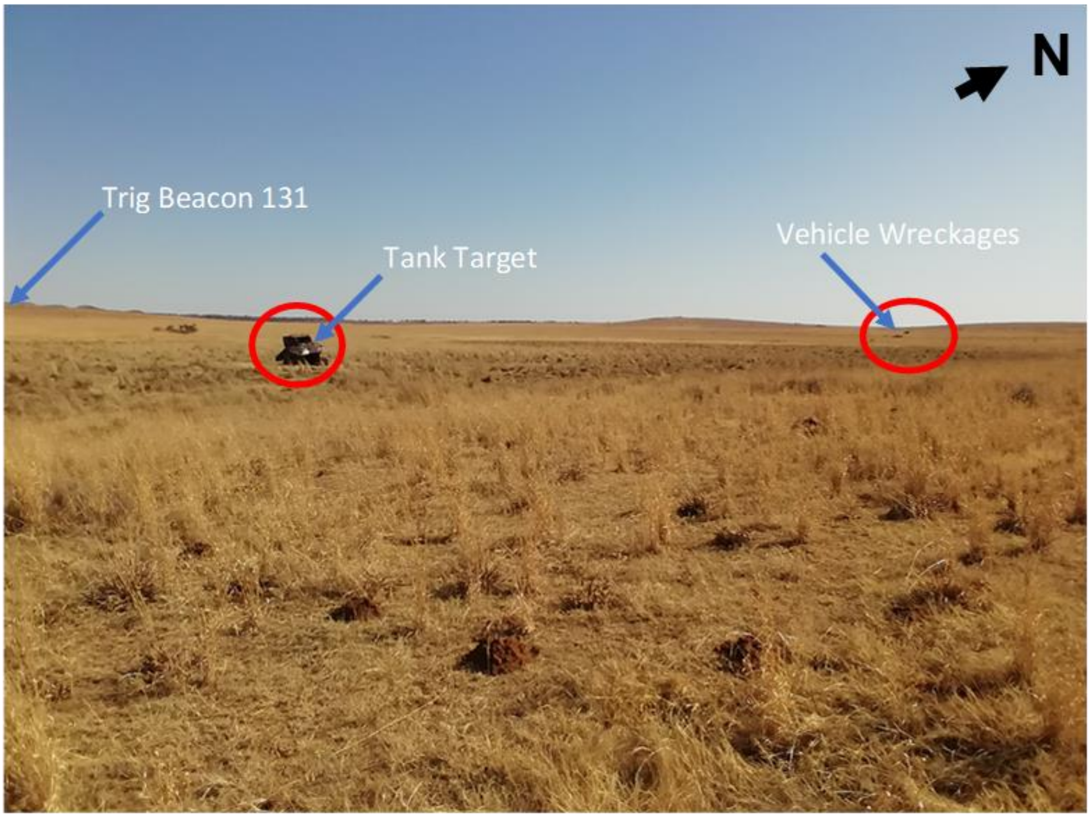


Figure 3.4:Artillery impact area at General De La Rey Training Area (Mokalapa, 2020)

3.2.4 Unexploded Ordnance (UXO) affected locations

A review of literature indicated that at least one in ten explosive munitions fired are duds (MacDonald et al., 2004; Pennington et al., 2008a). Chapter 1 demonstrates the fate of some of the Unexploded Ordnance (UXO) graphically. They may be embedded in the ground or suspended on surface soils. During range clearing operations, these are collected by expert personnel where possible for disposal or destruction. The same applies for excess propellant charges. Two types of UXO locations were identified at General De La Rey Training Area during the preliminary study; (1) UXO randomly occurring because they have failed to function as desired on targets and have not been subjected to onsite destruction or disposal and (2) UXO and/or remnants thereof stacked in OB/OD pits for disposal and destruction. Figure 3.5 illustrates types of UXO found in General De La Rey Training Area.

Figure 3.5:Unexploded Ordnance (UXO) at General De La Rey Training Area; (a) 120mm Mortar Bomb partially embedded in ground with fins exposed. (b) Ageing 155mm Round that failed to detonate on impact. (c) An assortment of UXO collected or disposed in a pit for destruction or burial (Images: Mokalapa, 2020)

3.2.4.1 UXO disposal locations

Nine UXO sites were located at the MTA and recorded as shown on Figure 3.6. Three UXO disposal/collection sites were discovered during the preliminary study. One was located north of Trig Beacon 116, one near a broken reservoir in Sector A and the other near a road north of Trig Beacon 186 in Sector B. The site near Trig Beacon 116 did not contain UXO, but exhibited evidence of Open Burning of munitions. About five burn pits of about five meters diameter and 1.5 m depth were counted. The site near Trig Beacon 186 contained a sizeable amount of UXO of various types and sizes ranging from 60 mm Mortars to 120 mm and 155 mm projectiles. The site in Sector A contained dispersed assortment of ageing remnants of projectiles.

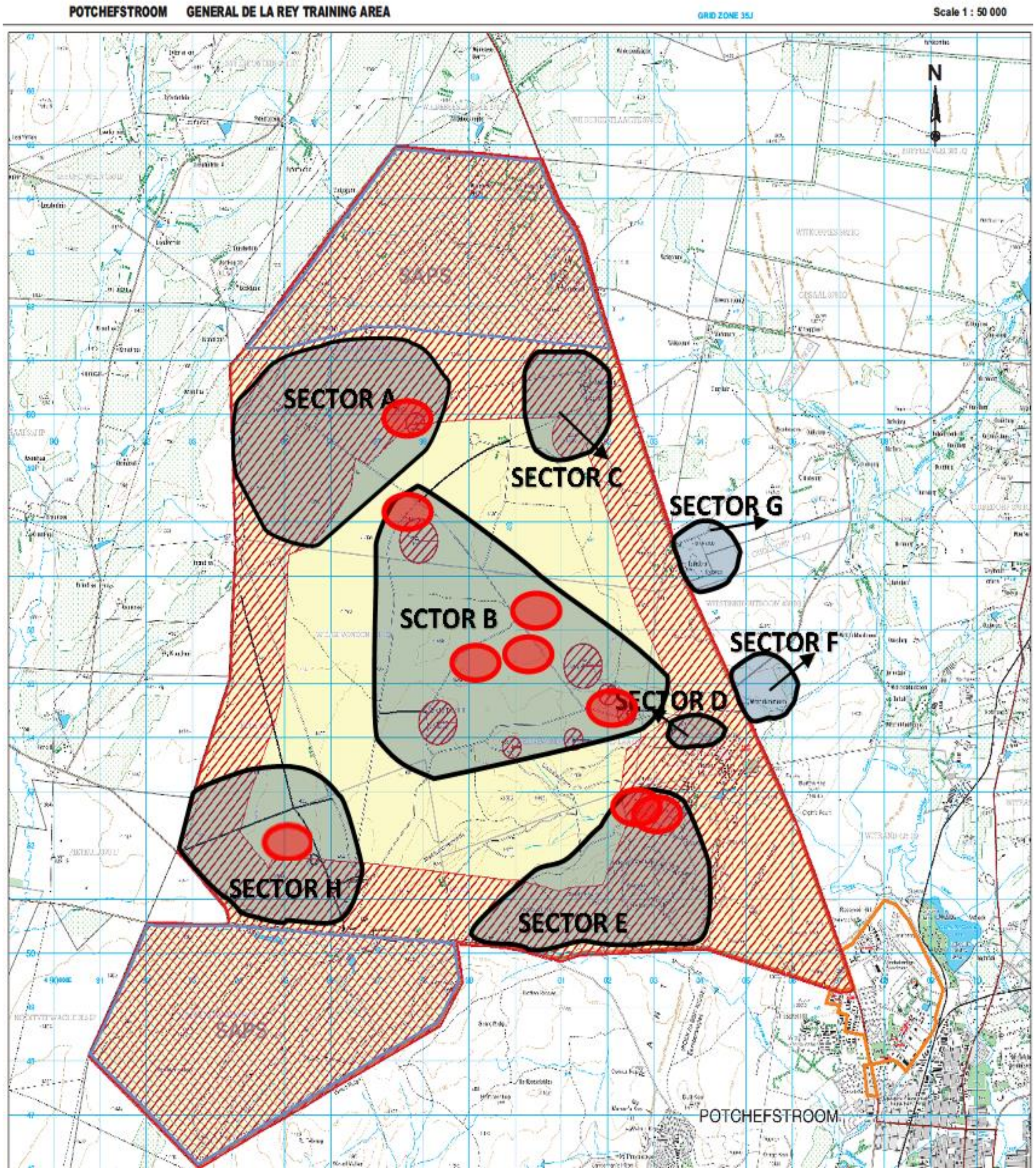


Figure 3.6: UXO disposal and destruction sites in the study area (Mokalapa, 2020)

Six other UXO sites were located during a detailed reconnaissance of the training area. Using Google Earth Pro, two burn sites were identified by the linear and cluster pattern of burn pits. The coordinates were recorded on Garmin GPS Montana 860 as waypoints and located by vehicle and foot navigation. One site was located at Sector B in the main target area and was overgrown with grass but showed evidence of past burning. The other was located in Sector H north of Trig Beacon 136. The site contained remnants of detonated UXO, suggesting past intensive use. Two sites in Sector E were pointed out by Ammunition Corps personnel during a field visit on 15 October

2020. These included about 25 burn pits. Three of the pits were filled with ageing 90 mm anti-tank rockets and Mortar projectiles. It is not clear whether these were HE or practice due to ageing. A large number of the ammunition pieces were fused. One UXO site next to a road between Sector B and Sector D, about 2 km from Leerdagstelling was littered on ground surface with practice M26 hand grenades, 120 mm Mortars, and 105 mm projectiles burned and/or corroded ordnance. Another OB/OD site consisting of three burn pits was located in Sector B east of the road that passes Trig Beacon 186 was pointed out by the Ammunition Corps members. A singe 155 mm fused round was found but evidence of burning and detonation fragments were present. Figure 3.6 provides a visual layout UXO sites. UXO locations were plotted using a portable Garmin GPS Montana 860. Coordinates of UXO sites are listed on Table 3.1.

Table 3.1: Location of UXO sites at General De La Rey Training Area

Serial	*Sector*	*Location ID*	*Coordinates*	*Description*
1	A	Wind Mill	26˚34'55.2" S 26˚58'58.8" E	UXO Disposal/ Target
2	B	∆116	26˚34'58.8" S 26˚58'01.8" E	UXO Demolition Pits
3	H	∆136	26˚39'05.3" S 26˚56'38.3" E	UXO Demolition Pits (OB/OD)
4	B	Artillery Target Area	26˚37'16.0" S 26˚59'25.0" E	UXO Demolition Pits (OB/OD)
5	B	OP Tree	26˚37'12.0" S 27˚00'14.4" E	UXO Disposal in Open Pit
6	B	OP Tree 2	26˚36'45.0" S 27˚00'03.0" E	UXO Demolition Pits (OB/OD)
7	B	Gonzales Firebreak	26˚37'05.8" S 27˚01'37.7" E	UXO Disposal Site
8	E	Old Weapons Range	26˚38'32.6" S 27˚01'24.6" E	UXO Disposal in Open Pit (OB/OD)
9	E	Old Weapons Range	26˚38'33.8" S 27˚01'14.0" E	UXO Disposal in Open Pit (OB/OD)

3.2.4.2 Random UXO locations

For the purpose of this study, randomly occurring UXO are Unexploded Ordnance located within the training area without any systematic distribution. This is due to the fact that UXO were found in different, spatially disjoint locations including areas not expected to be impact areas. This may be the result of long term changing patterns of use of the training area resulting in certain places changing from impact areas to firing positions or no longer used at all. Table 3.2 summarizes locations of UXO found during the preliminary study. Several reconnaissance trips were conducted to identify further random UXO locations to characterize the extent of the problem. Vehicle and foot reconnaissance were used to cover most of the accessible areas of the MTA.

Table 3.2: Randomly occurring UXO at General De La Rey Training Area

Serial	*Role Used*	*Coordinates*	*Observation*
1	Impact Area	26˚37'25.4" S 27˚00'16.7" E	120mm Mortar/Illum/Tank Target
2	Impact Area	26˚37'07.1" S 27˚00'14.6" E	Submunition/Road
3	Impact Area	26˚37'10.7" S 27˚00'00.8" E	120mm Mortar/HE/Rocks
4	Impact Area	26˚37'08.4" S 27˚00'16.2" E	120mm Mortar/Illum/Road
5	Impact Area	26˚37'09.5" S 26˚59'24.3" E	120mm Mortar/UXO Site
6	Impact Area	26˚37'09.0" S 26˚59'24.3" E	90mm HEAT Shape Charge
7	Impact Area	26˚37'04.9" S 26˚59'24.7" E	120mm Mortar Bomb
8	Firing Point	26˚37'05.9" S 26˚59'24.9" E	127mm MRL Rocket
9	Impact Area	26˚37'11.1" S 26˚59'25.4" E	120mm Mortar/Illum
10	Impact Area	26˚37'07.6" S 26˚59'35.8" E	120mm Mortar/Ilium/Road
11	Firing Point	26˚36'09.3" S 26˚58'05.2" E	127mm MRL Rocket

3.2.5 Shell fragments and heavy metals

The impact of heavy metals was discussed in Chapter 2. Explosive munitions disintegrate during detonation and bestrew fragments around the target. Erosion of metal fragments release heavy metal particulates to the environment, elevating the metal content at the affected areas. According to Stack et al. (2011) this type of erosion refers to the dimensionless quantity of metal mass loss expressed as a ratio between the initial and final mass of solid metal in the environment. Jenkins et al. (2012) also cited that propellant and high explosive mixtures contain some heavy metals as impurities. Metals such as Barium Nitrate, Lead Azide, Antimony Sulphide and Calcium Silicide were reported as impurities in explosive mixes (Jenkins et al., 2012). To investigate metal enrichment in the environment, hypothetically blank soil and water samples from control areas were compared with MTA samples. Potentially affected areas were identified for sampling by field observation of shell fragments and location around prominent target areas. Metals in water sources were expected to have settled, thus sub-surface samples were largely preferred for analyses. Results from MTA water samples and control blank samples were compared to determine if enrichment occurred as a result of the use of explosive munitions.

Parts of the training area including the entire Sector B were littered with varying sizes of shell fragments. Fragments ranged from centimetre size to whole projectiles (Figure 3.7). Four areas were remarkably littered with shell fragments (Sector B, Sector A, Sector E and Sector D). Sector B contained the highest concentration of shell fragments, being the most prominent impact area.

Sector A, about 1 km east of the UXO collection point, was classified as a firing point but has evidently been previously used as a target area for MRLs, owing to numerous 127 mm Rockets spotted protruding from the ground. Lower trajectory and the longer minimum target distance encourages firing MRLs from Sector H, in a north easterly direction towards Sector A. The third affected area was at Sector E around the dam near 4 Artillery Regiment. Ammunition Corps Officials reported the sector to have previously been used as a weapon testing range. Scattered shell fragments, 60 mm Mortar UXO and LODs were found in the vicinity of the dam and the area between the dam and the two Sector E OB/OD sites. At Sector D, shell fragments were concentrated at the one target area used for demonstrations. It was hypothesised that heavy metals were present in soil and water samples from the affected areas and therefore soil and water samples analysed for explosives would also be analysed for heavy metals.

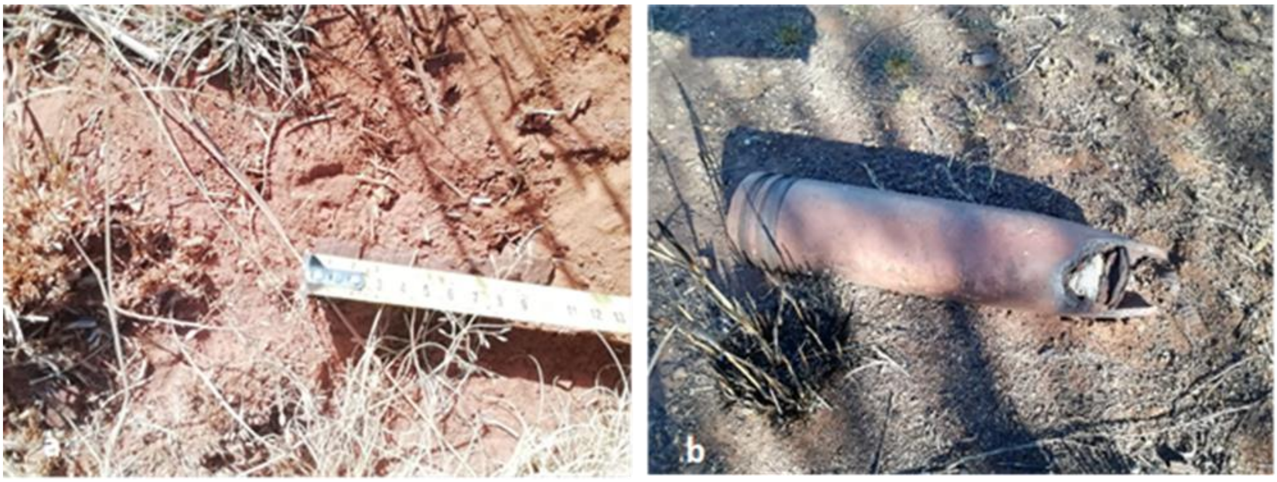


Figure 3.7: Metal shell fragments found at General De La Rey Training Area, (a) A 10cm metal fragment found at the impact area and (b) A large shell fragment from a low order detonation (Image: Mokalapa, 2020)

3.3 Data collection strategy

Sampling was the preferred method for characterising contamination of MTAs (Crockett et al., 1996). Explosive contamination was reported to be highly heterogeneous at MTAs ranging from less than detectable < 5 µg/kg and up to 10 000 mg/kg within several feet of sampled points (Pichtel, 2012; Jenkins et al., 2012). Determining effective sampling techniques is crucial where quantification of energetic contamination in MTAs is the subject of inquiry. Selected sampling strategies must addresses the balance between producing credible results and financial viability of obtaining results (Crockett et al., 1996). Collecting a high number of discrete samples will elevate analysis cost, but will also provide results representative of hotspot areas. Conversely, composite sampling averages out heterogeneity of contaminated sites and saves costs, but may fall short of exposing peak magnitudes of isolated hotspots due to mixing sample increments. Taherdoost (2016) provides a six stage model for selecting sampling techniques (Figure 3.8). This model was adapted in conjunction with methods derived from literature review to develop a data collection strategy.

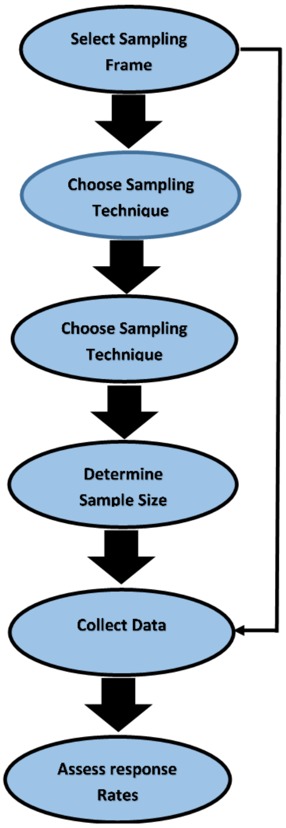


Figure 3.8: Process for selecting a sampling strategy (Taherdoost, 2016)

3.3.1 Identification of target population

According to Taherdoost (2016) the target population should be the entire list of subjects from which a research question arose. A sample is a miniature representation of the population. In this study, the population is defined in terms of the entity that is subjected to impact of explosive munitions. The entire 12 000 hectares of General De La Rey Training Area represents the target population as it was established for the purpose of executing military training with weapons including explosive munitions. No part of the training area is exempt from training exercises as long as necessary safety precautions are met. The soil and water resources of the MTA are identified as the main recipients of contaminants. In the face of changing weapon system technology and training methods in combination with the duration of use, the entire area of the MTA may have at any time or other have been used for training with explosive weapon systems. In Chapter 1 it was indicated that training at General De La Rey Training Area dates back to the end of World War II. This corresponds to more than half a century of usage. It was therefore hypothesised that the entire training area is potentially contaminated with energetic compounds.

Because energetic compounds are persistent in the environment, the assumption was that energetic contamination is potentially uniform throughout the MTA, a basic assumption suggested by Jenkins et al. (2012). It should be noted that the NFA of 1.3 km is only applicable to Artillery systems and that there is an entire spectrum of explosive weapons in use by other formations such as 40mm Multiple Grenade Launchers, Hand Grenades, Rifle Grenades and 60 mm Patrol Mortars that can be operated close to the boundaries of the MTA. Thus, focusing on Artillery systems in the study does not nullify the use of other weapon systems throughout the shooting range. Therefore detection of either type of energetics can be expected at any point within the study area. However, for Artillery weapon systems, propellants are expected to be enriched in higher concentrations at firing points than at impact areas and high explosives will be more concentrated at impact areas than firing positions.

3.3.2 Selection of sampling frame

A sampling frame reduces population to a list of specific subjects under investigation, which are representative of the population (Kabir, 2016; Taherdoost, 2016). Areas selected for sampling correspond to areas commonly used during live firing, thus possibly contaminated. The sampling frame was consistent with Figure 3.2 above. The shown sectors stratify the sectors into Firing Zones and Impact Zones. This does not insinuate non-use of other explosive weapon systems in these zones and intermediate areas. The Artillery system is arbitrarily selected to focus the study and to reduce the complexity of data collection and analysis. Sectors A, C, D, E and H on Figure 3.2 represent Firing Zones and Section B represents the impact area. It is noted that currently used firing positions may have previously been used as target areas and therefore detection of HE residues at firing positions or detection of propellant residues at target areas should not cause confusion. Section F and G are control sample locations for the study, having not been used for military deployments. Samples from these control areas are expected to exhibit the original physicochemical structure of the MTA before it was used for military purposes.

3.3.3 Selection of sampling techniques

Probability sampling and Non-probability sampling are two main techniques used in research where sampling is the preferred method of investigation (Kabir, 2016; Taherdoost, 2016).

Probability sampling is well suited for larger geographical areas and large populations. Using this sampling technique, every member of the dataset has the opportunity of being included in a sample. Non-probability sampling recognises that certain elements will not form part of the population under investigation. Non-probability sampling is inadequate for making statistical inferences in quantitative research and is well suited for smaller populations (Taherdoost, 2016).

Using Probability Sampling, the sampling frame served to separate sample areas within which Random Samples are expected to bear similar characteristics. Any Random Sample obtained from Sector B was expected to bear more HE residues than Propellants. The opposite would be expected at Sector D. Sampling makes statistical inferences to determine hotspot areas of contamination. Statistical inferences rejects Non-probability sampling techniques for the current study, therefore Stratified Random Sampling was preferred (Kabir, 2016).

A Multi-Stage Sampling technique was adopted to eliminate the need to sample the entire sampling frame for each event, significantly reducing the cost of sample analysis. Using this strategy samples decreased in number but increased in size (number of increments). Initially discrete samples were collected throughout the sampling frame and follow up samples were taken in areas affected by firing events. The Multi-Stage Sampling technique allows for the incorporation of Multi Incremental Sampling techniques (MIS). MIS was recommended by Jenkins et al. (2012) and Crockett et al. (1996) for explosive analyses as it averages out heterogeneity of the site with fewer composite samples.

3.3.4 Determination of sample size

Striking a balance between collecting representative samples and obtaining sustainable research results was critical. There were more firing positions than impact areas in the sampling frame. Taking too many samples per section of the frame would result in too many firing point samples and fewer impact area samples. By assuming uniform contamination of the MTA, it was possible to take fewer samples but to sufficiently cover the study area to prove the hypothesis. According to Jenkins et al. (2012) single discrete samples are not suited for exposing contamination distribution. This sampling technique produces a non-Gaussian distribution and a positively skewed distribution. To test this sampling theory the sample size was varied between single discrete samples and MIS. The MIS produces a normal distribution of error, providing better characterisation of sampled locations (Jenkins et al., 2012). Initially three discrete samples were taken for small areas such as Sector D or two sets of three discrete samples for larger sections such as Sector A. Samples were taken at 100 meter intervals focusing obvious targets and probable firing positions. Forty two discrete background firing point samples and 23 discrete background target area samples were obtained during Module X1. Only 6 increment composite samples were taken at OB/OD sites using Jenkins, et al. (2012) Sampling Wheel method. Discrete samples collected at UXO sites were considered random samples.

Sample size was varied with successive firing exercises. Six increment composite samples were collected from 10 m x 5 m grid patterns during the 4 Arty Regt Combat Readiness Exercise. Two composite samples were taken at two firing positions and one at the third position. The same sample size was used at explosion craters using the Sampling Wheel method around explosion craters. Sample radius was 1.5 m for 120 mm Mortars and about 0.5 m for 60 mm Mortars. Three spatially remote craters were sampled. During the 4 Special Forces Regiment Demonstration, one 8 increment background composite sample was taken from a 100 m x 10 m grid at the firing position before the exercise. A 10 m x 5 m grid was used to obtain a 6 increment composite background sample at the target. The demonstration area is small so only one launcher position and one target were sampled. Sixteen increment post firing composite samples were obtained at the launcher position on a 15 m x 15 m square grid and a 13 increment post firing composite was obtained at one explosion crater near the target background sample. During Module X2 samples were collected at all areas sampled during Module X1 but in single 30 increment composites from 30 m x 30 m grids for both firing points and explosion craters. One recent firing point composite and three recent explosion craters were sampled. The samples weighed just over 1 kg as recommended by Jenkins et al. (2012). Samples were collected only after the exercise which was executed over a week. Control point soil samples were also collected using MIS.

Water samples were collected in pairs at all times. One 1 000 ml surface water sample and a pool bottom sample were obtained at each water source except where water was too shallow. A total of 12 water samples were collected during a sampling session. Alternatively, 750 ml glass jars were used when 1 000 ml jars were not available. Sediment was taken along with subsurface samples.

3.4 Data collection process

Due to lack of onsite screening technology, determination of contaminated areas prior to sampling as recommended by Crockett, et al. (1996) was not possible. The knowledge and experience of the author was used to select sampling points. Physical observation of LODs, explosion craters, explosive chunks, UXO and knowledge of frequented deployment/target areas combined with the safety considerations elaborated in Section 3.1 were used to select sample locations. Figure 3.9 approximates sample locations in blue and brown dots. Blue dots represent water samples and brown dots represent soil samples.

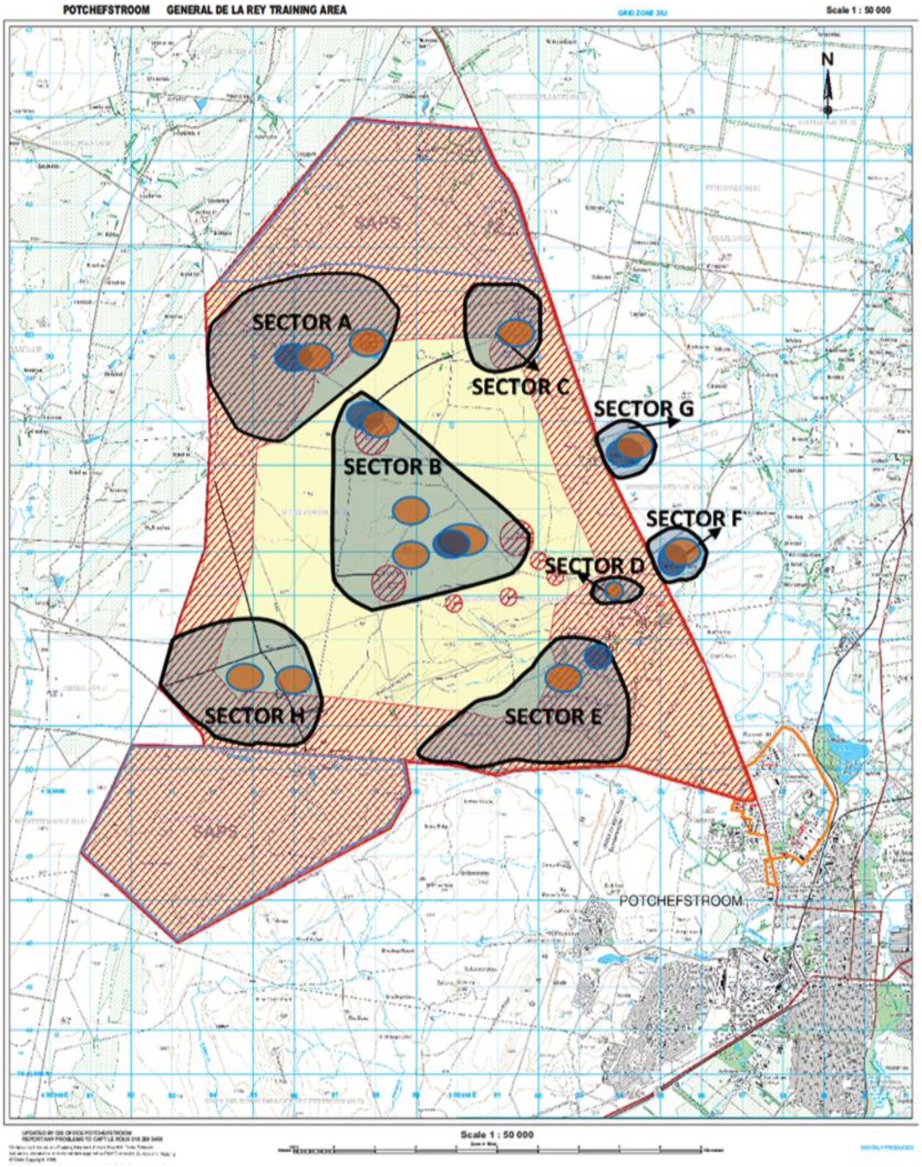


Figure 3.9:..Predetermined sample locations within the sample frame (Mokalapa, 2020)

3.4.1 Collection of soil samples

A total of 133 soil samples were collected. Soil samples were collected in laboratory grade 50 g Teflon screw top centrifuge tubes. A coring device obtained from the NWU was also used to obtain samples within a depth of 5 cm of the surface. Jenkins et al. (2012) suggested that energetic residues accumulate within the top 10 cm of soil surface. Equipment was wiped clean with a damp cloth treated with demineralised water and/or methylated spirit and air dried between samples to prevent cross contamination. Each soil core was obtained using the same technique. All UXO sites were sampled in 6 increment composites using the sampling wheel method (circular pattern) with five increments taken on circumference and one increment at the centre of the wheel. If it was not possible to reach the centre due to risk of disturbing UXO, all increment samples were taken on the inside edge of the danger area. A hand spade was used where the risk of underground UXO existed. The sampling wheel was used at the floor of the burn pit at empty OB/OD sites (Figure 3.10). Composite samples at explosion craters were taken using the sampling wheel method as shown on Figure 3.11, while samples at firing positions were taken on square or rectangular grids (Figures 3.12 and 3.13). Only sample SSB07C3 was taken on a 30 m x 30 m square grid at an explosion crater.

Composite soil samples were mixed in 500 g square plastic containers by emptying 50 g soil cores into the container and shaking the container. Larger samples were mixed in 1 kg containers. Samples were labelled with unique coding designed for the study and stored in a steel container at RWU NW Environmental Office. Coordinates of the sample locations were recorded using Garmin Oregon 750 and Garmin Montana 860, and tabled according to corresponding samples. The aim was to plot the locations on a 1:50 000 map of the study area in ARC GIS at Joint Tactical HQ North West (if the facilities were available).

Figure 3.10: Sampling at UXO areas; (a) soil sample collected at a OB/OD pit in Sector B and (b) sampling at an UXO disposal site near Gonzalespoort Fire break (Imagery: Mokalapa, 2020)

Figure 3.11: Application of the sampling wheel at explosion craters; (a) sampling at 1.5 m radius around an explosion crater and (b) composite sampling at a 60mm Mortar Crater near Gonzalespoort (Imagery: Mokalapa, 2020)

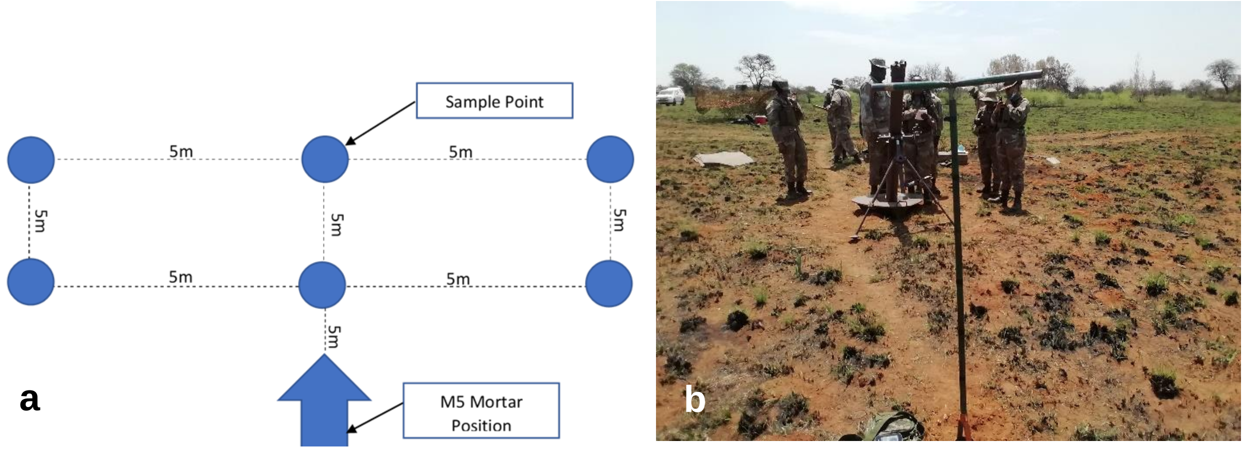


Figure 3.12: Sampling on a rectangular grid for launcher positions; (a) Layout of sampling in front of a 120mm Mortar position. (b) Obtaining a soil core in front of a 120mm Mortar during 4 Arty Regt Combat Readiness exercise (Imagery: Mokalapa, 2020)

Figure 3.13: MIS Sampling on a 15 m x 15 m sampling array at a 107mm MRL Position (Image: Mokalapa, 2020)

3.4.2 Collection of water samples

Four water points were identified for sampling within the MTA (Figure 3.14). Vandalism rendered all MTA boreholes inaccessible for extraction of water samples. The water hole in Sector A is located near the north western section of the MTA underlain by bedrock and holds water all year round. The water point in Sector B is located at an UXO site near Trig Beacon 116 and regularly contain water in the rainy season. It was hypothesised that water collecting in the burn pits will be contaminated with energetics. The third water point in Sector B lies on a marshy area where water accumulates in the wet season. This low lying area between three Trig Beacons serves as a sink for water draining from three surrounding hills forming a small catchment. The tank target on Figure 3.3 above stands in the centre of the marsh. The fourth water point is located in Sector E north of Valkop. This is a small artificial dam of approximately 300 m x 200 m downstream from the two Sector E UXO sites. It holds water throughout the year. Water flowing from the old weapons range was hypothesised to introduce energetics into this marine environment.

Two control water points (Figure 3.15) were located at two neighbouring farms outside the training area. The farm Sweet Cinnamon at Witstinkhoutboom is located in Sector F. Water samples were collected on a bridge between the MTA, at a small dam on the farm and at a borehole located next the farm house. Water from the MTA flows south-east from Sector B through Sector D into the farm and to with Mooi River further east. A borehole on the farm was also sampled. Aadil Farm at Oudedorp north of Sector F also has a borehole and a surface well. No surface flow channel links this farm to the training area. It was hypothesised that underground water systems may be linked and contamination from the MTA may reach groundwater on the farm.

Forty eight samples were collected in 1 000 ml glass jars marked with unique sample coding. One surface sample and one subsurface sample were collected per session. Subsurface samples were collected at pond bottom along with alluvial residues. Where water was too shallow, only one sample was collected. Where water had evaporated after background sampling, alluvial residues were collected and coded as water samples. Initial background samples were collected all water sources. For successive samples, only affected areas were sampled. Water samples from boreholes were taken when access to the farm was possible. Water samples were carried in ice filled cooler bags and stored at 4℃ at NWU's laboratory facilities.

Figure 3.14: Surface water sources in General De La Rey Training Area. The 300m x 200m dam at Sector E (top left). Sampling at the burn pit north of Trig Beacon 116 in Sector B (top right). The waterhole at Sector A (bottom left)and the marshy area at the target area in Sector B (bottom right). (Imagery: Mokalapa, 2020)

Figure 3.15: Water sampling at control areas; (a) sampling at a water pond on Aadil Farm and (b) sampling at a borehole at Sweet Cinnamon Farm (Imagery: Mokalapa, 2020)

3.5 Sample processing

Soil samples were kept at RWU NW Environmental Office and stored at room temperature in a dark room until analysis. Water Samples were kept at North West University Echo Analytica laboratory in a dark cold room at 4℃ until analysis. Soil and water samples were extracted and analysed for explosives using EPA SW 846-Method 8330a High Performance Liquid Chromatography (HPLC) as outlined in US EPA (2007b). Determinations were made using a UV Reverse Phase C-18 and CN Columns. Types and methods of HPLC are described in detail by Banzal et al. (2010). For heavy metal analyses, soil and water samples were extracted and analysed for heavy-metals using EPA SW 846-Method 3051a Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils. Determinations were made using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Method 3051a is detailed in US EPA (1997; 2007a).

3.5.1 Soil sample processing

Out of 181 total samples, 133 were soil samples and 48 water samples. Module X1 of February 2020 yielded 101 samples alone (62 background and 39 post firing). Soil samples were grouped in batches per exercise for analysis. All 74 soil samples for Module X1 were discrete soil samples (54.41% of total soil samples). The 4 Arty Regt exercise yielded 53 samples (39 background and 14 post firing samples). 34 background samples were soil samples of which 28 (20.59% of total soil samples) were discrete and 6 composite. All 8 post firing soil samples were composite. The 5 Special Forces Regiment demonstration produced 4 MIS soil composites (2.94% of total samples). Module X 2 produced a total of 23 samples 13 of which were soil composites (13.79% of total soil samples). This translates to a total of 102 discrete soil samples (75.74% of total soil samples) and

31 soil composites (23.31% of the study). The location of each sample was recorded in field notes with necessary description.

Analysis costs due to number of samples, particularly discrete samples, proved unacceptably high. The objective of sampling was to produce samples representative of the sampling frame. Module X1 yielded the largest number of samples in the study. Analysing only a portion of the samples to cut cost would result in unrepresentative sample coverage of the sample frame. Pooling samples and eliminating redundant samples was chosen as the closest possible solution. Redundant samples, including repeated background samples in areas not affected by firing between exercises were mixed, homogenised and subsampled for analysis as a single sample. As an example, Module X1 discrete background samples were combined with the 8 increment background composite from the 5 Special Forces Regiment exercise as no firing occurred from Sector D between the two exercises. In another instance, discrete background samples from the impact area were selected for analysis according to location to maintain sample coverage of the target area while the other samples were composited according to sub-zones and homogenised. Firing point discrete samples were also reduced by selecting individual samples for analysis as representative of the firing point. This strategy successfully reduced sample volume and analysis cost while ensuring site representatively of the samples.

Sample compositing involved blending samples in 500 g containers using a clean stainless steel Fisher Scoopula, shaking manually for 120 seconds and then sieving through a 2.36 mm Taeuber & Corssen Endecots sieve. The volume was then ground in Mortar and Pestle to homogenise the samples as recommended in Method 8330. The homogenised sample was then spread evenly in a pan and a 50 g multi increment subsample was collected from random areas and depths using the scoopula. Figure 3.16 illustrates the pooled subsamples used for analysis. The remaining sample was emptied in a zip bag for storage and possible later use.

The number of soil samples was reduced to a total of 50 samples. Annexure A details sample count, description and location of the pooled samples. 24 Samples from Module X1 were prepared for analysis (15 background and 9 post firing). For the 4 Arty Regt exercise, samples were collected primarily in 6 increment composites. One composite sample from each firing position and all three post firing samples were included for analysis. This sorting procedure was repeated for the 5 Special Forces exercise and only three MIS samples were considered from the exercise (two post firing samples and one target background sample). Seven MIS samples from Module X2 were also prepared for analysis. These included one sample from Sector F, one from Sector G, two from Sector D and three from engaged targets in Sector B. Heavy metal analysis was performed on 10 soil samples from different exercises and locations. Three were control samples from both control areas, two MTA samples were from UXO OB/OD Sites, three from target areas, one from a firing point and one from alluvial residues of a water sample from Sector E (See Table 3.3). Samples were digested with Microwave Assisted Acid Digestion and their metal content was analysed using Inductively Coupled Plasma Mass Spectrometry.

Figure 3.16: Pooled soil sub-samples in 50g Teflon centrifuge tubes (Image: Mokalapa, 2020)

Table 3.3: Soil Samples for Heavy Metal Analysis

Serial	*Sample Code*	*Location*	*Attribute*	*Description*
1	SSF01	Sector F	Control Sample	Sweet Cinnamon Farm
2	SSF07	Sector F	Control Sample	Sweet Cinnamon, Bridge
3	SSG01	Sector G	Control Sample	Aadil Farm
4	SSA07	Sector A	Firing Point	MRL Target Area
5	SSB07D1	Sector B	Impact Area	120mm Mortar Crater
6	SSB07C3	Sector B	Impact Area	120mm Mortar Crater
7	SSH02X	Sector H	Firing Point	UXO Disposal Site
8	SSB02AX	Sector B	Impact Area	UXO Disposal Site/ OB/OD
9	SSD07	Sector D	Firing Point	120mm Mortar Firing Point
10	SSE07	Sector E	Water Pond	Muddy Sludge

3.5.2 Water sample processing

A total of 48 water samples were collected throughout the study. Most of the samples were from the five prominent water sources in the MTA and control areas. About 23 water samples were collected during Module X1 (18 background and 5 post firing samples), accounting for 47.92% of total water samples. The 4 Arty Regt exercise yielded 11 water samples (5 background and 6 post firing samples), translating to 22.92% of total water samples. No water samples were collected for the 5 Special Forces exercise. Module X2 yielded 10 water samples (22.73% of total water samples). Module X1 contributed almost half the total water samples of the study.

Water samples analysed for heavy metals were selected among the pool of water samples analysed for explosive residues. Ten water samples from the five prominent water sources were selected for heavy metal analysis (See Figure 3.17). These were sub-sampled in 50 g Teflon centrifuge tubes for extraction and analysis. Water samples were not pooled together as was the case with discrete soil samples. Four samples analysed were from control areas (Sector F and Sector G) and six were from the MTA water points (Sectors A, B and E). A balanced mix between background samples and post firing samples was made to accommodate background samples, groundwater samples and surface water samples. The objective was to assess if there was a variation in heavy metal concentrations between MTA and control samples, between soil and water samples and between impact areas and firing positions. Table 3.4 summarises the descriptions of samples selected for heavy metal analysis. For Explosive analysis, an additional ten water samples were selected for explosive compound analysis. Due to the fact that some of the selected samples were common, the total number of water samples analysed for explosive compounds was seventeen. However, in Annexure C, the number of analysed samples is higher, owing to additional samples used in calibration of the HPLC apparatus. This occurred repeatedly as the sensitivity of the system and the accuracy of extraction protocols had to be established.

Figure 3.17: Water sub-samples in 50 g Teflon Tubes (Image: Mokalapa, 2020)

Table 3.4: Water Samples for Heavy Metal Analysis

Serial	*Sample Code*	*Location*	*Attribute*	*Description*
1	WSF03AWL	Sector F	Control Sample	Background, Sweet Cinnamon Dam
2	WSF07AWL	Sector F	Control Sample	Sweet Cinnamon, Bridge
3	WSG01BWL	Sector G	Control Sample	Aadil Farm, Pond
4	WSG07BWL	Sector G	Control Sample	Aadil Farm, Bore Hole
5	WSA01BWL	Sector A	Firing Point	Water Hole
6	WSA07BWL	Sector A	Firing Point	Water Hole
7	WSB01BWL	Sector B	Impact Area	Background, OB/OD Pits
8	WSB07BWL	Sector B	Impact Area	OB/OD Pits
9	WSE01BWL	Sector E	Firing Point	Artificial Dam
10	WSE07BWL	Sector E	Firing Point	Artificial Dam

3.6 Analytical methods and materials

3.6.1 Sample analysis for explosives on HPLC

An Agilent HPLC – 1100 system was used for all explosive analyses (Se Figure 3.18). The instrument was equipped with a Quaternary Pump, a degasser and an Auto-injector. Four samples can be delivered to the injector from four mobile phase reservoirs simultaneously. The mobile phase is fed through a 4.6 mm x 250 mm Reverse Phase Venusil XBP C-8 Column from Agela Technologies. The column packing (stationary phase) consist of 5 µm silica with 100 A pore size. Two mobile phases were prepared. A mobile phase of Methanol: Water 50: 50 (v/v) and one of 95% AcN Water. The 95% Acetonitrile: Water solution is recommended in Method 8330b when HMX is the target analyte. The mobile phases were prepared in 1 000 mL laboratory grade graduated glass bottles labelled A and B. The Methanol Water reservoir is favoured in most analyses as it accommodates a wide range of analytes. The system was flashed at 3 mL/min with mobile phase until a base to noise line was established on the calibration chromatogram before samples were injected.

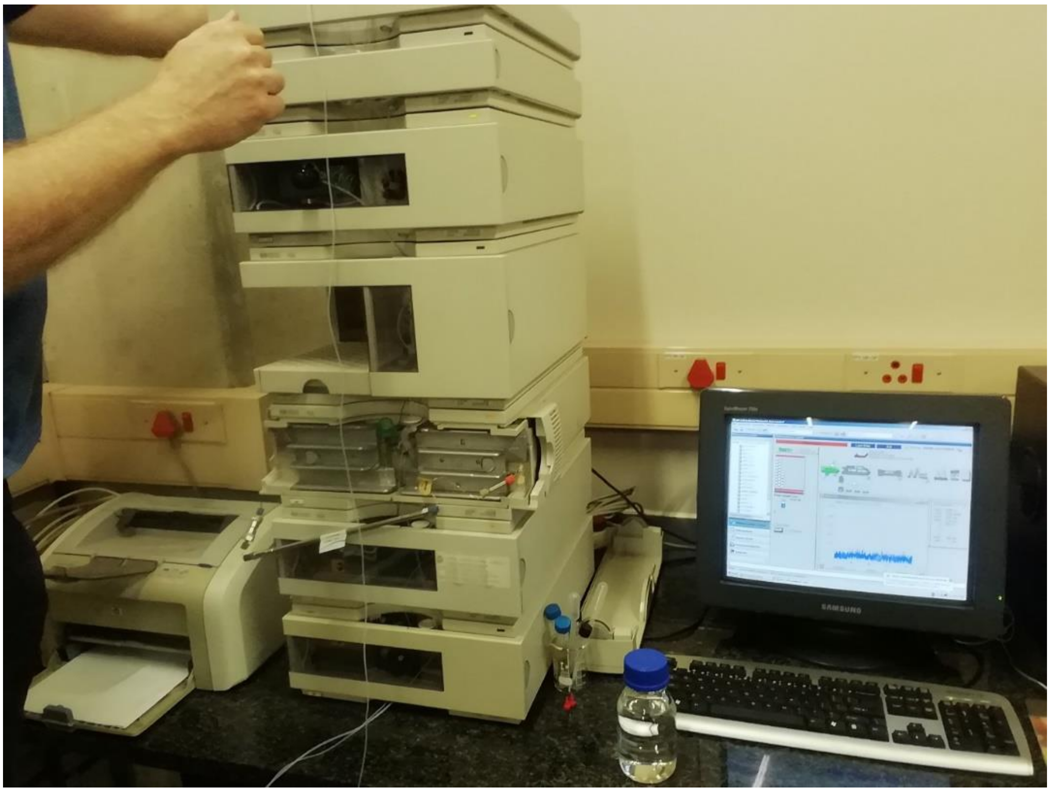


Figure 3.18: Agilent HPLC–1100 UV used for explosive compound analysis (Image: Mokalapa, 2020)

HPLC-RP uses a polar mobile phase, polar analyte and a non-polar stationery phase (Banzal et al., 2010). Injected analytes are separated by polarity as they interact with the stationery phase. Polar analytes elute faster than non-polar analytes. A UV detector maps analyte peak elution times and the wavelengths absorbed by the analytes. Calibrating the system by injecting diluted explosive mixes allows the chromatographer to identify elements by their peak elution times on the chromatograph. The peak represents a time interval during which maximum concentration of the analyte passed through the detector. For reproducible results, analytes are directly injected to a mobile phase and passed through the C-18 Column at 1.0 mL/min. The compounds are separated as they pass through the column based on the intermolecular forces between them and the stationery phase, which determines the speed with which the compounds travel between the ends of the column. The UV detector identifies each explosive compound based on its absorption spectrum and elution time. The detector must be set at wavelengths between 210 nm and 254 nm. The 254 nm was recommended for Method 8330 and was used in this study (US EPA, 2007b).

3.6.1.1 Preparation of primary standards

Certified Reference Materials (CRMs) from Restek (USA) were used for calibration of the HPLC. Certificates of Catalogue No 31450 for preparation of Method 8330 Calibration Mix #1 and Catalogue No 3145 for preparation of Method 8330 Calibration Mix #2 were used as primary standards. Both mixes contained seven explosive mixes each of concentration 1 000 µg/mL Nitroaromatics and Nitramines sealed in 1 mL glass vials (US EPA, 2007b). The fourteen explosive compounds recommended for analysis in Method 8330a are listed on Table 3.5.

The Primary Explosives standards are dissolved in 99% Acetonitrile (AcN). During preparation, the 1 mL glass vials were unsealed and the entire volume of CRMs transferred to airtight glass vials using a 0.25 mL syringe, rinsed five times with AcN between draws. Each explosive mix was sealed in a separate vial. Different syringes were used for Mix #1 and Mix #2. Mix #1 is colourless while Mix #2 is light yellow in colour. The airtight vials were stored in a refrigerator at 4°C in a light reflecting zip bag until used.

Table 3.5: Explosive Compositions in EPA Method 8330 Calibration Standards

Explosive Mix #1	*Explosive Mix #2*
1,3,5 - HMX	Methyl - 2,4,6 - Trinitrophenylnitramine (Tetryl)
1,3,5 - RDX	4-Amino - 2,6 - Dinitrotoluene (ADNT)
1,3,5 - Trinitrobenzene (TNB)	2 m- Amino - 4,6 - Dinitrotoluene (ADNT)
1,3 - Dinitrobenzene (DNB)	2,6 - Dinitrotoluene (DNT)
Nitrobenzene	2 - Nitrotoluene (NT)
2,4,6 - Trinitrotoluene (TNT)	3 - Nitrotoluene (NT)
2,4 - Dinitrotoluene (DNT)	4 - Nitrotoluene

3.6.1.2 Preparation of intermediate standards

The concentration of primary explosives is extremely high and intermediate standards must be prepared for HPLC analyses by diluting small volumes of the primary standards to 1 ppm concentrations. Intermediate standards are used for calibration of HPLC and deriving injection standards by diluting primary standards and injecting the diluted mix or spiking blank samples with dilute explosive mix to determine the system sensitivity and establish detection limits. Intermediate standards are prepared afresh when a period of one month has passed or if they get exposed to direct sunlight. The 1000 µg/mL primary standards were diluted to 1µg/mL with Acetonitrile in a volumetric flask. Simple titration calculations are instrumental in finding the amount of AcN required to dilute a volume of primary standard. The general term;

$$C_1V_1 = C_2V_2 \tag{1}$$

Provides a solution, where C_1 is the known concentration of the mix in the primary standard, V_1 is the unknown volume of the primary standard to be withdrawn, C_2 is the desired known concentration of the intermediate standard and V_2 is the desired known volume of the intermediate standard required. A 25 mL volumetric flask was used to gauge the required volume of intermediate standard. To obtain a 1 ppm mix, 25 µL of primary standard was syringed into the flask. The remaining volume was filled with AcN to the 25 mL mark (Figure 3.19). The same procedure was followed for Mix #1 and Mix #2. A new syringe was used for each dilution.

Figure 3.19:. Preparation of intermediate explosive standards (Image: Mokalapa, 2020)

3.6.1.3 Preparation of working standards

Working standards are also called injection or calibration standards. Concentration of explosives in intermediate standards is determined using equation (1) until HPLC sensitivity and detection limits are established. Working standards are valid for only one day and results were accepted when injected standards or spiked blank samples produced the method signature chromatogram supplied with the standards, and analyte concentrations and retention times on the report match method recommendations. Working standard chromatograms assist in determining method detection limits by comparing measured peak concentrations against injected concentrations. From the 1ppm intermediate standards 10 ppb standards were prepared. About 0.25 µL of the intermediate solution was injected in a new 25 mL volumetric flask and the remaining volume filled with reagent grade water and not AcN. 20 µL of each 10 ppb mix was syringed into injection vials and analysed on HPLC at 1µl/min. Explosive chromatograph peaks were visible but too small for HPLC to resolve individual explosive peaks (figure 3.20). When the injection volume was increased to 50 µl/min, only HMX (3.9 ppb), 1,3,5-TNB (4.4 ppb), RDX (3.4 ppb), and 1,3-DNB (4.6 ppb) were detected (Figure 3.21). The other three peaks were visible at the expected positions but below HPLC resolution.

Adjusting flow rate to 100 µL/min did not improve peak height, but all explosives were detected with increased peak concentration. Detections were in the order 2,4,6-TNT (10 ppb), RDX (9.9 ppb), 1,3,5-TNB (9.8), HMX (9.4), 1,3-DNB (8.8 ppb), NB (7.2 ppb), and 2-ADNT (5.9 ppb). This observation indicates that the entire range of explosives was detectable when a 10 ppb standard was eluted at between 50 µL/min and 100 µL/min. The peaks were significantly improved by increasing the injection standard to 100 ppb at 100 µL/min. Detected concentrations were all above 100 ppb except HMX at 97 ppb. Injecting a 100 ppb standard of Mix #2 at 100 µL/min produced similar results.

To create a composite injection standard, 1 mL of Mix #1 and 1 mL of Mix #2 were mixed in a 10 mL solution of 50% Methanol: Water (v/v). Injecting this standard under the same conditions produced consistent results. All detections were over 100 ppb (average 140 ppb) as seen on Figure 3.22). This observation indicated that the mobile phase eluted faster than the explosive compounds. The retarded flow of analytes through the stationery phase increases the elution concentration of the analytes. Increasing the flow rate does not change the elution sequence but increases the elution concentration and signal strength. Notice that the chromatograms on Figure 3.20 through to Figure 3.22 exhibit similar peak times but different peak heights at increasing with flow rate. All chromatographic information is detailed in Annexure C.

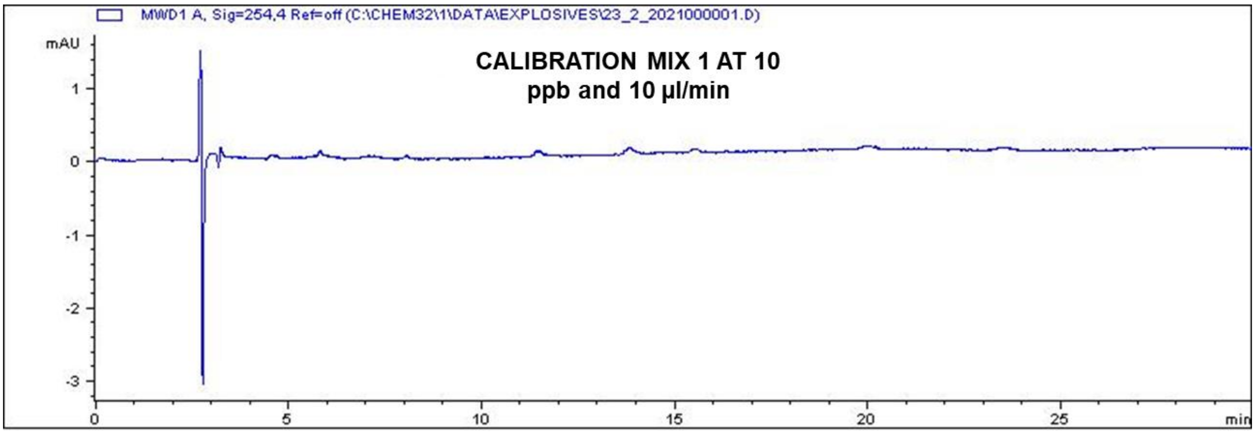


Figure 3.20: Chromatogram of 10 µg/L Explosive Mix #1 at 1 µl/min (Image: Mokalapa, 2020)

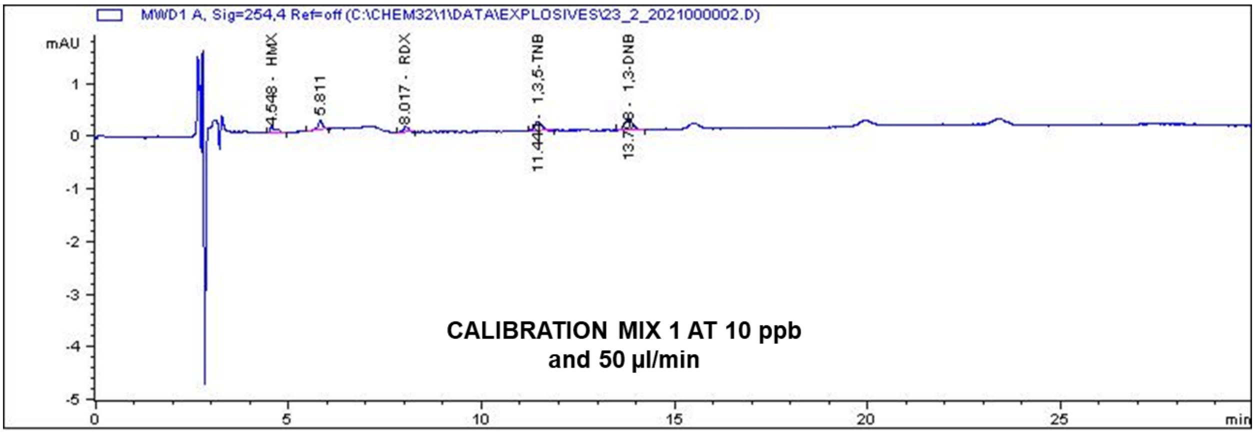


Figure 3.21: Chromatogram of 10 µg/L Explosive MIX #1 at 50µl/min (Image: Mokalapa, 2020)

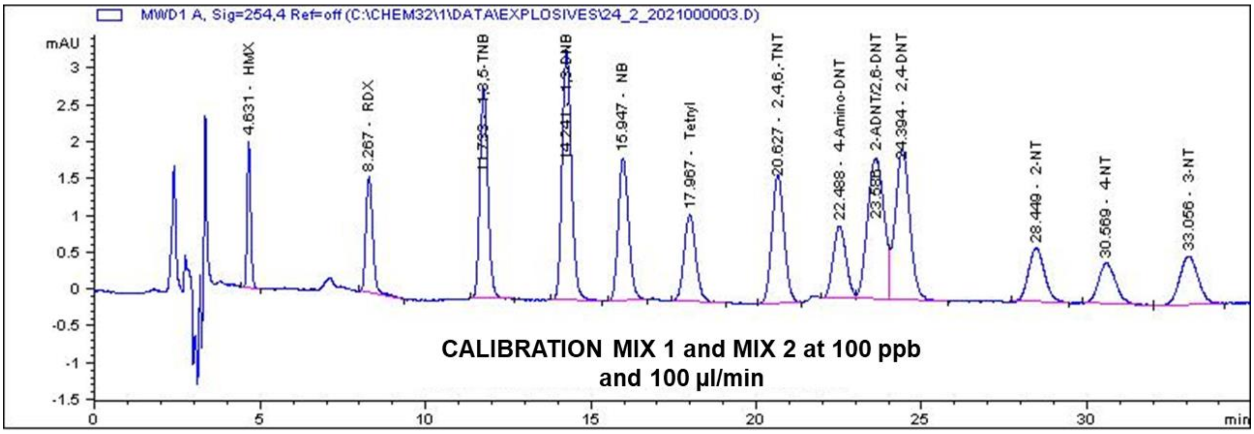


Figure 3.22: Chromatograph of 100 µg/L combined Explosive Mix at 100µl/min (Image: Mokalapa, 2020)

3.6.1.4 Soil sample extraction for explosives

To test HPLC efficiency against field conditions, live samples were extracted and analysed using EPA SW-846 Method 8330a HPLC protocols. Soil samples were passed through a 2.36 mm Taeuber & Corssen Endecots sieve, ground and homogenised with Mortar and Pestle (Figure 3.23). Using a Model HH120 Ohaus digital scale, 2 grams of ground soil sub-sample was weighed in 15 mL Teflon centrifuge tubes. A Dragon 1 000 – 5 000 µL calibrated syringe was used to transfer 5 ml of 95% AcN to the ground material. The tubes were shaken manually by hand for 10 seconds and placed in a Sonorex ultrasonic bath illustrated on Figure 3.24 for 15 minutes, then refrigerated at 4°C for 2 hours, followed by a further 15 minutes of sonication before centrifuge. Ultrasonic bath separates the liquid from solid soil matrix for extraction using a syringe. The 2 mL extracts were filtered into new 15 mL tubes through 0.45 µm Teflon filters. One mL of AcN and 3 mL of

50% Methanol Water were added to the matrix and shaken. The samples were further filtered through a 0.45 µm Teflon membrane into glass vials for analysis in HPLC.

Figure 3.23: A 2.36 mm Taeuber & Corssen sieve and ceramic mortar and pestle (Image: Mokalapa, 2020)

HPLC sensitivity on field samples was tested with three un-spiked soil samples; one control sample from Sector G (SSG01), one sample was from beneath a 155 mm LOD Shell from Sector B and one sample from one Sector B UXO site (LIC 1). These samples were sub-sampled in duplicates for verification of the method. No peaks were observed from all three un-spiked sub-samples. A 155mm duplicate was spiked with 100 ppb of the composite explosive mix. The HPLC produced low signature peaks but concentrations were below detection level. The control blank sample was spiked with a 200 ppb of the composite mix and injected. Signature peaks were clearly observed and explosive concentrations were populated on chromatograph. It was concluded that HPLC could detect explosives in field soil samples and that detected explosive concentration is likely higher than measured by the method. This indicates that concentration of the standard was lowered when introduced to sample matrix, thus detected concentrations on soil samples may be higher than reported, depending of the extraction protocols used.

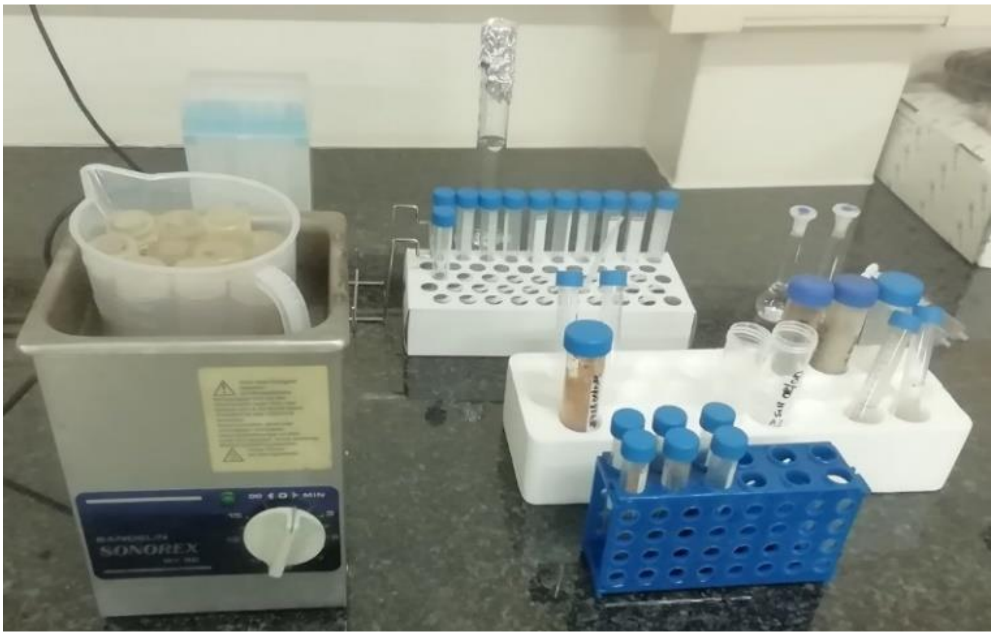


Figure 3.24:Sonorex ultrasonic bath used for soil sample extraction (Imagery: Mokalapa, 2020)

3.6.1.5 Water Sample Extraction for Explosives

HPLC and Solid Phase Extraction (EPA Method 3535) were used for water sample extraction and analysis. Preparation of water samples for HPLC involved multistage filtration of water samples using Solid Phase Extraction (SPE) Manifold and Agilent Sample Preparation Solutions. Filtration removed solid residues and prepared the sample matrix for extraction and analysis. The 1 000 mL samples were shaken and sub-sampled into 50 mL centrifuge tubes and allowed to settle at room temperature. Using a 1 000 mL volumetric flask, a Halden Wanger ceramic funnel (Figure 3.25) and 110 mm diameter glass microfiber filters, settled sub-samples were filtered into the flask one sub-sample at a time. New filters were wet slowly to saturation by initially dripping the sample to prevent sample contents flowing under the filter. A Rocker 410 vacuum pump (Figure 3.26) was connected to the flask and filtration was achieved by applying negative pressure under the filter. The apparatus was rinsed with 99% AcN and de-ionised water between samples.

Filtered samples were decanted into new 50 mL centrifuge tubes. Three samples were used for a test run. The SPE manifold has 20 valves in two rows onto which Agilent Bond Elut LMS cartridges containing the mobile phase can be connected. Three LMS cartridges were attached to valves 1, 3 and 5 and only those valves were opened. The dry packing was pre-treated with 1 mL AcN, which was allowed to drip under gravity, followed by 1 mL of reagent water. Samples were introduced into the cartridges until the centrifuge tubes were empty. Filtered water dripped into an airtight glass container connected to the vacuum pump through a pressure gauge. Rubber seals under the manifold maintain vacuum. Samples SSE07B, SSA07A and SSA07B were used for the test run. Samples dripped at 1-2 mL/min. One mL reagent grade water was injected after each sample. Cartridges were then dried for 1.5 minutes with the vacuum pump. The cartridges were ready for elution. Vial racks supplied with the SPE manifold can hold 14 mL centrifuge tubes. Filtered sample water was decanted and clean centrifuge tubes were loaded on the racks and placed in the jar. The manifold needles now dripped eluent into the tubes (Figure 3.2). Elution was achieved by injecting 2 mL AcN into the cartridges. Eluted samples were dried under a Nitrogen evaporator. The dried residue was reconstituted to 2 mL of 50% Methanol Water. The resulting solution was 25 times the concentration of the analyte in the 50 mL sample. The extracted matrix was injected into 1 mL glass vials for HPLC analysis.

Figure 3.25:A Halden Wanger ceramic funnel on a glass volumetric flask (Image: Mokalapa, 2020)

Figure 3.26:The Rocker 410 vacuum pump connected to the SPE manifold (Image: Mokalapa, 2020)

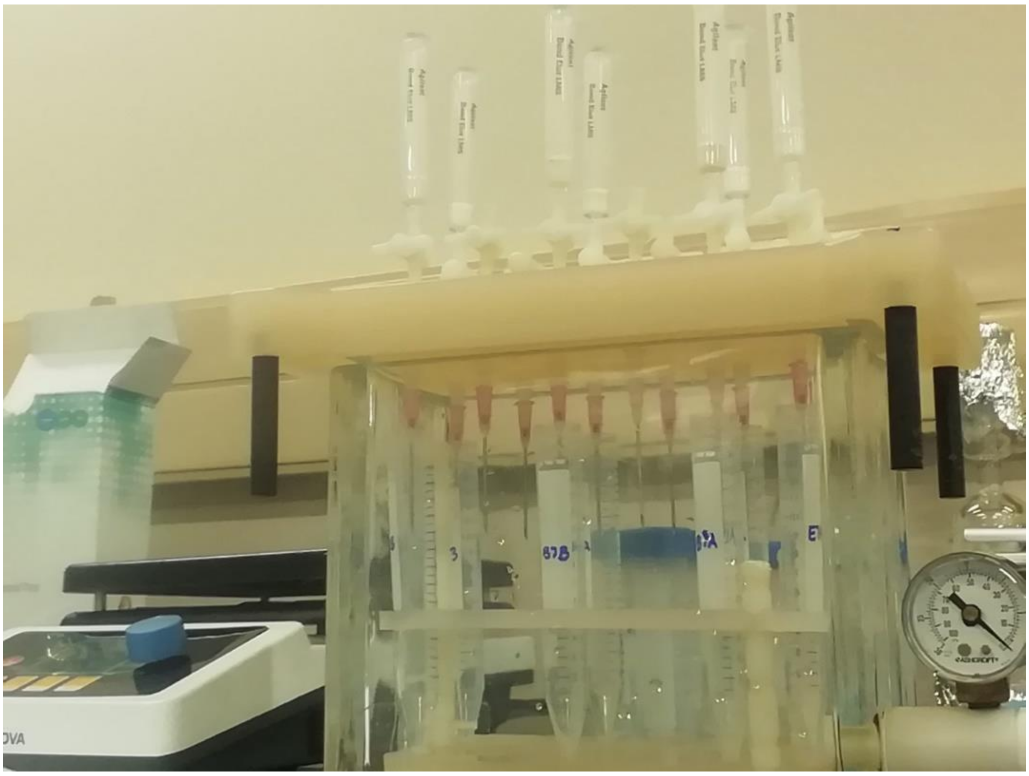


Figure 3.27:.SPE Manifold loaded with seven LMS cartridges (Image: Mokalapa, 2020)

3.6.2 Sample Analysis for heavy metals

3.6.2.1 Soil Sample Extraction and Analysis

The US EPA introduced two methods for soil sample analyses. Both involve extraction by acid digestion of samples (US EPA, 1996; US EPA, 2007a). Conflict exists among authors with regard to the efficiency and authenticity of the protocols used in these methods. One method involves the total digestion of the sample, while the other involves the digestion of only the material bounded to the soil particles, which can otherwise be mobile in the environment. This conflict arises around the understanding of whether total digestion of the sample or washing the elements off the soil particles would be suitable for determining introduced elements in the sample matrix. Method 3050b extracts analytes by addition of concentrated Nitric acid (HNO_3) and Hydrogen Peroxide (H_2O_2) to samples to dissolve all elements present in the sample except those bound by the silicate material in soil particles. HCL is also added if certain metals such as Antimony are target analytes. The extract is then heated and brought to volume for analysis using either Flame Atomic Absorption Spectrometry (FLAA) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Alternatively the extract is analysed using Graphite Furnace Atomic Absorption (GFAA) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Method 3051a, used in this study, also uses continuous addition of strong acids (HNO_3 and HCL) to dissolve most of the environmentally available elements. Method 3051a is similar to Method 3050b except that the acid digestion of the sample in Method 3051a is not total and occur under microwave-heated conditions for a specified period, then allowed to cool and settle before being centrifuged or filtered for determinations using ICP-AES or ICP-MS. In this study ICP-MS was used for analysis.

Samples prepared for explosive analyses were sub-sampled in 50 g Teflon tubes. Sub-samples were already sieved through a 2 mm mesh sieve, homogenized and ground in mortar and pestle. The ground samples were spread on paper trays and left to air dry for 14 days. About 200 mg sub-samples were placed in Teflon centrifuge tubes. A volume of 9 ml of 65% nitric acid (HNO_3) and 3 ml of 32% hydro chloric acid (HCL) were added to the tube. The tube was capped and placed in a Milestone Ethos UP Maxi 44 High Performance Microwave digestion system. A period of 20 minutes allowed the system to reach 1800 MW at a temperature of 200°C which was maintained for 15 minutes. After cooling, the sample was brought up to a final volume of 50 ml and analysed on the Agilent 7500 series ICP-MS (Figure 3.28). This system is optimized for detection of samples requiring ultra-high sensitivity using plasma mass spectrometry. Trace elements as low as 1 part per trillion (ppt) can be measured using this system.

Figure 3.28: Agilent 7500 series Inductively Coupled Plasma Mass Spectrometry (Image: Mokalapa, 2020)

3.6.2.2 Water sample extraction and analysis

While Microwave Assisted Acid Digestion extracts soil samples, this step is not necessary for water samples as they are already in liquid form and analytes are expected to be dissolved or in solution phase. Water Samples were subsampled from the 1000 mL samples analysed for explosives. The samples were shaken vigorously by hand and decanted into 50 mL Teflon centrifuge tubes. Each sub-sample was filtered through a 25 mm x 0.45 micron Clarinet™ Nylon syringe filter manufactured by Agela Technologies to remove solid particulates larger than 0.45 mm. The filtration procedure is an adaptation of EPA SW 846 Method 3051a and 3005a. 1 ml of the filtrate was removed using a Dragon 1000 µg calibrated syringe and placed in a 14 ml centrifuge tube, then diluted to volume with 9 ml of 2% Suprapure Nitric HNO_3 from MERCK. All instruments were pre-cleaned with acid and reagent grade water before use. Analyses were conducted using Agilent 7500CE Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The results were recorded in tabular format per sample, discussed in Chapter 4.

Chapter 4 Results and Data Analysis

4.1 Explosive contamination

4.1.1 Explosive concentration in soil samples

Annexure C exhibits the chromatographic data for all analysed samples. Out of 50 soil samples analysed 16 samples were contaminated with explosive compounds. This translates to 32% of the samples. Six of the samples were contaminated with Tetryl, three were contaminated with 4-Nitrotoluene (NT), four were contaminated with 1,3,5-Trinitrobenzene (TNB), two were contaminated with HMX, one was contaminated with 2,4,6-Trinitrotoluene (TNT), and one was contaminated with 3-Nitrotoluene. Table 4.1 summarizes the contaminated samples and concentrations of detected explosives.

Table 4.1: Explosive compound concentrations in soil samples

SAMPLE CODE	CONTAMINANT	CONCENTRATION (µg/kg)
SSD06	Tetryl	15.342
SSB07D	Tetryl	19.268
SSH01B	1,3,5-TNB	19.268
SSB01B	4-NT	41.826
SSC02	4-NT	46.010
SSA01B	4-NT	18.049
SSF01	3-NT	28.586
SSB02A	HMX	36.588
SSD07B	HMX	60.390
SSB02D1	1,3,5-TNB	5.774
SSE02BX	Tetryl	17.426
SSE02AX	Tetryl	21.061
SSB02DX1	1,3,5-TNB	8.497
SSB02CX2	Tetryl	29.016
SSH02AX	Tetryl	28.020
SSB02EX	1,3,5-TNB	7.997
	2,4,6-TNT	11.728

Most of the contaminated samples were from Sector B, the main target area. The seven contaminated samples accounted for just over 43% of all contaminated samples. Explosives detected were 4-NT, Tetryl, HMX, 1,3,5-TNB and 2,4,6-TNT. Six of the samples contained only one type of explosive and one sample from an UXO site contained two. The highest frequency of occurrence was that of 1,3,5-TNB , appearing in three samples, two of which were from UXO sites. SSB07D contained 12.3 µg/kg of Tetryl, SSB01B contained 41.8 µg/kg of 4-NT, SSB02A contained 36.6 µg/kg of HMX and SSB02D1 contained 5.8 µg/kg of 1,3,5-TNB. Five increment samples from Sub-sector D UXO site (SSB02DX1) and the UXO site at Gonzalespoort Firebreak (SSB02EX) contained 8.5 and 8.0 µg/kg of TNB, respectively. The latter sample also contained 11.7 µg/kg of 24,6-TNT. The highest contamination at a Sector B UXO site was in SSB02CX2, the UXO demolition pits north of OP Tree, at 29 µg/kg of Tetryl.

From Sector A, only the discrete sample SSA01B, was contaminated with 18 µg/kg of 4-NT. This sample was expected to contain no explosive residues. In Sector C, only sample SSC02 measured 46 µg/kg of 4-NT, the highest concentration of the compound in the study. Two samples from Sector D, SSD06 and SSD07B, contained Tetryl at 15.3 µg/kg and HMX at 60.4 µg/kg, respectively. A further two samples from Sector E (SSE02AX and SSE02BX), both from UXO demolition pits, contained Tetryl at 21.1 µg/kg and 17.4 µg/kg, respectively. A control sample from Sector F (SSF01), the farm Sweet Cinnamon, was contaminated with 28.6 µg/kg of 3-NT, the only soil sample detection of the compound in the study. No detection of explosive compounds was found in Sector G soil samples. In Sector H, two samples (SSH01B and SSH02AX), were contaminated with 19.3 µg/kg of 1,3,5-TNB and 28µg/kg of Tetryl, respectively.

Figure 4.1 indicates the concentration distribution of explosive compounds in contaminated soil samples. The sampling codes on the figure are more clearly presented on Table 4.1 and follow sequentially. The range of concentrations was from 5.8 to 60.4 µg/kg. Only three samples had concentrations below 10 µg/kg. All three detections were of 1,3,5-TNB from Sector B, the main impact area. Two of these were from UXO sites. Five samples had explosive concentrations ranging between 10 and 20 µg/kg. Three of the five samples contained Tetryl, one contained 1,3,5-TNB and the other contained 4-NT. Four samples had explosive concentrations between 20 and 30 µg/kg. Three of them contained Tetryl and one contained 3-NT. All samples containing Tetryl in in this concentration range were collected at UXO sites. Only one sample contained explosive concentration between 30 and 40 µg/kg (HMX) and two had concentrations in the range 40 to 50 µg/kg (both contained 4-NT). Only one sample from Sector D had a concentration of HMX of just under 60 µg/kg, the highest concentration of the compound in soil samples. This data indicates that over half of explosive concentrations in samples was below 20 µg/kg. Detections in this concentration bracket were dominated by Tetryl and 1,3,5-TNB.

A review of cumulative concentrations per type of explosive compound (Figure 4.2) indicates that Tetryl, HMX and 4-NT had the highest cumulative concentrations at 114.7 µg/kg, 97 µg/kg and

105.9 µg/kg, respectively. 2,4,6-TNT had the lowest cumulative concentration at 11.7 µg/kg, followed by 3-NT at 28,6 µg/kg and 1,3,5 TNB at 41.5 µg/kg. Despite a high frequency of detection, TNB concentrations were generally low relative to 4-NT, which had low frequency of detection but had high concentration per sample.

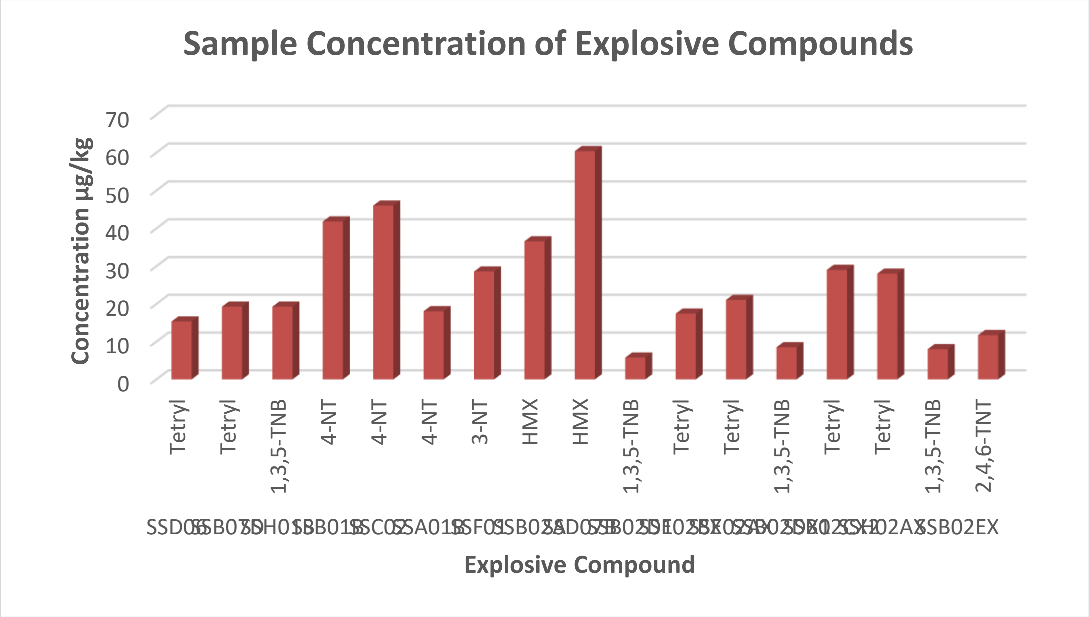


Figure 4.1: Explosive compound concentrations in soil samples

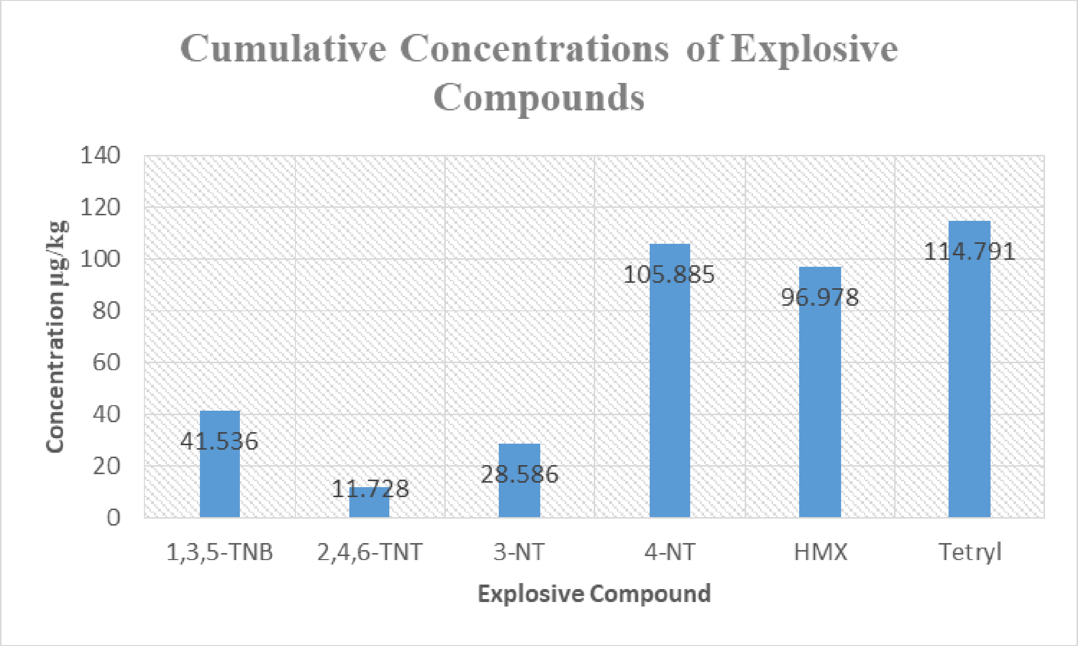


Figure 4.2: Cumulative explosive compound concentrations in soil samples

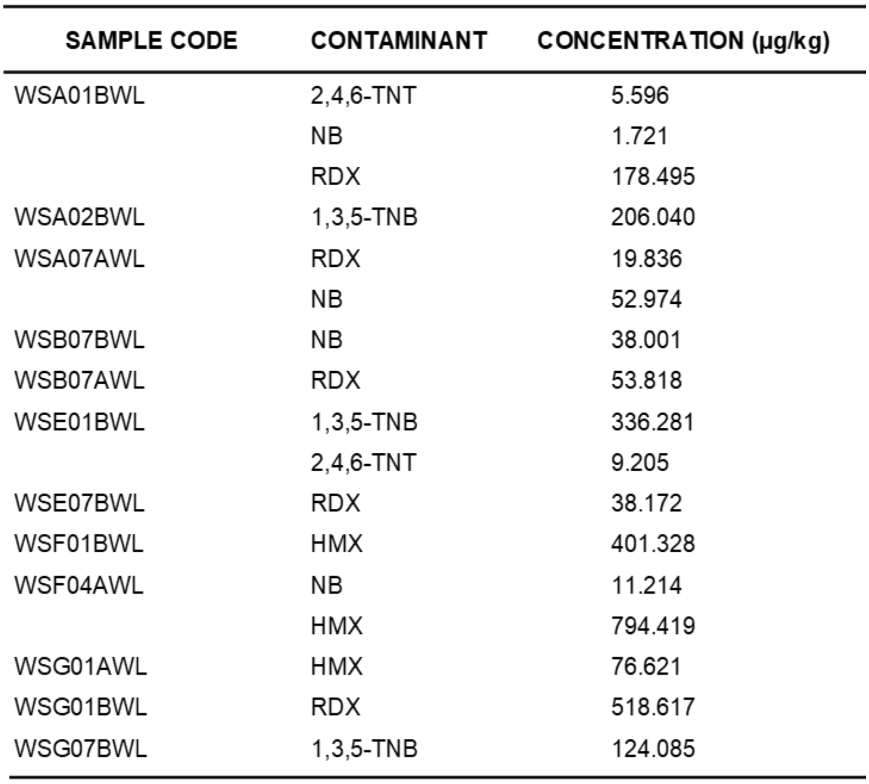
4.1.2 Explosive concentration in water samples

Twenty water samples were analysed in HPLC using US EPA Method 8330a. Twelve of the samples tested positive for at least one explosive compound. This translates to 60% of the analysed samples. The highest frequency of explosive detections was of RDX which was in five water samples (WSA01BWL, WSA02BWL, WSG01BWL, WSA07AWL and WSE07BWL). NB had the second highest frequency of detection and was detected in four samples (WSB07BWL, WSA07AWL, WSB07AWL and WSA01BWL). 2,4,6-TNT was detected in two samples (WSA01BWL and WSE01BWL). 1,3,5-TNB was detected in samples WSG07BWL, WSA02BWL and WSE02BWL. HMX was detected in samples WSF04AWL, WSF01BWL and WSG01AWL. All detections of HMX were in control areas including an underground water sample from Sector G. 3-NT, 4-NT, and 2-NT were not detected in water samples. No other explosive compounds were detected in the analysed water samples.

Table 4.2 exhibits concentrations of the detected compounds. All types of explosive compounds detected in water samples were present in samples from Sector A. Three samples from Sector A water pond, two obtained before and after Module X1 and the other a year later, were contaminated with an assortment of explosive compounds. The Module X1 background sample (WAS01BWL) contained more explosive compounds than the post-firing sample (WSA02BWL). 2,4,6-TNT was detected at 5.6 µg/kg, NB at 1.7 µg/kg and RDX at 178.6 µg/kg in the background sample. The post firing sample contained only 1,3,5-TNB at 206 µg/kg and none of the other compounds detected in the background sample. Both samples were collected within feet of each other using the same method. The third sample (WSA07AWL) was collected during Module X2 at the pond surface when the water level lower. The sample contained RDX at 19.8 µg/kg and NB at 53 µg/kg.

Two water samples from Sector B collected in the same pond on the same day, one surface (WSB07AWL) and one sub-surface (WSB07BWL) were found contaminated with RDX at 53.8 µg/kg and NB at 38 µg/kg, respectively. RDX was not detectable in sediments at this pond, unlike in Sector A. All analysed Sector E samples were collected at sub-surface including sediment. Two explosive compounds detected in WSE01BWL were 1,3,5-TNB at 336.3 µg/kg and 2,4,6-TNT at 9.2 µg/kg. This result was consistent with observations from Sector A samples, suggesting that 2,4,6-TNT concentrations may have been higher but have metabolized to 1,3,5-TNB due to degradation, resulting in elevated concentration of 2,4,6-TNB and less 2,4,6-TNT. Conversely, RDX was the only explosive compound detected in the sub-surface sample of the same pond a year later at 38.2 µg/kg.

Table 4.2: Explosive compound concentrations in water samples



SAMPLE CODE	CONTAMINANT	CONCENTRATION (µg/kg)
WSA01BWL	2,4,6-TNT	5.596
	NB	1.721
	RDX	178.495
WSA02BWL	1,3,5-TNB	206.040
WSA07AWL	RDX	19.836
	NB	52.974
WSB07BWL	NB	38.001
WSB07AWL	RDX	53.818
WSE01BWL	1,3,5-TNB	336.281
	2,4,6-TNT	9.205
WSE07BWL	RDX	38.172
WSF01BWL	HMX	401.328
WSF04AWL	NB	11.214
	HMX	794.419
WSG01AWL	HMX	76.621
WSG01BWL	RDX	518.617
WSG07BWL	1,3,5-TNB	124.085

Six samples from control areas were contaminated with explosive compounds. WSF01BWL contained 401.3 µg/kg of HMX. The sample was collected at the bridge connecting General De La Rey Training Area with the farm Sweet Cinnamon. This was the second highest concentration of HMX in the study. The highest concentration of HMX was in sample WSF04AWL at 794.4 µg/kg at a dam located in the farm. The sample also contained 11.2 µg/kg of NB. These observations suggest that explosive compounds may have reached neighbouring area from the MTA. No contamination was detected in borehole samples from Sweet Cinnamon farm. Three Samples from Aadil Farm to the north were contaminated with HMX, RDX and 1,3,5-TNB. Two of the pond samples (WSG01AWL and WSG01BWL) collected on the same day contained HMX at 76.6 µg/kg and RDX at 518.6 µg/kg, respectively. RDX was detected in a subsurface sample while HMX was detected in a surface sample. The RDX concentration was the highest in the study. No water seeps connect Aadil Farm with the MTA, thus it is suspected that contamination could be from groundwater. WSG07BWL was collected from a borehole at this farm and contained 124 µg/kg of 1,3,5-TNB. This observation invokes the suspicion that explosives may be present in groundwater and may reach outlying areas via rising and falling water table.

Graphical representation of individual water sample detections is shown in Figure 4.3. The sampling codes on the figure are more clearly presented on Table 4.2 and follow sequentially.

Comparison between soil and water samples revealed that explosive concentrations in water samples were generally higher than in soil samples. For the same number of detections observed in both soil and water samples, all soil sample detections were below 100 µg/kg while several water samples contained significantly high concentrations of explosive compounds. Ten out of 17 detections in water samples were below 100 µg/kg. Four detections were in concentrations between 100 µg/kg and 400 µg/kg. Three of these were of 1,3,5-TNB in Sector A, Sector E and Sector G. The other detection was of RDX in Sector A. Three explosive detections were between 400 µg/kg and 800 µg/kg. Two detections of HMX in Sector F and one of RDX in Sector G. The majority of water samples containing very high concentrations of explosive compounds were from control samples, suggesting significant mobility of these compounds. HMX, RDX and 1,3,5-TNB were the most highly enriched explosive compounds in water resources sampled.

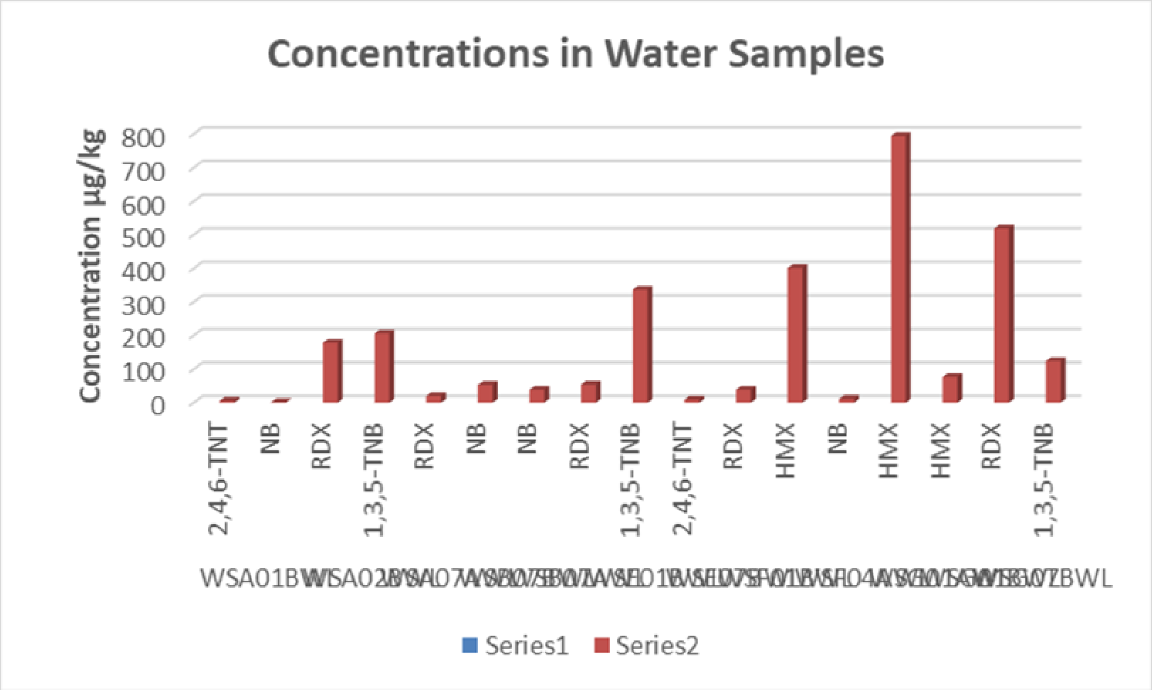
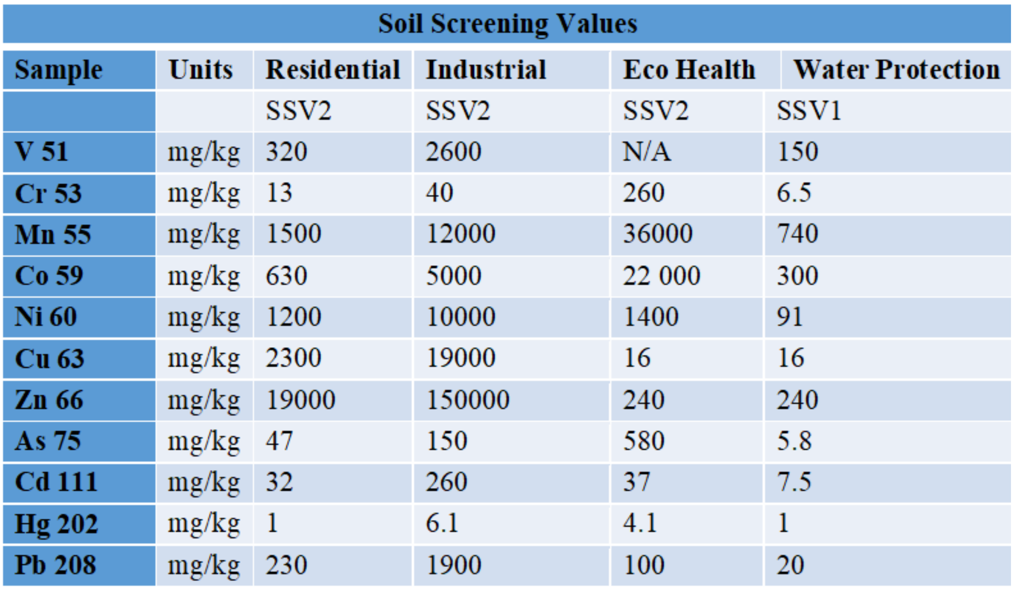


Figure 4.3: Explosive compound concentrations in water samples

4.2 Heavy metal contamination

Heavy metals are non-volatile or only volatile in minute quantities and have high potential for bioaccumulation in soils more than in water resources (Su et al., 2014; Tangahu et al., 2011). Heavy metals in water ponds may settle and accumulate in soil sediments or carried downstream in water courses. Soil and water samples were collected and analysed for heavy metals. Results are comparable to existing Soil Screening Values (Table 4.3) available in the National Environmental Management Act (NEMA): Waste Act (Act No. 59 of 2008) and water sample results were compared with the World Health Organisation (WHO) Guidelines and literary sources (Su et al., 2014; Tchounwou et al., 2012). Eleven heavy metals have been identified by (NEMA, 2008) as environmentally hazardous heavy metals (Fe, Co, Zn, As, Pb, Hg, Ni, Cu, Mn, Cr and V). Concentration limits were established above which remediation will be required. Soil Screening Values are divided into two categories. The SSV2 include limits for Residential, Industrial and Ecosystem Protection. SSV1, which is also the most sensitive category, is for water protection. SSV1 was selected for all analyses in this study due to the fact that the study area is also sanctuary to Tops wild life species and sensitive vegetation, therefore protection of water resources is critical.

Table 4.3: National Soil Screening Values for toxic heavy metals in South Africa (Adaptation of NEMA, 2008)

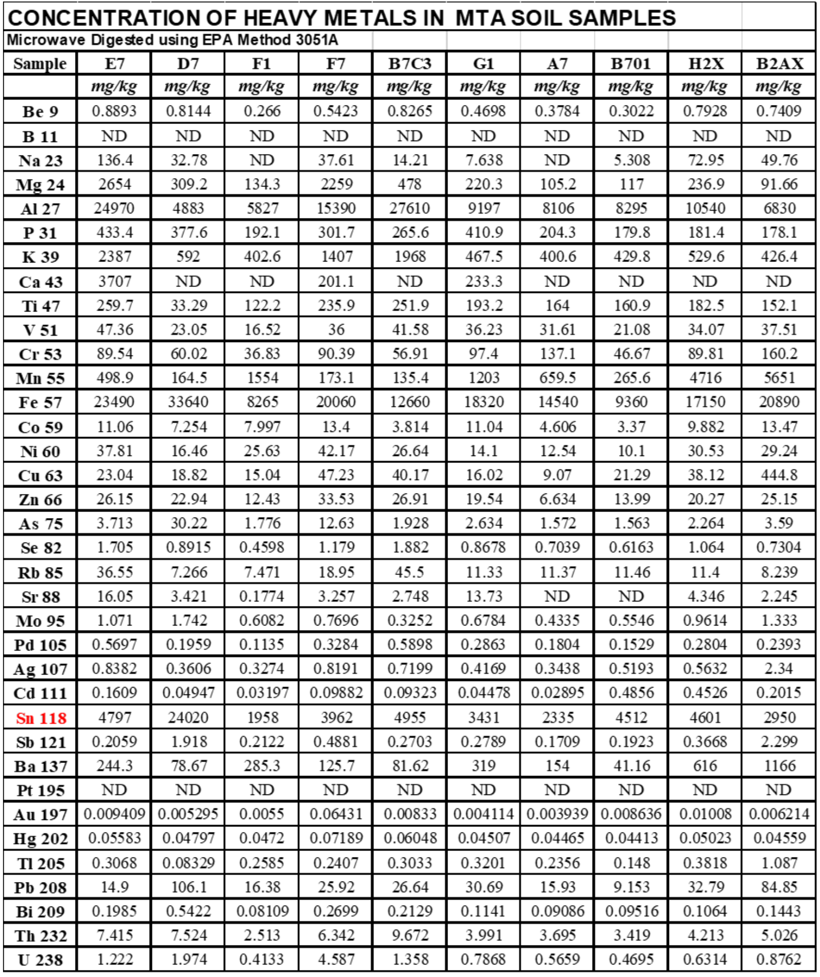


Soil Screening Values					
Sample	**Units**	**Residential**	**Industrial**	**Eco Health**	**Water Protection**
		SSV2	SSV2	SSV2	SSV1
V 51	mg/kg	320	2600	N/A	150
Cr 53	mg/kg	13	40	260	6.5
Mn 55	mg/kg	1500	12000	36000	740
Co 59	mg/kg	630	5000	22 000	300
Ni 60	mg/kg	1200	10000	1400	91
Cu 63	mg/kg	2300	19000	16	16
Zn 66	mg/kg	19000	150000	240	240
As 75	mg/kg	47	150	580	5.8
Cd 111	mg/kg	32	260	37	7.5
Hg 202	mg/kg	1	6.1	4.1	1
Pb 208	mg/kg	230	1900	100	20

4.2.1 Heavy metals in soil samples

Table 4.4 provides concentrations of 36 heavy metals from ten soil samples analysed using Environmental Protection Act (EPA) Method 3051a. Table 4.5 includes only the heavy metals of concern listed in the NEMA Waste Act. Table 4.6 includes control samples and their average concentrations. Several elements, such as Mg, Al, Fe and Sn, were detected in significantly high concentrations, mostly above 1000 mg/kg and some in the order of 10 000 mg/kg. These elements are not listed in the Soil Screening Values and WHO Guidelines as environmentally hazardous, potentially due to their naturally high background concentrations. Control samples were separated from MTA samples and individual element concentrations were averaged out in order to obtain a reference value representative of the control samples. Detections from field samples were compared with SSV1 (NEMA, 2018), other literary sources (Su et al., 2014; Tchounwou et al., 2012; WHO, 2017) Guidelines. The extent of environmental risk was determined by calculating Enrichment Factor (EF) and Geo-accumulation Index (Igeo) of each element per sample site to determine if remediation was necessary for the sampled areas.

Table 4.4: Concentrations of 36 heavy metals from ten soil samples

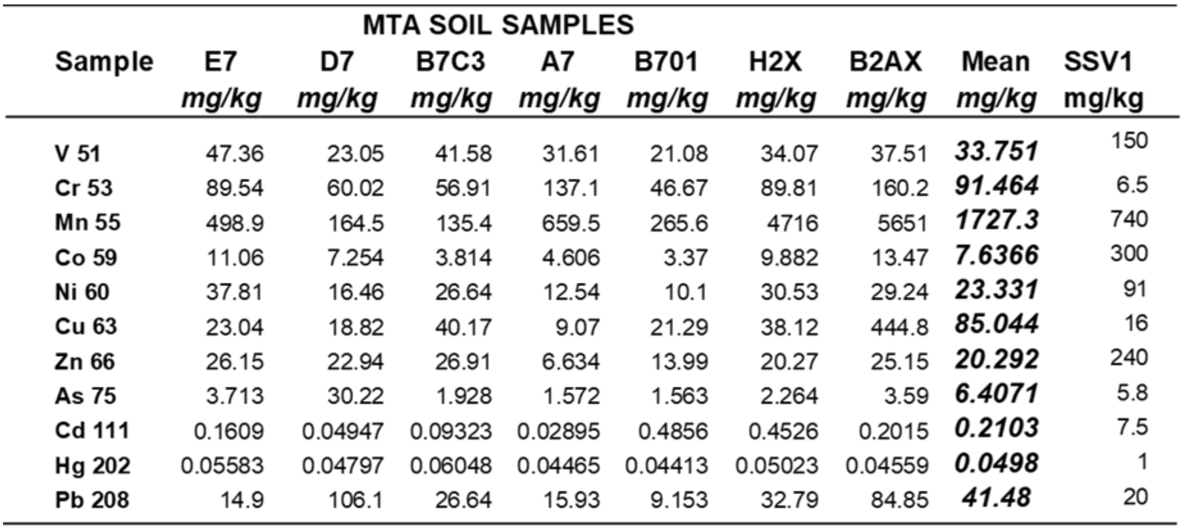


CONCENTRATION OF HEAVY METALS IN MTA SOIL SAMPLES

Microwave Digested using EPA Method 3051A

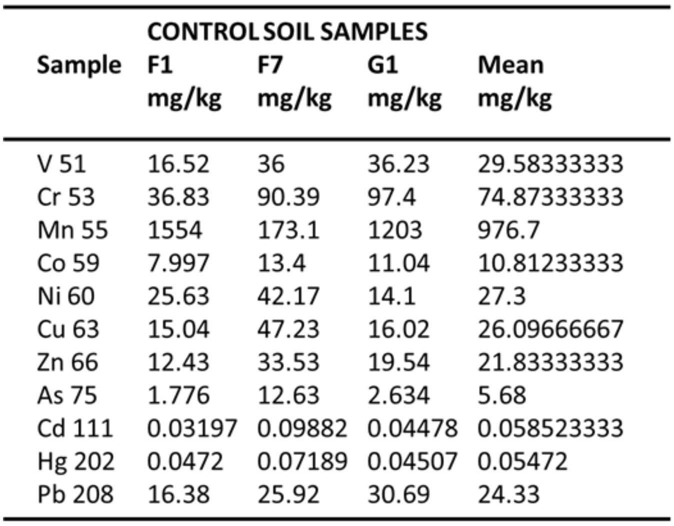
Sample	**E7**	**D7**	**F1**	**F7**	**B7C3**	**G1**	**A7**	**B701**	**H2X**	**B2AX**
	mg/kg	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*
Be 9	0.8893	0.8144	0.266	0.5423	0.8265	0.4698	0.3784	0.3022	0.7928	0.7409
B 11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Na 23	136.4	32.78	ND	37.61	14.21	7.638	ND	5.308	72.95	49.76
Mg 24	2654	309.2	134.3	2259	478	220.3	105.2	117	236.9	91.66
Al 27	24970	4883	5827	15390	27610	9197	8106	8295	10540	6830
P 31	433.4	377.6	192.1	301.7	265.6	410.9	204.3	179.8	181.4	178.1
K 39	2387	592	402.6	1407	1968	467.5	400.6	429.8	529.6	426.4
Ca 43	3707	ND	ND	201.1	ND	233.3	ND	ND	ND	ND
Ti 47	259.7	33.29	122.2	235.9	251.9	193.2	164	160.9	182.5	152.1
V 51	47.36	23.05	16.52	36	41.58	36.23	31.61	21.08	34.07	37.51
Cr 53	89.54	60.02	36.83	90.39	56.91	97.4	137.1	46.67	89.81	160.2
Mn 55	498.9	164.5	1554	173.1	135.4	1203	659.5	265.6	4716	5651
Fe 57	23490	33640	8265	20060	12660	18320	14540	9360	17150	20890
Co 59	11.06	7.254	7.997	13.4	3.814	11.04	4.606	3.37	9.882	13.47
Ni 60	37.81	16.46	25.63	42.17	26.64	14.1	12.54	10.1	30.53	29.24
Cu 63	23.04	18.82	15.04	47.23	40.17	16.02	9.07	21.29	38.12	444.8
Zn 66	26.15	22.94	12.43	33.53	26.91	19.54	6.634	13.99	20.27	25.15
As 75	3.713	30.22	1.776	12.63	1.928	2.634	1.572	1.563	2.264	3.59
Se 82	1.705	0.8915	0.4598	1.179	1.882	0.8678	0.7039	0.6163	1.064	0.7304
Rb 85	36.55	7.266	7.471	18.95	45.5	11.33	11.37	11.46	11.4	8.239
Sr 88	16.05	3.421	0.1774	3.257	2.748	13.73	ND	ND	4.346	2.245
Mo 95	1.071	1.742	0.6082	0.7696	0.3252	0.6784	0.4335	0.5546	0.9614	1.333
Pd 105	0.5697	0.1959	0.1135	0.3284	0.5898	0.2863	0.1804	0.1529	0.2804	0.2393
Ag 107	0.8382	0.3606	0.3274	0.8191	0.7199	0.4169	0.3438	0.5193	0.5632	2.34
Cd 111	0.1609	0.04947	0.03197	0.09882	0.09323	0.04478	0.02895	0.4856	0.4526	0.2015
Sn 118	4797	24020	1958	3962	4955	3431	2335	4512	4601	2950
Sb 121	0.2059	1.918	0.2122	0.4881	0.2703	0.2789	0.1709	0.1923	0.3668	2.299
Ba 137	244.3	78.67	285.3	125.7	81.62	319	154	41.16	616	1166
Pt 195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Au 197	0.009409	0.005295	0.0055	0.06431	0.00833	0.004114	0.003939	0.008636	0.01008	0.006214
Hg 202	0.05583	0.04797	0.0472	0.07189	0.06048	0.04507	0.04465	0.04413	0.05023	0.04559
Tl 205	0.3068	0.08329	0.2585	0.2407	0.3033	0.3201	0.2356	0.148	0.3818	1.087
Pb 208	14.9	106.1	16.38	25.92	26.64	30.69	15.93	9.153	32.79	84.85
Bi 209	0.1985	0.5422	0.08109	0.2699	0.2129	0.1141	0.09086	0.09516	0.1064	0.1443
Th 232	7.415	7.524	2.513	6.342	9.672	3.991	3.695	3.419	4.213	5.026
U 238	1.222	1.974	0.4133	4.587	1.358	0.7868	0.5659	0.4695	0.6314	0.8762

Table 4.5: Heavy Metal concentrations in MTA vs. Soil Screening Values



	MTA SOIL SAMPLES								
Sample	E7 *mg/kg*	D7 *mg/kg*	B7C3 *mg/kg*	A7 *mg/kg*	B701 *mg/kg*	H2X *mg/kg*	B2AX *mg/kg*	Mean *mg/kg*	SSV1 *mg/kg*
V 51	47.36	23.05	41.58	31.61	21.08	34.07	37.51	***33.751***	150
Cr 53	89.54	60.02	56.91	137.1	46.67	89.81	160.2	***91.464***	6.5
Mn 55	498.9	164.5	135.4	659.5	265.6	4716	5651	***1727.3***	740
Co 59	11.06	7.254	3.814	4.606	3.37	9.882	13.47	***7.6366***	300
Ni 60	37.81	16.46	26.64	12.54	10.1	30.53	29.24	***23.331***	91
Cu 63	23.04	18.82	40.17	9.07	21.29	38.12	444.8	***85.044***	16
Zn 66	26.15	22.94	26.91	6.634	13.99	20.27	25.15	***20.292***	240
As 75	3.713	30.22	1.928	1.572	1.563	2.264	3.59	***6.4071***	5.8
Cd 111	0.1609	0.04947	0.09323	0.02895	0.4856	0.4526	0.2015	***0.2103***	7.5
Hg 202	0.05583	0.04797	0.06048	0.04465	0.04413	0.05023	0.04559	***0.0498***	1
Pb 208	14.9	106.1	26.64	15.93	9.153	32.79	84.85	***41.48***	20

Table 4.6: Background values obtained from control samples



	CONTROL SOIL SAMPLES			
Sample	F1 mg/kg	F7 mg/kg	G1 mg/kg	Mean mg/kg
V 51	16.52	36	36.23	29.58333333
Cr 53	36.83	90.39	97.4	74.87333333
Mn 55	1554	173.1	1203	976.7
Co 59	7.997	13.4	11.04	10.81233333
Ni 60	25.63	42.17	14.1	27.3
Cu 63	15.04	47.23	16.02	26.09666667
Zn 66	12.43	33.53	19.54	21.83333333
As 75	1.776	12.63	2.634	5.68
Cd 111	0.03197	0.09882	0.04478	0.058523333
Hg 202	0.0472	0.07189	0.04507	0.05472
Pb 208	16.38	25.92	30.69	24.33

Detected Vanadium (V) concentration was below NEMA in all seven-field samples. Concentrations of Vanadium were in the range 21.08 to 47.36 mg/kg in MTA samples with an average of 33.75 mg/kg. This was slightly above control point average of 29.58 mg/kg but well below the allowable national limit of 150 mg/kg. Chromium detections in the MTA ranged between 46.67 and 160.2 mg/kg. Average concentration of Cr in the MTA was 91.46 mg/kg, which was slightly higher than the control point average of 74.87 mg/kg. Cr concentrations were much higher than NEMA, (2008) recommendation of 6.5 mg/kg. Literary sources indicate that a concentration of 100 mg/kg is normal for soil media. Manganese (Mn) concentrations in MTA ranged from 135.4 to 5651 mg/kg. Four of the samples contained concentrations below the legal limit of 740 mg/kg. Samples from UXO sites (H2X and B2AX) measured 4716 and 5651 mg/kg, respectively, resulting in average MTA concentration of 1727.3 mg/kg. This average is also higher than control background concentration of 976.7 mg/kg. This observation suggest that Mn occurs in higher concentrations at UXO sites and that the local environment already exhibits high Mn concentrations.

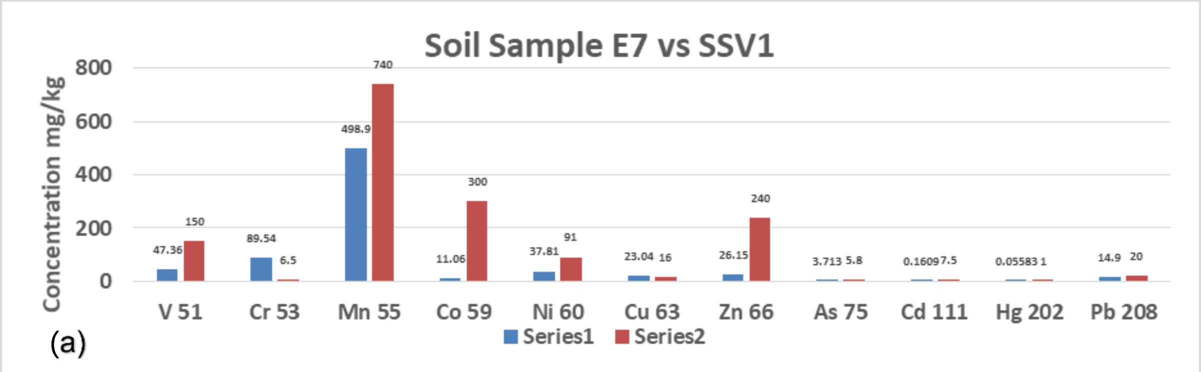
Cobalt (Co) concentrations were significantly lower than the legal limit of 300 mg/kg in all ten samples. Cobalt concentrations ranged from 3.37 to 13.47 mg/kg for MTA samples with average concentration of 7.64 mg/kg. This is lower than control concentration of 10.81 mg/kg. Another element that was found with lower MTA average concentrations than control average was Nickel (Ni) with concentration range of 10.1 to 37.81 mg/kg and average concentration of 23.33 mg/kg, which is lower than control average of 27.3 mg/kg. Both are much lower than the national limit of 91 mg/kg.

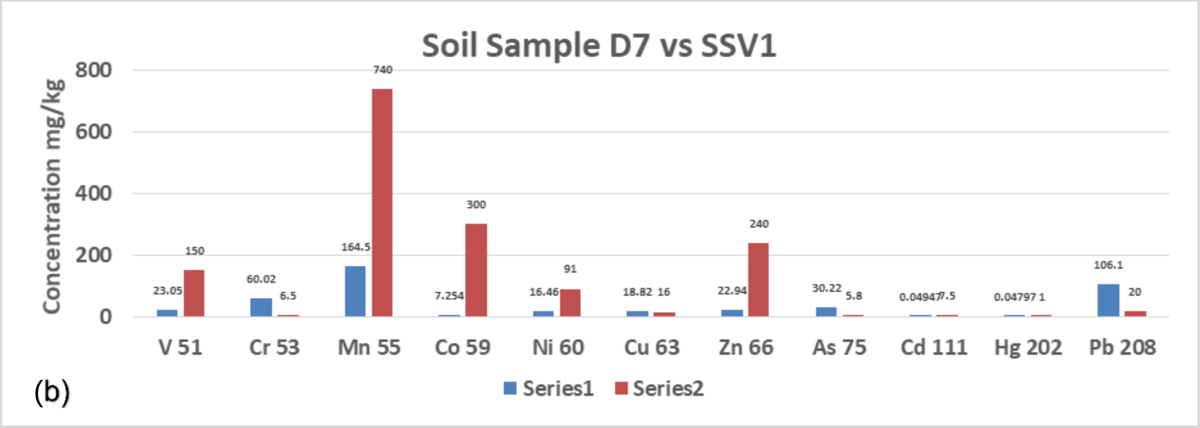
Average concentration of Copper (Cu) in the MTA was 85.04 mg/kg, with concentration range from 9.07 to 444.80 mg/kg and which is higher than control average of 26.1 mg/kg. The higher average MTA value is associated with a single detection of 444.8 mg/kg at an UXO site (B2AX). More than 80 percent of Cu concentrations in both control and MTA samples were above the legal limit of 16 mg/kg. All concentrations of Zinc (Zn) in both MTA and control sites were significantly below the legal limit 240 mg/kg. MTA concentration of Zn ranged from 6.63 to 26.91 mg/kg with an average of 20.29 mg/kg. The highest concentration of Zn was 33.53 mg/kg detected in a control point sample. Control average concentration of Zn was higher than MTA average.

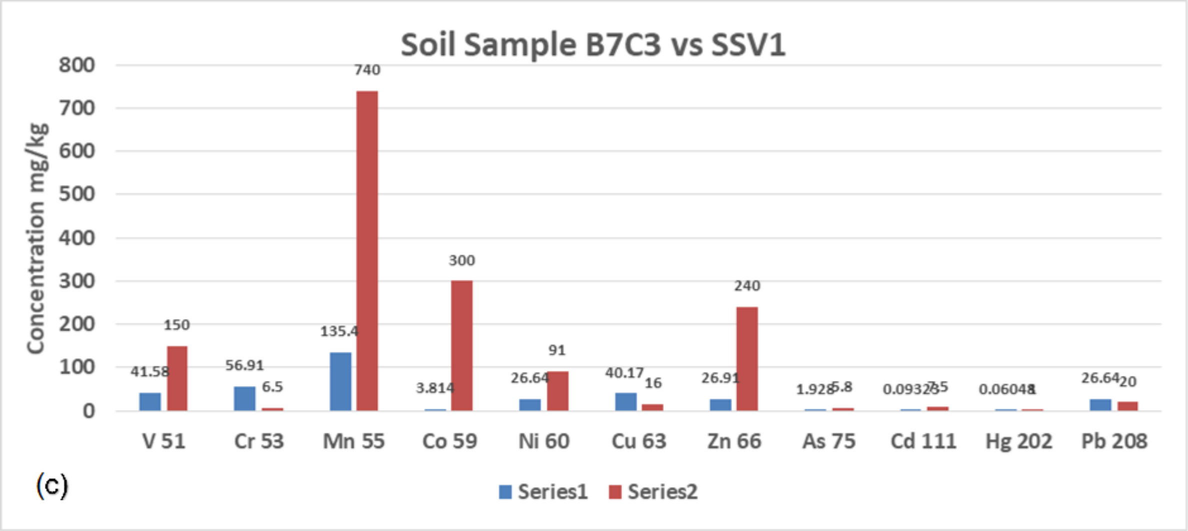
Arsenic (As) in both MTA and control sites was nearly equal to the legal limit of 5.8 mg/kg. As concentrations ranged from 1.56 to 30.22 mg/kg at the MTA with concentration of 6.41. Reference concentration was 5.68 mg/kg. Sample D7 measured 30.22 mg/kg, which suggests that the firing point at Leerdagstelling contained about five times the legal limit and directly affected the average concentration value. Sample F7 also measured twice the legal limit of As at 12.63 mg/kg. All Cadmium (Cd) concentrations were well below the legal limit of 7.5 mg/kg in both control and MTA samples. Cd concentrations ranged from 0.03 to 0.49 mg/kg and an MTA average of 0.21 mg/kg. Cd concentration in MTA was higher that control concentration of 0.06 mg/kg.

Mercury (Hg) detections were almost equal between MTA and control area at averages 0.05 and 0.06 mg/kg, respectively. MTA concentration ranged from 0.04 to 0.06 mg.kg. The legal detection limit of Hg is 1 mg/kg. Hg concentration in MTA was less that the reference concentration. There was low variability in concentrations of MTA and control Hg concentrations. For this reason, Hg was used as a normalization element in EF calculations. Lead (Pb) was above the legal limit of 20 mg/kg in both MTA and control points. The average detection in MTA was 41.48 mg/kg and an average of 24.33 mg/kg was detected at control points. The range of Pb concentrations was 9.15 to 106.1 mg/kg. Three of the six MTA samples contained higher concentrations that the legal limit. These include sample D7, H2X and B2AX. D7 measured over ten times the legal limit at 106.1 mg/kg, followed by B2AX (81.85 mg/kg) and H2X (32.79 mg/kg). Two control samples, including F7 and G1, measured 25. 92 and 30.69 mg/kg, respectively.

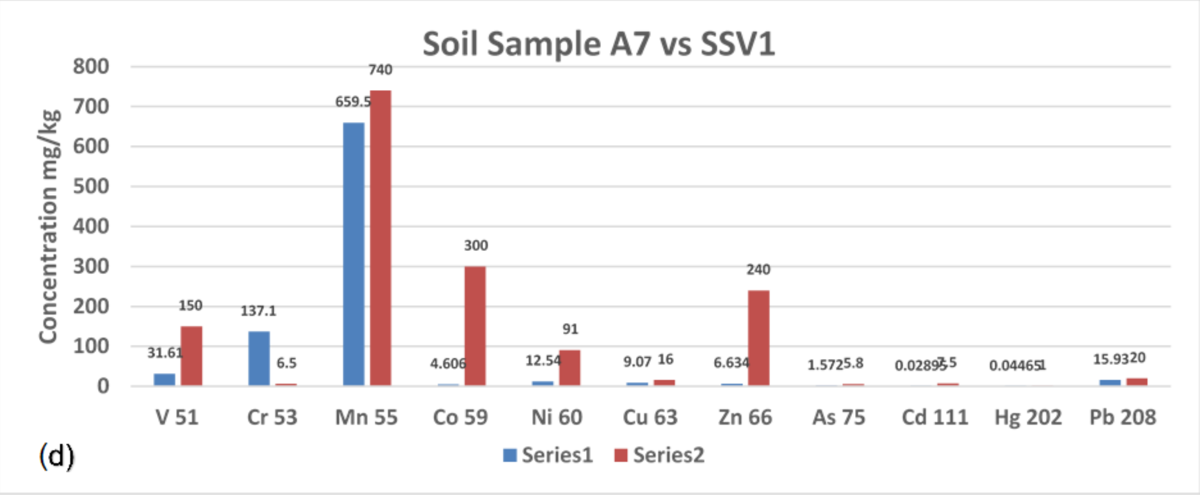
Figure 4.4 illustrate a graphical comparison between heavy metal concentrations in General De La Rey Training Area and Control Points. Series 1 represent the MTA soil samples while Series 2 represents control samples. Figure 4.5 illustrates averaged concentrations of MTA samples compared to average background values per element. Dataset 1 represents mean MTA samples while Dataset 2 represents background samples. Manganese included, the data range of Dataset 1 has a maximum of above 5000 mg/kg and Dataset 2 reaches 4000 mg/kg, particularly in sample H2X and B2AX, dwarfing out the rest of the metals. Removing Mn from both datasets allows better graphical comparison. One to one analysis of the data in Figure 4.5 shows that MTA samples have generally higher average concentrations of heavy metals than background samples.



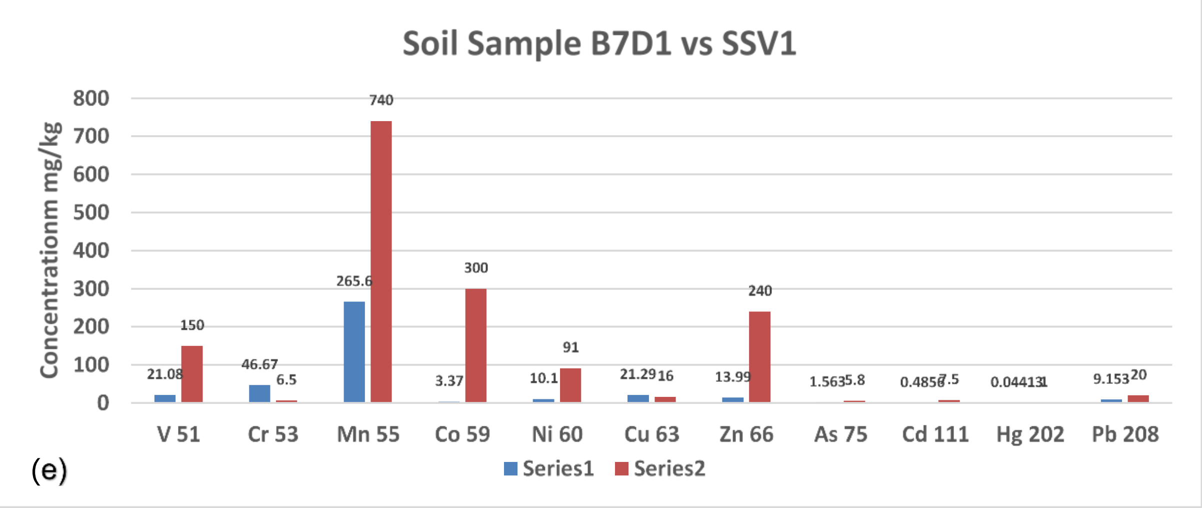



Soil Sample B7C3 vs SSV1
Concentration mg/kg
800
700
600
500
400
300
200
100
0
41.58
150
56.91
6.5
135.4
740
3.814
300
26.64
91
40.17
16
26.91
240
1.9285.8
0.093237.5
0.06048
26.6420
V 51
Cr 53
Mn 55
Co 59
Ni 60
Cu 63
Zn 66
As 75
Cd 111
Hg 202
Pb 208
Series1
Series2

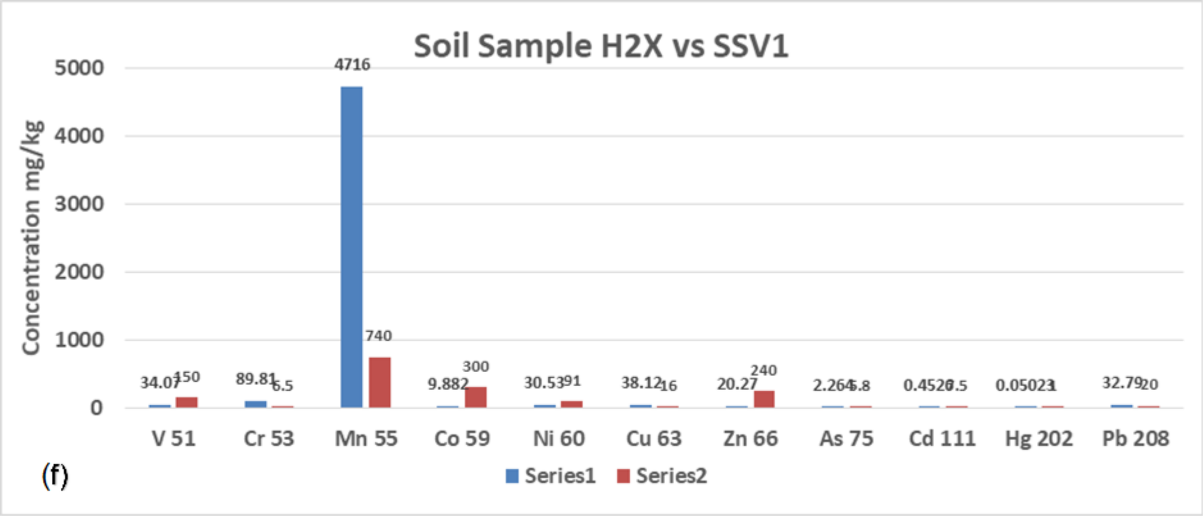
(c)


Soil Sample A7 vs SSV1
Concentration mg/kg
800
700
600
500
400
300
200
100
0
31.61
150
137.1
6.5
659.5
740
4.606
300
12.54
91
9.07
16
6.634
240
1.5725.8
0.028957.5
0.04465
15.9320
V 51
Cr 53
Mn 55
Co 59
Ni 60
Cu 63
Zn 66
As 75
Cd 111
Hg 202
Pb 208
Series1
Series2

(d)


Soil Sample B7D1 vs SSV1
Concentrationm mg/kg
800
700
600
500
400
300
200
100
0
21.08
150
46.67
6.5
265.6
740
3.37
300
10.1
91
21.29
16
13.99
240
1.5635.8
0.48567.5
0.04413
9.153
20
V 51
Cr 53
Mn 55
Co 59
Ni 60
Cu 63
Zn 66
As 75
Cd 111
Hg 202
Pb 208
Series1
Series2

(e)



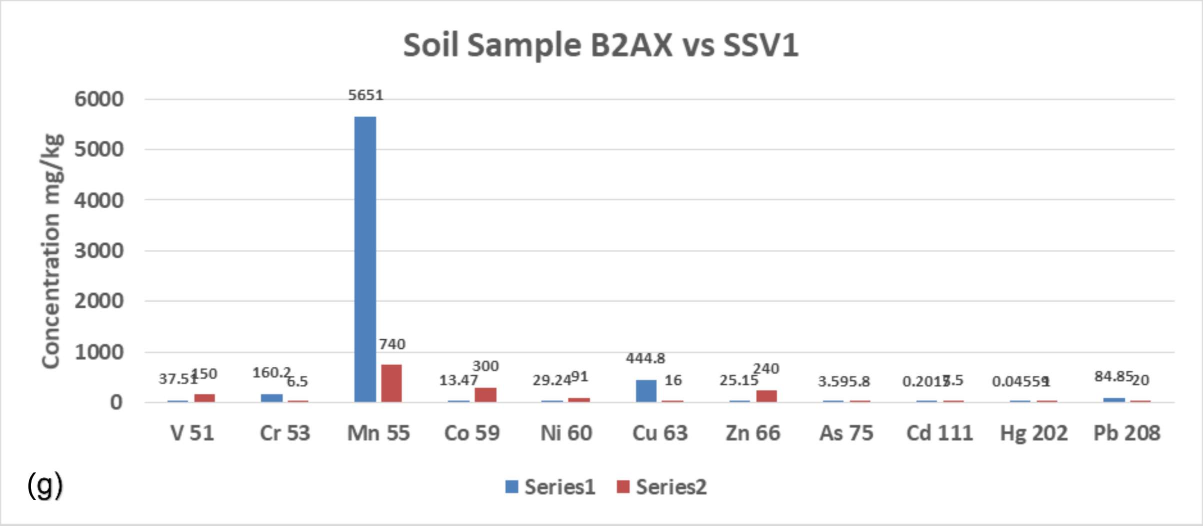


Figure 4.4:Comparison between MTA heavy metal concentrations in samples (a) SSE07, (b) SSD07, (c) B7C3, (d) SSA07, (e) SSB07D1, (f) SSH02X, and (g) SSB02AX with NEMA guideline concentrations

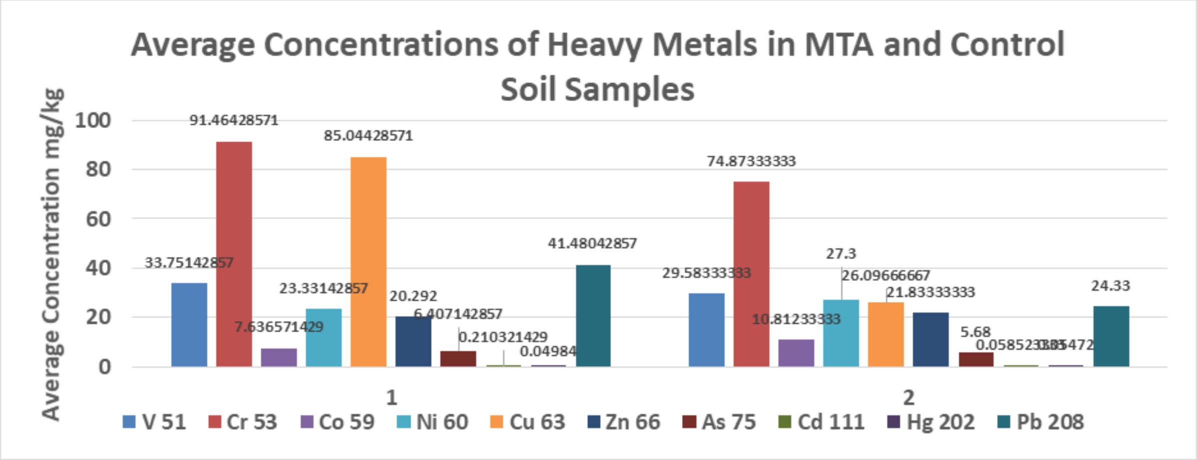


Figure 4.5: Heavy metal concentrations in MTA soil samples vs. control samples

Calculation of Enrichment Factor (EF) and Geo-accumulation Index (Igeo) are used by analysts to determine the level of anthropogenic enrichment of heavy metals to above natural content (Abrahim and Parker, 2008; Bern, et al, 2019; Muzerengi, 2017). Using Mercury (Hg) as the normalization factor, the average concentration of Hg in control samples was used in all calculations of EF. The average concentration of Hg mg/kg in control samples was 0.0547 mg/kg. Contamination is measured as the ratio between the concentration of heavy metals in samples and the concentration of heavy metals in reference material (Abrahim and Parker, 2008). According to Muzerengi, (2017) EF can be used to differentiate heavy metals originating from anthropogenic activity and those naturally occurring in the environment. The EF was calculated using the general term;

$$EF = [C_x / C_{ref}] / [B_x / B_{ref}] \qquad (2)$$

Where C_x is the concentration of a certain heavy metal in a field sample, C_{ref} is the concentration of the heavy metal in a reference sample. B_x is the concentration of a reference heavy metal in a field sample (measured environment) while B_{ref} is the concentration of the reference heavy metal in a reference sample (control sample). Values obtained from the calculation of enrichment falls within six categories proposed by Muzerengi, (2006) and are populated on Table 4.7.

Table 4.7: Enrichment levels for heavy metals in the environment (Muzerengi, 2006)

EF VALUE	IMPLIED MTA ENRICHMENT LEVEL
< 2	Deficiency to Minimal Enrichment
2 – 5	Moderate Enrichment
5 – 20	Significant Enrichment
20 – 40	Very High Enrichment
> 40	Extremely High Enrichment

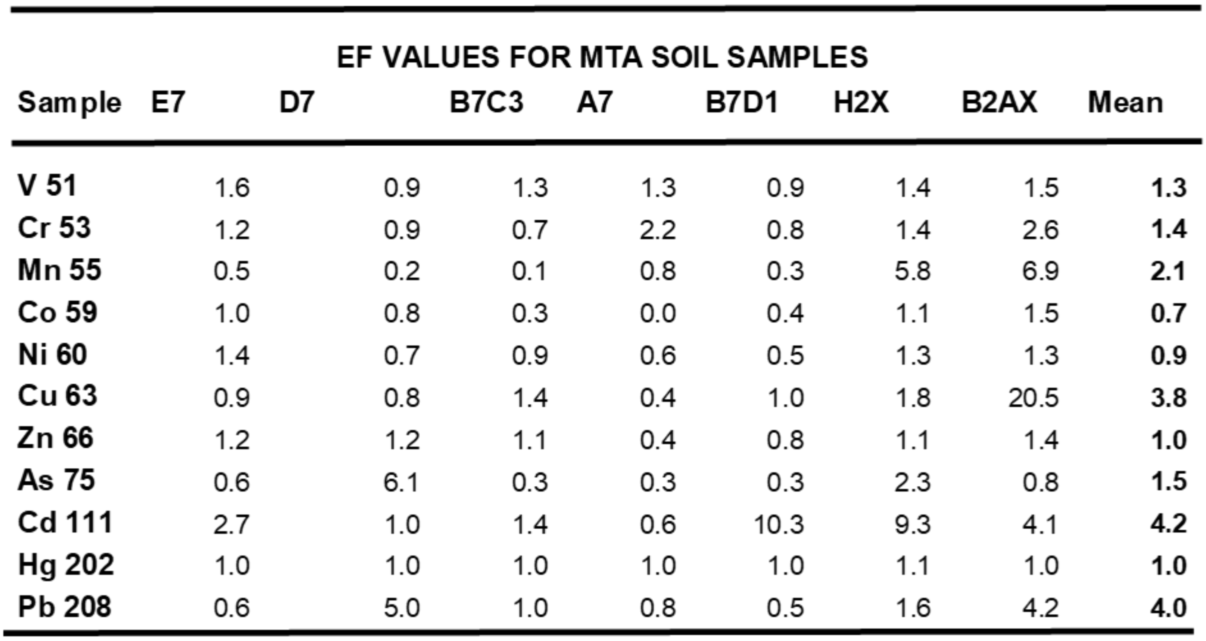
Table 4.8 provides the EF values for each element and average values for each sample. All EF of Vanadium were < 2, indicating Deficiency to minimal enrichment. The highest EF value of V is 1.6 in sample SSE07 and a mean EF value of 1.3 for the MTA. Six of the MTA samples had EF values of < 2 for Cr. Only SSA07 exhibited moderate enrichment with an EF value of 2.2 for Cr. Mean EF value of Cr was 1.4. Five Mn samples had EF valued below 2 with two UXO site samples (SSH02X and SSB02AX) having EF values of 5.8 and 6.9, respectively, suggesting moderate

enrichment. Average MTA EF value for Mn was 2.1, implying moderate enrichment. EF values for Co were all < 2 with an average EF value of 0.7 for the MTA (deficiency to moderate enrichment). The highest EF value was 1.5 at SSB02AX. Ni also had EF values ranging from 0.5 to 1.4 and a mean EF value of 0.9 (deficiency to minimal enrichment).

Copper (Cu) had EF values ranging from 0.4 to 20.5 and an average EF value of 3.8 (moderate enrichment). Only sample SSB02AX with EF value of 20.5 (very high enrichment) had an EF value above 2. Zinc had EF values ranging from 0.4 to 1.4n mg/kg (deficiency to moderate enrichment) for all MTA samples. Arsenic also had deficiency to moderated enrichment with EF values ranging from 0.3 to 6.1 and an average EF value of 1.5 (deficiency to moderate enrichment). Only sample SSD07 had an EF value of 6.1 (significant enrichment). Sample SSD07 was significantly enriched with EF value of 6.1 while sample SSH02 was moderately enriched with EF value of 2.3.

Cadmium (Cd) had EF values in the range 0.6 to 10.3 with an average EF value of 4.2 (moderate enrichment). Only sample SSB07D1 and SSH02AX had EF values of 10.3 and 9.3, respectively (significant enrichment). Mercury (Hg), which was used as a reference element had all EF values < 2 ranging from 1.0 to 1.1 with an average of 1.0 (deficiency to moderate enrichment). Lead (Pb) was moderately enriched in the MTA with an average EF value of 4.0 and an EF range of 0.5 to 5.0. Only SSB07C3 and SSB02AX had EF values > 2 (5.0 and 4.2, respectively).

Table 4.8: Enrichment factors for MTA soil samples



EF VALUES FOR MTA SOIL SAMPLES

Sample	E7	D7	B7C3	A7	B7D1	H2X	B2AX	Mean
V 51	1.6	0.9	1.3	1.3	0.9	1.4	1.5	**1.3**
Cr 53	1.2	0.9	0.7	2.2	0.8	1.4	2.6	**1.4**
Mn 55	0.5	0.2	0.1	0.8	0.3	5.8	6.9	**2.1**
Co 59	1.0	0.8	0.3	0.0	0.4	1.1	1.5	**0.7**
Ni 60	1.4	0.7	0.9	0.6	0.5	1.3	1.3	**0.9**
Cu 63	0.9	0.8	1.4	0.4	1.0	1.8	20.5	**3.8**
Zn 66	1.2	1.2	1.1	0.4	0.8	1.1	1.4	**1.0**
As 75	0.6	6.1	0.3	0.3	0.3	2.3	0.8	**1.5**
Cd 111	2.7	1.0	1.4	0.6	10.3	9.3	4.1	**4.2**
Hg 202	1.0	1.0	1.0	1.0	1.0	1.1	1.0	**1.0**
Pb 208	0.6	5.0	1.0	0.8	0.5	1.6	4.2	**4.0**

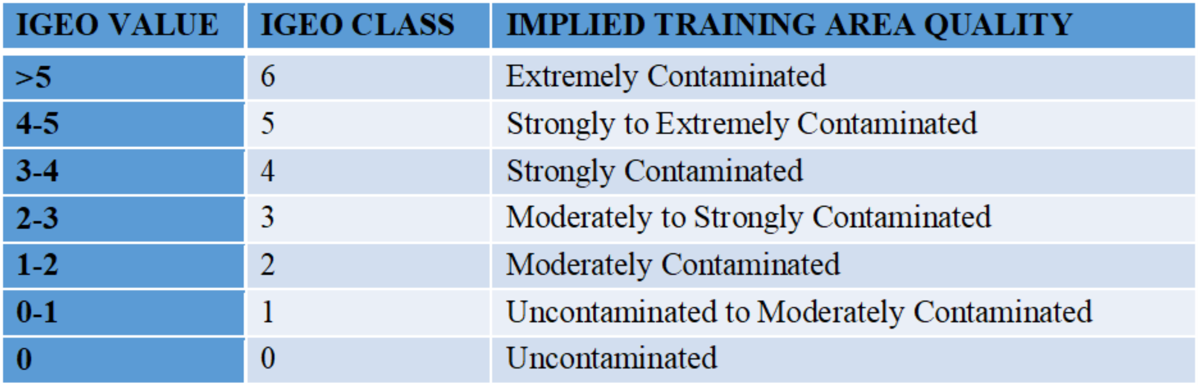
Muzerengi, (2017) suggested that results of EF can be verified using geo-accumulation index (I*geo*). I*geo* is a base 2 logarithmic function that determines the weighted average concentration of heavy metal enrichment within the study area by using the average concentration of a heavy metal in the MTA using the general term;

$$Igeo = \log 2 \; [\; Cn / 1.5 \text{ x } Bn \;] \tag{3}$$

Where I*geo* is the geo-accumulation index, Cn is the average concentration of the heavy metal in the sample and Bn is the average concentration of the heavy metal in the control area. 1.5 is a constant factor that minimizes the data variability between different samples in the study area. Similar to EF, I*geo* uses an index to classify the level of contamination. Results from equation 3 fall in one of seven classes of contamination.

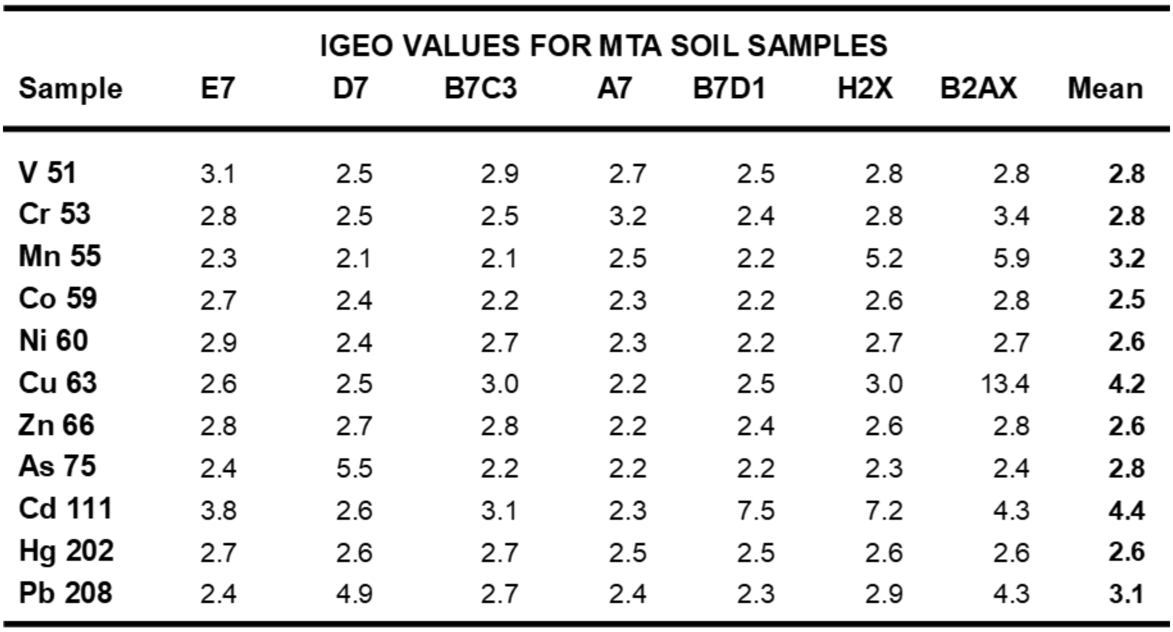
Table 4.9 lists the geo-accumulation indices for the heavy metals. Calculations were done in Excel statistics and verified on Casio fx-82ZA PLUS scientific calculator. Table 4.10 lists the calculated geo-accumulation indices for heavy metals in MTA soil samples. Average I*geo* values for the training area ranged from 2.6 (moderate to strong contamination) to 4.6 (strong to extreme contamination) with a mean of 4.4 (strong to extreme contamination). Most of the elements were generally at I*geo* < 3 for most of the samples, suggesting a lower MTA average. However, some sites presented very high contamination and a few samples had I*geo* values in the extreme contamination bracket, raising the MTA average and leading to a false assessment of the mean.

Table 4.9: Geo-accumulation index classes for heavy metal contamination



IGEO VALUE	IGEO CLASS	IMPLIED TRAINING AREA QUALITY
>5	6	Extremely Contaminated
4-5	5	Strongly to Extremely Contaminated
3-4	4	Strongly Contaminated
2-3	3	Moderately to Strongly Contaminated
1-2	2	Moderately Contaminated
0-1	1	Uncontaminated to Moderately Contaminated
0	0	Uncontaminated

Table 4.10: Geo-accumulation Indices for heavy metals in MTA soil samples



IGEO VALUES FOR MTA SOIL SAMPLES

Sample	E7	D7	B7C3	A7	B7D1	H2X	B2AX	Mean
V 51	3.1	2.5	2.9	2.7	2.5	2.8	2.8	**2.8**
Cr 53	2.8	2.5	2.5	3.2	2.4	2.8	3.4	**2.8**
Mn 55	2.3	2.1	2.1	2.5	2.2	5.2	5.9	**3.2**
Co 59	2.7	2.4	2.2	2.3	2.2	2.6	2.8	**2.5**
Ni 60	2.9	2.4	2.7	2.3	2.2	2.7	2.7	**2.6**
Cu 63	2.6	2.5	3.0	2.2	2.5	3.0	13.4	**4.2**
Zn 66	2.8	2.7	2.8	2.2	2.4	2.6	2.8	**2.6**
As 75	2.4	5.5	2.2	2.2	2.2	2.3	2.4	**2.8**
Cd 111	3.8	2.6	3.1	2.3	7.5	7.2	4.3	**4.4**
Hg 202	2.7	2.6	2.7	2.5	2.5	2.6	2.6	**2.6**
Pb 208	2.4	4.9	2.7	2.4	2.3	2.9	4.3	**3.1**

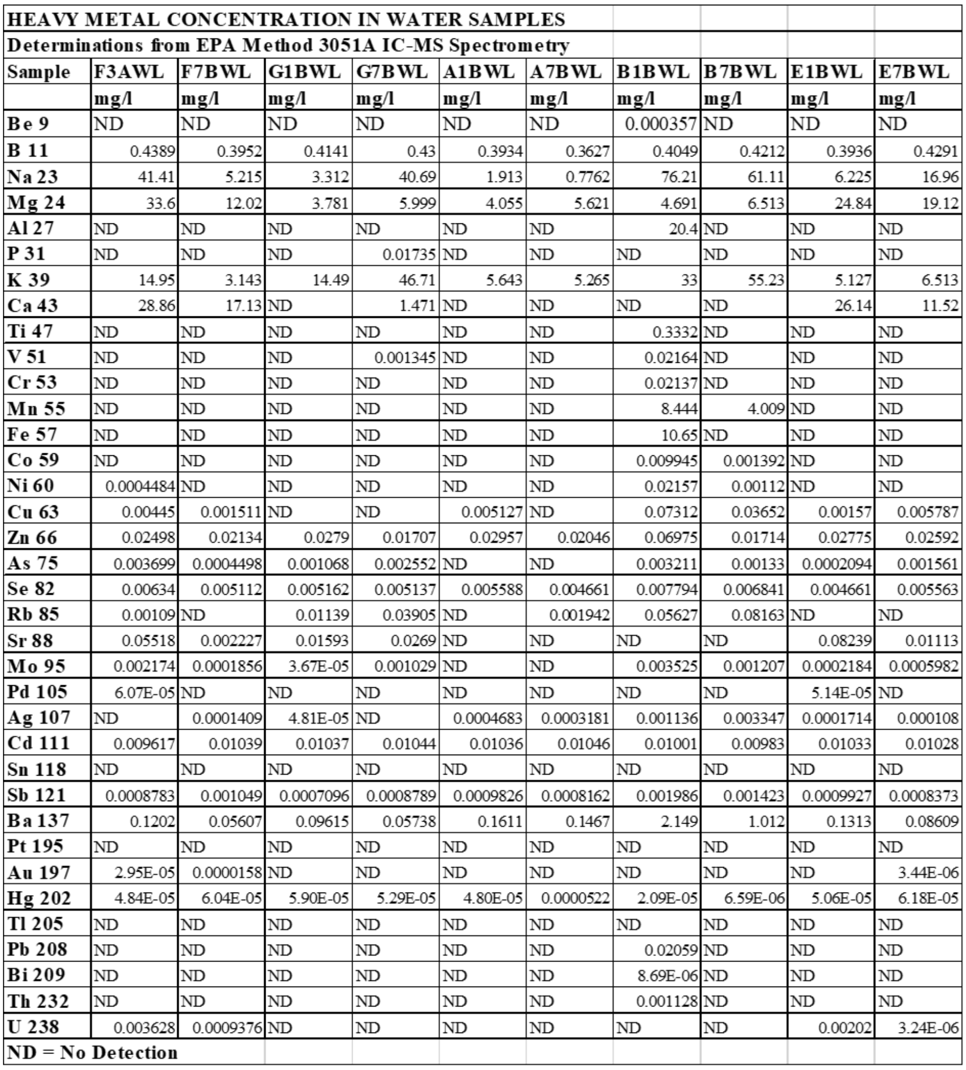
Vanadium (V) had I*geo* range of 2.5 to 3.1 with an MTA average of 2.8 (Moderate to strong contamination). The highest contamination was in SSE07 (I*geo* = 3.1) and SSB07C3 (I*geo* = 2.9). The samples were collected at a firing point and an explosion crater, respectively. V contamination was biased towards the upper half of the class (2.5 < I*geo* < 3). Chromium (Cr) also had average I*geo* value of 2.8 with range 2.4 to 3.4. The highest contamination was at the two UXO sites and the firing point at Sector E. Strong contamination was in SSB02AX, which exceeded moderate to strong contamination level with only decimal amount. Manganese (Mn) contamination was strong at MTA average I*geo* of 3.2. However, five of the seven samples were in the moderate to strong contamination, which was biased towards the lower segment of the class (2 < I*geo* < 2.5). The strong average MTA value is the result of very high contamination in UXO sites (SSH02X and SSB02AX with I*geo* = 5.2 and 5.9, respectively). Cobalt (Co) contamination was moderate to strong with I*geo* range of 2.2 to 2.8 and an MTA average of 2.5. Nickel (N) contamination was moderate to strong contamination with average I*geo* of 2.2 to 2.9 and an MTA average of 2.6.

Copper (Cu) had an MTA average I*geo* of 4.2 (strong to high contamination) with I*geo* range of 2.2 to 13.4. Six of the samples had moderate to strong contamination. The high MTA average was due to I*geo* value of 13.4 at an UXO site in Sector B (SSB02AX). Zinc (Zn) I*geo* values were all within the moderate to strong classification with a range of 2.2 to 2.8 and an MTA average of 2.8. A similar trend was observed with As, except that very high As contamination was observed in SSD07 at I*geo* = 5.5. Cadmium (Cd) contamination had I*geo* value range of 2.3 to 7.5 and an MTA average of 4.4 (strong to extreme contamination). Five of the seven samples had I*geo* >3 , signifying a bias towards high MTA contamination. The highest I*geo* values were at SSB07D1 and SSH02X at 7.5 and 7.2, respectively. Contamination with Hg was moderate to strong in across all samples at the range of 2.5 to 2.7 and an MTA average of 2.6. Lead (Pb) had generally the same trend with only two samples (SSD07 and SSB02AX) having strong to extreme contamination with the metal at I*geo* values of 4.9 and 4.3, respectively.

4.2.2 Heavy metal concentration in water samples

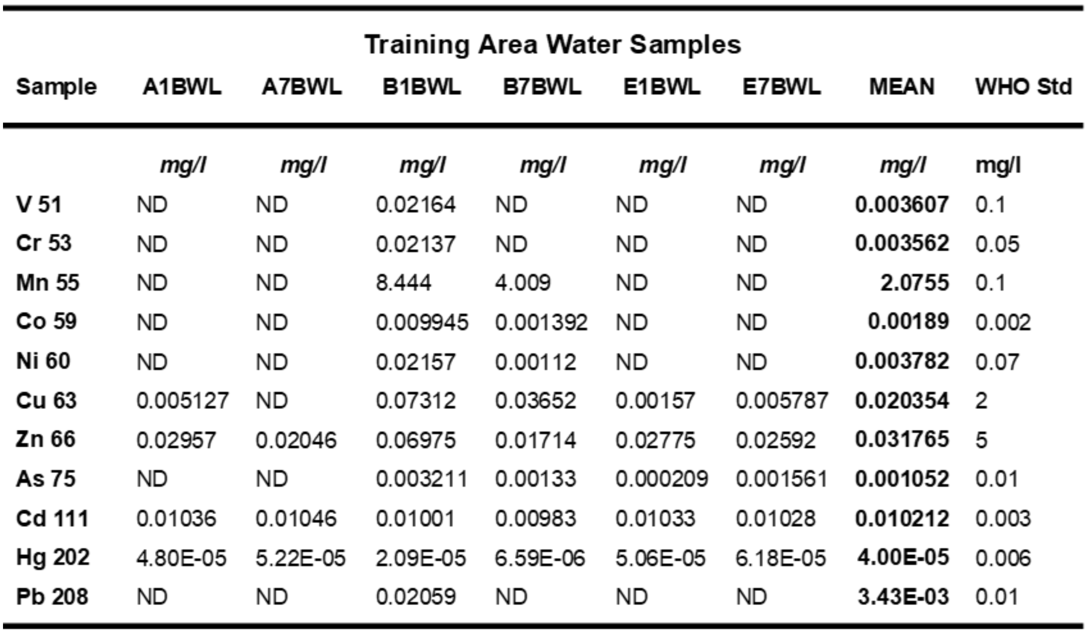
Table 4.11 exhibits concentrations of heavy metals in Water Samples. Samples were analysed for heavy metals and results were compared with WHO Guidelines and other literary sources. Local background values for acceptable concentrations of heavy metals in drinking water have not been found. Table 4.12 lists metals identified by NEMA, (2008) as environmentally hazardous. Data was explored using Excel statistics. The last column on Table 4.3 (SSV1) provides allowable concentrations for water sources. Allowable background values may vary due to different indices used in different literary sources. Results on Table 4.13 exhibit generally very low elemental concentrations of heavy metals in control water samples. In contrast to soil samples, water samples from both MTA and control areas had a significant number of ‘no detections’. As an example, Beryllium (Be), with average concentrations of 1 ppm in both MTA and control soil samples, was only detected in one water sample (B1BWL) at 0.000357 mg/l. Iron (Fe) which is known to have high natural concentrations, which was detected in the order of 10 000 mg/kg several MTA soil samples, was detected in only one water sample(B1BWL) at 10.6 mg/l. Out of 36 heavy metals analysed, only six heavy metals (Na, Mg, Al, K, Ca and Fe) measured concentrations above 1 mg/l. The highest concentration was of Sodium (Na) detected at 76.21 mg/l at B1BWL.

Table 4.11: Heavy metal concentrations in MTA and Control water samples



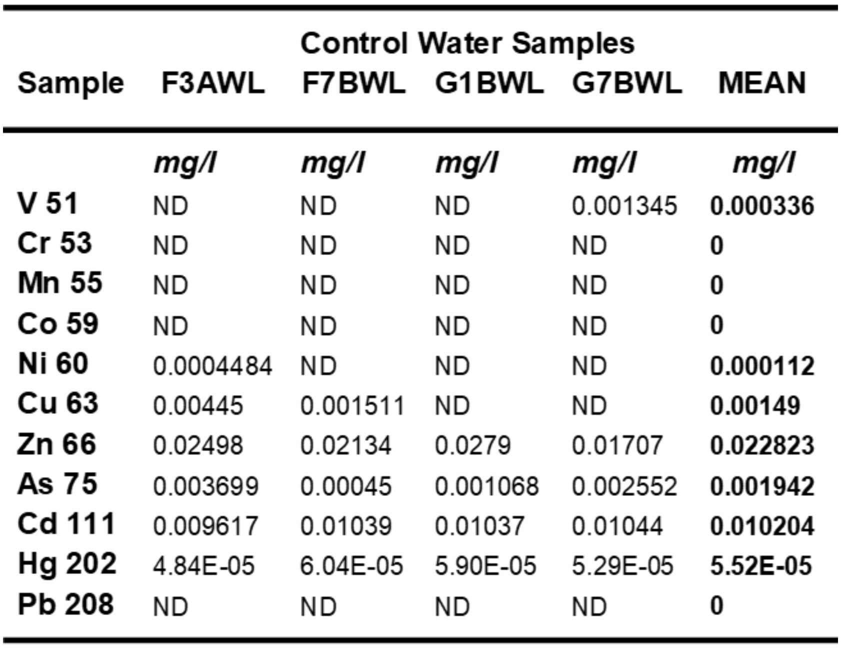
HEAVY METAL CONCENTRATION IN WATER SAMPLES										
Determinations from EPA Method 3051A IC-MS Spectrometry										
Sample	**F3AWL**	**F7BWL**	**G1BWL**	**G7BWL**	**A1BWL**	**A7BWL**	**B1BWL**	**B7BWL**	**E1BWL**	**E7BWL**
	mg/l	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
Be 9	ND	ND	ND	ND	ND	ND	0.000357	ND	ND	ND
B 11	0.4389	0.3952	0.4141	0.43	0.3934	0.3627	0.4049	0.4212	0.3936	0.4291
Na 23	41.41	5.215	3.312	40.69	1.913	0.7762	76.21	61.11	6.225	16.96
Mg 24	33.6	12.02	3.781	5.999	4.055	5.621	4.691	6.513	24.84	19.12
Al 27	ND	ND	ND	ND	ND	ND	20.4	ND	ND	ND
P 31	ND	ND	ND	0.01735	ND	ND	ND	ND	ND	ND
K 39	14.95	3.143	14.49	46.71	5.643	5.265	33	55.23	5.127	6.513
Ca 43	28.86	17.13	ND	1.471	ND	ND	ND	ND	26.14	11.52
Ti 47	ND	ND	ND	ND	ND	ND	0.3332	ND	ND	ND
V 51	ND	ND	ND	0.001345	ND	ND	0.02164	ND	ND	ND
Cr 53	ND	ND	ND	ND	ND	ND	0.02137	ND	ND	ND
Mn 55	ND	ND	ND	ND	ND	ND	8.444	4.009	ND	ND
Fe 57	ND	ND	ND	ND	ND	ND	10.65	ND	ND	ND
Co 59	ND	ND	ND	ND	ND	ND	0.009945	0.001392	ND	ND
Ni 60	0.0004484	ND	ND	ND	ND	ND	0.02157	0.00112	ND	ND
Cu 63	0.00445	0.001511	ND	ND	0.005127	ND	0.07312	0.03652	0.00157	0.005787
Zn 66	0.02498	0.02134	0.0279	0.01707	0.02957	0.02046	0.06975	0.01714	0.02775	0.02592
As 75	0.003699	0.0004498	0.001068	0.002552	ND	ND	0.003211	0.00133	0.0002094	0.001561
Se 82	0.00634	0.005112	0.005162	0.005137	0.005588	0.004661	0.007794	0.006841	0.004661	0.005563
Rb 85	0.00109	ND	0.01139	0.03905	ND	0.001942	0.05627	0.08163	ND	ND
Sr 88	0.05518	0.002227	0.01593	0.0269	ND	ND	ND	ND	0.08239	0.01113
Mo 95	0.002174	0.0001856	3.67E-05	0.001029	ND	ND	0.003525	0.001207	0.0002184	0.0005982
Pd 105	6.07E-05	ND	ND	ND	ND	ND	ND	ND	5.14E-05	ND
Ag 107	ND	0.0001409	4.81E-05	ND	0.0004683	0.0003181	0.001136	0.003347	0.0001714	0.000108
Cd 111	0.009617	0.01039	0.01037	0.01044	0.01036	0.01046	0.01001	0.00983	0.01033	0.01028
Sn 118	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sb 121	0.0008783	0.001049	0.0007096	0.0008789	0.0009826	0.0008162	0.001986	0.001423	0.0009927	0.0008373
Ba 137	0.1202	0.05607	0.09615	0.05738	0.1611	0.1467	2.149	1.012	0.1313	0.08609
Pt 195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Au 197	2.95E-05	0.0000158	ND	ND	ND	ND	ND	ND	ND	3.44E-06
Hg 202	4.84E-05	6.04E-05	5.90E-05	5.29E-05	4.80E-05	0.0000522	2.09E-05	6.59E-06	5.06E-05	6.18E-05
Tl 205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pb 208	ND	ND	ND	ND	ND	ND	0.02059	ND	ND	ND
Bi 209	ND	ND	ND	ND	ND	ND	8.69E-06	ND	ND	ND
Th 232	ND	ND	ND	ND	ND	ND	0.001128	ND	ND	ND
U 238	0.003628	0.0009376	ND	ND	ND	ND	ND	ND	0.00202	3.24E-06
ND = No Detection										

Table 4.12: Heavy metal concentrations in MTA water samples



	Training Area Water Samples							
Sample	**A1BWL**	**A7BWL**	**B1BWL**	**B7BWL**	**E1BWL**	**E7BWL**	**MEAN**	**WHO Std**
	mg/l	***mg/l***	***mg/l***	***mg/l***	***mg/l***	***mg/l***	***mg/l***	**mg/l**
V 51	ND	ND	0.02164	ND	ND	ND	**0.003607**	0.1
Cr 53	ND	ND	0.02137	ND	ND	ND	**0.003562**	0.05
Mn 55	ND	ND	8.444	4.009	ND	ND	**2.0755**	0.1
Co 59	ND	ND	0.009945	0.001392	ND	ND	**0.00189**	0.002
Ni 60	ND	ND	0.02157	0.00112	ND	ND	**0.003782**	0.07
Cu 63	0.005127	ND	0.07312	0.03652	0.00157	0.005787	**0.020354**	2
Zn 66	0.02957	0.02046	0.06975	0.01714	0.02775	0.02592	**0.031765**	5
As 75	ND	ND	0.003211	0.00133	0.000209	0.001561	**0.001052**	0.01
Cd 111	0.01036	0.01046	0.01001	0.00983	0.01033	0.01028	**0.010212**	0.003
Hg 202	4.80E-05	5.22E-05	2.09E-05	6.59E-06	5.06E-05	6.18E-05	**4.00E-05**	0.006
Pb 208	ND	ND	0.02059	ND	ND	ND	**3.43E-03**	0.01

Table 4.13: Heavy metal concentrations in control water samples



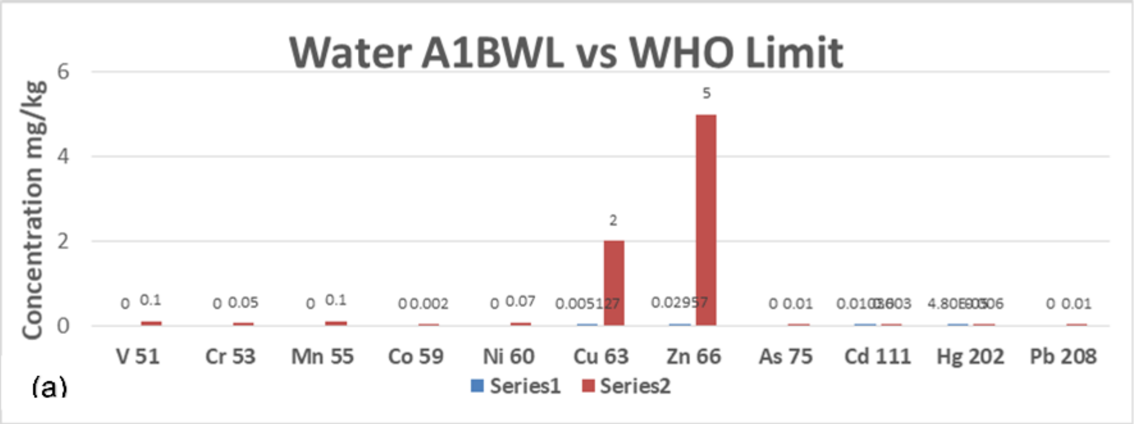
Sample	Control Water Samples F3AWL	F7BWL	G1BWL	G7BWL	MEAN
	mg/l	***mg/l***	***mg/l***	***mg/l***	***mg/l***
V 51	ND	ND	ND	0.001345	**0.000336**
Cr 53	ND	ND	ND	ND	**0**
Mn 55	ND	ND	ND	ND	**0**
Co 59	ND	ND	ND	ND	**0**
Ni 60	0.0004484	ND	ND	ND	**0.000112**
Cu 63	0.00445	0.001511	ND	ND	**0.00149**
Zn 66	0.02498	0.02134	0.0279	0.01707	**0.022823**
As 75	0.003699	0.00045	0.001068	0.002552	**0.001942**
Cd 111	0.009617	0.01039	0.01037	0.01044	**0.010204**
Hg 202	4.84E-05	6.04E-05	5.90E-05	5.29E-05	**5.52E-05**
Pb 208	ND	ND	ND	ND	**0**

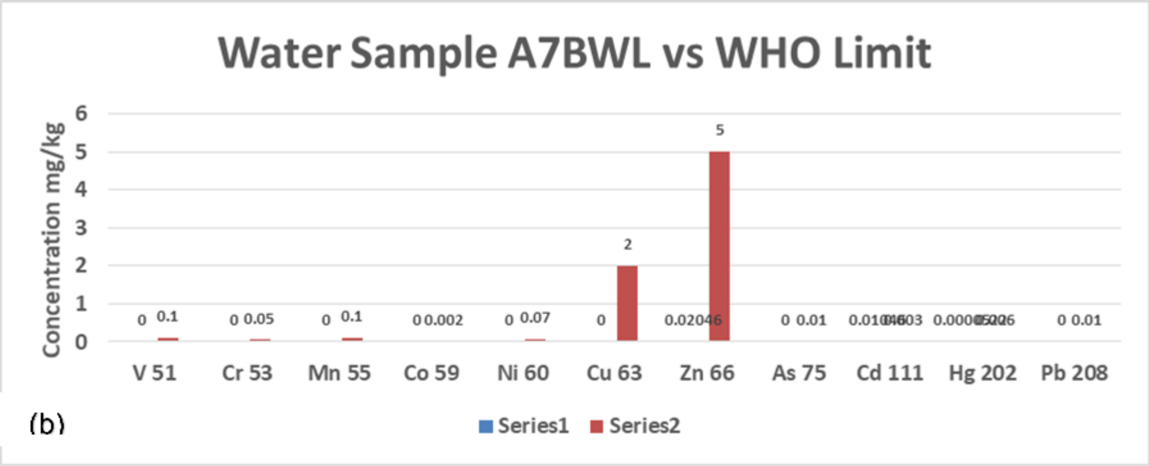
A new reference element was determined for water sample analyses. Cadmium (Cd) exhibited the best consistency in occurrence and average concentrations in both MTA and control samples with concentration range of 0.00983 to 0.01046 mg/l and average concentration of 0.01 mg/l for both MTA and control samples, including borehole samples. Six MTA samples and four control samples were analysed for heavy metals. These were obtained from five locations one year apart. The sites included the well in Sector A, the UXO site in Sector B, The dam at Sector E, The water pond at Sector F (including a borehole) and the water pond at Sector G (including a borehole). This translates to two samples per site.

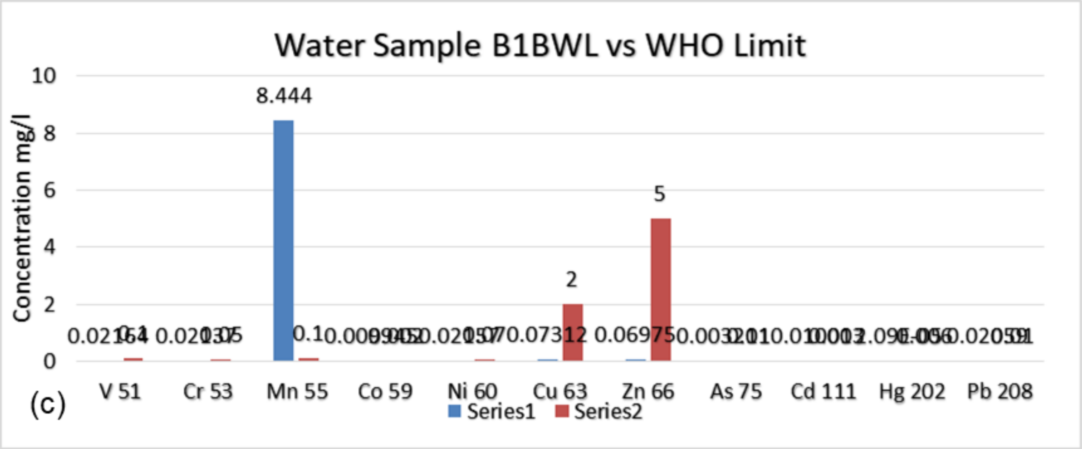
Vanadium was detectable in only one MTA sample (WSB01BWL) at 0.022 mg/l. It was also detected in only one borehole water sample from Sector G at 0.0014 mg/l. A concentration of 0.1 mg/l is allowable for V, suggesting significantly low contamination. Chromium (Cr) was also detected in only one MTA sample (WSB01BWL) at 0.02 mg/l. It was not detected in control samples. Chromium (Cr) concentration was lower than guideline limit of 0.05 mg/l. Mn was detected in two water samples from the same pond (WSB01BWL and WSB07BWL) at 8.44 and 4.01 mg/l and not detected in control samples. Allowable concentration of Mn is 0.1 mg/l, suggesting significant contamination of the UXO site. Cobalt (Co) was also detected in both water samples (WSB01BWL and WSB07BWL) at 0.01 and 0.001 mg/l, respectively, and none in control samples. A limit concentration of 0.002 mg/l is allowable, indicating some contamination in WSB01BWL. Nickel (Ni) was detected in both sector B samples at 0.02 mg/l and 0.001 mg/l, respectively. Average concentration of Ni in control samples was 0.000112 mg/l. This low average resulted from detection of Ni in only one of four samples (SSF03AWL) at 0.0005 mg/l. MTA samples exhibited higher average concentration of 0.004 mg/l than control samples. A concentration of 0.07 mg/l is permissible. This suggests significantly low contamination in both MTA and control samples.

Copper (Cu) concentration in water samples ranged from 0.002 to 0.07 mg/l with an average of 0.02 mg/l. Control samples of Cu had an average concentration of 0.002 mg/l. Copper (Cu) concentrations were significantly lower than permissible limit of 2 mg/l. Zinc (Zn) concentrations in the study area ranged from 0.02 to 0.07 mg/l with average concentration of 0.03 mg/l. A concentration of 5 mg/l is environmentally permissible for water sources. Zinc (Zn) concentrations are significantly lower than allowable the limit. Arsenic (As) concentrations were in the range 0.0002 to 0.0032 mg/l in MTA samples with an average of 0.001 mg/l. Control average concentration of As was 0.002 mg/l. A limit of 0.01 mg/l of As is allowed in water sources. This suggests low As contamination in the study area. Cadmium (Cd) concentrations were 0.01 mg/l in all MTA and control samples. A concentration of 0.003 mg/l is allowed in water sources. Cadmium (Cd) was three times lower than legal allowable limit. Mercury (Hg) was detectable in minute concentrations ranging from of 0.00002 to 0.00005 mg/l and an average of 0.00004 mg/l in MTA samples. Average control concentration was 0.00006 mg/l, suggesting higher Mercury (Hg) average in control samples than MTA samples. Mercury (Hg) legal limit concentration is 0.006 mg/l, which is significantly higher than all detections. Lead (Pb) was only detected in one MTA sample (SSB01BWL) at 0.021 mg/l and was not detectable in control samples. Allowable concentration limit of Pb is 0.01 mg/l, suggesting contamination in sample WSB01BWL with twice the legal limit of Pb concentration.

It is clear from the data that elemental concentration of heavy metals in water samples from both control and MTA is very low. Results indicate that Manganese (Mn) concentrations are very high at the UXO site in Sector B. The Mn was not detected in any of the control water samples in the study. Graphical representation of Mn dwarfs out the other metals and makes comparison difficult. To make a better comparison between background samples and control samples, Mn was removed from both datasets. In Figure 4.6 see that the rest of the elements were detected at concentrations below 0.1 mg/l. However, nine of the eleven metals detected in MTA water samples had higher concentration than control samples. This translates to over 80% of the elements. Only Hg and As were found in concentrations lower than control samples. Figure 4.7 shows graphical comparisons between MTA and control sample concentrations.


Water A1BWL vs WHO Limit
Concentration mg/kg
6
4
2
0
0 0.1
0 0.05
0 0.1
0 0.002
0 0.07
0.005127
2
0.02957
5
0 0.01
0.01036603
4.80E-05006
0 0.01
V 51
Cr 53
Mn 55
Co 59
Ni 60
Cu 63
Zn 66
As 75
Cd 111
Hg 202
Pb 208
(a)
Series1
Series2


Water Sample A7BWL vs WHO Limit
Concentration mg/kg
6
5
4
3
2
1
0
0 0.1
0 0.05
0 0.1
0 0.002
0 0.07
0
2
0.02046
5
0 0.01
0.01046603
0.00006006
0 0.01
V 51
Cr 53
Mn 55
Co 59
Ni 60
Cu 63
Zn 66
As 75
Cd 111
Hg 202
Pb 208
(b)
Series1
Series2


Water Sample B1BWL vs WHO Limit
Concentration mg/l
10
8
6
4
2
0
8.444
5
2
0.02164
0.02137
0.1
0.0009405
0.02157
0.07312
0.06975
0.003201
0.01003
V 51
Cr 53
Mn 55
Co 59
Ni 60
Cu 63
Zn 66
As 75
Cd 111
Hg 202
Pb 208
(c)
Series1
Series2

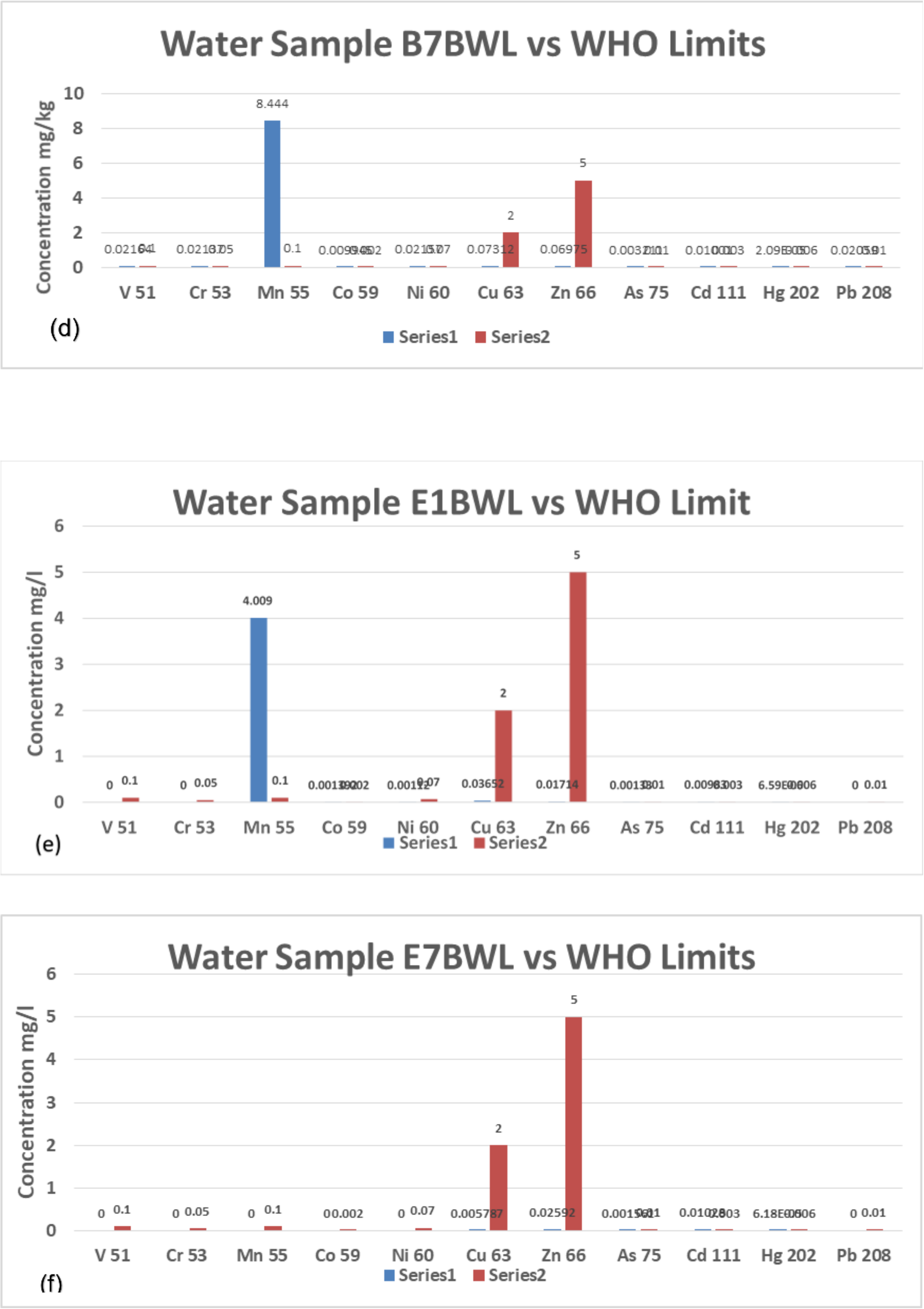


Figure 4.6:Comparison between MTA heavy metal concentrations in water samples; (a) WSA01BWL, (b) WSA07BWL, (c) WSB01BWL, (d)WSB07BWL, (e) WSE01BW, (f) WSE07BWL, with NEMA guideline concentrations

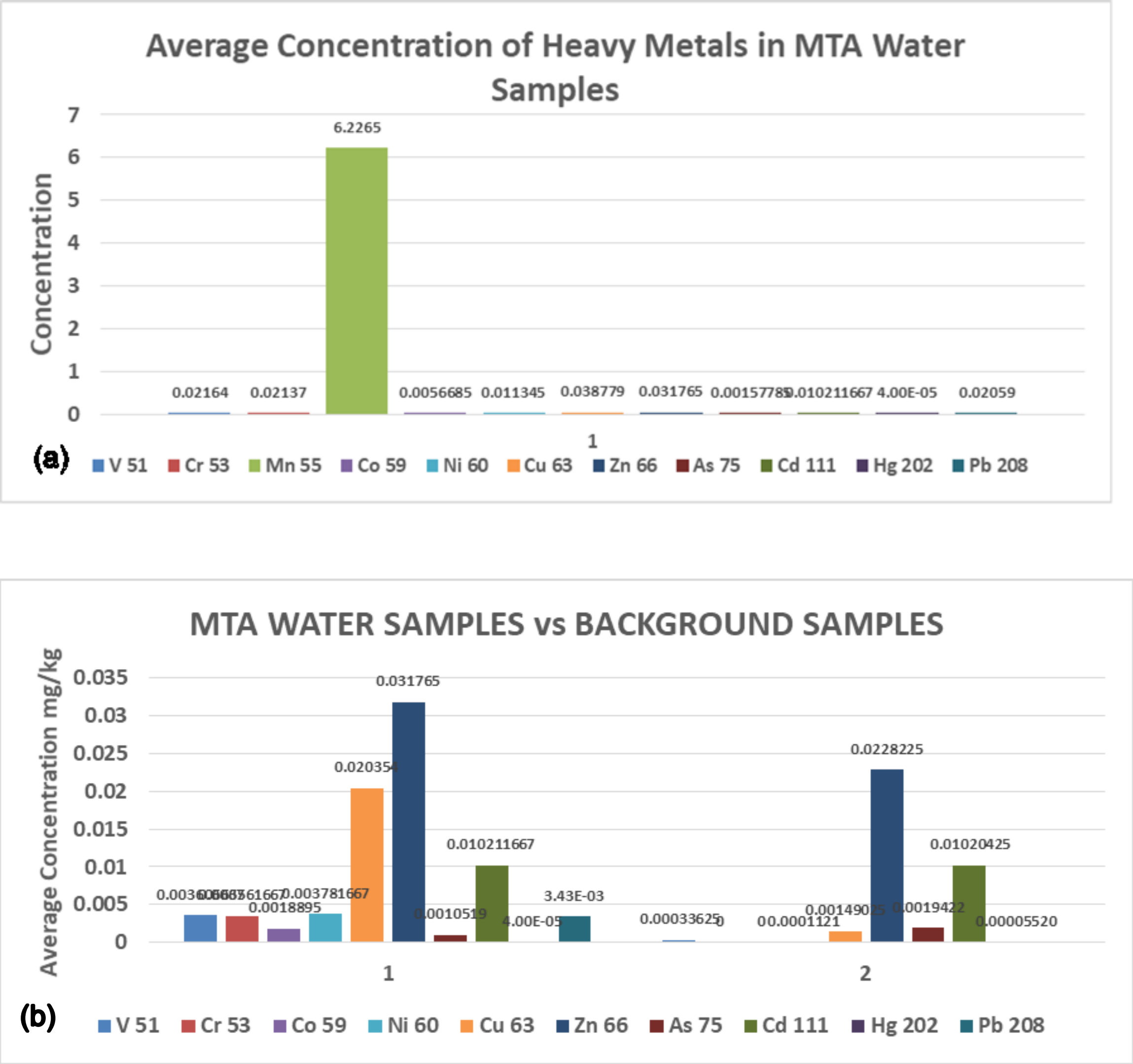
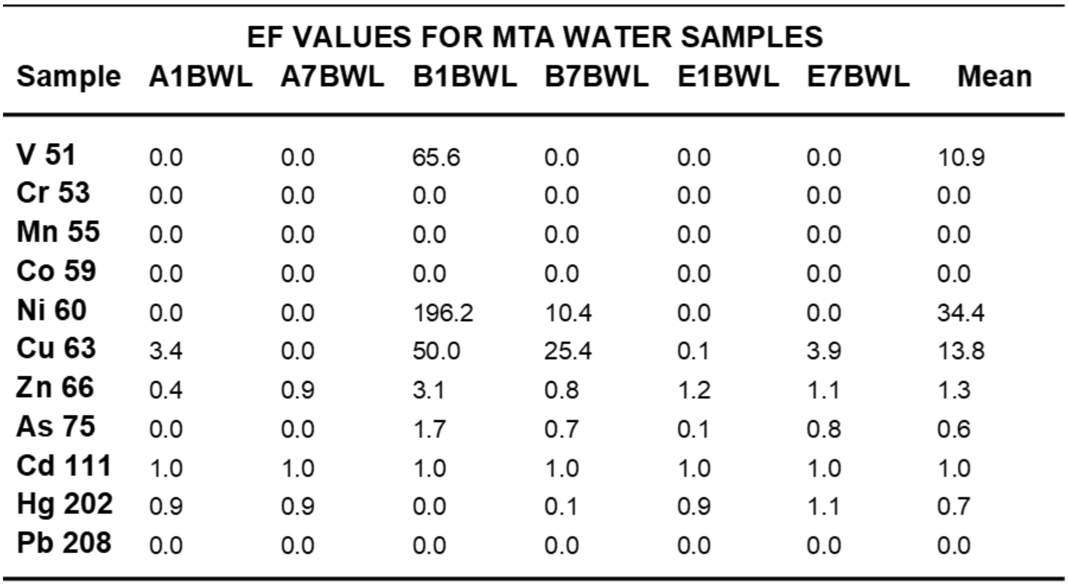


Figure 4.7:Average heavy metal concentrations in (a) MTA water samples and (b) background control samples

The EF and I*geo* of the data was calculated using equation (2) and (3). Cd was used as the reference element due to its constant concentration between MTA and control samples of 0.01 mg/l. Table 4.14 provides the calculated EFs. Five samples out of six were uncontaminated with Vanadium. One sample WSB01BWL had an EF value of 65.6 which suggests extremely high enrichment. An average of 10.9 suggests significant enrichment for the study area. Co, Cr, Pb and Mn were uncontaminated with EF values of 0.0, respectively. Four of six Ni samples were not contaminated with EF values of 0.0. Sample WSB01BWL was extremely contaminated with EF value of 196.2 and sample WSB07BWL had an EF value of 10.4, suggesting significant enrichment. The two EF values account for the MTA average EF value of 34.4 suggesting very high enrichment. Copper (Cu) had EF values ranging from 0.1 to 50.0 with an average MTA value of 13.8 (significant enrichment). Sample WSA01BWL and WSE07BWL were moderately enriched with EF values of

3.4 and 3.9, respectively. The WSB07BWL had very high enrichment at EF value of 25.4. WSB01BWL was extremely contaminated with an EF value of 50.0.

Table 4.14: Enrichment factors for heavy metals in MTA water samples



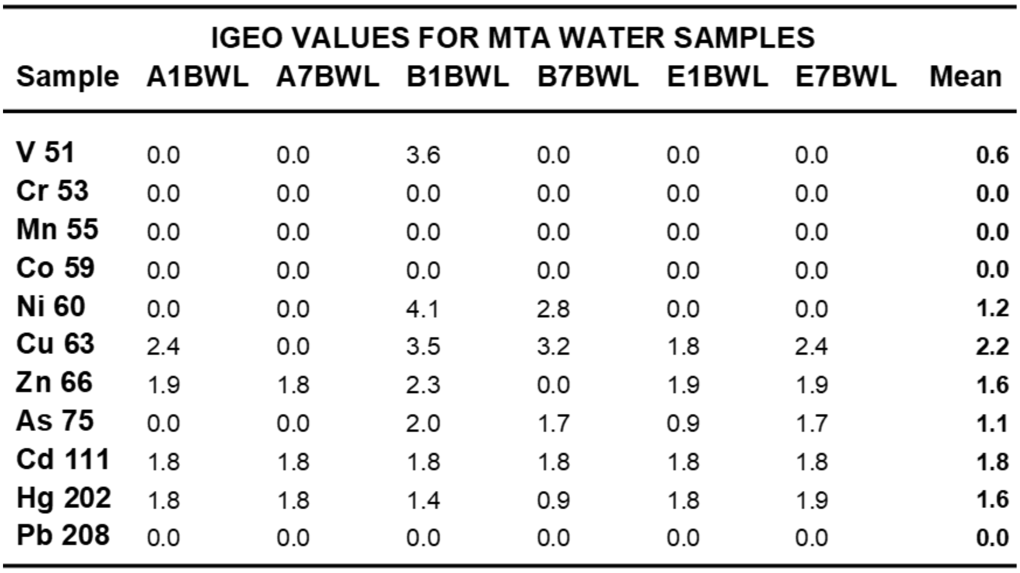
EF VALUES FOR MTA WATER SAMPLES

Sample	A1BWL	A7BWL	B1BWL	B7BWL	E1BWL	E7BWL	Mean
V 51	0.0	0.0	65.6	0.0	0.0	0.0	10.9
Cr 53	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mn 55	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Co 59	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ni 60	0.0	0.0	196.2	10.4	0.0	0.0	34.4
Cu 63	3.4	0.0	50.0	25.4	0.1	3.9	13.8
Zn 66	0.4	0.9	3.1	0.8	1.2	1.1	1.3
As 75	0.0	0.0	1.7	0.7	0.1	0.8	0.6
Cd 111	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Hg 202	0.9	0.9	0.0	0.1	0.9	1.1	0.7
Pb 208	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Zinc (Zn) had EF values ranging from 0.4 (minimal enrichment) to 3.1 (moderate enrichment) with an NTA average of 1.3 (minimal to moderate enrichment). Arsenic (As) had EF values ranging from 0.0 (minimal enrichment to 1.7 (minimal to moderate enrichment), with an MTA average of 0.6, suggesting very little As enrichment of the MTA. Cadmium (Cd) had EF values of 0.1 in all samples, suggesting minimal enrichment in the MTA. Mercury (Hg) results suggest minimal to moderate enrichment with an EF value range of 0.0 to 0.9 and an MTA average of 0.7. The data suggests that only V, Ni and Cu had concerning enrichment levels. However, it is clear from Table 4.14 that high enrichment values corresponded to a single UXO site in Sector B.

The I*geo* values for the study area are presented in Table 4.15. Mean I*geo* values for the study area ranged from 0.0 (uncontaminated) to 2.2 (moderate to strong contamination). Only one sample (WSB01BWL) with I*geo* value of 3.6 was strongly contaminated with Vanadium. All other samples had I*geo* values of 0.0 (uncontaminated). The Cr, Mn, Co and Pb had I*geo* values of 0.0 each (uncontaminated). Nickel (Ni) had I*geo* values 4.1 (strongly to extremely contaminated) and 2.8 (moderately to strongly contaminated) in WSB01BWL and WSB07BWL, respectively. This suggests that Ni contamination was also a hotspot at the UXO site in Sector B. Copper (Cu) had I*geo* values ranging from 0.0 (uncontaminated) to 3.5 (strongly contaminated). Only two out of six samples (WSB01BWL and WSB07BWL) were in the strongly contaminated category with I*geo* values above 3. Zinc (Zn) I*geo* values ranged from 0.0 (uncontaminated) to 1.9 (moderate contamination). The As, Cd and Hg followed the same trend as Zn with all I*geo* values < 2, suggesting moderate contamination.

Table 4.15: Geo-Accumulation Indices for heavy metals in MTA water samples



IGEO VALUES FOR MTA WATER SAMPLES							
Sample	**A1BWL**	**A7BWL**	**B1BWL**	**B7BWL**	**E1BWL**	**E7BWL**	**Mean**
V 51	0.0	0.0	3.6	0.0	0.0	0.0	**0.6**
Cr 53	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
Mn 55	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
Co 59	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
Ni 60	0.0	0.0	4.1	2.8	0.0	0.0	**1.2**
Cu 63	2.4	0.0	3.5	3.2	1.8	2.4	**2.2**
Zn 66	1.9	1.8	2.3	0.0	1.9	1.9	**1.6**
As 75	0.0	0.0	2.0	1.7	0.9	1.7	**1.1**
Cd 111	1.8	1.8	1.8	1.8	1.8	1.8	**1.8**
Hg 202	1.8	1.8	1.4	0.9	1.8	1.9	**1.6**
Pb 208	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**

4.3 Unexploded Ordnance (UXO)

The UXO have been defined as explosive munitions that have been fired, dropped, placed or otherwise prepared for employment against a target, but have failed to function as required and therefore still pose a risk to the environment and humans (McDonald et al., 2004; US Army, 2006). Fired UXO are most likely to be found around impact areas while emplaced UXO are likely to be located in disposal sites. Two types of UXO disposal sites were identified in this study. Those that were used as UXO dumping sites and those used as UXO destruction sites. Destruction of UXO can be carried out by Open Detonation (OD) or by Open Burning (OB). The latter is likely to be used when the material to be disposed includes charges. The UXO locations were characterised and the results are represented in the next sub sections. The quantity and variety of identified UXO is significantly higher than reported here due to only surface count even where UXO occurred in a heap such as Sector E disposal site. This is illustrated in Appendix B.

4.3.1 UXO disposal sites

A total of nine UXO sites were identified. One was located in Sector A, five in Sector B, one in Sector H and two in Sector E. Dumped UXO were located at four locations (Sector A Reservoir, Sector E Old Weapons Range, Sector B OP Tree and Sector B Gonzalespoort Firebreak). Open Burning was identified by darkened soil around burn pits with only a few shell fragments, suggesting munitions were not destroyed at the site. This is a characteristic identified at the OB site at Sector B target area and the pits near Trig Beacon 116. The second set of disposal pits at Sector E (Old Weapons Range), the pits at Sector H and the pits in Sector B North West of Trig Beacon 186 were all littered with fragments from detonated shells and had strong evidence of multiple use.

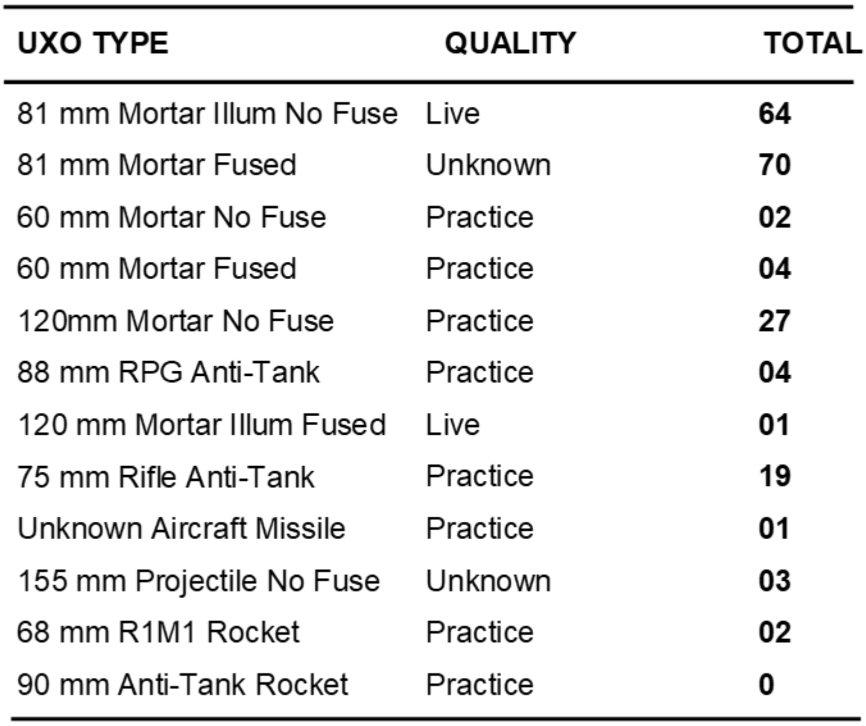
The UXO disposal sites at Sector E near Valkop consisting of three disposal pits contained a very large quantity of UXO. Characterisation was difficult due to the absence of an explosives expert, thus only UXO at the surface was counted. The assortment of the UXO is detailed in imagery in Appendix A. Table 4.16 summarises the quantities and types of UXO found at the three disposal pits in Sector E. The highest quantity of UXO found at the site Sector E are 60 mm Mortar bombs. A total of 392 bombs were counted of which 286 were unfused duds while 106 were fused. Mortar bombs (81 mm) were 191 in total and 127 of these were fused while 64 were duds. Only one 120 mm Mortar Bomb was found in Pit 3. Twelve Hand Grenades and 73 Rifle Grenades were counted and all were in Pit 1. No intact 90 mm Rockets were found on site, although remnants of this monition accounted for the bulk of the metal content in the pits due to the fact that most of the rockets have exploded high order, leaving only fins intact. UXO quantity was in the order Pit 1 > Pit 2 > Pit3. Almost all the identified UXO appeared to be Practice rounds. A total of 672 ammunition items were counted.

Table 4.16: Type and quantity of UXO found at Sector E1 UXO site

UXO TYPE	QUALITY	QUANTITY			TOTAL
		PIT 1	PIT 2	PIT 3	
81 mm Mortar No Fuse	Practice	28	20	16	**64**
81 mm Mortar Fused	Practice	84	21	22	**127**
60 mm Mortar No Fuse	Practice	188	67	31	**286**
60 mm Mortar Fused	Practice	49	25	32	**106**
120mm Mortar	Practice	-	-	01	**01**
M2642 Hand Grenade	Practice	15	-	-	**15**
M791A1 Rifle Grenade	Practice	73	-	-	**73**
90 mm Anti-Tank Rocket	Practice	-	-	-	**0**

The UXO found disposed at Sector B next to OP Tree had the highest complexity but less quantity than at Sector E. Eight types of munitions were identified at the site (see Table 4.17). These ranged from various calibres of Mortars (120 mm, 81 mm and 60 mm), Anti-Tank Rockets and even air delivered bombs. One hundred and ninety-seven ammunition pieces were counted. The highest number of UXO was from 81 mm Mortar rounds at 134 pieces, of which 70 were impact fused and 64 were Illuminating rounds. The next highest number was 120 mm Mortars at 28 pieces of which one was an intact and clearly identifiable Illuminating round fused. Twenty seven pieces were severely rusted and it could not be determined if they were HE or practice. Nineteen rounds were identifiable 75 mm Rifle Anti-Tank Practice Rockets. Only six 60 mm Mortars were counted with four of them attached with fuses. Four 88 mm RPG Practice rounds were also counted. This number was followed by three 155 mm Projectiles which could not be identified. Two air delivered bombs were counted. One was a practice missile and the other looked like a discarded souvenir. A single 68 mm Practice Rocket was also found at this site.

Table 4.17: Type and quantity of UXO found at Sector B UXO disposal site



UXO TYPE	QUALITY	TOTAL
81 mm Mortar Illum No Fuse	Live	**64**
81 mm Mortar Fused	Unknown	**70**
60 mm Mortar No Fuse	Practice	**02**
60 mm Mortar Fused	Practice	**04**
120mm Mortar No Fuse	Practice	**27**
88 mm RPG Anti-Tank	Practice	**04**
120 mm Mortar Illum Fused	Live	**01**
75 mm Rifle Anti-Tank	Practice	**19**
Unknown Aircraft Missile	Practice	**01**
155 mm Projectile No Fuse	Unknown	**03**
68 mm R1M1 Rocket	Practice	**02**
90 mm Anti-Tank Rocket	Practice	**0**

A total of 163 pieces of ammunition were found at Gonzalespoort next to a firebreak. The remnants of ammunition were scattered on ground surface (images in Annexure 2). Table 4.18 summarises the quantity and type of UXO found at Gonzalespoort Firebreak. The most abundant munitions at this site were M791A1 Practice Rifle Grenades (65 pieces) > 90 mm Anti-Tank Practice Rockets (42 pieces) > M26 Practice Hand Grenades (31 pieces) > 105 mm Shells. For other UXO types including 120 mm Mortar bombs, 81 mm Mortar bombs, 88 mm RPG Anti-Tank Practice Rockets and 60 mm Mortar bomb were one item each was found on the site. Many of the UXO such as sub-munitions and Anti-Tank Rockets were rusted and could not be identified as Practice or HE.

The least UXO contaminated site found in the MTA during the study was the UXO site at Sector A next to the broken Reservoir. Table 4.19 exhibits the assortment of UXO located at the site. Only 22 pieces of UXO were found at the site. Almost all ammunition was rusted and could not be characterised as HE or Practice. A 127 mm MRL Rocket found sticking in the ground on the site was classified as disposed UXO as it appeared to have been fired and became a dud. About 13 pieces of 90 mm Anti-Tank Rockets were, three 155 mm Projectiles and three 105 mm Shells were found at the site. The disposal appears to have been from a clean-up operation to establish a temporary base nearby where a cluster of blue gum trees formed a canopy.

Table 4.18: Type and quantity of UXO disposed at Gonzalespoort Firebreak

UXO TYPE	QUALITY	QUANTITY
120 mm Bomb	Unknown	01
M791A1 Rifle Grenades	Practice	65
M2642 Hand Grenades	Practice	31
105 mm Shells	Unknown	21
90 mm Anti-Tank Rocket	Unknown	42
81 mm Mortar Bomb	Red Phos	01
88 mm RPG ATk	Practice	01
60 mm Mortar No Fuse	Unknown	01

Table 4.19: Type and quantity of UXO found at Sector H UXO site

UXO TYPE	QUALITY	QUANTITY	TOTAL
155 mm Projectile	Unknown	03	**03**
105mm Shells	Unknown	06	**06**
90 mm Anti-Tank Rocket	Unknown	13	**13**

Table 4.20 exhibits a summary of the UXO quantification data for General De La Rey Training Area by listing the types and cumulative quantities of UXO found in the MTA. A total of 1054 UXO items were counted. A review of the data indicated that 60 mm Mortars were the most abundant UXO in the MTA at 399 pieces. This is followed by 81 mm Mortars at 326 and Rifle grenades at 138, respectively. The rest of the UXO types numbered between10 and 100. Graphical representation of the data is provided in Figure 4.8 expressing the percent distribution of the UXO. 60 mm Mortars made 38 percent of the total UXO counted, followed by 81mm Mortars at 31

percent. Thirteen percent of the UXO was Rife Grenades. The rest of the UXO ranged between just over 0 percent (88 mm Anti-Tank) and 5% (90 mm Anti-Tank Rockets).

Table 4.20: Total counted UXO by type and quantity

UXO TYPE	**TOTAL**
81 mm Mortar	**326**
60 mm Mortar	**399**
120mm Mortar	**30**
M791A1 Rifle Grenades	**138**
M2642 Hand Grenades	**46**
88 mm RPG Anti-Tank	**05**
75 mm Rifle Anti-Tank	**19**
Unknown Aircraft Missile	**01**
155 mm Projectile	**06**
105 mm Shells	**27**
68 mm R1M1 Rocket	**02**
90 mm Anti-Tank Rocket	**55**

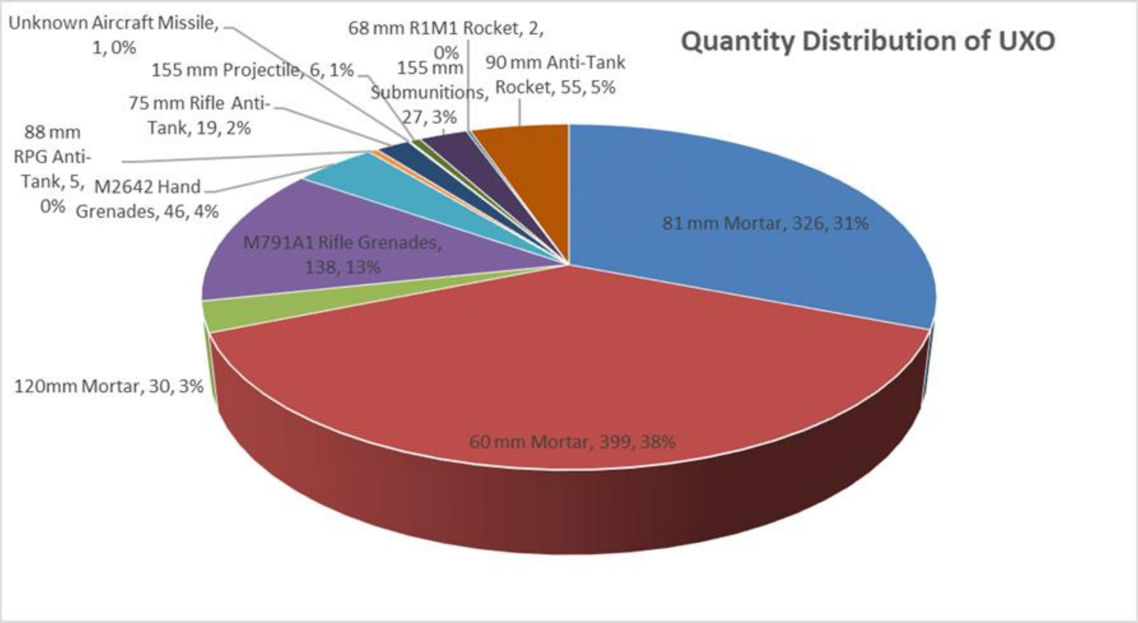


Figure 4.8: Quantity distribution of UXO in the study area

4.3.2 Randomly occurring UXO

Randomly occurring UXO were located at various locations in the MTA. Table 4.20 lists the locations, quantity and types of the UXO found during the study. Some UXO such as 122mm MRL Rockets are largely found in Sector A, which has been identified has a firing location. Note must be taken that it was explained in Chapter 2 that Sector A was previously used as MRL target due to the longer range it offers when firing from south west to north east. As a result, the Sector is also referred as Target Area when describing MRL UXO Locations.

Table 4.21: Random UXO Locations at General De La Rey Training Area

SERIAL	**FUNCTION**	**LOCATION COORDINATES**	**OBSERVATION**
1	Impact Area	26˚37'25.4" S 27˚00'16.7" E	120mm Mortar/Illum/Tank
2	Impact Area	26˚37'07.1" S 27˚00'14.6" E	105 mm Projectile/Road
3	Impact Area	26˚37'10.7" S 27˚00'00.8" E	120mm Mortar/HE/Rocks
4	Impact Area	26˚37'08.4" S 27˚00'16.2" E	120mm Mortar Bomb/Illum/Road
5	Impact Area	26˚37'09.5" S 26˚59'24.3" E	120mm Mortar/UXO Site
6	Impact Area	26˚37'09.0" S 26˚59'24.3" E	90mm HE Anti-Tank Rocket
7	Impact Area	26˚37'04.9" S 26˚59'24.7" E	120mm Mortar Bomb
8	Impact Area	26˚37'05.9" S 26˚59'24.9" E	127mm MRL Rocket
9	Impact Area	26˚37'11.1" S 26˚59'25.4" E	120mm Mortar/Illum
10	Impact Area	26˚37'07.6" S 26˚59'35.8" E	120mm Mortar/Ilium/Road
11	Firing Position	26˚36'09.3" S 26˚58'05.2" E	127mm MRL Rocket In Ground
12	Firing Position	26˚35'00.2" S 26˚58'56.7" E	127mm MRL Rocket In Ground
13	Impact Area	26˚37'54.1" S 27˚01'37.8" E	120mm Mortar Bomb In Ground
14	Impact Area	26˚37'06.7" S 26˚59'35.8" E	120mm Mortar Illum In Ground
15	Impact Area	26˚37'12.5" S 26˚59'24.9" E	90mm HEAT Rocket On Ground
16	Impact Area	26˚37'15.8" S 26˚59'25.8" E	120mm Mortar In Ground
17	Impact Area	26˚37'26.0" S 26˚59'17.0" E	120mm Mortar On Ground
18	Impact Area	26˚37'12.2" S 26˚59'06.6" E	155mm Projectile Broken Fuse
19	Impact Area	26˚37'16.1" S 26˚59'00.3" E	120mm Mortar In Ground
20	Impact Area	26˚36'45.3" S 27˚00'03.1" E	155mm Projectile Fuzzed
21	Impact Area	26˚36'45.3" S 27˚00'03.1" E	120mm Mortar In Ground
22	Firing Position	26˚35'41.0" S 26˚58'34.7" E	127mm MRL Rocket In Ground
23	Impact Area	26˚35'51.1" S 26˚58'33.4" E	90mm HEAT Rocket On Ground
24	Impact Area	26˚36'03.3" S 26˚59'02.3" E	155mm Projectile/Broken Fuse/TB 116
25	Firing Position	26˚35'16.6" S 26˚58'50.9" E	127mm MRL Rocket In Ground
26	Firing Position	26˚34'52.3" S 26˚59'02.2" E	127mm MRL Rocket In Ground
27	Firing Position	26˚34'49.4" S 26˚59'05.7" E	127mm MRL Rocket In Ground
28	Firing Position	26˚34'48.2" S 26˚59'04.1" E	127mm MRL Rocket In Ground
29	Firing Position	26˚34'48.2" S 26˚59'04.1" E	155mm Illum On Ground/ Broken Fuse
30	Firing Position	26˚34'45.7" S 26˚59'06.9" E	127mm MRL Rocket In Ground
31	Firing Position	26˚34'45.5" S 26˚59'06.4" E	127mm MRL Rocket In Ground
32	Firing Position	26˚34'44.2" S 26˚59'04.8" E	127mm MRL Rocket In Ground
33	Firing Position	26˚34'41.3" S 26˚59'11.7" E	127mm MRL Rocket In Ground
34	Firing Position	26˚34'41.7" S 26˚59'15.7" E	127mm MRL Rocket In Ground

The data indicated that most of the random UXO discovered were 127 mm Multi Rocket Launcher darts and 120 mm Mortars. Thirteen MRL and 13 Mortars were counted in total (Figure 4.9). Most of the MRL rounds were found in Sector A. With over half the length of the projectiles in the ground, it was not easy to determine if the projectiles had exploded, partially exploded or darts. This was also the case with 120 mm Mortars, which were mostly identified by their fins sticking out of the ground. Due to the fact that tempering with UXO is prohibited and dangerous, all munitions protruding were recorded as UXO. The second highest number of UXO were 155 mm Projectiles in use by GV5/GV6 howitzers of the Artillery. A total of three projectiles were found lying on ground surface with intact fuses. It was evident that the projectiles have been fired but have failed to function properly and have ricocheted from the intended target as whole munitions. Only three 90 mm Fin Stabilised Practice rounds were found at Sector B. These also were whole munitions lying above ground with fuses intact.

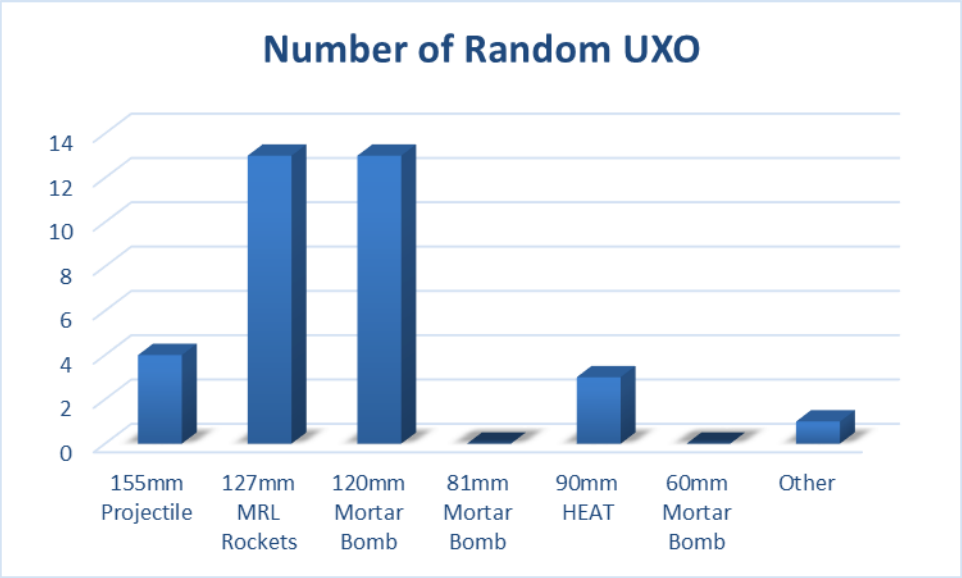


Figure 4.9: Type and number of Randomly located UXO

Chapter 5 Discussion, Conclusion and Recommendations

5.1 Introduction

The Defence Review (2015) states common environmental problems experienced in Military Training Ranges under the custody of the SANDF. These problems include, but not limited to, deposition of explosive residues, remnants of munitions, heavy metals and unexploded ordnance (Dontsova, et al., 2006; GICHD, 2017; Walsh, et al., 2009). A review of literature revealed that explosive residues are the result of incomplete consumption of explosive compounds during detonations Penningtn, et a., 2008b). This occur at detonation craters during live firing exercises and at UXO sites during Blow in Place (BIP) operations and Open Burning/Open Detonation (OB/OD) of munitions (Dontsova, et al., 2006; Walsh, et al., 2009). Explosives may also leach from UXO in ambient shooting range environments. UXO can be dangerous to personnel and animals should be assumed to be unstable at all times. In addition, they contribute to enrichment of the environment with heavy metals and leaching explosives (Cross et al., 2016). Exploded ordnance release heavy metals through deposition of metal fragments from fragmentation of ammunition shells. This results in enrichment of heavy metals in the long run, increasing the mass balance of heavy metals.

This combination of environmental problems are detrimental to the long term strategy of the SANDF to hand over some of the unused military properties back to public when it is no longer required. The Defence Review (2015) also indicated that the SANDF did not possess the necessary expertise to deal with these environmental problems. Several studies have demonstrated that civilian communities occupying territories formerly used by the armed forces have experienced problems with remnants of munitions and contaminated lands. Military institutions around the world have taken to expanding research in effort to characterise these environmental problems with a view to find remedial solutions (Hibert, 2012; Magagula, 2014). The current study sought to inspire the SANDF to review possibilities of developing and capacitating itself with an internal skills base for scientific environmental impact assessments at training areas. This would bridge the gap of lack of expertise and reduce dependence on procured skilled, while remaining compliant with environmental legislation.

5.2 Review of hypotheses tested

The study consisted of four objectives and three hypothesis, namely; to investigate the impact of explosive munitions on soil resource, the impact on water resources, the presence of UXO in ambient MTA environment and at disposal sites, and the enrichment of heavy metals in the MTA as a result of explosive munitions. The study also intended to use an environment external to the study area measuring variation between MTA and control areas. The study hypothesised that soil and water samples collected from the MTA will be contaminated with energetic materials from explosive munitions, including watercourses leading from impacted areas. It was also hypothesised that munitions that failed to detonate may be present in random locations, resulting in an increasing presence of UXO at the study area. A further hypothesis was that both exploded and unexploded munitions cause elevated heavy metal concentrations in soil and water resources of the MTA.

5.3 Summary of findings

5.3.1 The nature of explosive contamination

Explosive compounds are not naturally occurring but are synthetic industrial products (US Army, 1990). At military institutions, their occurrence is likely the result of military activity involving explosive munitions (Pichtel, 2012). This study was conducted in a military training area with the goal of determining the existence of contamination in soil and water media. Literature studies have reported that contamination of military installations around the world with explosive residues has become an important environmental problem as this has often complicated land redistribution efforts when the land had to be transferred back to civilians. This was one of the major problems cited by the Defence Review (2015). Physico-chemical characteristics, environmental impacts and toxicity of explosive compounds is covered in Chapter 2.

Eight explosive compounds were detected in soil and water samples from all sectors of the MTA and adjacent farms (TNT, RDX, HMX, TNB, 3-NT, 4-NT, NB, and Tetryl). The TNT has over twenty transformation products listed by Walsh et al. (1995) but not all are target analytes in Method 8330a. Degradation products of TNT were reported to be less toxic than the TNT in decreasing order of degradation (Kalderis et al., 2011). According to Walsh et al. (1995) 2,4,6-TNT in water is readily photolysed into 1,3,5-TNB when exposed to sunlight. When in soil, TNT exposed to sunlight in anhydrous conditions is photolysed into 2,4-DNT and 2,6-DNT. These intermediate isomers were not detected in the study area from both water and soil samples but are target analytes in Method 8330a. Further photolysis of the two isomers result in the formation of n-Nitrotoluene (2-NT, 3-NT and 4-NT). Detection of 3-NT was only in one of the control areas (Sector F) and 4-NT was detected in Sector B near the OB/OD pits at Trig Beacon 116, at Sector B near the water pond and at Sector C around a firing point. The NT is highly soluble at the rate of 440 mg/L in water and is immediately mobile to deeper soil layers once introduced. This observation explains the absence of Nitrotoluene in surface water samples.

The presence of TNB in soil samples may be explained by phototransformation of TNT in the presence of interstitial water in the soil (Monteil-Rivera et al., 2009; Walsh et al. 1995). Formation of TNB does not appear to be a pathway for formation of DNTs or NTs. TNB, known to be a co-contaminant of TNT, was detected in higher concentrations than TNT in all samples in which the compounds were detected. The concentration of TNB was higher in water samples (up to 336.3 µg/kg) than in soils samples (up to 11.7 µg/kg). The TNB was also detected in a borehole sample at concentration of 124 µg/kg in Aadil Farm. The above information indicates that over half of the contamination detected in this study was related to TNT and its transformation products.

The RDX and HMX undergo limited phototransformation (Jenkins et al., 2012) and have been detected in water samples in pure form. Transformation derivatives of the two compounds are not target analytes in Method 8330a used in this study. The two compounds are less water soluble and have less sorption tendency than TNT. Thus these compounds are mobile in soil, explaining their limited detection in surface soil samples (Jenkins et al., 2012). The RDX was not detected in any soil samples while HMX was detected in two soil samples from Sector D and Sector B. The detection at Sector D was at a site where excess propellant was burnt after Module X 1. The detection at Sector B was in an explosion crater from a 120 mm Mortar during Module X2. Both RDX and HMX were detected in water samples from both MTA and control sites. The highest RDX detections were at Sector A and Sector G surface ponds in the order of above 100 µg/kg. HMX was detected only in control water samples in Sector F and Sector G. The highest detections were in Sector F at Sweet Cinnamon Dam.

Tetryl can remain in soil for decades despite discontinuation of its production and use (Alfaraj et al., 2016). It is highly unstable and is readily water transported deeper into soil than by runoff, explaining its non-detection in water accumulation ponds. Its detection was largely at OB/OD sites as it is used as a blasting agent during UXO destruction. It was detected in soil samples from four UXO sites and two explosion craters at concentrations ranging between 15.3 µg/kg and 29 µg/kg.

Nitrobenzene (NB) is an additive in propellant formulations. Method 8330a used in this study does not include standards for analysing propellant formulations. Detection of NB in samples suggests that contamination with propellants is probable. Nitrobenzene was, however, not detected in soil samples. It was detected in water samples from Sector A, Sector B and Sector F. The highest detections were in Sector A and Sector B. Further investigation using EPA Method 8330b is required to determine propellant contamination. All NB detections were less than 55 µg/kg.

5.3.2 UXO accumulation in the study area

Unexploded Ordnance are explosive devices that have been set up, fired, placed or dropped on a target but have failed to function as planned, remaining in the environmental as an explosion or contamination hazard (EPA, 2002). The occurrence of UXO in MTAs and former theatres of war remains a global problem, particularly in countries that experienced large scale bombings and major combat operations during the two World Wars. In recent decades, literature studies reported that newly introduced UXO were becoming a problem in military training ranges (EPA, 2002, Pennington et al., 2008b).

Two types of UXO locations were investigated at general De La Rey Training Area. Random UXO were identified and recorded by type and location. Their description and location data is tabulated in Appendix A. Some of these were still fused while some were not fused but contained explosive fill. A total of 34 UXO pieces were found in ambient terrain on the MTA. The largest number of UXO was thirteen 127 mm Multi Rocket Launcher darts and thirteen 120 mm Mortar Bombs. These accounted for over 70% of randomly located UXO. Almost all Mortar Bombs were located in Sector B and almost all MRL rockets were located in Sector A. As explained in Chapter 4, Sector A, although classified as a firing position in this study, was favoured for MRL targeting due to the dimensions of the MTA. Large scale sighting of shell fragments indicated that the area has previously been targeted with Mortars and 155 mm projectiles. This suggests that the use of the MTA has changed dynamics over time, probably due to temporal changes in training methods. This observation was also encountered in other parts of the MTA such as Sector E. Only three of 155 mm and none f 90 mm Antitank UXO were found in the main target area, suggesting that 120 mm Mortars and 127 mm MRL rockets have a higher dart rate than other munitions. Alternatively, it could mean that these munitions are used more extensively than other munitions and the dart rate is a function of the percentage of ammunition fired. Some of the located remnants of munitions were Low Order Detonations, some half the size of the projectile, with part explosive fill visible.

These were not counted as UXO but the area next to them was sampled for analysis. None of the LODs exhibited detectable amounts of explosive compounds.

Certain areas at General De La Rey Training Area were used for UXO disposal. A total of Nine UXO sites were located. Description of the sites is also tabulated in Annexure A. Four UXO sites were used as UXO dumping sites and the other five as OB/OD sites. All UXO sites were sampled for explosive and heavy metal contamination. The UXO site at Sector E1 contained at least 672 pieces of ammunition, more than half of which were 60 mm Mortar Bombs, followed by 81 mm Mortar Bombs. From the imagery in Annexure B, it is clear that the UXO was off loaded at the site. About three OB/OD pits contained various types and quantities of UXO. The disposal site at Sector B had similar characteristics but with relatively smaller quantity of UXO (197 pieces counted). The discovery of air delivered UXO at Sector B disposal site also suggested that some of the UXO were off loaded there. It could not be determined whether these were collected from the MTA or intentionally disposed there from remote locations. At Gonzalespoort and Sector A, the discarded UXO was done on open soil and not in prepared pits. The site at Gonzalespoort consisted mostly of Hand Grenades, Rifle Grenades and 105 mm projectiles, while Sector A consisted of a few 155 mm Shells. The ammunition at these sites appeared to have been gathered there from cleaning operations from within the MTA. A total of 1054 UXO items were counted at the disposal sites. The amount of UXO is extremely higher than counted due to the fact that UXO cannot be handled and therefore only items on the surface of the pile were counted. A more comprehensive quantitation would have been achieved with expert participation.

The rest of the UXO sites were OB/OD sites. These are distinguishable by burnt soil, remnants of exploded ammunitions and detection of explosive residues in samples from the sites. Soil samples from these sites contained detectable concentrations of explosives. These included the UXO dumping site at Gonzalespoort, Sector H, Sector B (Trig Beacon 116, Main Target Area and north east of OP Tree) and both UXO sites at Sector E. Explosives detected at these sites included Tetryl, 2,4,6-TNT and 1,3,5-TNB. All detections were below 30 µg/kg. The highest detections were of Tetryl in samples SSB02C2 and SSH02AX. The RDX and NB were detected in two water samples from the UXO site at Trig Beacon 116 (WSB07AWL and WSB07BWL) at 53.8 µg/kg and 38 µg/kg, respectively.

5.3.3 The nature of heavy metal contamination in the study area

Heavy metals occur in the environment both naturally through pedological processes in trace concentrations less than 1000 mg/kg (Addis & Abebaw, 2016; Gautam et al, 2016; Wuana & Okieimen, 2011). Some metals are used by plants and other living organisms in biological processes. When the removal of heavy metals is less than their introduction, pollution risk increases (Masindi & Muedi, 2018). This topic is discussed at length in Chapter 2. Many heavy metals have been reported to have carcinogenic effects of organisms such as attack on central nervous systems, liver and blood systems of vertebrates (Addis & Abebaw, 2016; Tangahu et al., 2011). Monitoring the pathways of heavy metal introduction to environments is of utmost importance to prevent future costly remediation.

Eleven heavy metals of interest listed in NEMA (2008) were selected for analysis. Although the list of heavy metals analysed was longer, these were listed as the most environmentally hazardous and therefore undesirable metals in the South African context. While metals such as Iron (Fe) were detected in higher concentrations, they are already naturally occurring in high background concentrations and slight enrichment will not constitute statistically significant contamination. The heavy metals were Vanadium (V), Chromium (Cr), Cobalt (Co), Zinc (Zn), Arsenium (As), Copper (Cu), Cadmium (Cd), Mercury (Hg), Lead (Pb), Nickel (Ni) and Manganese (Mn). Soil and water samples were collected from the MTA and control sites to make statistical inferences of potentially contaminated areas. Sample locations are detailed in Annexure A.

Heavy metal content was analysed using EPA Method 3051a: Microwave Assisted Acid Digestion and determinations achieved on an ICP-MS. Sample processing and analysis methods are detailed in Chapter 3. Analysis results are presented in Chapter 4. Average concentrations of heavy metals in MTA field samples were generally higher than background samples in both soil (V, Cr, Mn, Cu, As, Cd, and Pb) and water samples (Cr, Mn, Co, Zn, Ni, and Pb). This translates to 63.64% of soil samples and 54.55% of water samples. Most of the analysed samples had concentrations below the legal limit set out in NEMA (2008) and WHO (2017). Six soil samples (V, Co, Ni, Zn, Cd and Hg) had concentration below the recommended reference limit. As was only slightly higher than the limit. Eight water samples (V, Cr, Ni, Cu, Zn, As, Hg and Pb) had concentrations below the legal limit. Cobalt had a concentration equal to the legal limit. This translates to 54.55% of soil samples and 72.73% of water samples. Although NEMA stipulates 6.5 mg/kg as the risk level soil concentration of Cr, WHO (2017) soil screening values recommends 100 mg/kg. Consideration of this screening value would liberate Cr to a significantly below legal limit. A review of literature suggests that reference concentrations must be checked against local characteristics (Herselman et al., 2005).

Heavy Metal concentrations also varied between individual samples. Severe contamination with Mn was observed in two soil samples from OB/OD sites (SSB02AX and SSH02AX) with concentrations above 1 000 mg/kg while the other five samples contained concentrations below the recommended 750 mg/kg. This trend was observed in water samples from Sector B where individual metal concentrations caused elevated MTA average value. This suggests that some average MTA concentrations stipulated present a false positive due to small sample bias from just a few samples. Results in this study are expected to generate inferences for further characterisation and mapping out of the contaminated sites using more rigorous sampling methods. Five of the analysed heavy metals had very high concentrations in individual soil samples. Chromium (Cr) in SSB2AX measured 1.5 times the legal limit (assuming a WHO limit of 100 mg/kg). Manganese (Mn) in SSH01AX and SSB02AX measured six and seven times the NEMA limit, respectively. Copper (Cu) in SSB02AX measured 27.8 times the limit. Lead (Pb) in SSD07 and SSB02AX measured five and four times the NEMA limit, respectively, and AS in SSD07 wast five times the limit. Four water samples with high contamination included Mn in WSB01BWL and WSB07BWL which was 84 and 40 times the recommended limit, respectively, Co in WSB01BWL with five times the limit, Cr in all samples, including control samples, with above NEMA limit and Pb in WSB01BWL with twice the limit.

Enrichment Factor (EF) and Geo-accumulation Index (I*geo*) were used to determine enrichment levels of heavy metals as recommended by Abrahim & Parker, (2008), Gupta et al., (2014) and Muzerengi, (2017). Mercury (Hg) was used as the normalization factor for soil analyses and Cd was used as normalisation factor for water samples. EF values for soil and water samples fall within six categories determining the level of enrichment as discussed in Chapter 4. In soil samples V, Cr, Co, Ni, Zn, As and Hg were categorised between deficiency to moderate contamination (average EF < 2) while Mn, Cu, Cd, Pb were categorised in moderate enrichment (average EF between 2 and 5). Individual samples indicated that Mn was significantly enriched in SSH02AX at EF=5.6 and SSB02AX at EF=6.9. Copper (Cu) was extremely enriched in SSB02AX at EF=20.5. Cadmium (Cd) was strongly enriched in SSB07D and SSH02AX at EF=10.9 and EF=9.1, respectively. With averaged MTA EF values for water samples Cr, Mn, Co, Zn, As, Cd, Hg and Pb were classified as deficiency to moderate enrichment (EF < 2). Vanadium (V) and Copper (Cu) were classified as significantly enriched with MTA average EF=10.9 and 13.8, respectively. Nickel (Ni) was classified in very high enrichment category with MTA average

EF=31.4. A review of individual metal compounds per sample indicated that some metals were more severely enriched locally and fall in a more severe category than the MTA average classification. Vanadium (V) was detected in a single MTA sample (WSB01BWL) and the EF value was 65.6 (extreme enrichment). Nickel (Ni) enrichment was in only two samples (WSB01BWL and WSB07BWL) at EF=196.2, extreme contamination and EF=25.4, very high enrichment, respectively. Copper (Cu) was extremely enriched in WSB01BWL at EF=50 and very highly enriched in WSB07BWL at EF=25.4. This data also indicates that averaging may result in false negative assessment of contamination. One important observation was of Mn. While this compound was detected in very high concentrations in MTA samples, the zero detection in control samples have resulted in a zero enrichment factor due to non-detection in control samples, resulting in a false negative.

The MTA average I*geo* values per heavy metal in soil suggested a pollution index between I*geo*=2.5 in Co (moderate to strong contamination) to I*geo*=4.4 (strong to extreme contamination) in Cd. Seven metals exhibited moderate to strong contamination (V, Cr, Co, Ni, Zn, As, and Hg). Mn and Pb were in the strongly contaminated category. The Cu and Cd were classified in strongly to extremely contaminated category. Reviewing individual metals in samples revealed that Mn contamination in SSH02AX and SSH02AX was in the extremely contaminated category at 5.2 and 5.9, respectively. Chromium (Cr) contamination in SSA07 was 3.2 and in SSB02AX it was 3.4 (strong to extreme contamination). Copper (Cu) contamination in SSA02AX exhibited extreme contamination at I*geo*=13.4. The same was observed with As in SSD07 at I*geo*=5.5 and Cd in SSH02AX and SSB02AX at I*geo*=7.7 and 7.2, respectively. Lead (Pb) in SSD07 and SSB02AX exhibited strong to extreme contamination. In water samples no contamination from Cr, Mn, Co and Pb was observed. Vanadium (V) was in the uncontaminated to moderately contaminated category, although this observation emanates from averaging the only contaminated sample, WSB01BWL, which had I*geo*=3.6 (strong contamination). Nickel (Ni) was classified in the moderately contaminated category for MTA, but WSB01BWL was strongly to extremely contaminated with Ni at I*geo*=4.1 and WSB07BWL moderately to strongly contaminated with Ni at I*geo*=2.8. Copper (Cu) was classified in moderate to strong contamination. Individual samples (SSB01BWL and WSB07BWL) exhibited strong contamination with Cu I*geo*=3.5 and I*geo*=3.2, respectively. A similar trend was observed in Zn and As, both of which had an MTA classification of moderate contamination but one sample (WSB01BWL) had I*geo*=2.3 for Zn and I*geo*=2 for As.

5.4 Potential limitations in the Study

Explosive analyses in this study were conducted on SW846 Method 8330a HPLC-RP with fixed UV detection. HPLC is the favoured and most popular method for analysing samples for explosive residues (Jenkins et al., 1988). The HPLC has a detection limit between 0.3 µg/kg to 1000 µg/kg. All samples analysed in this study were below the upper limit. This is important since severity of environmental impact is based on the higher magnitude. All protocols recommended in the method were followed with only slight variations to accommodate available laboratory materials and reagents. All procedures relating to sampling, sample processing and extraction were followed closely to avoid erroneous observations. The following conditions, which have not been elaborated in consulted literature, may affect the quality of the obtained results and observations:

Samples were obtained in systematic manner by altering sample size per sampling session. Due to apparent analysis cost, it became necessary to pool samples in order to limit the number of samples without compromising sample coverage of the study area (Crockett et al., 1996). Three or six discrete soil cores were collected per sector. During pooling of samples, a set of three discrete samples from each sector were collected at 100 meter intervals were blended and subsampled as discrete sub-samples for analysis, significantly reducing the number of analysed samples while maintaining representativity as each set was obtained at a single target. A few discrete soil cores from different sections of the MTA were also analysed as discrete samples. This is also the basis of Multi Increment Sampling as recommended by Jenkins et al. (2012) and Creockett et al., (1996). According to Crockett et al., (1996), MIS has the advantages of physically averaging out error and providing a higher level of confidence than discrete sampling. However, in a hypothetical 30 increment sample, if only 10% of the soil cores were highly contaminated with explosives, an observed low concentration may be the result of the averaging procedure, exhibiting a false negative. Similarly, a single soil core may suggest a larger area is contaminated, resulting in a false positive observation. Onsite technology can be instrumental in pre-determining contaminated sites before sampling techniques can be employed.

According to Jenkins et al. (1998), commercial laboratory filters can sieve out some analytes, reducing actual sample concentrations. Although laboratory grade 0.45 µm Teflon filters were used in this study, no guarantee could be afforded against filtration loss, physically reducing observed analyte concentrations. Acetonitrile was used for sample extraction and elution as recommended in the Method. Samples were allowed to stand 15 minutes after ultrasonication to allow complete flocculation. No guarantee can be afforded in studies that entire analytes are removed from the sample matrix during the salting out process as the degree to which explosive compounds are irreversibly sorbed to soil particulates is unknown.

For Heavy Metal analyses using EPA Method 3051a, a 2 gram sized soil sun-sample was digested under microwave conditions and the extract was analysed in mass spectrometry ICP-MS. This method is designed to detect as low as part per trillion concentrations of heavy metals in soil and water sample extracts. The only limitations related to the method relate to the soil sampling procedures (averaging), in a similar manner as for explosive analyses. Water samples are also extracted using filtration techniques used in Method 8330. Samples were mainly collected at the edge of the water source as resources for deeper water sampling were limited. It is not known if different water levels may have uncovered untouched layers of contamination, resulting in different observations from samples collected at the same site. These limitations are not expected to alter the interpretation of results obtained in this study. These potential errors have not been the focus of most of the literature studied, thus more effective methods of data collection and analysis need further research in order to eliminate error and produce the most reliable results.

5.5 Conclusion and recommendations

Explosive compounds are persistent, toxic and environmentally undesirable as they are not naturally occurring (xenobiotic). The TNT was reported to be is toxic in raw chemical form and its toxicity decreases with its subsequent degradation metabolites (Kalderis et al. 2017; Lotufo, 2013). Raw TNT is more lethal than RDX and HMX to microbes, invertebrates and algae, retarding some important ecosystem functions. At concentrations of 360 mg/kg, TNT was reported to cause 70% mortality in earthworms. It took an even higher concentration of RDX (540 mg/kg) and HMX (1 000 mg/kg) to achieve 60% earthworm mortality. In combination, the three explosive compounds were observed to cause 100% earthworm mortality at 180 mg/kg. Metabolites of explosives were also reported to have reduced toxicity. Explosive compounds were detected in concentrations of less than 1 mg/kg in the current study. This leads to the conclusion that contamination of the MTA with explosive compounds exists but has not reached toxic levels to warrant immediate remediation. Measured maximum concentrations in this study were significantly lower than reported in other studies (Jenkins et al., 2001; 2012). This is based on comparison with findings in some USA bases where concentrations as high as 1750 µg/kg of TNT, 51 200 µg/kg of RDX and transformation products of TNT were measured. Around 100 µg/kg of RDX was also reported in MTA groundwater (Jenkins et al., 2001; 2012). As in the current study, determining whether the measured concentrations were recent or old is a daunting process.

Environmental managers are expected to continuously monitor contamination and generate remediation strategy well in advance to prevent adverse future environmental problems emanating from explosive contamination. Future research on vegetation and large animals is required to investigate current health effects related to intake of contaminated water and soil constituents. Explosives were found in control areas outside the MTA. This is an indication that some these compounds are mobile in the environment as documented in literature and have the potential of causing environmental and health problems at civilian installations neighbouring the MTA. Cooperation between interested and affected parties and the SANDF can help develop sustainable training area management practices by investigating the sources of contamination and jointly determining viable solutions to prevent adverse environmental impacts.

Sampling is the single most preferred method for investigating contamination. Mapping contamination in soil requires extensive employment of systematic discrete sampling, recording the sequence and position of each soil core and analysing each soil core in order to map out the dimensions of contamination. When inferences have been made such as in the current study, Multi Incremental Sampling techniques are the next step to effectively characterise the extent contamination, potentially exposing the pattern of heterogeneity. These can be implemented economically by employing onsite detection technology in order that contaminated sites can be determined before sampling, thereby reducing analysis costs. The vertical dimension must also be explored per site by sampling at variable depths in order to determine sites where contamination is likely to reach groundwater. This will assist in identifying pathways of contamination into neighbouring environments. No conclusive evidence was found in this study pointing to pathways of contamination in control areas, although it is highly evident that contamination at Sweet Cinnamon farm was through runoff water from the MTA.

No indices were found regarding the quantity of UXO constituting an environmental hazard. However, mere presence of UXO in the training area is an explosive hazard and these pose a risk to personnel during training. The large quantity of random UXO found at target areas indicate that range sweeps, after the various training exercises, fell short of detecting and marking the UXO for destruction or removal by ammunition experts. This problem should be treated as a matter of emergency for the purpose of general safety. Although most of the UXO in disposal sites appear to be inert practice explosives, most have aged, corroded and cannot be easily distinguished as HE or practice. There was significantly more explosive munitions at collection sites than reported in this study due to inability to count UXO beneath piles of these devices due to safety considerations.

Environmental and training area managers should initiate programs to remove or render safe UXO from the training area. Explosive compounds and heavy metals have been detected at many of the UXO and OB/OD sites, suggesting that some of the UXO is leaching explosive residues and heavy metals into the ground (Wilkinson and Watt, 2006). No characterisation of the vertical dimension of contamination was done. In addition, more extensive sampling is required to map out horizontal dimensions of contamination. This exercise is expected to come at a high cost due to the lack of onsite detection technology and the need to analyse individual discrete samples.

Contamination with UXO at the study area did not reflect the magnitude of the problem experienced in other parts of the word. Martin et al. (2019) indicated that South East Asia is the most UXO infested region in the world due to millions of tons of UXO including land mines and cluster bombs form the Vietnam War contaminating over 20% of the land in Vietnam, Cambodia and Laos. Sulineyadeth (2014) listed eleven UXO infested countries in the word in millions of tons. The three highest were Laos (80), Egypt (23) and Iran (11). African countries included Angola (10) and Mozambique (3) in Sub-Saharan Country. Currently South Africa does not experience the threat of UXO as most is contained in MTAs, thus controlled, than in former conflict areas, as is the case with neighbouring Mozambique and Angola.

The SANDF needs to explore sustainable and green methods for UXO processing and disposal. Environmentally viable disposal methods have been well documented (Pennington et al., 2008a; Walsh et al., 2009). Using the right technology, munitions can be clinically dissected. The explosive fill can be recovered for reuse and the metal components can be recycled. The SANDF has a corps of munitions trained personnel (The South African Ammunition Corps), which can provide a starting point for characterising hazards, recovering and disposing UXO. SANDF also has internal engineering skills from the Army Engineering Corps, who are trained in mine detection. The existing technology should be sufficient for detection of buried UXO, or minor upgrades can made to reach the objective. Additional explosive detecting devices can be included for onsite detection of explosive residues during live firing exercises for real time monitoring of contamination. Failure to address the issues may result in attraction of looters from local civilian settlements looking for scrap metals in the MTA, which is currently poorly fenced, exposing civilians and unsuspecting persons to explosion hazards. Incidents have been reported where civilians were injured by explosive devices while trying to recover metals components of munitions or apprehended while collecting remnants of munitions from the MTA.

Heavy metals are non-volatile and recalcitrant to biodegradation (Gautam et al., 2016; Masindi & Muedi, 2018; Vasarevicius, & Greiciute, 2004). Contamination of the MTA with heavy metals is suspected to elevate concentrations of heavy metals at General De La Rey Training Area. Comparison between metal concentrations between the MTA and control samples indicated that the MTA had elevated heavy metal concentrations than control areas. Contamination was higher in soil samples than in water samples. Because heavy metals are not significantly mobile in soil, it is clear that contamination of water sources was minimal. Almost all heavy metals under analysis in water samples were below the WHO (2018) reference limits for drinking water, considering averaged values.

Some individual samples exhibited higher concentrations of heavy metals than reference limits. These samples corresponded mostly to the UXO sites at Sector B and Sector H. Cr, Mn, Cu, As and Pb had the highest concentrations in soil samples from these sites. However, the concentrations did not reach toxic levels. Enrichment Factor calculations indicated that heavy metals are generally deficiently to moderately enriched in the study area with the few mentioned exceptions being strongly to extremely enriched in specific areas. Most of the enrichment was at the UXO site in Sector B (Trig Beacon 116) in both water and soil samples. EF calculations depend on ratios of analyte concentrations between MTA and control area relative to the ratio of a reference element to its MTA concentration to determine the magnitude of enrichment.

Using averaged I*geo* values from soil samples to determine pollution level, the MTA was classified as moderately to strongly contaminated with most of the heavy metals discussed above. High AS and Pb contamination was observed at Sector D where excess charges were burnt. Strong to extreme contamination with Mn, Cd, and Cu was observed in samples from Sector H and Sector B OB/OD sites. Most water samples were classified in uncontaminated to moderately contaminated, with a few exceptions from individual samples. Similar to soil samples, metals detected in Sector B at the OB/OD site were moderately to strongly contaminated with V, Cu, Ni, Zn and As. The I*geo* values depend solely on the ratio between MTA and control concentration. I*geo* values in soil samples suggest that closer monitoring is required as MTA loading of heavy metals is much higher than control samples, despite their concentrations being below recommended limits. This is more so for Sector H and Sector B. Contamination at General De La Rey Training Area with heavy meats is way below the reported contamination at USA bases. Bricka et al. 1994) reported that about 920 out of 1200 MTAs surveyed across USA needed intervention. Concentrations as high as 3 000 mg/kg (Cr), 4 900 mg/kg (Pb) , and 453 mg/kg (Cd) were reported. Cr, Pb, Cd and HG were frequently above the allowed concentration at these bases.

The Environmental impact of explosive munitions at General De La Rey Training Area is that of three types of contaminations. Explosive compounds were detected in the study area but in ppb concentrations, therefore not considered enriched enough to cause environmental problems. Contamination with UXO is considered extreme judging by the amount of UXO in ambient environment and at disposal sites. The reported quantities are much less than the actual quantities. Intervention is required to remove UXO from the study area. Contamination with heavy metals in soil and water sources has also not reached toxic levels (less than recommended concentrations). The elevated concentrations are suspected to emanate from erosion of metal constituents of explosive munitions. Lower levels of heavy metals in water samples and control areas indicate that most of the contamination is in soil corresponding to areas affected by employment of explosive munitions such as UXO demolition pits and explosion craters.

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Annexures

Annexure A: Samples analysed for explosive and heavy metal contamination

MTA Soil Samples						
Serial	**Sample**	**Sector**	**Role Used**	**Coordinates**	**Sample Type**	**Remarks**
1	SSA01A	Sector A	Firing Point	26˚35'00.8" S 26˚57'17.4" E	Soil Sample	Water Hole
2	SSA01B	Sector A	Firing Point	26˚34'56.3" S 26˚57'19.2" E	Soil Sample	Water Hole
3	SSA04A	Sector A	Firing Point	26˚35'08.9" S 26˚57'28.3" E	Soil Sample	Water Hole/Thorn Bushes
4	SSA04D	Sector A	Firing Point	26˚35'08.5" S 26˚58'59.8" E	Soil Sample	Reservoir/Wind Mill South
5	SSA07	Sector A	Firing Point	26˚34'55.0" S 26˚59'10.0" E	Soil Sample	MRL Target
6	SSB01B	Sector B	Impact Area	26˚37'33.6" S 26˚59'00.0" E	Soil Sample	Trig Beacon 131, Low Ground
7	SSB02A	Sector B	Impact Area	26˚35'52.8" S 26˚58'30.0" E	Soil Sample	UXO Demolition Site/B01
8	SSB02C1	Sector B	Impact Area	26˚37'36.3" S 27˚00'02.5" E	Soil Sample	Small Bush, Near Tank, Illum
9	SSB02C2	Sector B	Impact Area	26˚37'30.8" S 27˚00'09.8" E	Soil Sample	Tank Target
10	SSB02C3	Sector B	Impact Area	26˚37'33.3" S 26˚59'52.9" E	Soil Sample	Armored Vehicle
11	SSB01D2	Sector B	Impact Area	26˚37'03.9" S 26˚59'24.3" E	Soil Sample	Wagon Wreckage Target
12	SSB02B2	Sector B	Impact Area	26˚37'29.2" S 26˚59'21.5" E	Soil Sample	Trig Beacon 131, Lower Hill
13	SSB02D1	Sector B	Impact Area	26˚37'06.7" S 26˚59'35.8" E	Soil Sample	Mortar Crater/Dirt Road
14	SSB02D2	Sector B	Impact Area	26˚37'03.9" S 26˚59'24.3" E	Soil Sample	Wagon Wreckage Target
15	SSB04	Sector B	Impact Area	26˚37'07.1" S 26˚59'37.0" E	Soil Sample	Next to Road
16	SSB04C	Sector B	Impact Area	26˚37'25.4" S 27˚00'16.7" E	Soil Sample	Tank Target
17	SSB04D1	Sector B	Impact Area	26˚37'07.1" S 26˚59'37.0" E	Soil Sample	Next to Road
18	SSB04D2	Sector B	Impact Area	26˚37'08.2" S 26˚59'34.5" E	Soil Sample	On Dirt Road

19	SSB07D	Sector B	Impact Area	26˚37'08.2" S 26˚59'34.5" E	Soil Sample	Sector B/On Dirt Road
20	SSB07C1	Sector B	Impact Area	26˚37'25.4" S 27˚00'16.7" E	Soil Sample	Op Tree Junction
21	SSB07C3	Sector B	Impact Area	26˚37'25.4" S 27˚00'16.7" E	Soil Sample	Tank Target
22	SSC02	Sector C	Firing Point	26˚34'04.8" S 27˚00'46.8"E	Soil Sample	Trig Beacon 187
23	SSD01A2	Sector D	Firing Point	26˚35'52.8" S 26˚58'30.0" E	Soil Sample	UXO Demolition Site
24	SSD02A	Sector D	Firing Point	26˚37'59.3" S 27˚02'26.6" E	Soil Sample	Open Burn of Charges
25	SSD05A	Sector D	Firing Point	26˚38'00.4" S 27˚02'23.4" E	Soil Sample	Leerdagstelling
26	SSD05B	Sector D	Impact Area	26˚38'06.1" S 27˚01'55.2" E	Soil Sample	Yellow Target/Pre-Firing
27	SSD06	Sector D	Impact Area	26˚38'06.1" S 27˚01'55.2" E	Soil Sample	Yellow Target/Post Firing
28	SSD07A	Sector D	Firing Point	26˚37'56.0" S 27˚02'23.7" E	Soil Sample	Open Burning of Charges
29	SSD07B	Sector D	Firing Point	26˚37'59.3" S 27˚02'26.6" E	Soil Sample	120mm Mortar Firing Position
30	SSE01B	Sector E	Firing Point	26˚38'59,9" S 27˚01'35.0" E	Soil Sample	120mm Mortar Firing Position
31	SSE02A	Sector E	Firing Point	26˚39'04.0" S 27˚01'29.6" E	Soil Sample	120mm Mortar Firing Position
32	SSE02B	Sector E	Firing Point	26˚39'01.5" S 27˚01'33.8" E	Soil Sample	120mm Mortar Firing Position
33	SSF01	Sector F	Control Point	26˚37'40.7" S 27˚02'55.4" E	Soil Sample	Sweet Cinnamon Bridge
34	SSF07	Sector F	Control Point	26˚37'40.7" S 27˚02'55.4" E	Soil Sample	Sweet Cinnamon Bridge
35	SSG01	Sector G	Control Point	26˚36'24.6" S 27˚02'16.6" E	Soil Sample	Aadil Farm
36	SSH01A	Sector H	Firing Point	26˚39'18.8" S 26˚57'22.4" E	Soil Sample	Trig Beacon 136, Flat Terrain
37	SSH01B	Sector H	Firing Point	26˚39'18.2" S 26˚57'24.8" E	Soil Sample	Trig Beacon 136, Flat Terrain
38	SSH03	Sector H	Firing Point	26˚37'32.3" S 26˚57'00.1" E	Soil Sample	Spookbos/Bushes
39	SSH04	Sector H	Firing Point	26˚37'32.3" S 26˚57'00.1" E	Soil Sample	Spookbos/Bushes
40	LIC 1	Sector B	Impact Area	26˚35'52.9" S 26˚58'30.4" E	Soil Sample	OB/OD Pit/ Bottom/Discrete/SSB02B

41	155 MM	Sector B	Impact Area	26˚35'58.3" S 26˚58'36.1" E	Soil Sample	Corroding Shell/Trig 116/SSB02B
42	OP TREE	Sector B	Impact Area	26˚37'01.2" S 27˚00'07.2" E	Soil Sample	OP Tree/Junction/36 Increment
Unexploded Ordnance Destruction Site Samples						
43	SSA02AX	Sector A	UXO Site	26˚34'55.2" S 26˚58'58.8" E	Soil Sample	UXO Disposal/ Reservoir
44	SSB02AX	Sector B	UXO Site	26˚34'55.2" S 26˚58'58.8" E	Soil Sample	UXO Disposal/Reservoir
45	SSB02EX	Sector B	UXO Site	26˚37'05.8" S 27˚01'37.7" E	Soil Sample	Gonzalespoort Firebreak
46	SSB02CX2	Sector B	UXO Site	26˚36'45.0" S 27˚00'03.0" E	Soil Sample	OP Tree 2/ OB/OD Site
47	SSB02CX1	Sector B	UXO Site	26˚37'12.0" S 27˚00'14.4" E	Soil Sample	OP Tree/UXO Dumping
48	SSB02DX	Sector B	UXO Site	26˚37'16.0" S 26˚59'25.0" E	Soil Sample	UXO Pits/ OB/OD Site
49	SSB02DX1	Sector B	UXO Site	26˚37'16.0" S 26˚59'25.0" E	Soil Sample	UXO Pits/ OB/OD Site
50	SSE02BX1	Sector E	UXO Site	26˚38'32.6" S 27˚01'24.6" E	Soil Sample	Weapons Range/ UXO Dumping
51	SSE02BX2	Sector E	UXO Site	26˚38'33.8" S 27˚01'14.0" E	Soil Sample	Weapons Range/UXO OB/OD Site
52	SSH02AX	Sector H	UXO Site	26˚39'05.3" S 26˚56'38.3" E	Soil Sample	UXO OB/OD Site
Water Samples						
53	WSA01BWL	Sector A	Firing Point	26˚34'58.3" S 26˚57'17.9" E	Water Sample	Water Hole/Below Surface
54	WSA02BWL	Sector A	Firing Point	26˚34'58.3" S 26˚57'17.7" E	Water Sample	Water Hole/ Below Surface
55	WSB02BWL	Sector B	Firing Point	26˚35'52.8" S 26˚58'03.0" E	Water Sample	UXO Site//Below Surface
56	WSE01BWL	Sector E	Firing Point	26˚38'54.5" S 27˚02'12.7" E	Water Sample	Sector E/Dam/Below Surface
57	WSF01BWL	Sector F	Firing Point	26˚37'40.7" S 27˚02'55.4" E	Water Sample	Sweet Cinnamon Bridge/Below Surface
58	WSF04AWL	Sector F	Firing Point	26˚37'42.7" S 27˚03'04.4" E	Water Sample	Sweet Cinnamon/Dam/Surface
59	WSF04BWL	Sector F	Firing Point	26˚37'45.8" S 27˚03'02.4" E	Water Sample	Sweet Cinnamon/Borehole
60	WSG01AWL	Sector G	Control Point	26˚36'24.6" S 27˚02'16.6" E	Water Sample	Aadil Farm/Pond/Surface
61	WSG01BWL	Sector G	Control Point	26˚36'24.6" S 27˚02'16.6" E	Water Sample	Aadil Farm/Pond/Below Surface

62	WSG04BWL	Sector G	Control Point	26˚36'24.0" S 27˚02'15.7" E	Water Sample	Aadil Farm/Pond/Below Surface
63	WSA07AWL	Sector A	Firing Point	26˚34'58.3" S 26˚57'17.9" E	Water Sample	Water Hole/ Surface
64	WSA07BWL	Sector A	Firing Point	26˚34'58.3" S 26˚57'17.9" E	Water Sample	Water Hole/Below Surface
65	WSB07AWL	Sector B	UXO Site	26˚35'52.8" S 26˚58'03.0" E	Water Sample	OB/OD Pits, Surface
66	WSB07BWL	Sector B	UXO Site	26˚35'52.8" S 26˚58'03.0" E	Water Sample	OB/OD Pits/Below Surface
67	WSE07AWL	Sector E	Firing Point	26˚38'42.1" S 27˚02'01.7" E	Water Sample	Sector E/Dam/Surface
68	WSE07BWL	Sector E	Firing Point	26˚38'42.1" S 27˚02'01.7" E	Water Sample	Sector E/Dam/ Below Surface
69	WSF07AWL	Sector F	Control Point	26˚37'40.7" S 27˚02'55.4" E	Water Sample	Sweet Cinnamon, Bridge/Surface
70	WSF07BWL	Sector F	Control Point	26˚37'40.7" S 27˚02'55.4" E	Water Sample	Sweet Cinnamon, Bridge/Below Surface
71	WSG07AWL	Sector G	Control Point	26˚36'24.6" S 27˚02'16.6" E	Water Sample	Aadil Farm, Pond/Surface
72	WSG07BWL	Sector G	Control Point	26˚36'24.0" S 27˚02'15.7" E	Water Sample	Aadil Farm, Borehole/Below Surface

Annexure B: Imagery of researched items

Section A: Explosive munitions commonly in use at General De La Rey Training Area

Example of a TNT filled 120 mm High Explosive Mortar Bomb at an ammunition depot of Army Support Base Potchefstroom.

120 mm Mortar Illuminating Round at ASB Potchefstroom ammunition depot complete with a complement of propellant charges

Example of a 155 mm High Explosive artillery shell filled with RDX and TNT (60/40) at the ammunition depot

155 mm Illumination rounds in storage at ASB Potchefstroom ammunition depot. Notice that heavy artillery shells are not fitted with a complement of propellant charges as is with Mortars

155 mm propellant formulations in use by heavy artillery. The explosive composition of the charges has not been determined during this study

Section B: Random UXO and UXO disposal sites

UXO collection point at Sector A near a vandalised reservoir

Disposal of UXO in prepared collection pits in Sector B near OP Tree. The OP Tree is seen at the top right edge of the image. Five disposal pits are located at this area

UXO demolition Pits in Sector B near the main target area overgrown with grass. Explosive compounds were detected in both discrete and composite samples from the site. About eleven pits were counted.

Collection of a 6 Increment surface soil sample at a surface UXO disposal Sector B near Gonzalespoort

6 Increment Sample collected at Sector E old Weapons Test Range in an UXO demolition pit

UXO disposal in a pit in Sector E near the old weapon testing range. Only the area around the lip of the pit was sampled for explosives as handling UXO would be dangerous and not permitted

UXO destruction site located at Sector H near Trig Beacon 136. Remnants of explosive munitions were found around the eleven burn pits. Explosive compounds were detected in samples from one of the pits.

Recording a randomly located 127 mm Multi Rocket Launcher darts stuck in ground at Sector B target area

Recording location of a buried 120 mm Mortar Bomb exposed by a grade at a fire break in Sector B near the main target area

Locating and recording a 120 mm Mortar Bomb stuck in ground in Sector B target area


155 mm HE UXO found on surface near Trig Beacon 116 in Sector B. Others were randomly located within the sector and recorded

Section C: Discrete soil sampling


Discrete soil sample collected at the bottom of an UXO demolition pit in Sector B during a dry season


Discrete sampling near two ageing UXO in Sector B target area.


Collection of discrete background surface sample at a 120 mm Mortar position before the deployment of the launcher at Sector E during Exercise Module X 1


Discrete surface soil sample collected at the location where excess charges were burnt after Exercise Module X 1

Discrete surface soil sample collected near a 155 mm Illumination canister after Exercise Module X 1 in Sector B target area

Discrete surface soil sample collected under a Low Order Detonated 155 mm Round with leaking explosive fill in Sector B target area

Discrete surface soil sampling next to a vehicle wreckage in Sector B target area

Section D: Multi Increment Sampling (MIS)

7 Increment soil sample collected at Sector B Road during 4 Artillery Regiment Exercise. The 120 mm Mortar Bomb exploded High Order

Collecting one soil core of 8 Increment Background Sample during 5 Special Forces Demonstration at Leerdagstelling. The length of the position extends towards the vehicle in the background

13 Increment Post Firing Sample collected in front of a target During 5 Special Forces Demonstration. The 60 mm Extended Range Mortar exploded High Order

16 Increment Sampling of a Multi Rocket Launcher back blast after the 5 Special Forces Demonstration at Leerdagstelling

36 Increment sampling at an impact crater of a 120 mm Mortal Bomb during Exercise Module X 2. The round exploded High Order next to the road junction near OP Tree.

36 Increment sampling at Sector C firing position. The target area is beyond in the horizon. A sample from this scarcely used area was contaminated with Nitrobenzene (NB)

Section E: Water samples

Collection of pond water samples at the water point in Sector A. Explosive compounds were detected in both surface and sub-surface water samples

Water accumulated in a UXO demolition pit at Sector B near Trig Beacon 116 during the rainy season. Explosive compounds were detected in both surface and sub-surface water samples

Surface water samples collected in Sector E at a dam near 4 Artillery Regiment. Explosive compounds were detected in both surface and sub-surface samples

Water sample collection point at a bridge connecting General De La Rey Training Are and Sweet Cinnamon Farm

Surface water sampling at Sweet Cinnamon farm at a dam fed by a water course from General De La Rey Training Area through the Sweet Cinnamon Bridge

Collection of a borehole water sample from a surface tap at Sweet Cinnamon farm (Sector F)

Collection of water samples at a surface pond at Aadil Farm (Sector G). The pond water was found contaminated with explosive compounds

Collection of borehole samples from a surface tap at Aadil Farm. Explosive compounds were detected in the groundwater

Section F: UXO types at General De La Rey Training Area

Two 90 mm Anti-Tank rounds

Practice Rifle Grenades (Blue)

60 mm Patrol Mortar Practice Bomb

Ageing 81 mm Mortar Bomb

120mm Mortar Practice Bomb

Unidentified heavy artillery projectile

Aged 105 mm Projectiles

76 mm fin-stabilised Rifle Anti-tank Rocket (Top of pile)

M26 Practice Hand Grenades (Powder Blue)

Unidentified fin stabilised air craft bomb

88 mm RPG 7 Anti-tank Rocket

Unidentified fin stabilised munition

Unidentified Aircraft Missile

120 mm Illuminating Mortar Bomb fused

60 mm Illuminating Mortar Bomb

40 mm Practice Rifle Grenade

SNEB 68 mm Anti-armour Rocket

Rifle Anti-tank rocket next to a Practice SNEB 68 mm Practice Rocket

81 mm Illuminating Mortar Bomb

Section G: Metal fragments

Fragment from a 60 mm Mortar Low Order Detonation

Metal fragment from a 120 mm Low Order Detonation

81 mm Mortar fragment from LOD

120 mm Mortar Tail Section

A typical fragment from a High Order Detonation of a 155 mm round

155 mm fragment from LOD

Section H: Materials and Methods

Discrete samples grouped by sector before laboratory analyses

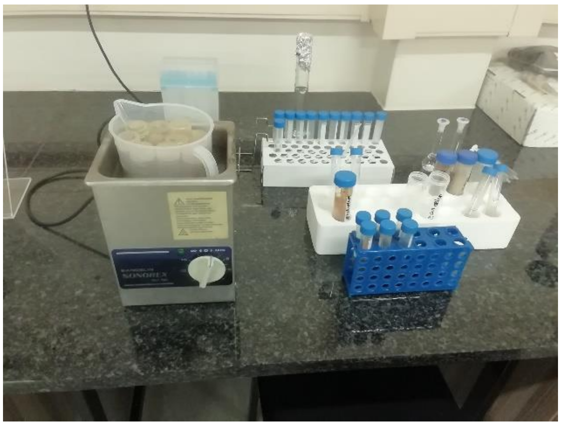
5 Increment samples prepared for processing and analyses

Pooling and Sieving of soil samples through a 10 mesh sieve

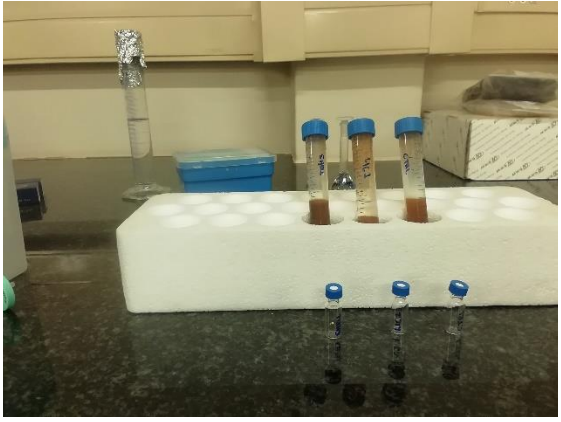
Soil sample homogenisation and grinding in Mortar and Pestle

50 Pooled samples ready for extraction and analysis

Subsampling of 2 gram subsamples for extraction on Ohaus 120 digital scale



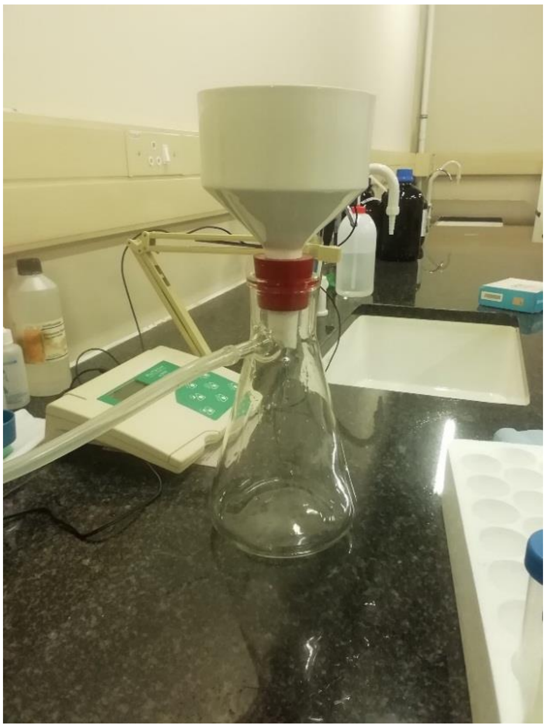
50 mL sample extracts in Sonorex ultrasonic bath



Extracts in 14 mL centrifuge tubes and filtration into 2 mL vials For HPLC

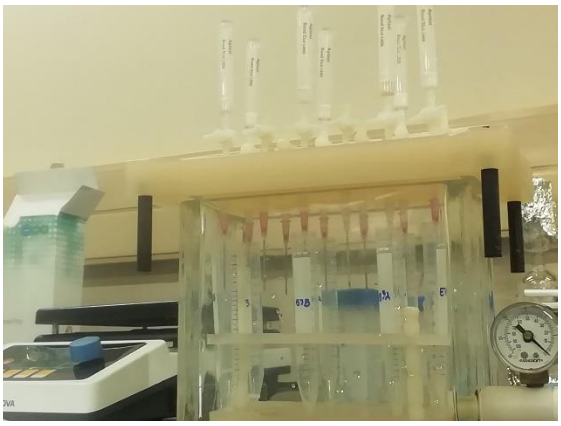
Water samples prepared for laboratory analyses

Water samples prepared in laboratory for Solid Phase Extraction (SPE)



Filtration of water samples for SPE

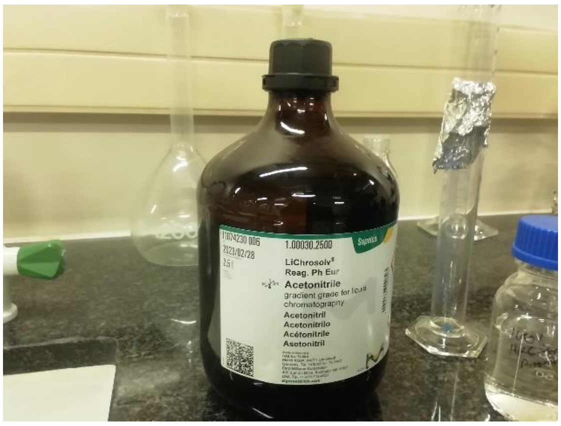
Subsampling of filtered samples for SPE

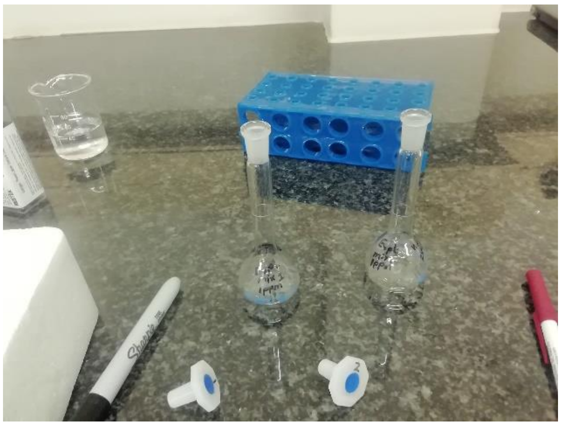


Injection of water samples in SPE for preparation of HPLC grade extracts


Optima water purifier for de-ionising HPLC reagent water

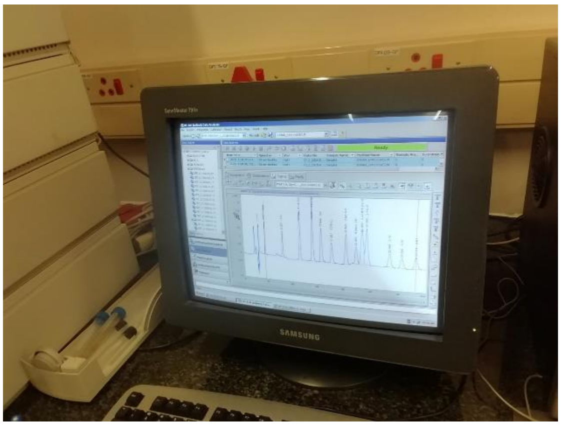

Certified Reference Material for explosive standards from RESTEK (Mix #1 and Mix #2)


Acetonitrile was used to clean equipment and to extract analytes


Prepared 1 ppm Intermediate standards for calibration of HPLC in 25 µL volumetric flasks


Measuring cylinder for preparation of mobile phases (50% Methanol Water)

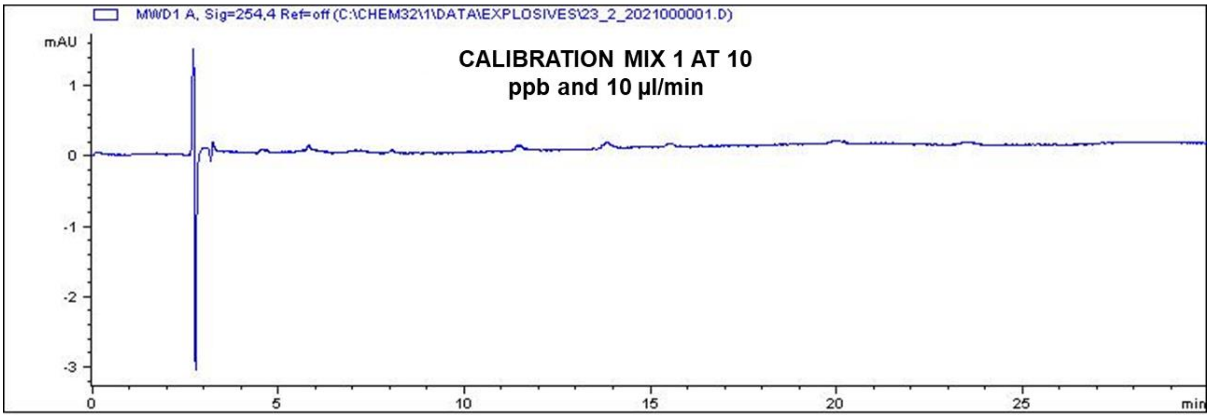

Agilent HPLC-100 for explosive analyses fitted with -18 Column for EPA Method 8330a

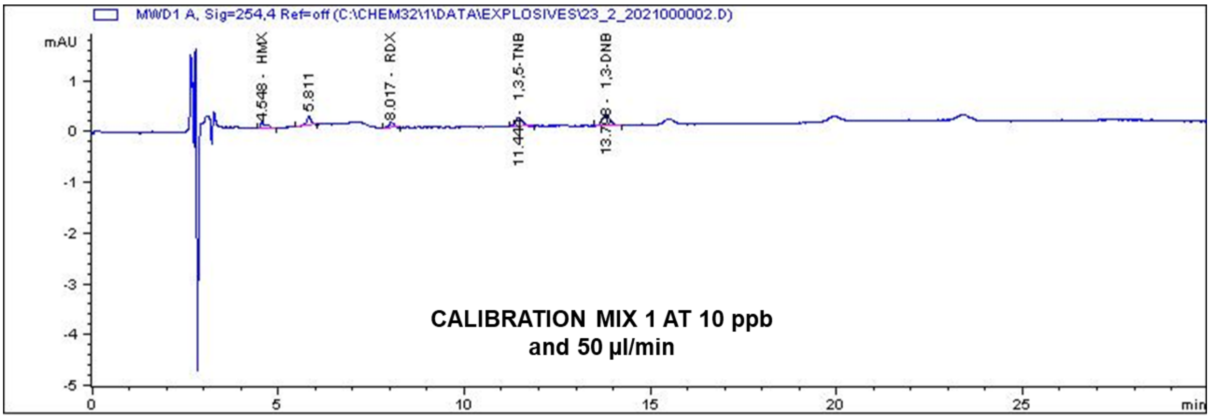


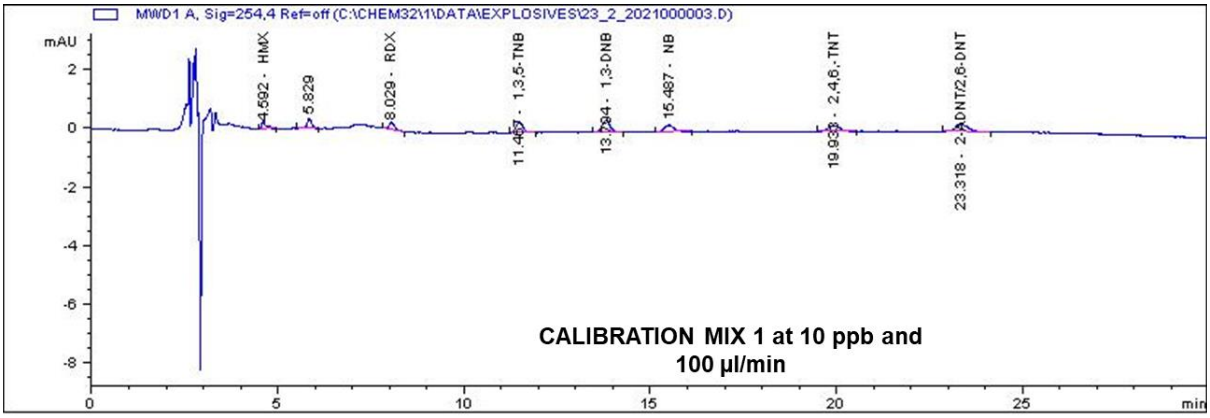
Typical Chromatogram for explosives contaminated sample analysed in HPLC

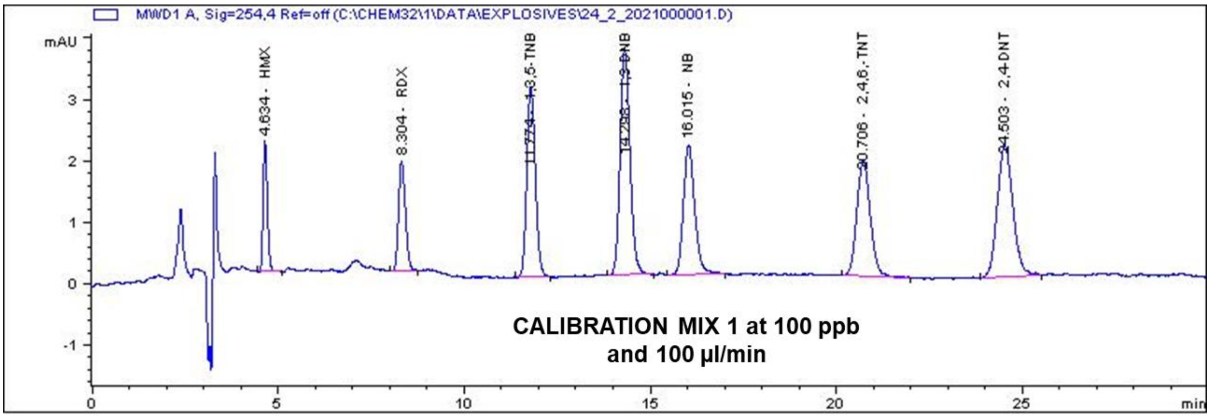
Annexure C: Chromatographs of HPLC results

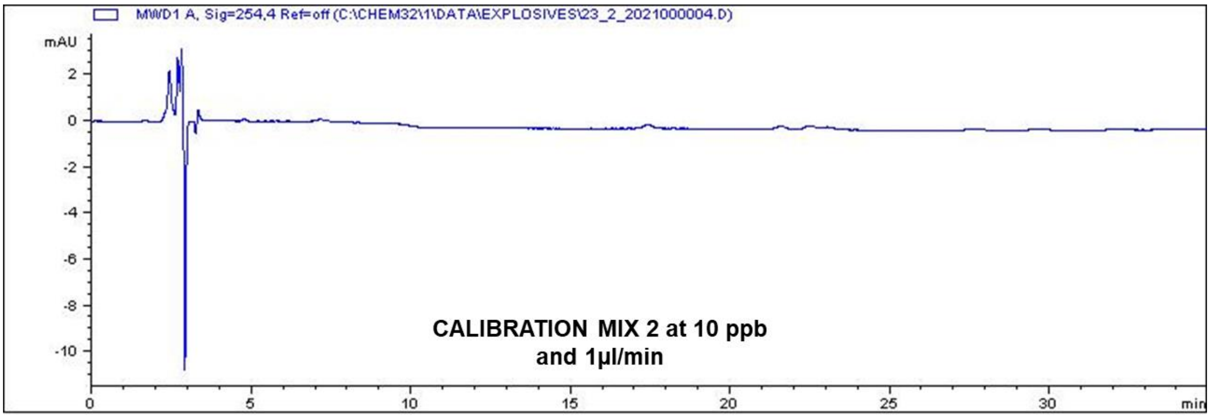
Calibration of HPLC using pure explosive mixes







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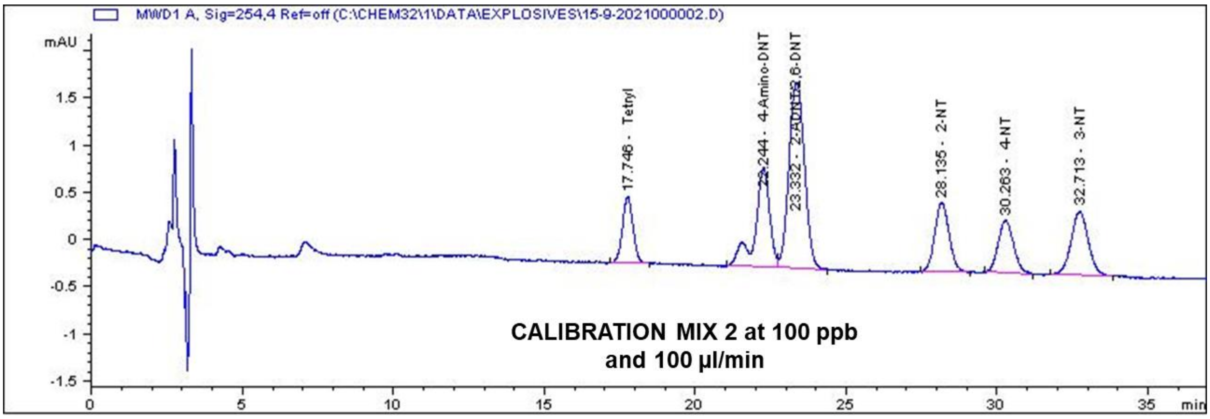
mAU
2
0
-2
-4
-6
-8
-10
0
5
10
15
20
25
30
min
CALIBRATION MIX 2 at 10 ppb
and 1µl/min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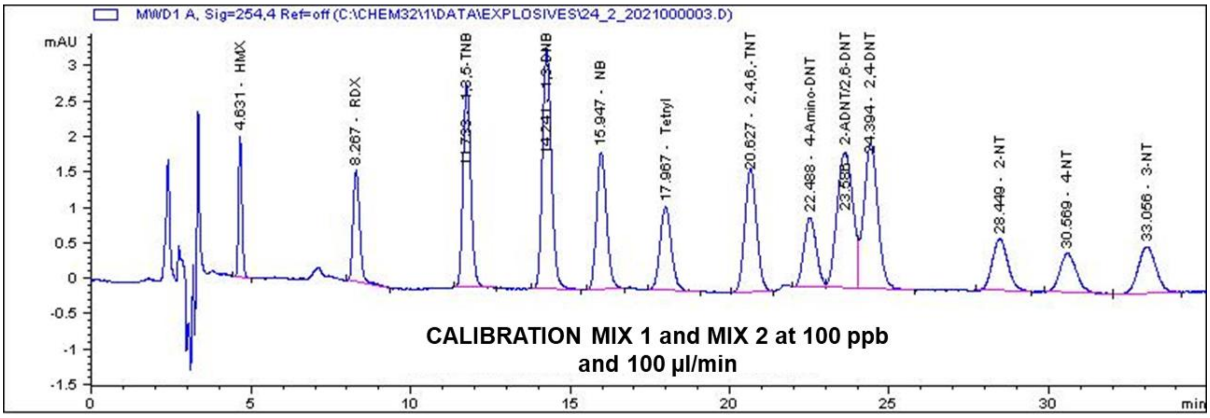
mAU
1.5
1
0.5
0
-0.5
-1
-1.5
17.746 - Tetryl
22.244 - 4-Amino-DNT
23.332 - 2-ADNT/2,6-DNT
28.135 - 2-NT
30.263 - 4-NT
32.713 - 3-NT
0
5
10
15
20
25
30
35
min
CALIBRATION MIX 2 at 100 ppb
and 100 µl/min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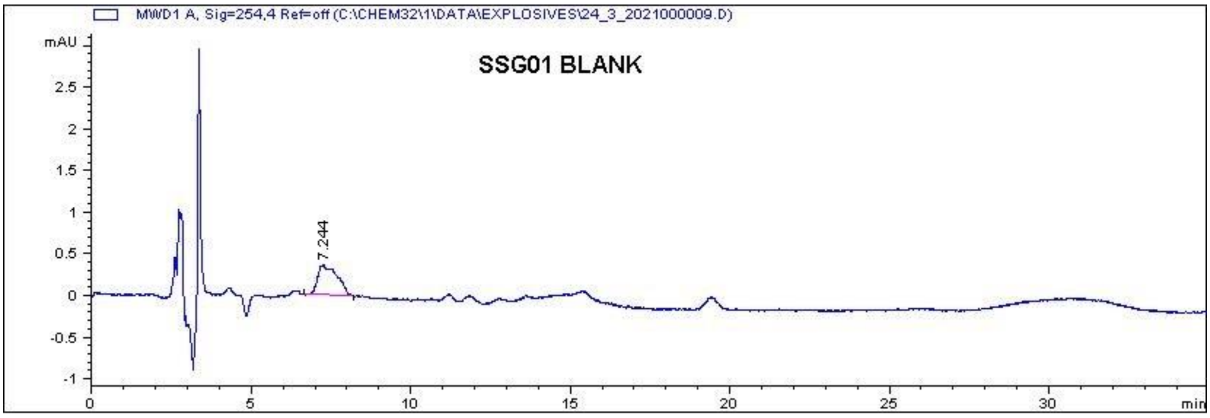
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
4.631 - HMX
8.267 - RDX
11.733 - 1,3,5-TNB
14.241 - 1,3-DNB
15.947 - NB
17.967 - Tetryl
20.627 - 2,4,6,-TNT
22.488 - 4-Amino-DNT
23.580 - 2-ADNT/2,6-DNT
24.394 - 2,4-DNT
28.449 - 2-NT
30.569 - 4-NT
33.056 - 3-NT
0
5
10
15
20
25
30
min
CALIBRATION MIX 1 and MIX 2 at 100 ppb
and 100 µl/min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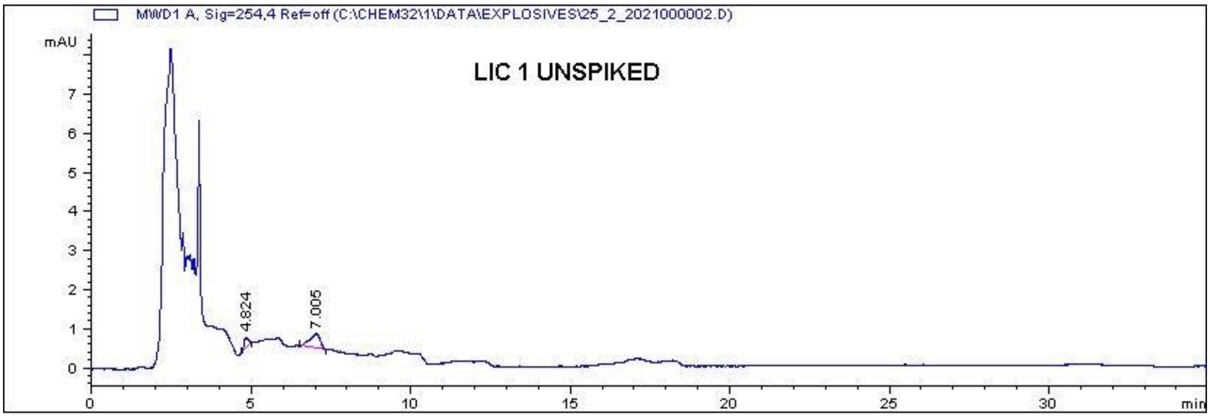
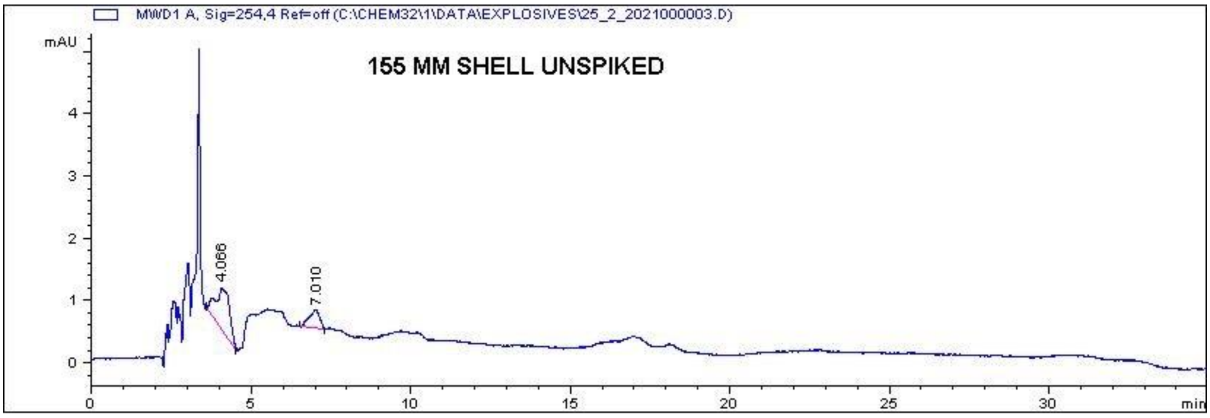
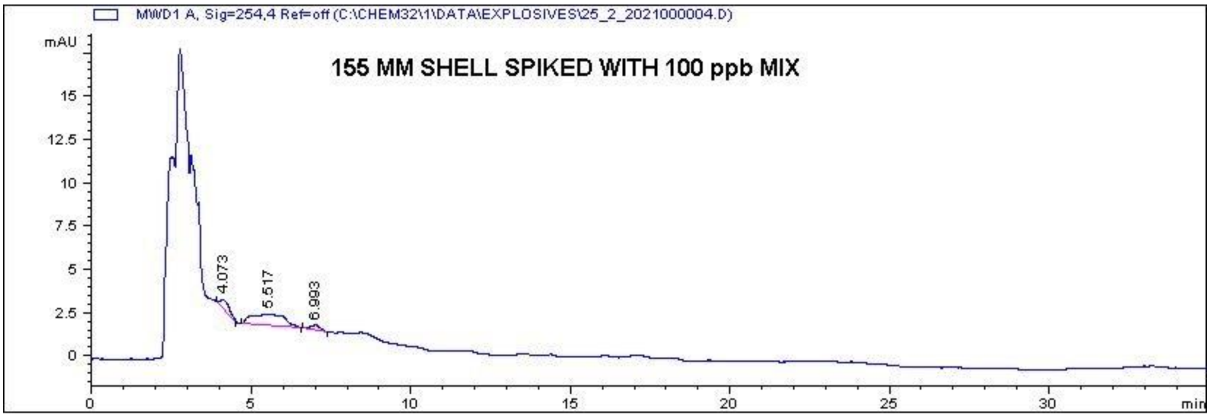
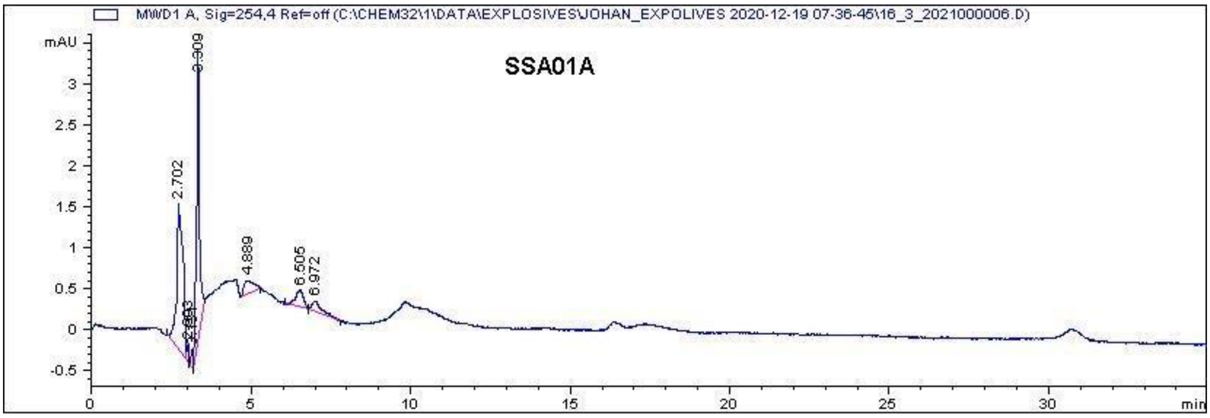
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
7.244
0
5
10
15
20
25
30
min
SSG01 BLANK

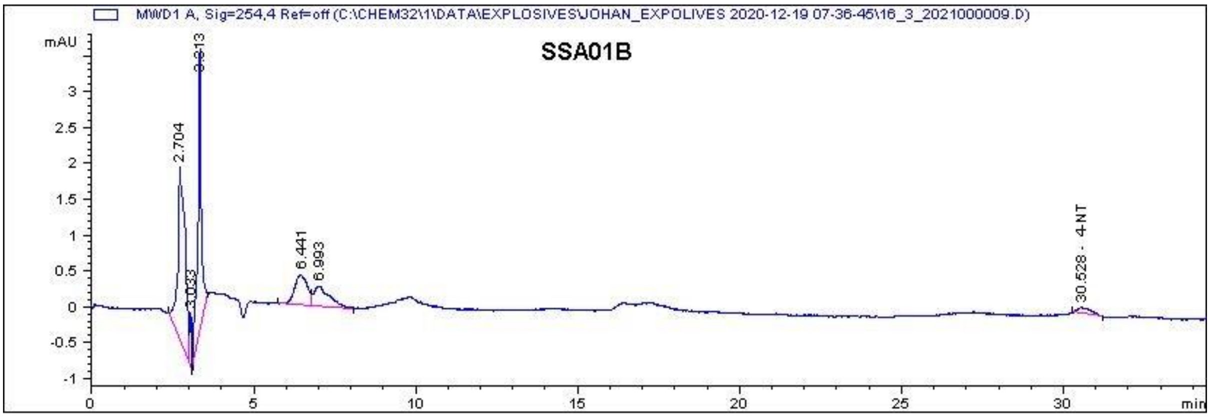






MTA and Control soil samples

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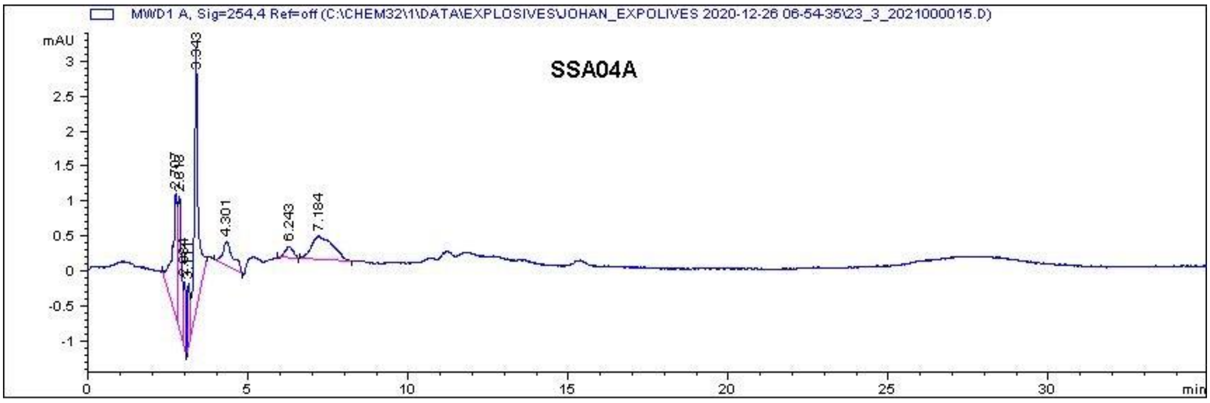
SSA01B
mAU
3.313
2.704
3.033
6.441
6.993
30.528 - 4-NT
3
2.5
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min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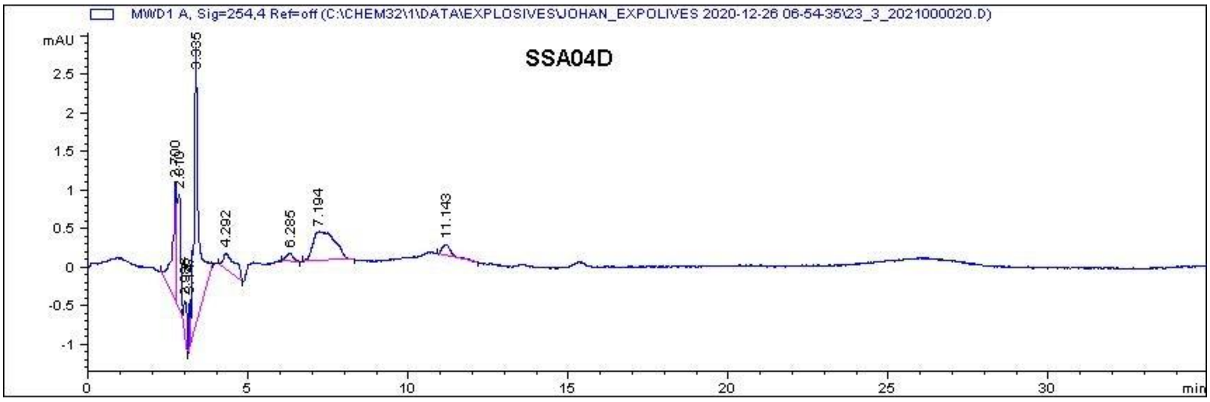
SSA04A
mAU
3.343
4.301
6.243
7.184
3
2.5
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min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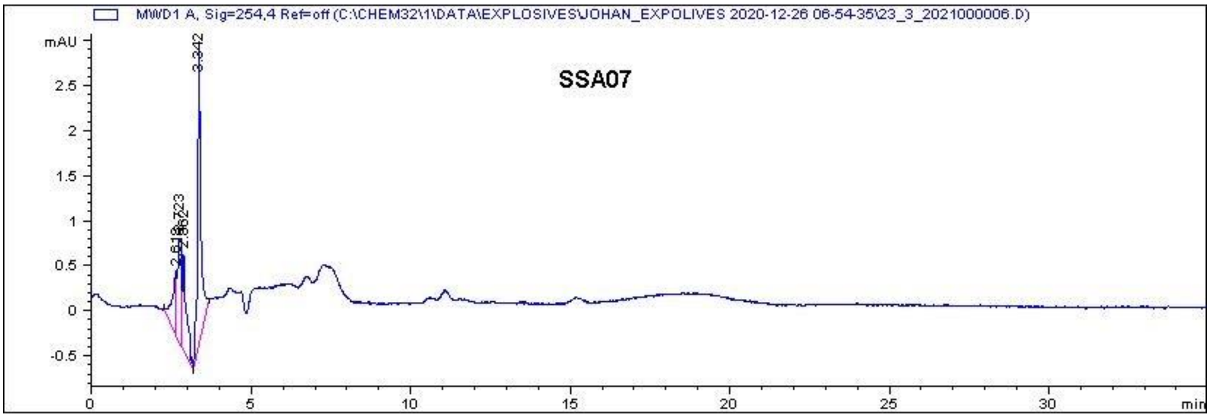
SSA04D
mAU
3.335
2.700
2.810
4.292
6.285
7.194
11.143
2.5
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min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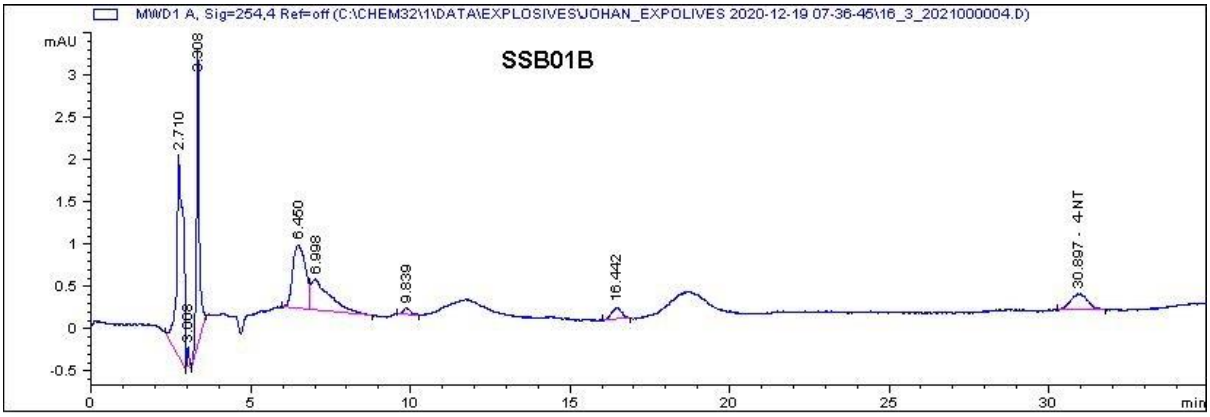
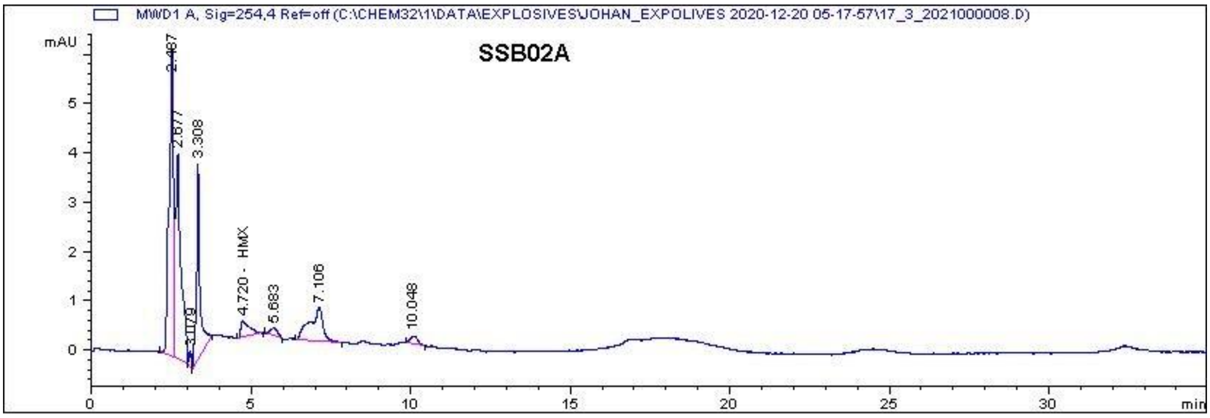
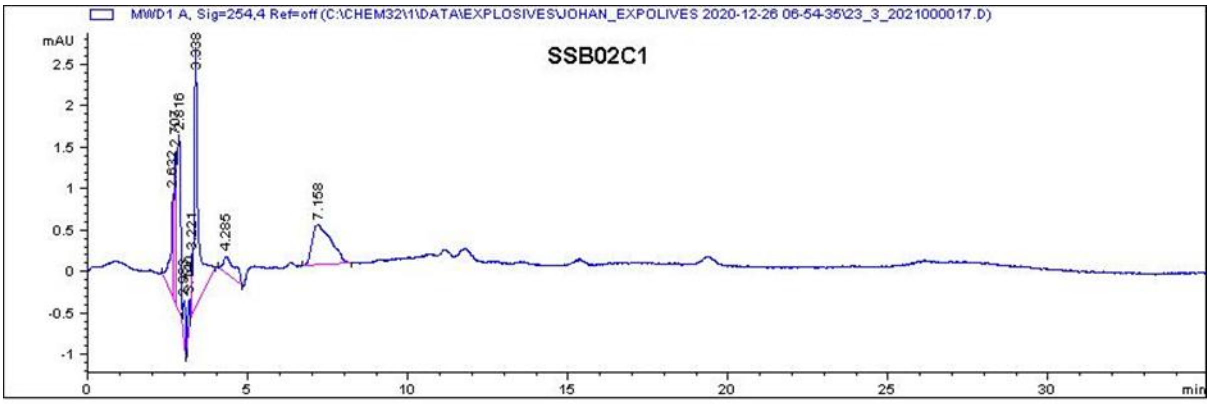
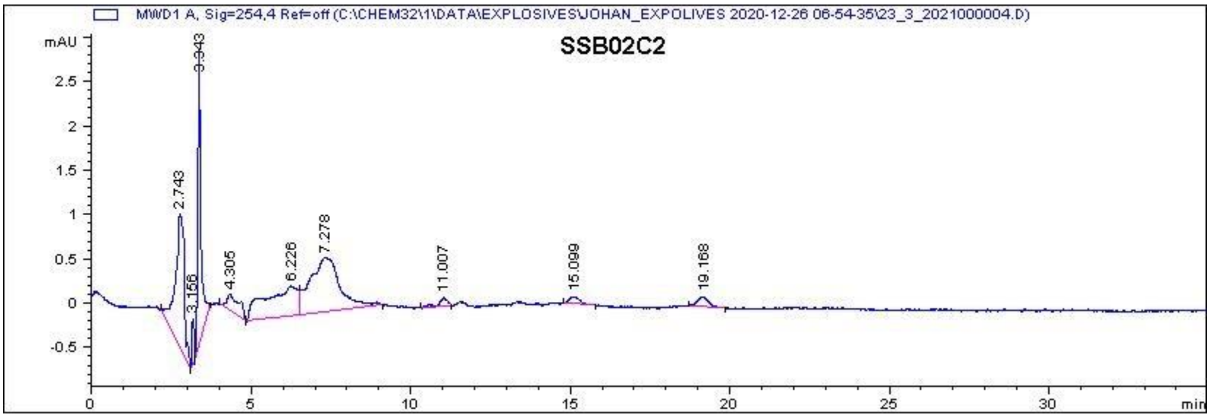
SSA07
mAU
3.342
2.723
2.862
2.5
2
1.5
1
0.5
0
-0.5
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-19 07-36-45\16_3_2021000004.D)
SSB01B
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
3.308
2.710
3.008
6.450
6.998
9.839
16.442
30.897 - 4-NT
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-20 05-17-57\17_3_2021000008.D)
SSB02A
mAU
5
4
3
2
1
0
2.487
2.677
3.308
3.079
4.720 - HMX
5.683
7.106
10.048
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000017.D)
SSB02C1
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
3.338
2.816
2.703
2.632
3.221
4.285
7.158
0
5
10
15
20
25
30
min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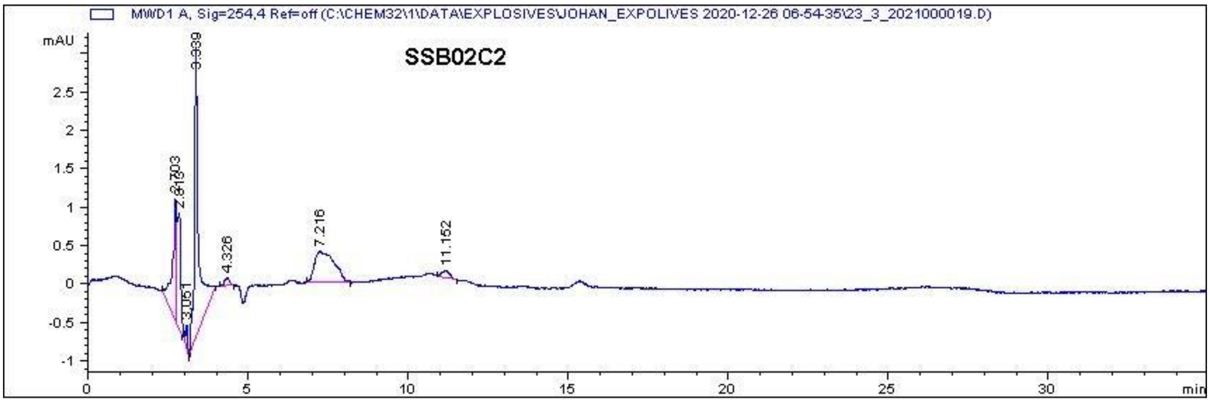
SSB02C2
mAU
2.5
2
1.5
1
0.5
0
-0.5
3.343
2.743
3.156
4.305
6.226
7.278
11.007
15.099
19.168
0
5
10
15
20
25
30
min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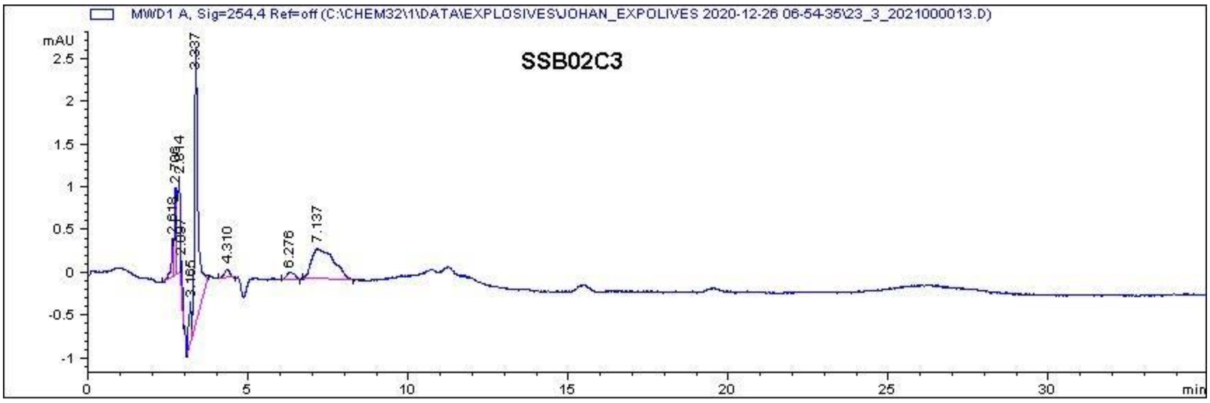
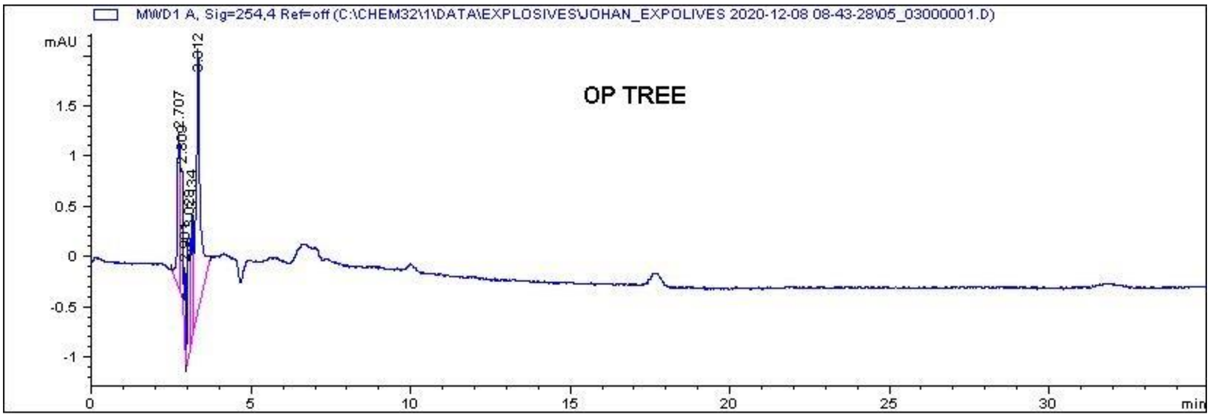
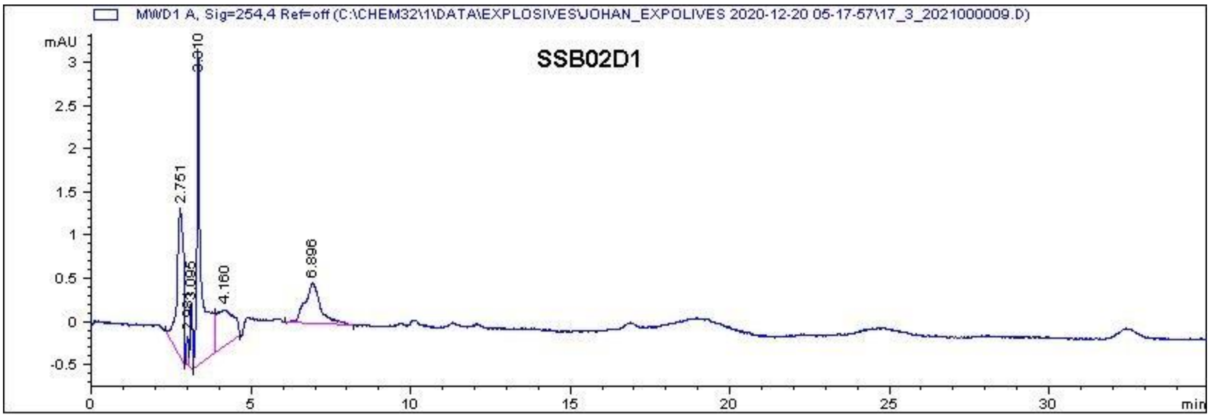
SSB02C2
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
3.339
2.703
3.051
4.326
7.216
11.152
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000013.D)
SSB02C3
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
3.337
2.619
3.165
4.310
6.276
7.137
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-08 08-43-28\05_03000001.D)
OP TREE
mAU
1.5
1
0.5
0
-0.5
-1
3.312
2.707
0
5
10
15
20
25
30
min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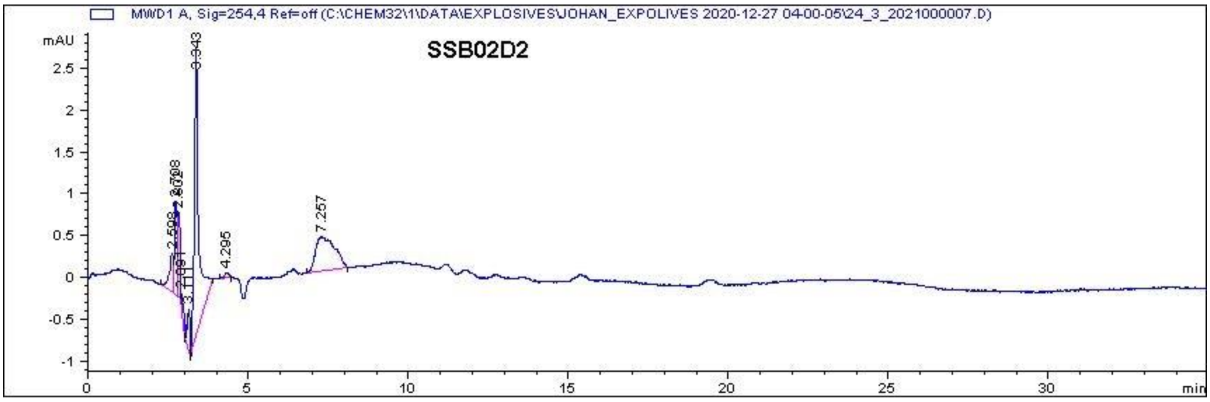
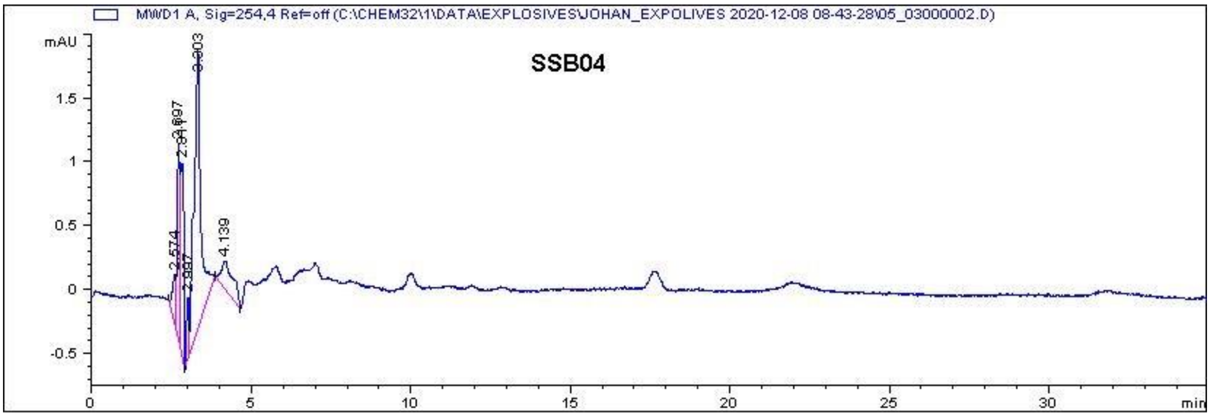
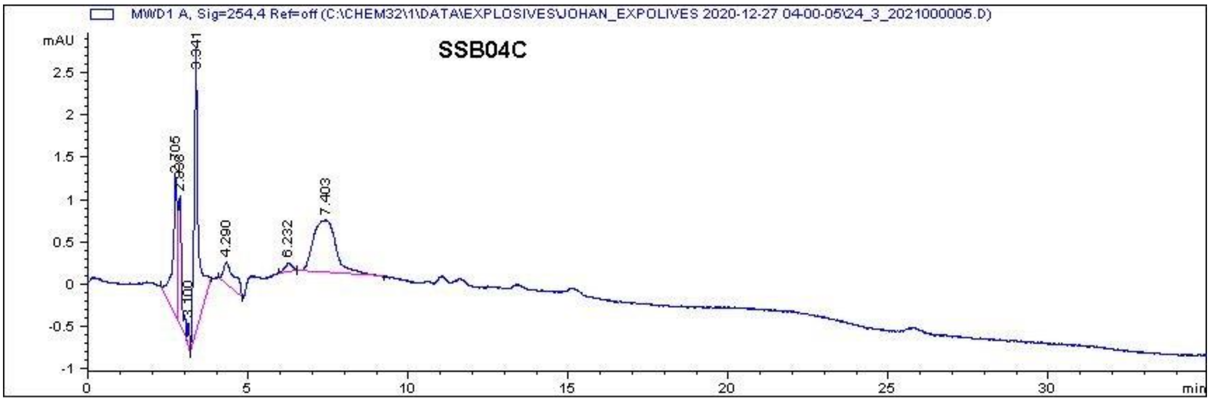
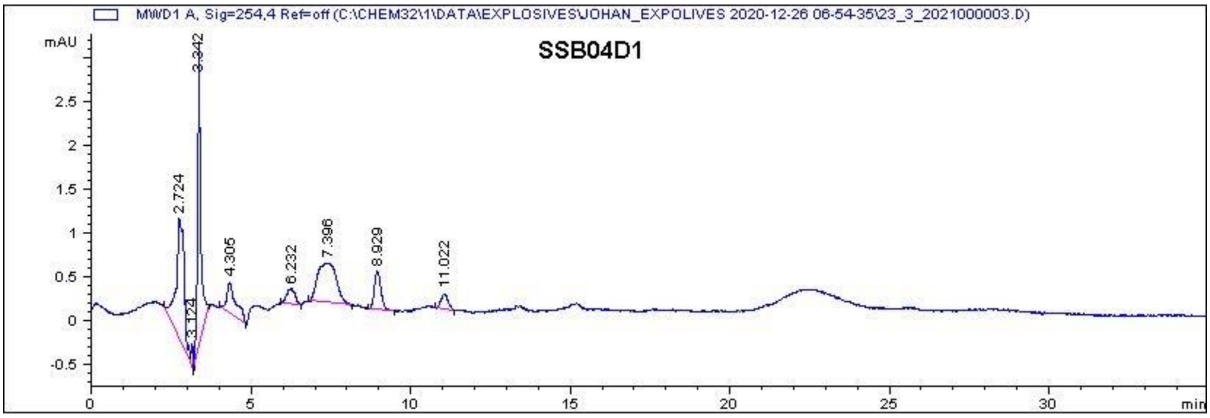
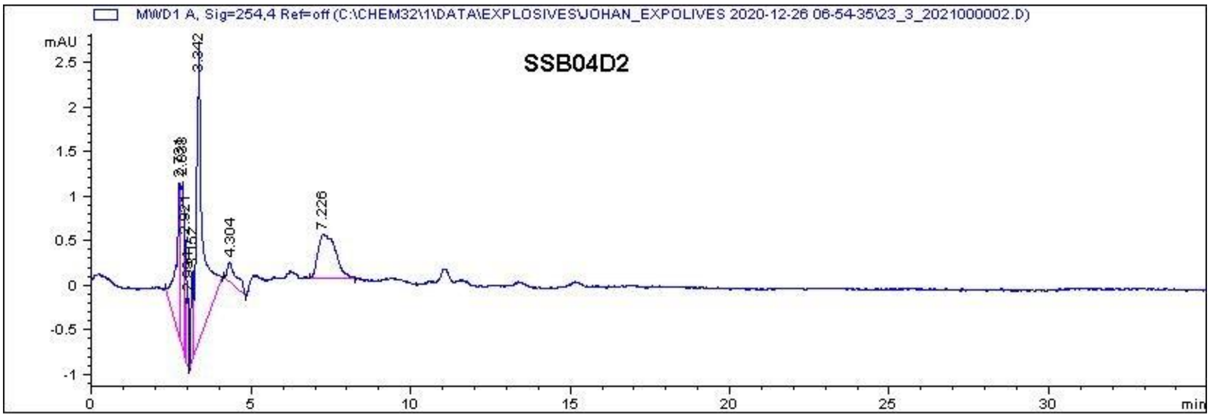
SSB02D1
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
3.310
2.751
3.095
4.160
6.896
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-27 04-00-05\24_3_2021000007.D)
SSB02D2
mAU
min
3.343
2.598
7.257
4.295
3.111
0
5
10
15
20
25
30
2.5
2
1.5
1
0.5
-0.5
-1


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-08 08-43-28\05_03000002.D)
SSB04
mAU
min
3.303
2.574
2.997
4.139
0
5
10
15
20
25
30
1.5
1
0.5
-0.5


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-27 04-00-05\24_3_2021000005.D)
SSB04C
mAU
min
3.341
2.705
3.100
4.290
6.232
7.403
0
5
10
15
20
25
30
2.5
2
1.5
1
0.5
-0.5
-1


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000003.D)
SSB04D1
mAU
min
3.342
2.724
3.124
4.305
6.232
7.396
8.929
11.022
0
5
10
15
20
25
30
2.5
2
1.5
1
0.5
-0.5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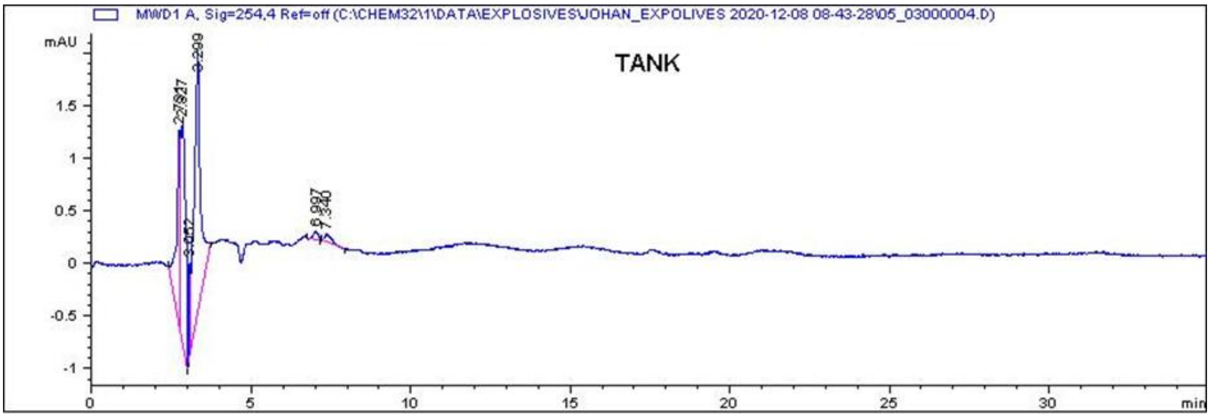
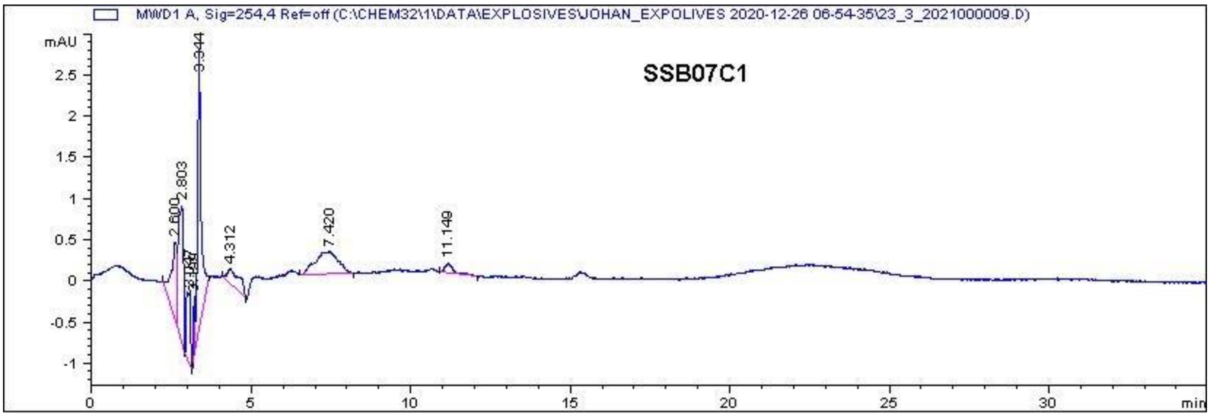
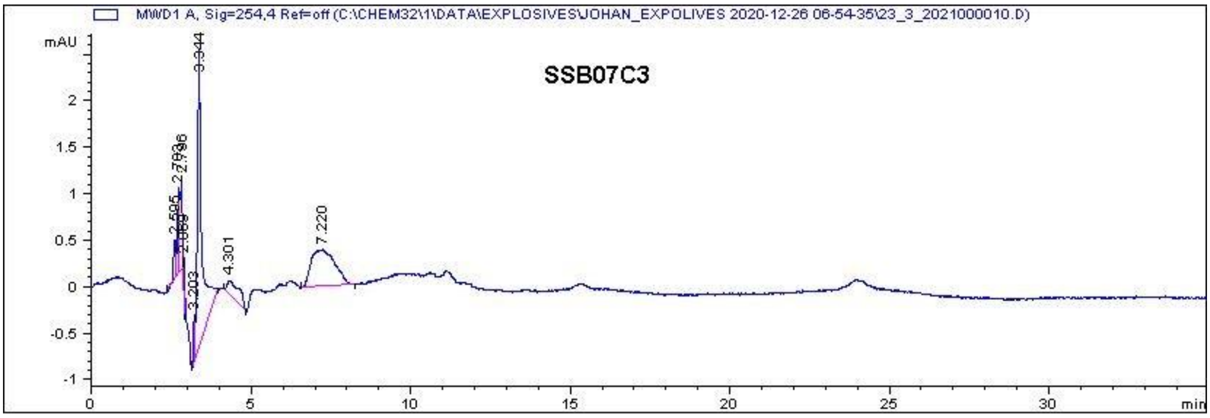
SSB04D2
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min
3.342
2.921
4.304
7.226


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-08 08-43-28\05_03000004.D)
TANK
mAU
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min
3.299
3.062
6.997
7.340


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000009.D)
SSB07C1
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min
3.344
2.803
2.600
4.312
7.420
11.149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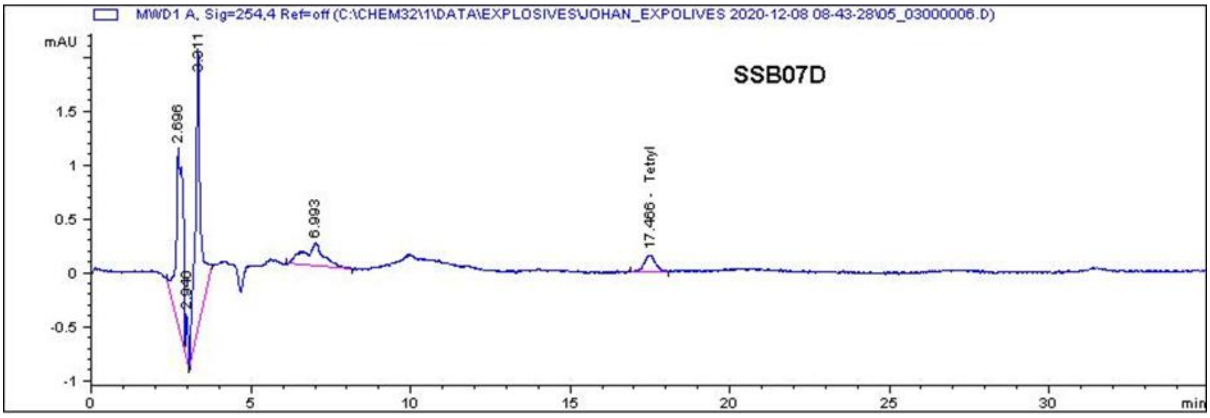
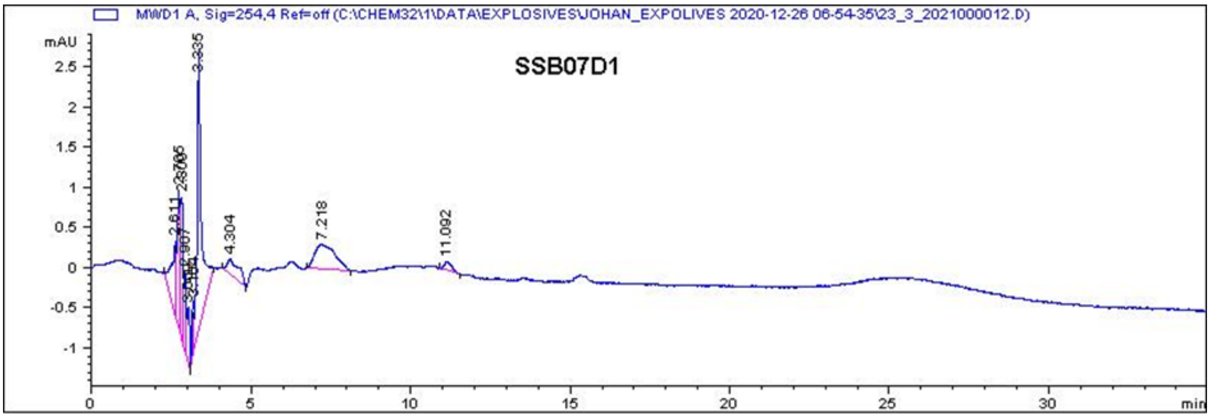
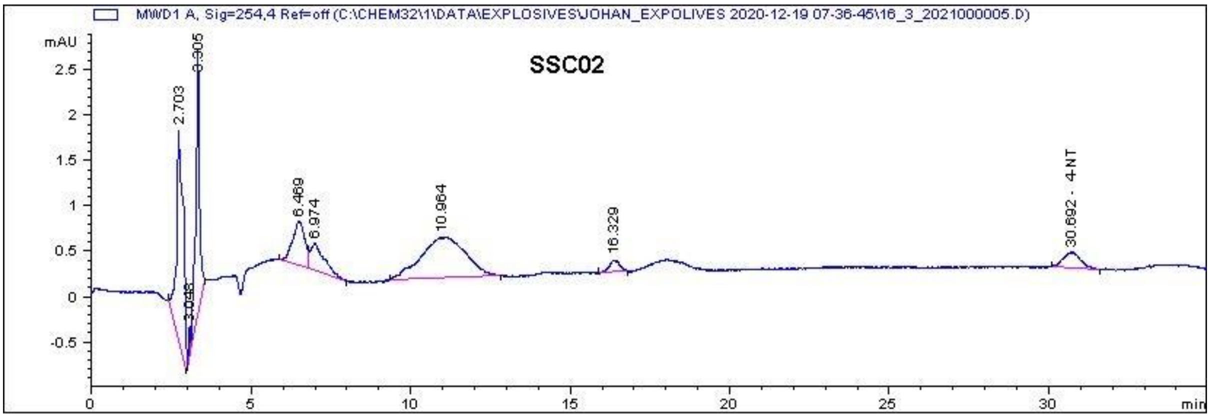
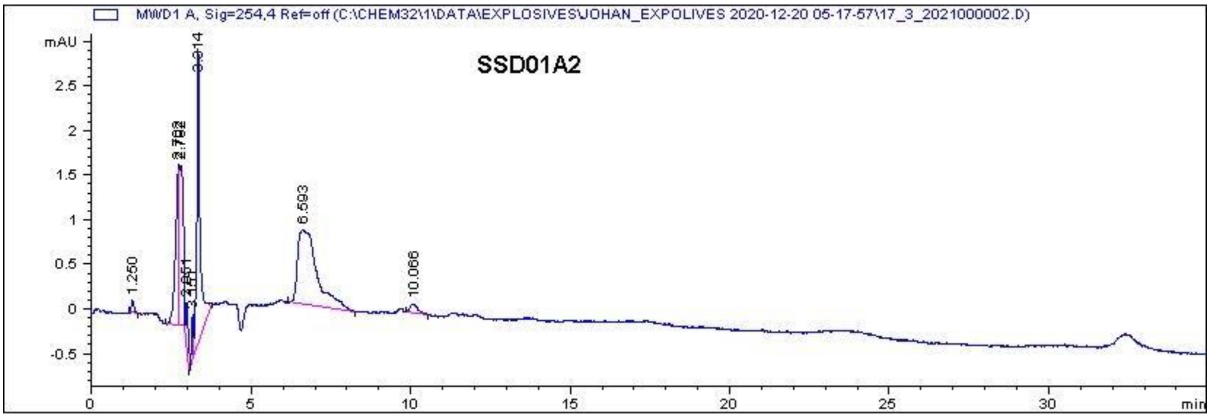
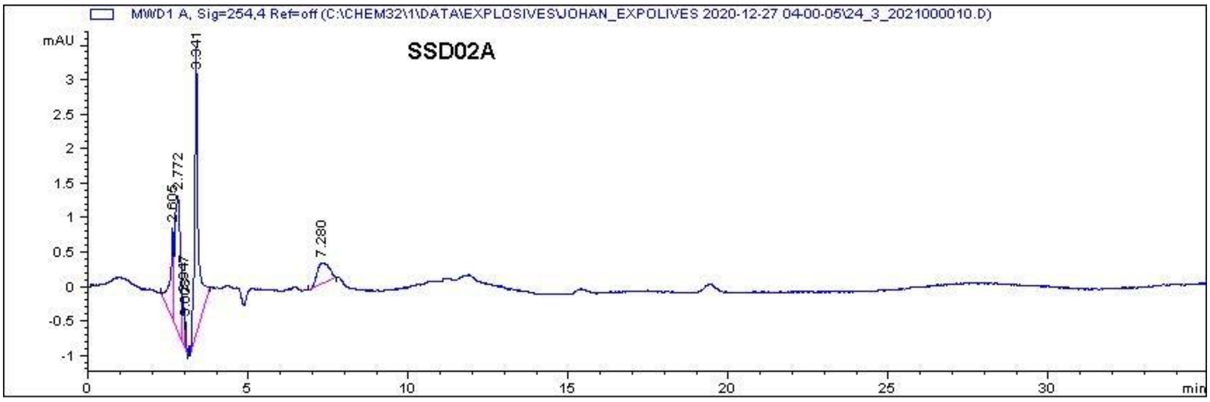
SSB07C3
mAU
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min
3.344
2.796
2.595
3.203
4.301
7.220


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-08 08-43-28\05_03000006.D)
SSB07D
mAU
1.5
1
0.5
0
-0.5
-1
3.311
2.696
2.940
6.993
17.466 - Tetryl
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000012.D)
SSB07D1
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
3.335
2.806
2.611
2.907
4.304
7.218
11.092
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-19 07-36-45\16_3_2021000005.D)
SSC02
mAU
2.5
2
1.5
1
0.5
0
-0.5
3.305
2.703
3.048
6.469
6.974
10.964
16.329
30.692 - 4-NT
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-20 05-17-57\17_3_2021000002.D)
SSD01A2
mAU
2.5
2
1.5
1
0.5
0
-0.5
3.314
2.762
1.250
2.951
6.593
10.066
0
5
10
15
20
25
30
min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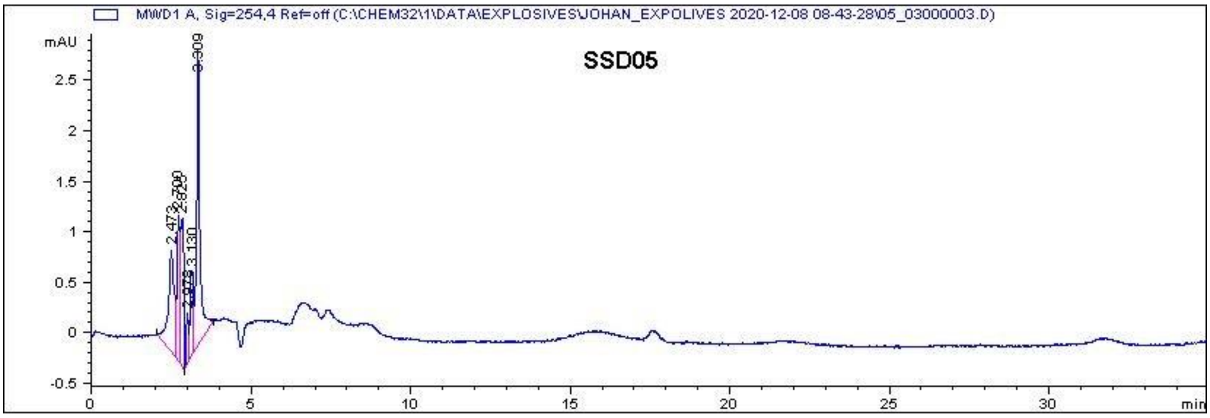
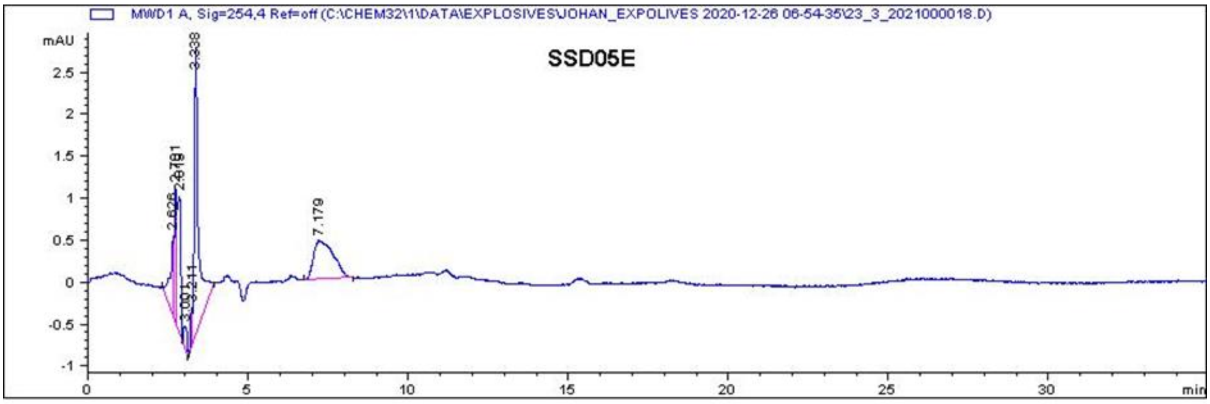
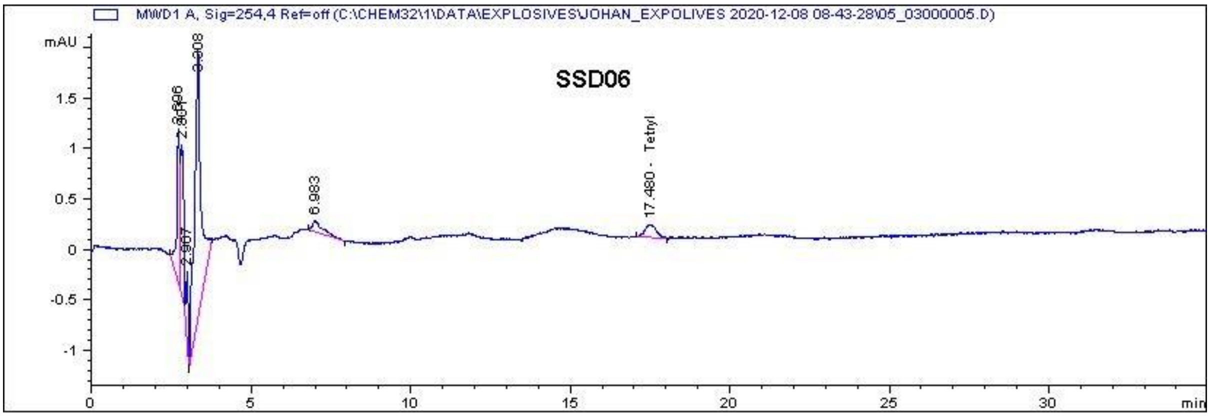
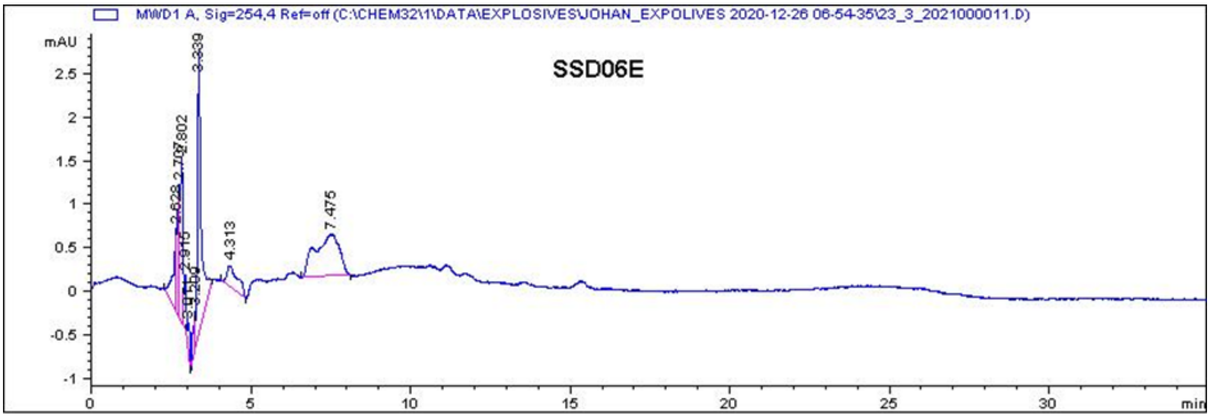
SSD02A
mAU
3.341
2.772
2.605
7.280
3
2.5
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-08 08-43-28\05_03000003.D)
SSD05
mAU
3.309
2.700
2.473
2.829
3.130
2.5
2
1.5
1
0.5
0
-0.5
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000018.D)
SSD05E
mAU
3.338
2.781
2.626
7.179
3.001
3.111
2.5
2
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-08 08-43-28\05_03000005.D)
SSD06
mAU
3.308
2.806
2.861
2.907
6.983
17.480 - Tetryl
1.5
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
min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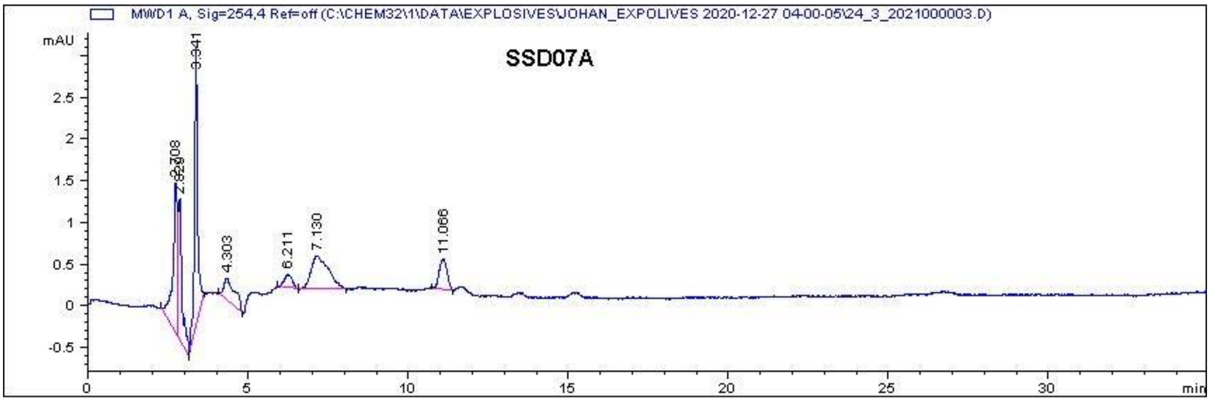
SSD06E
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
3.339
2.802
2.628
2.915
4.313
7.475
0
5
10
15
20
25
30
min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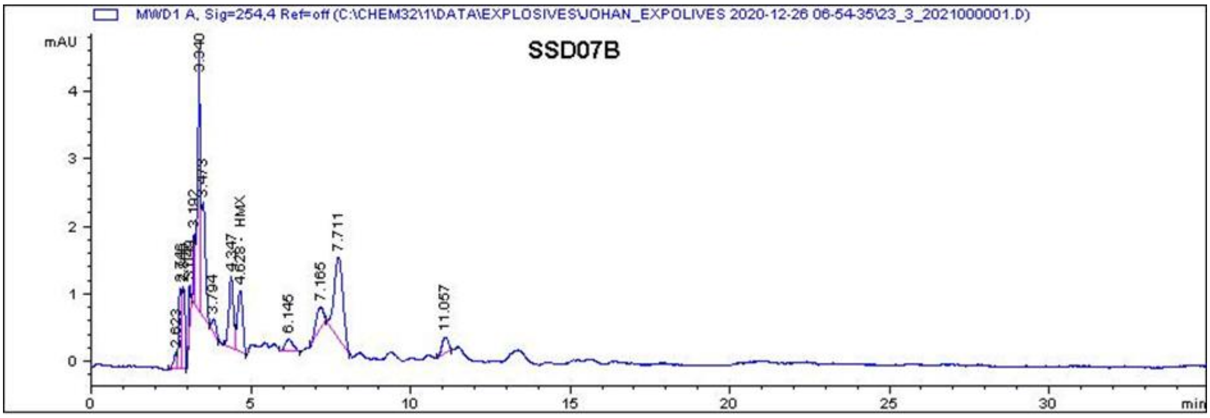
SSD07A
mAU
2.5
2
1.5
1
0.5
0
-0.5
3.341
2.708
4.303
6.211
7.130
11.066
0
5
10
15
20
25
30
min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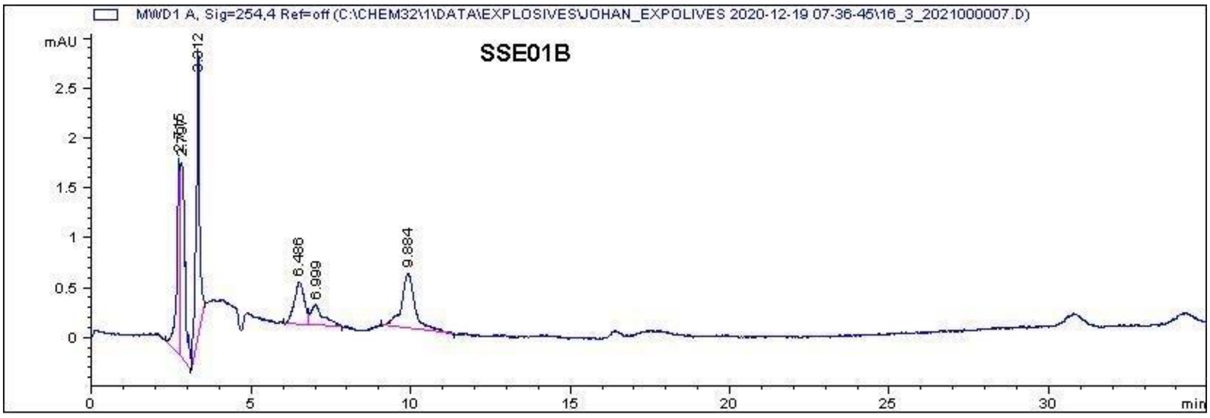
SSD07B
mAU
4
3
2
1
0
3.340
3.473
3.192
HMX
4.347
4.628
3.794
2.623
6.145
7.165
7.711
11.057
0
5
10
15
20
25
30
min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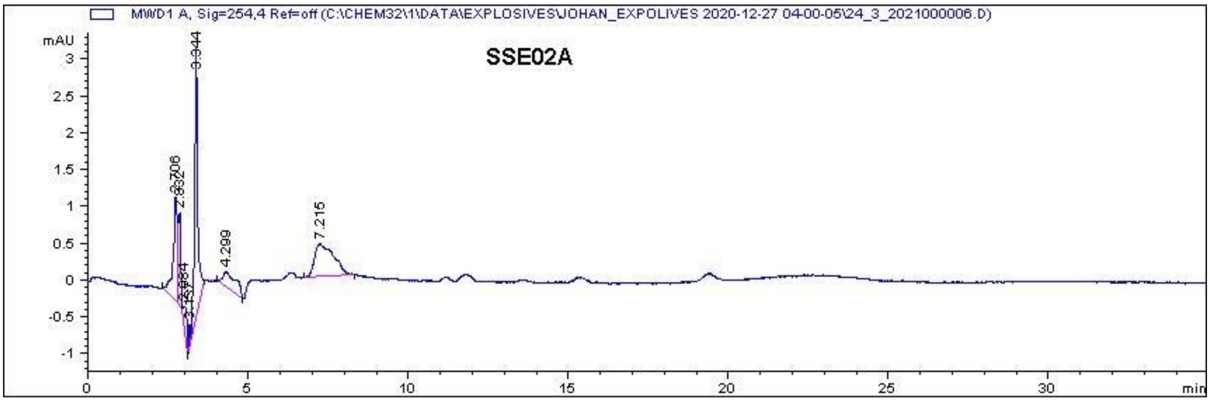
SSE01B
mAU
2.5
2
1.5
1
0.5
0
3.312
6.486
6.999
9.884
0
5
10
15
20
25
30
min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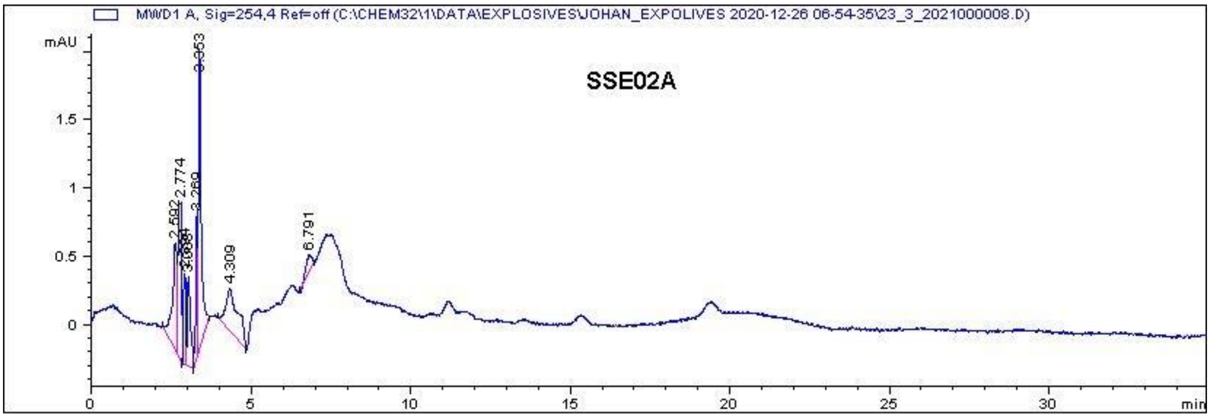
SSE02A
mAU
3.344
2.706
2.832
4.299
7.215
min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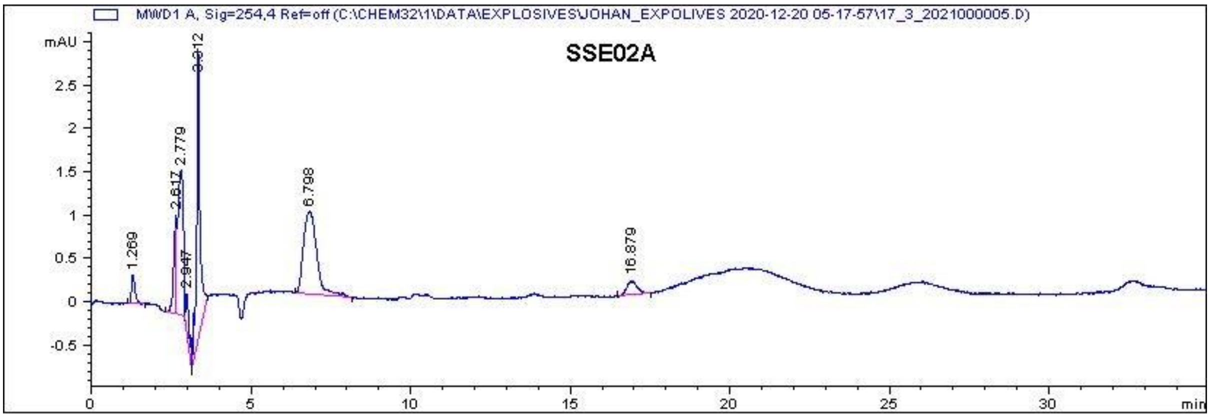
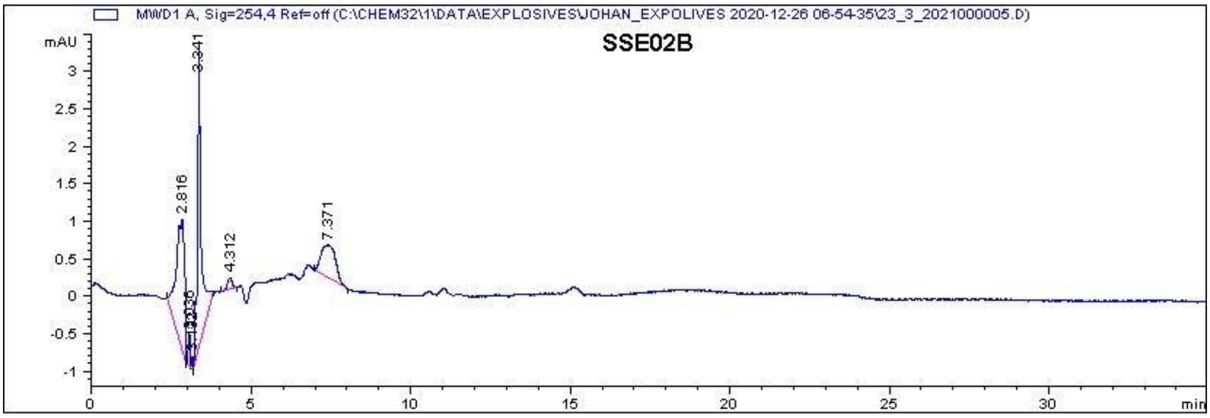
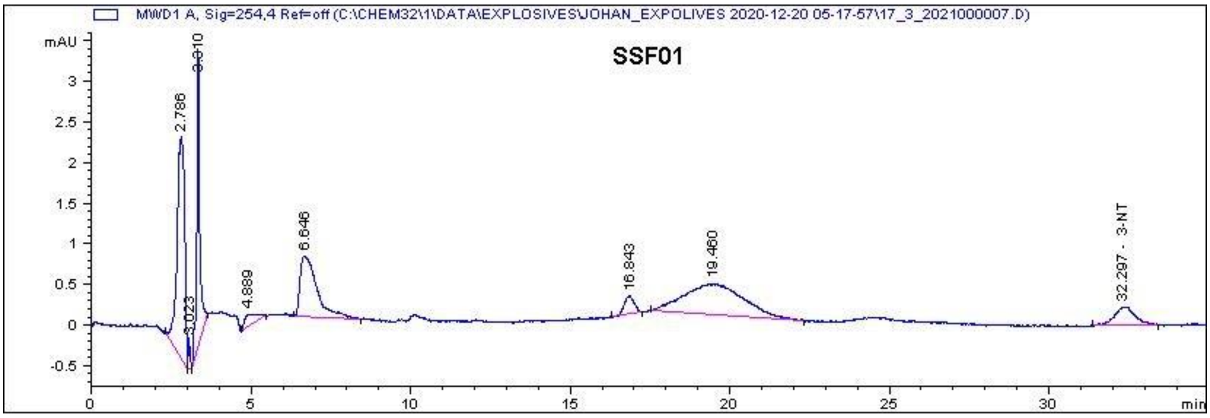
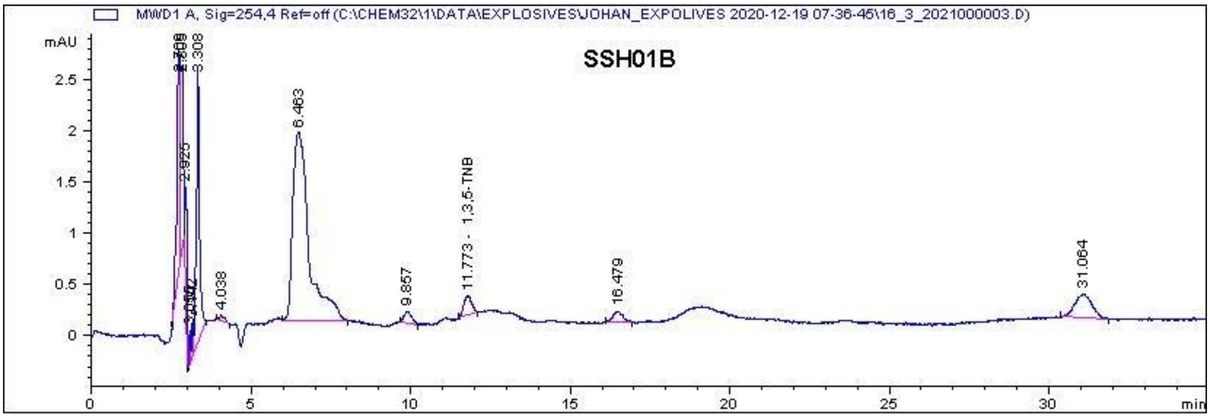
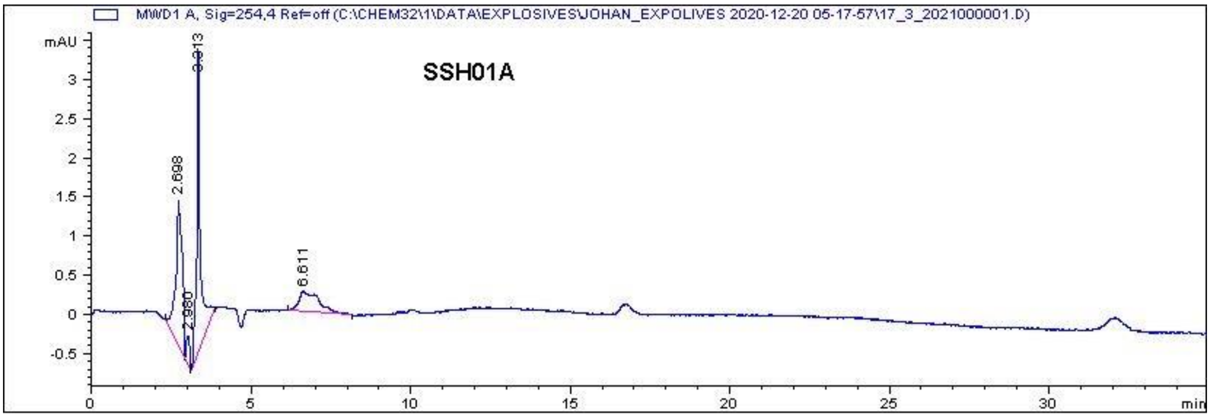
SSE02A
mAU
3.353
2.774
2.592
3.269
4.309
6.791
min

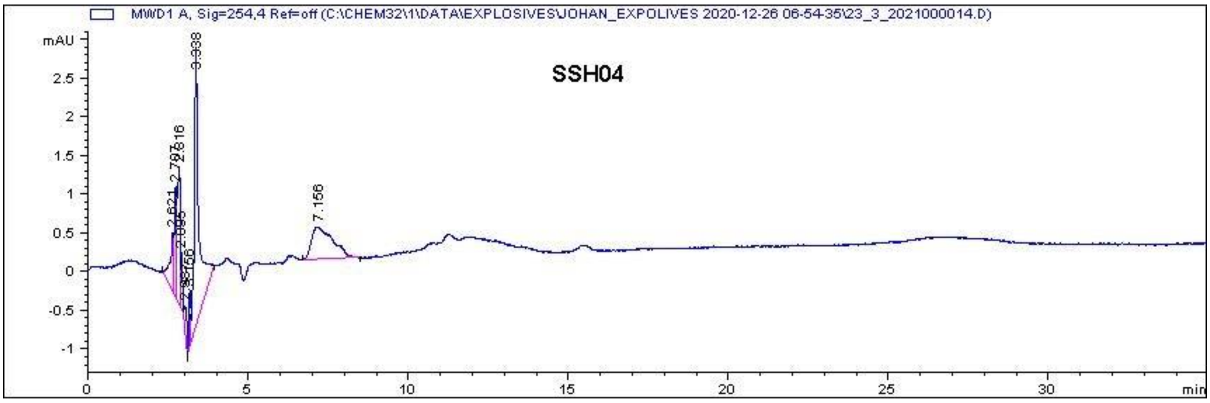

MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-20 05-17-57\17_3_2021000005.D)
SSE02A
mAU
3.312
2.779
2.617
1.269
2.947
6.798
16.879
min

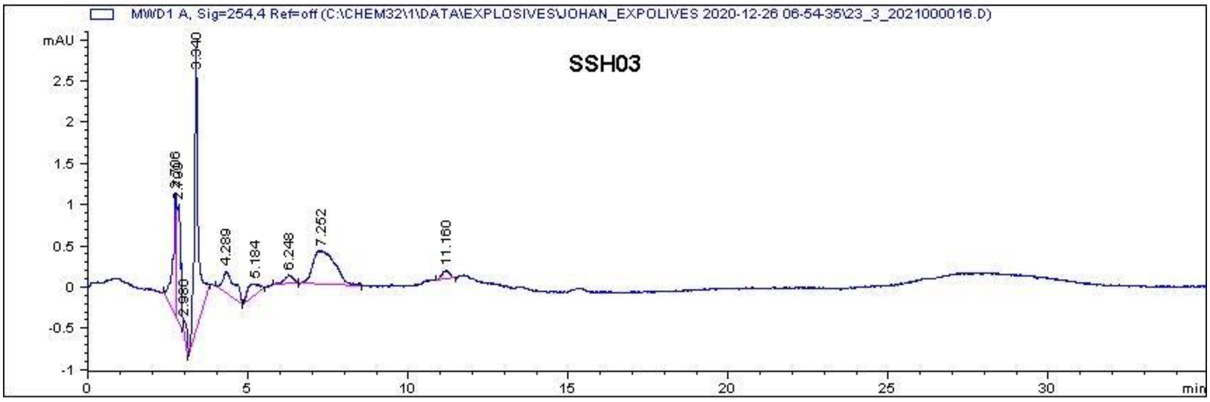

MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000005.D)
SSE02B
mAU
3.341
2.816
4.312
7.371
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-20 05-17-57\17_3_2021000007.D)
SSF01
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
2.786
3.310
3.023
4.889
6.646
16.843
19.460
32.297 - 3-NT
0
5
10
15
20
25
30
min

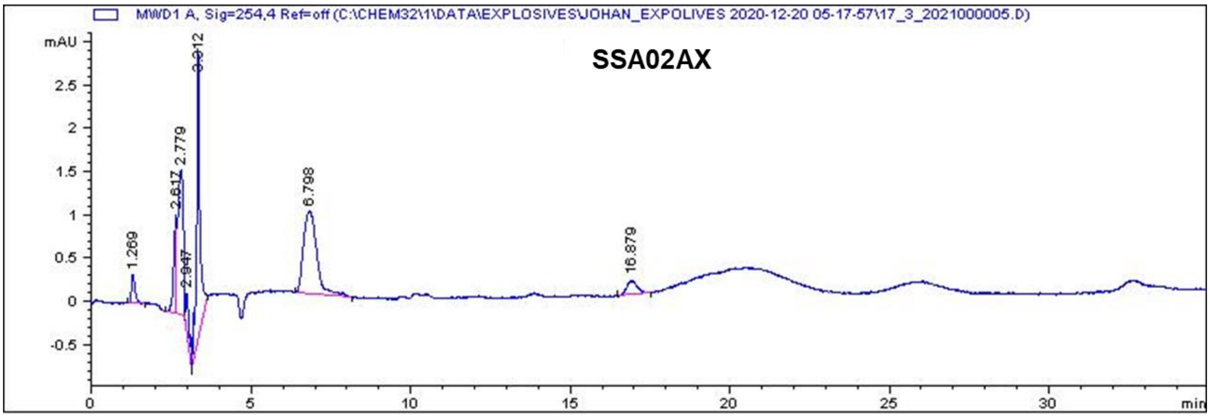

MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-19 07-36-45\16_3_2021000003.D)
SSH01B
mAU
2.5
2
1.5
1
0.5
0
3.308
2.925
4.038
6.463
9.857
11.773 - 1,3,5-TNB
16.479
31.064
0
5
10
15
20
25
30
min

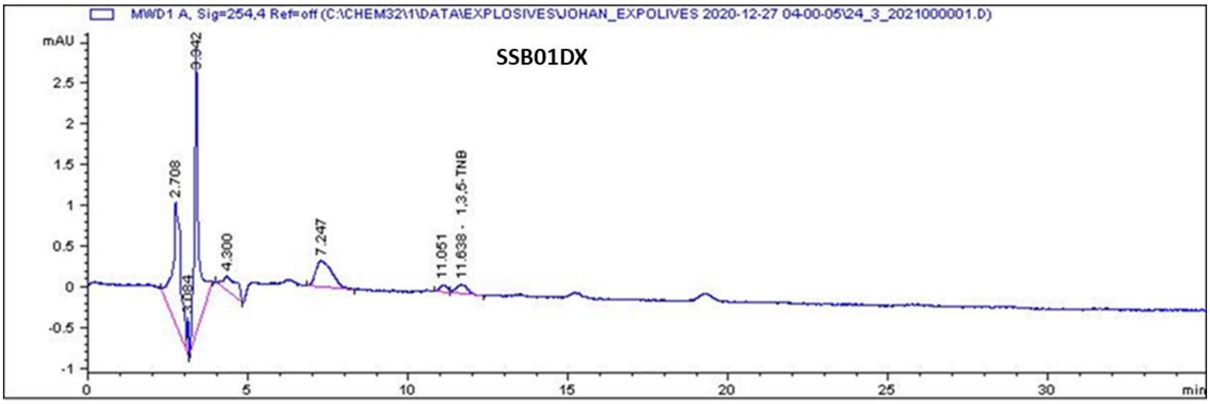

MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-20 05-17-57\17_3_2021000001.D)
SSH01A
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
2.698
3.313
2.980
6.611
0
5
10
15
20
25
30
min

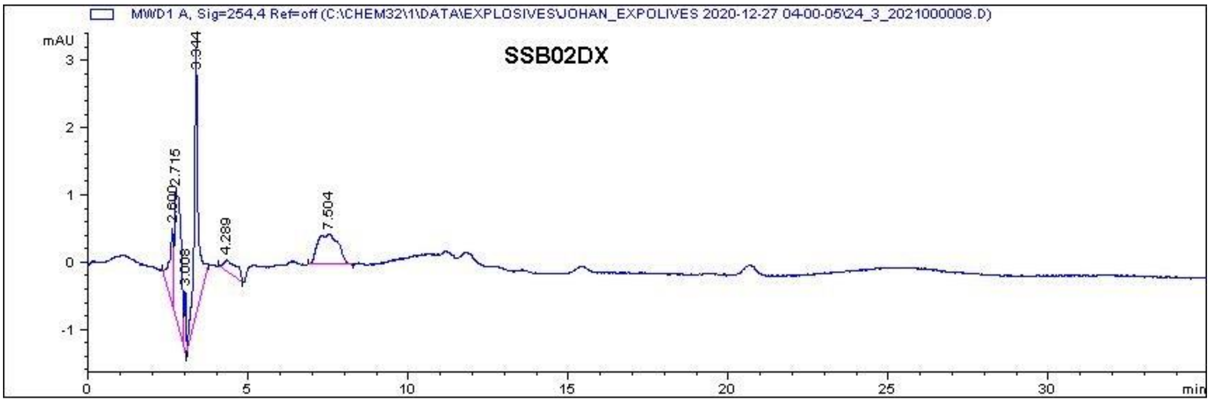

MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-26 06-54-35\23_3_2021000014.D)
SSH04
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
3.338
2.816
2.797
2.621
2.885
3.156
7.156
0
5
10
15
20
25
30
min

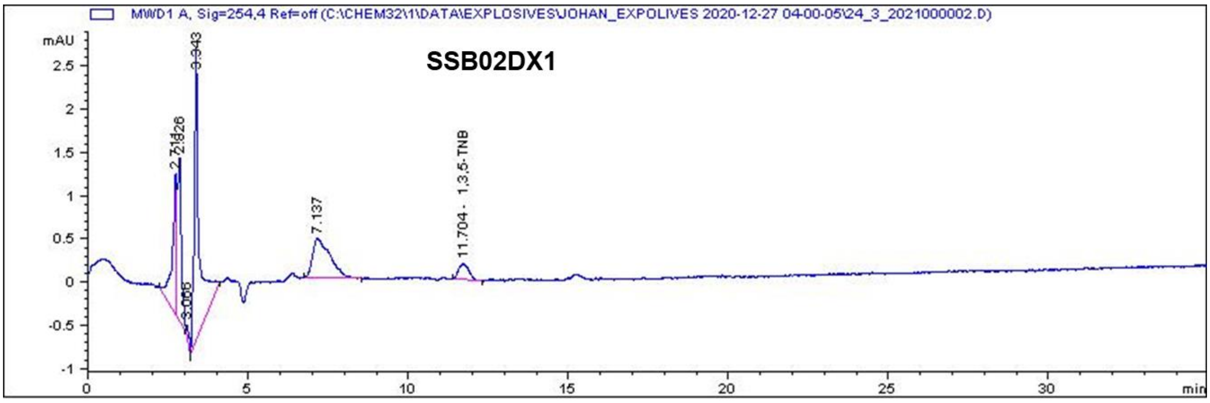


UXO Site soil samples





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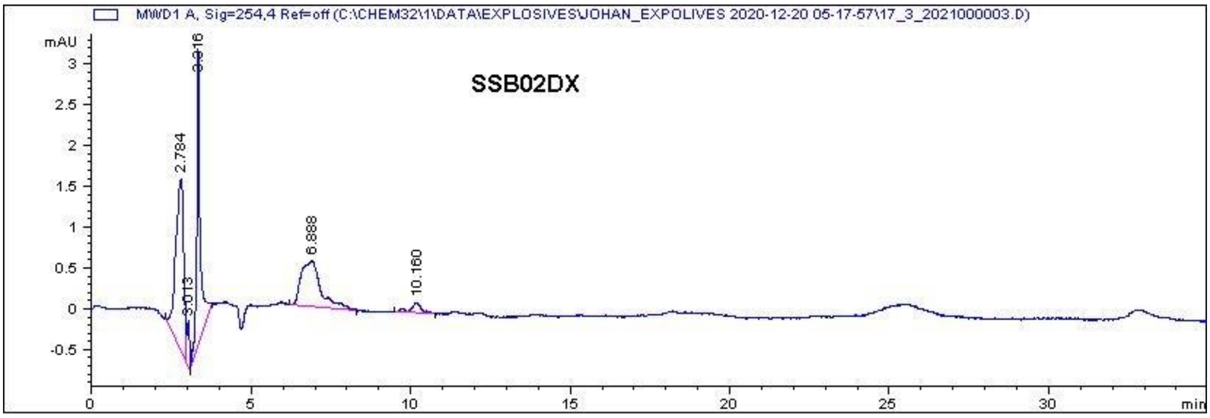
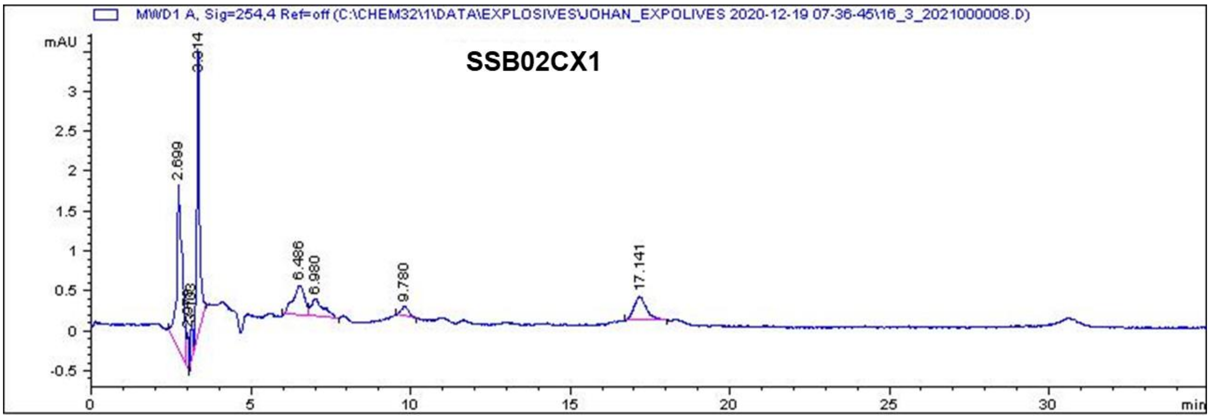
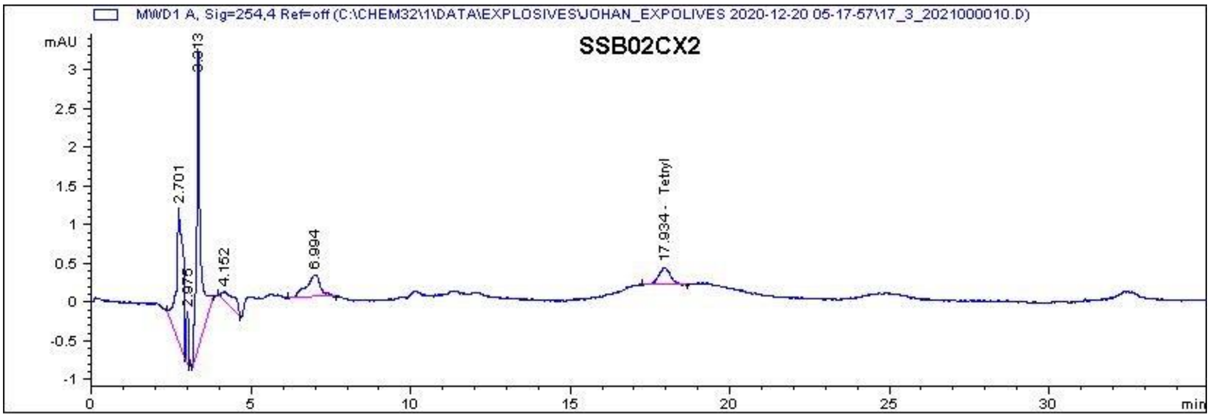
SSB02DX1
mAU
2.5
2
1.5
1
0.5
0
-0.5
-1
3.343
2.726
3.066
7.137
11.704 - 1,3,5-TNB
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-20 05-17-57\17_3_2021000003.D)
SSB02DX
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
3.316
2.784
3.013
6.888
10.160
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2020-12-19 07-36-45\16_3_2021000008.D)
SSB02CX1
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
3.314
2.699
6.486
6.980
9.780
17.141
0
5
10
15
20
25
30
min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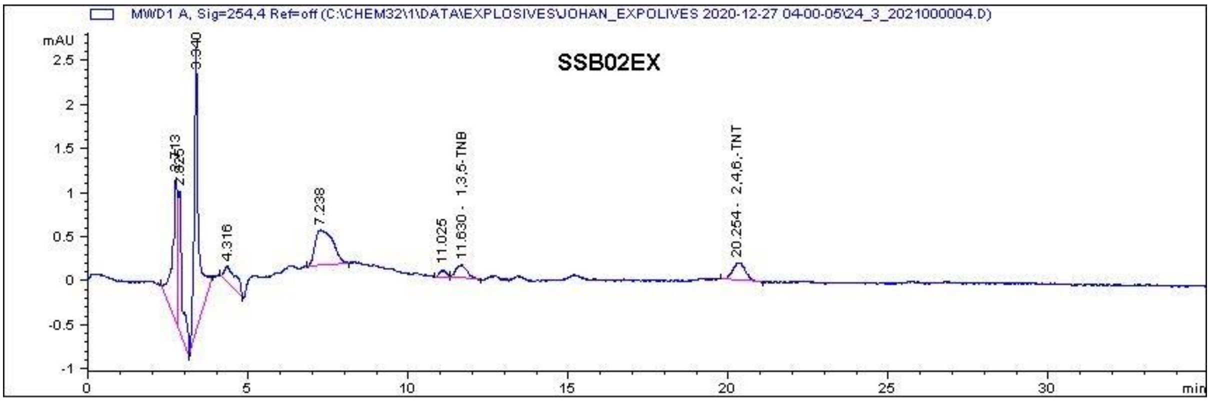
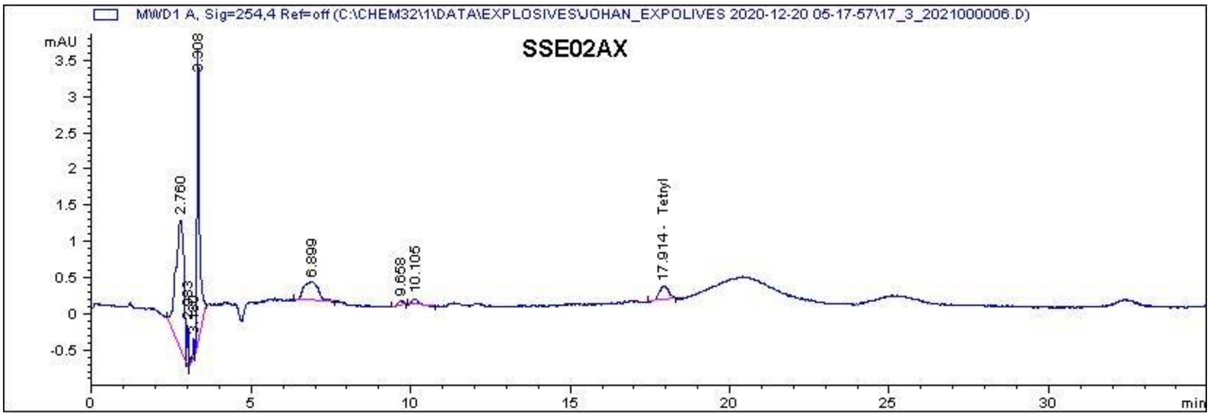
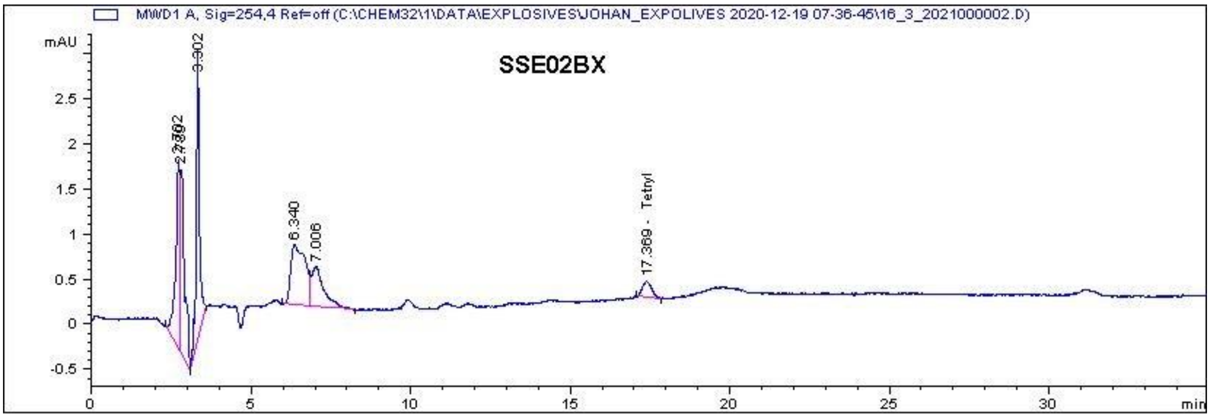
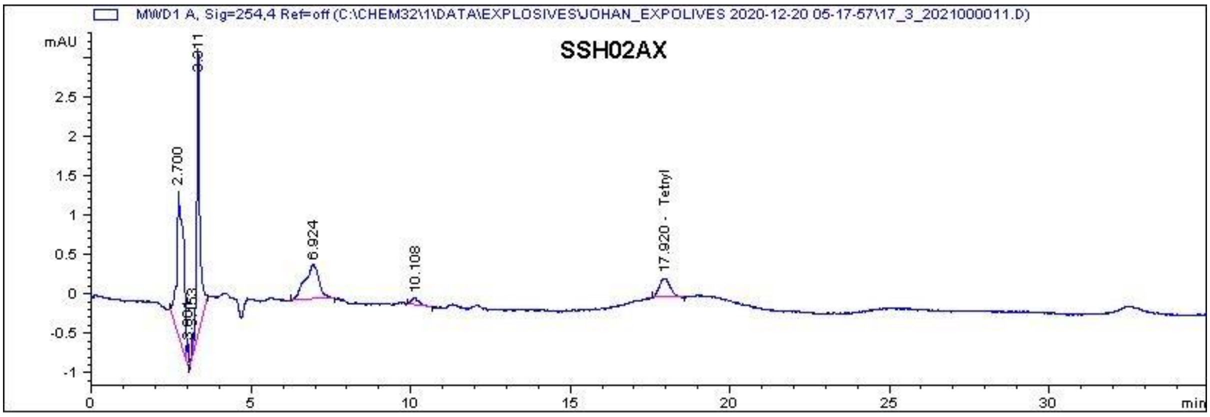
SSB02CX2
mAU
3
2.5
2
1.5
1
0.5
0
-0.5
-1
3.313
2.701
2.975
4.152
6.994
17.934 - Tetryl
0
5
10
15
20
25
30
min

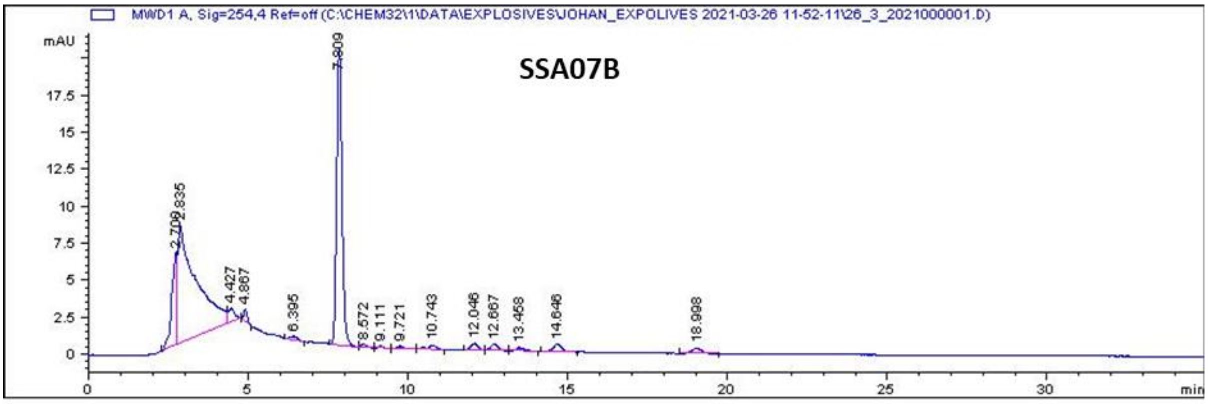








Water wamples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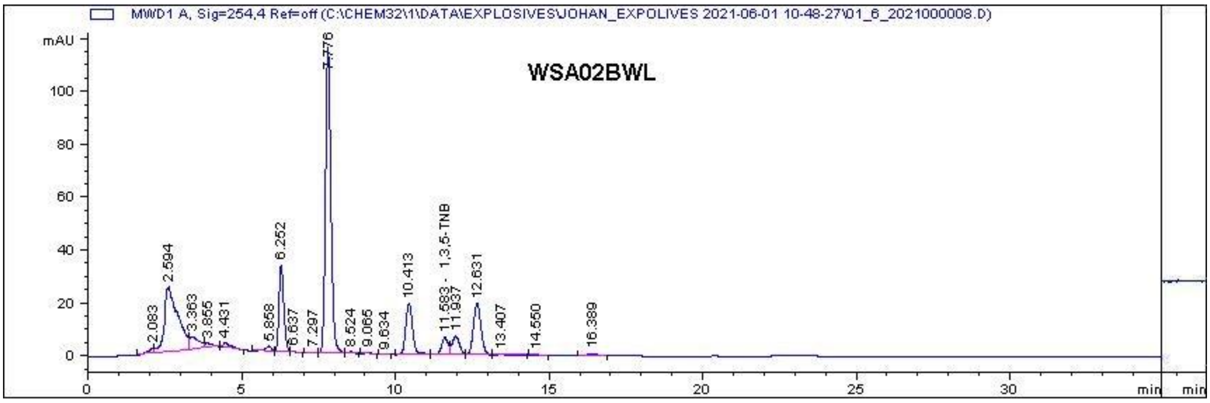
SSA07B
mAU
17.5
15
12.5
10
7.5
5
2.5
0
2.709
2.835
4.427
4.867
6.395
7.809
8.572
9.111
9.721
10.743
12.046
12.667
13.458
14.646
18.998
0
5
10
15
20
25
30
min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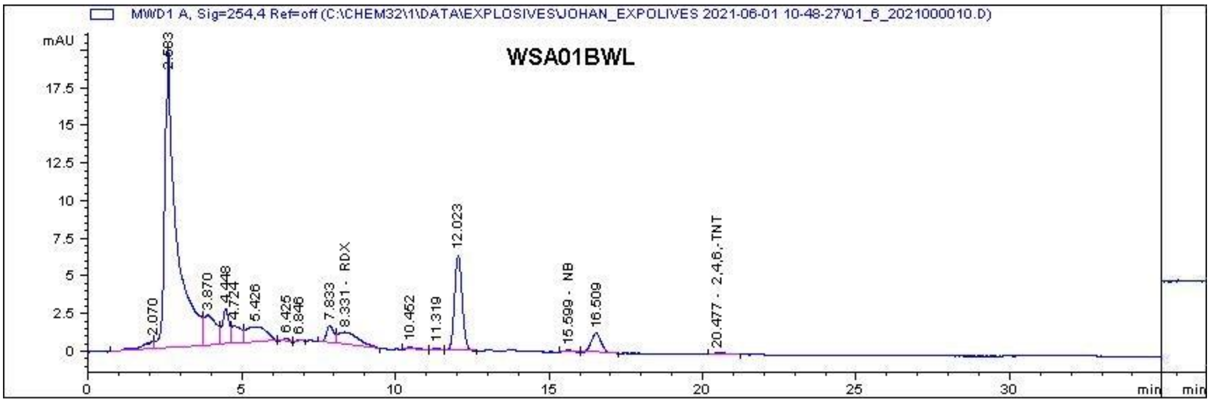
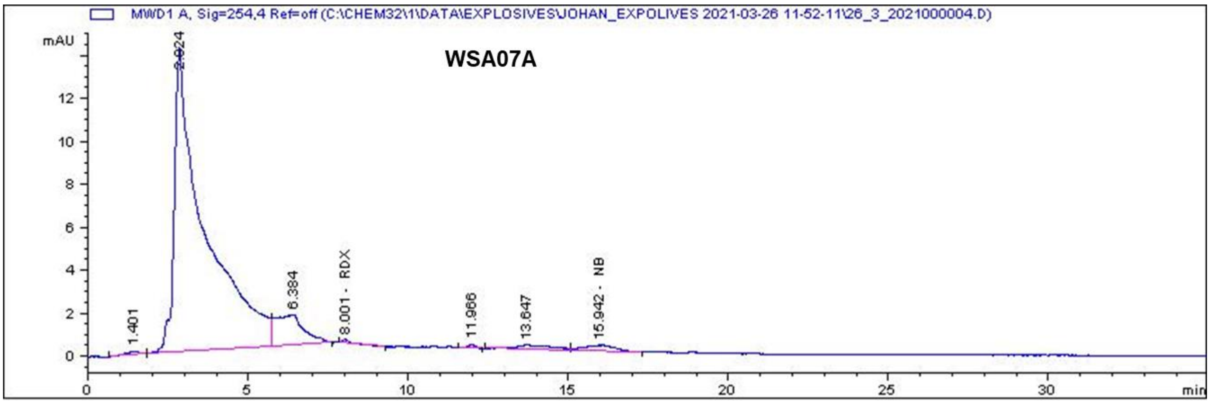
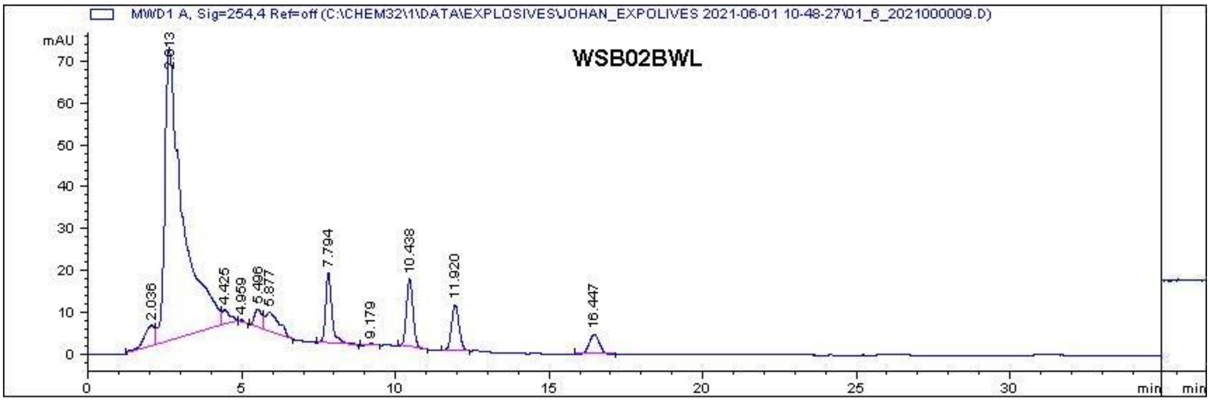
WSA02BWL
mAU
100
80
60
40
20
0
2.083
2.594
3.363
3.855
4.431
5.858
6.252
6.637
7.297
7.776
8.524
9.065
9.634
10.413
11.583 - 1,3,5-TNB
11.937
12.631
13.407
14.550
16.389
0
5
10
15
20
25
30
min
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-06-01 10-48-27\01_6_2021000010.D)
WSA01BWL
mAU
17.5
15
12.5
10
7.5
5
2.5
0
2.070
2.583
3.870
4.448
4.724
5.426
6.425
6.846
7.833
8.331 - RDX
10.452
11.319
12.023
15.599 - NB
16.509
20.477 - 2,4,6,-TNT
0
5
10
15
20
25
30
min
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-03-26 11-52-11\26_3_2021000004.D)
WSA07A
mAU
12
10
8
6
4
2
0
1.401
2.924
6.384
8.001 - RDX
11.966
13.647
15.942 - NB
0
5
10
15
20
25
30
min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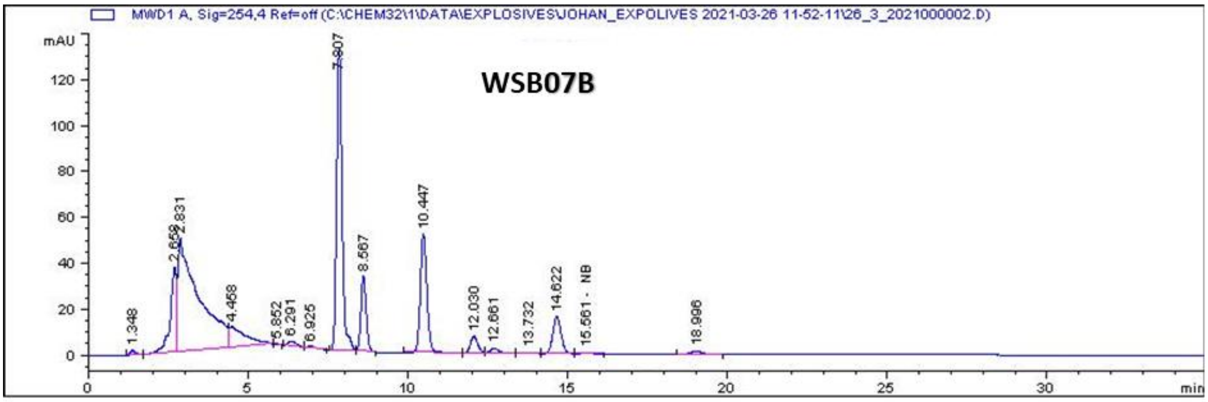
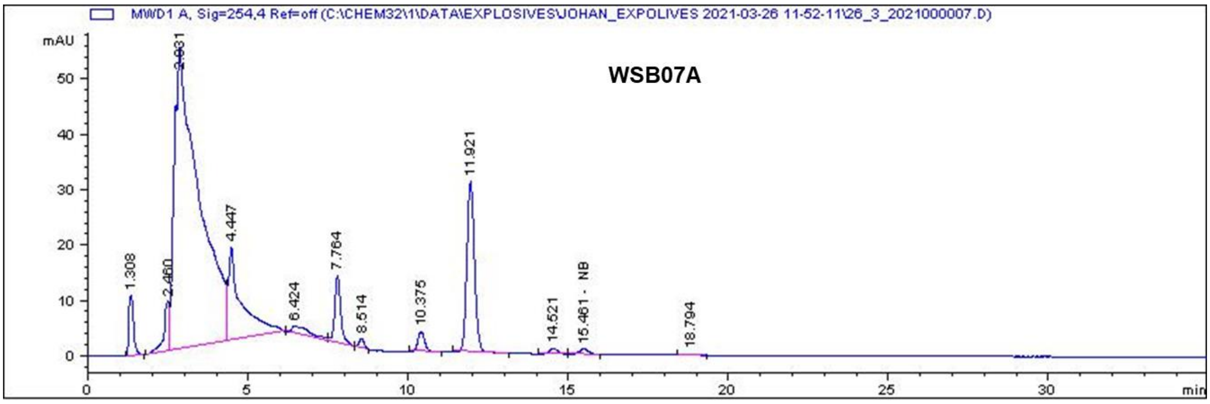
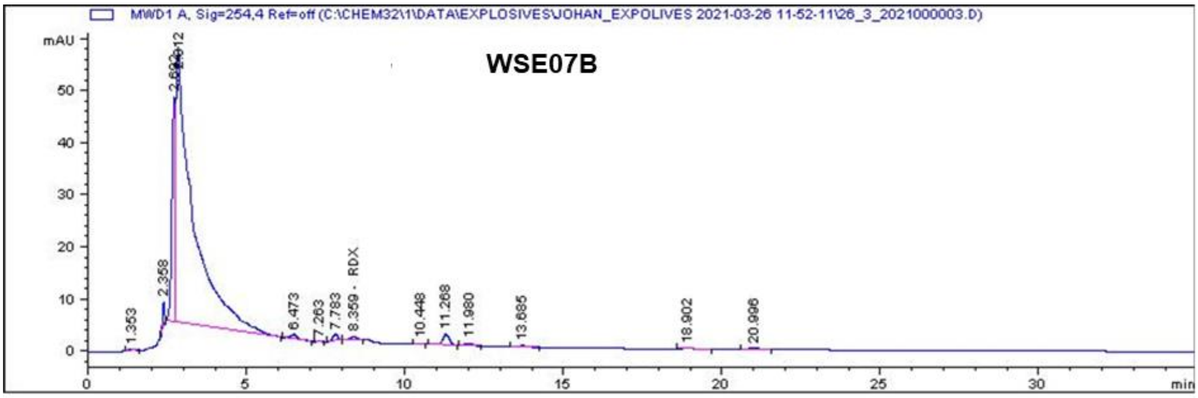
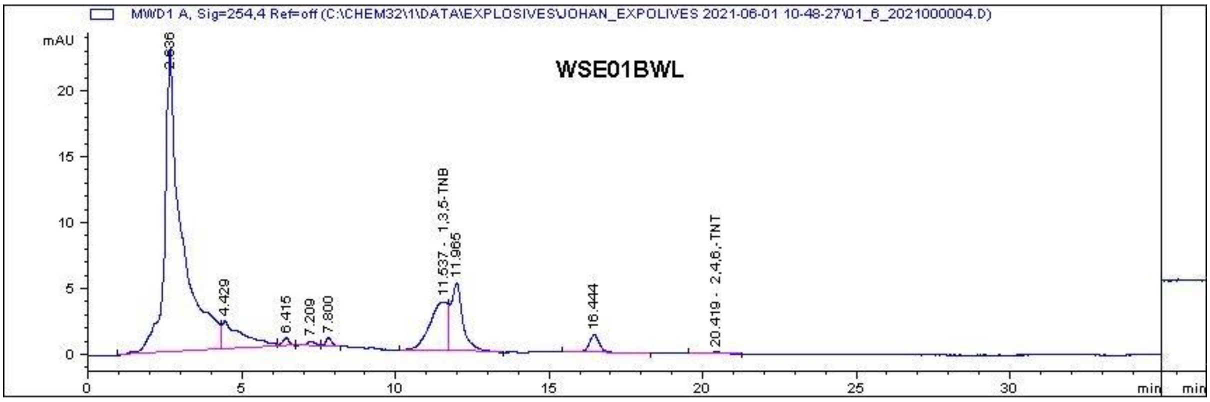
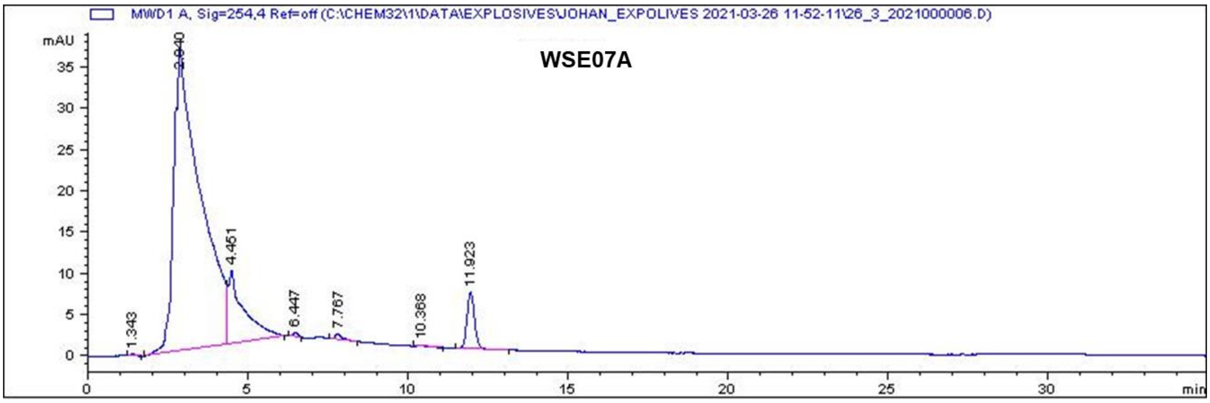
WSB02BWL
mAU
70
60
50
40
30
20
10
0
2.036
2.613
4.425
4.959
5.496
5.877
7.794
9.179
10.438
11.920
16.447
0
5
10
15
20
25
30
min
min

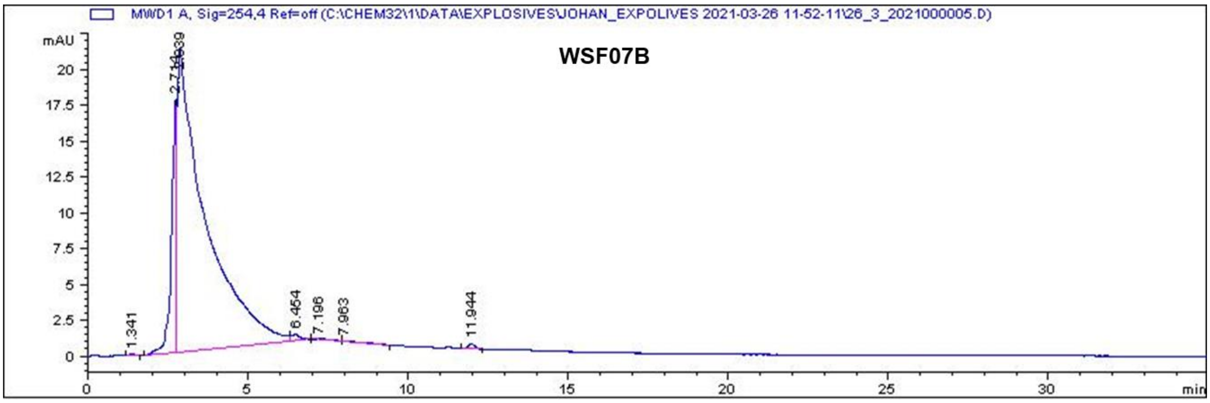

MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-03-26 11-52-11\26_3_2021000002.D)
WSB07B
mAU
120
100
80
60
40
20
0
1.348
2.652
2.831
4.458
5.852
6.291
6.925
7.807
8.567
10.447
12.030
12.661
13.732
14.622
15.561 - NB
18.996
0
5
10
15
20
25
30
min

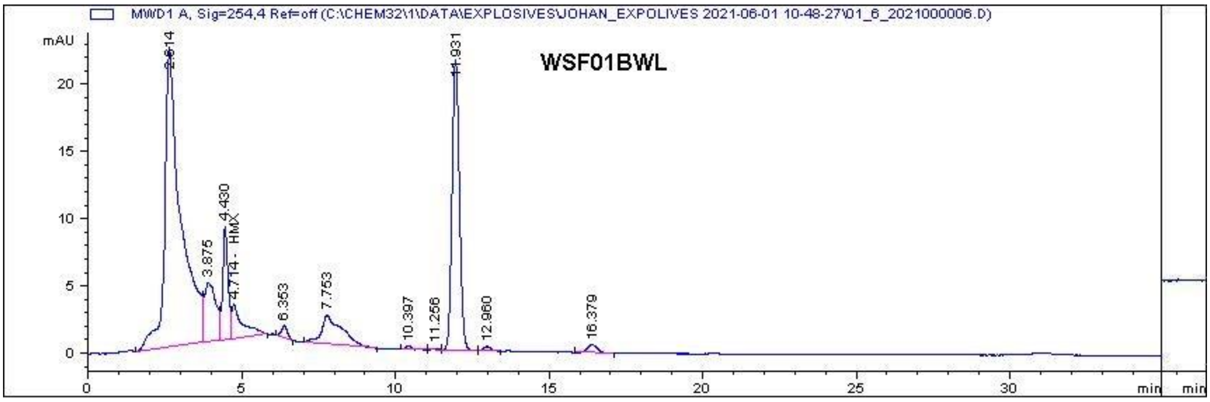

MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-03-26 11-52-11\26_3_2021000007.D)
WSB07A
mAU
50
40
30
20
10
0
1.308
2.460
2.931
4.447
6.424
7.764
8.514
10.375
11.921
14.521
15.461 - NB
18.794
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-03-26 11-52-11\26_3_2021000003.D)
WSE07B
mAU
50
40
30
20
10
0
1.353
2.358
2.662
2.912
6.473
7.263
7.783
8.359 - RDX
10.448
11.268
11.980
13.685
18.902
20.996
0
5
10
15
20
25
30
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-06-01 10-48-27\01_6_2021000004.D)
WSE01BWL
mAU
2.636
4.429
6.415
7.209
7.800
11.537 - 1,3,5-TNB
11.965
16.444
20.419 - 2,4,6,-TNT
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-03-26 11-52-11\26_3_2021000006.D)
WSE07A
mAU
1.343
2.940
4.451
6.447
7.767
10.368
11.923
min


MWD1 A, Sig=254,4 Ref=off (C:\CHEM32\1\DATA\EXPLOSIVES\JOHAN_EXPOLIVES 2021-03-26 11-52-11\26_3_2021000005.D)
WSF07B
mAU
1.341
2.744
2.939
6.454
7.196
7.963
11.944
min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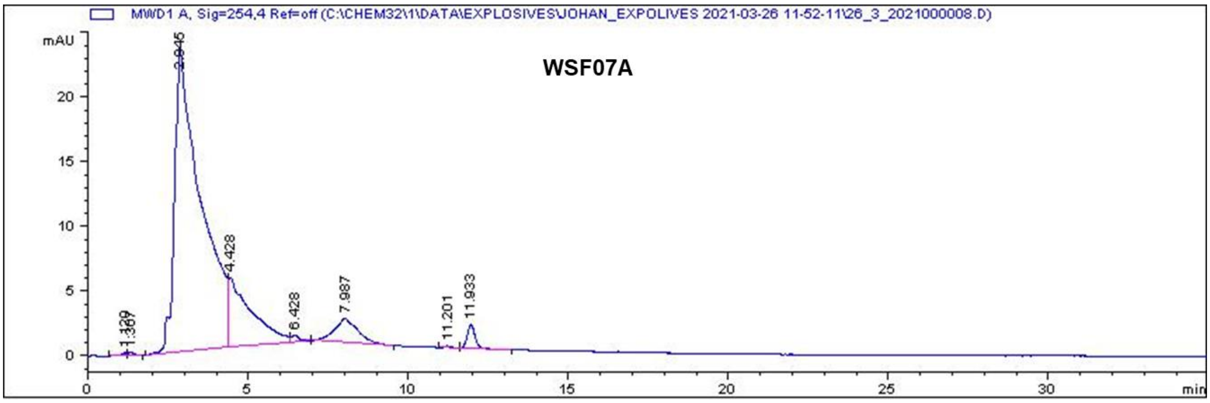
WSF01BWL
mAU
2.614
3.875
4.430
4.714 - HMX
6.353
7.753
10.397
11.256
11.931
12.960
16.379
min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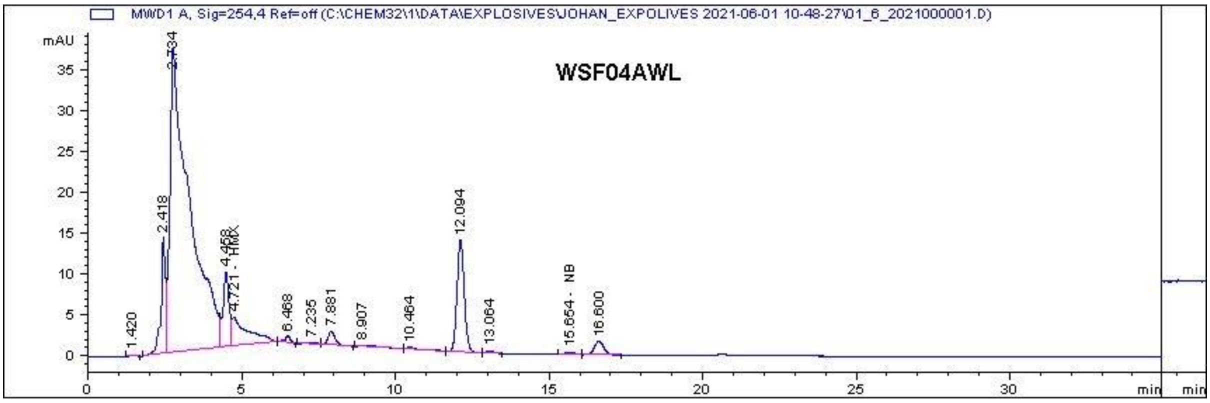
WSF07A
mAU
20
15
10
5
0
1.329
1.367
2.945
4.428
6.428
7.987
11.201
11.933
0
5
10
15
20
25
30
min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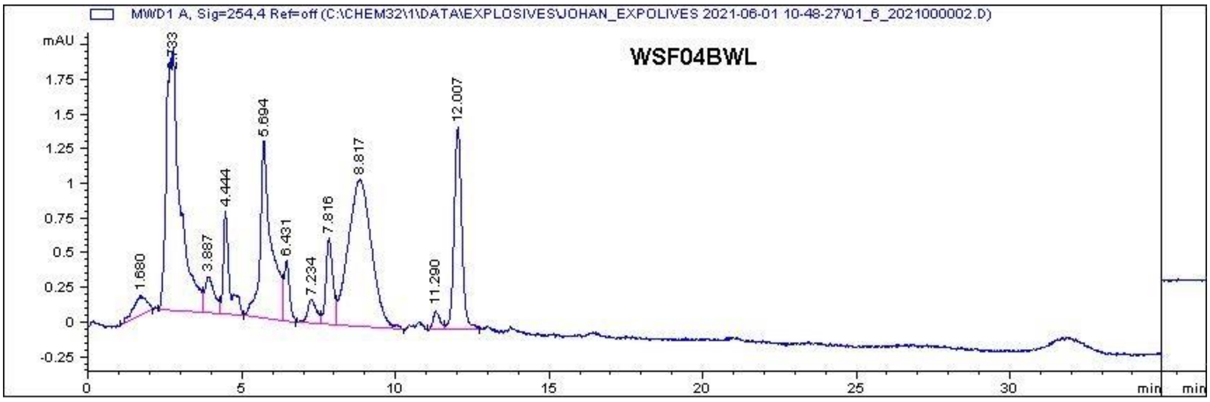
WSF04AWL
mAU
35
30
25
20
15
10
5
0
1.420
2.418
2.734
4.458
4.721 - HMX
6.468
7.235
7.881
8.907
10.464
12.094
13.064
15.654 - NB
16.600
0
5
10
15
20
25
30
min
min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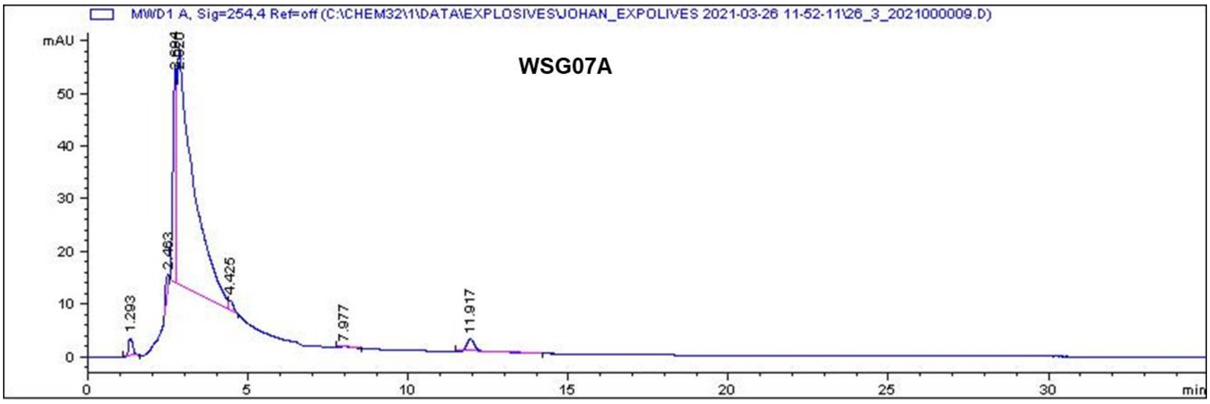
WSF04BWL
mAU
1.75
1.5
1.25
1
0.75
0.5
0.25
0
-0.25
1.680
2.733
3.887
4.444
5.694
6.431
7.234
7.816
8.817
11.290
12.007
0
5
10
15
20
25
30
min
min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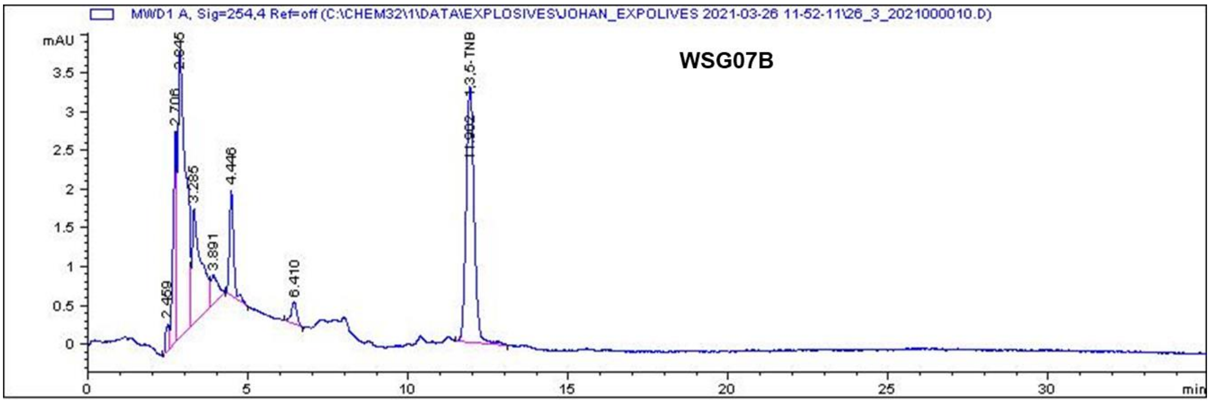
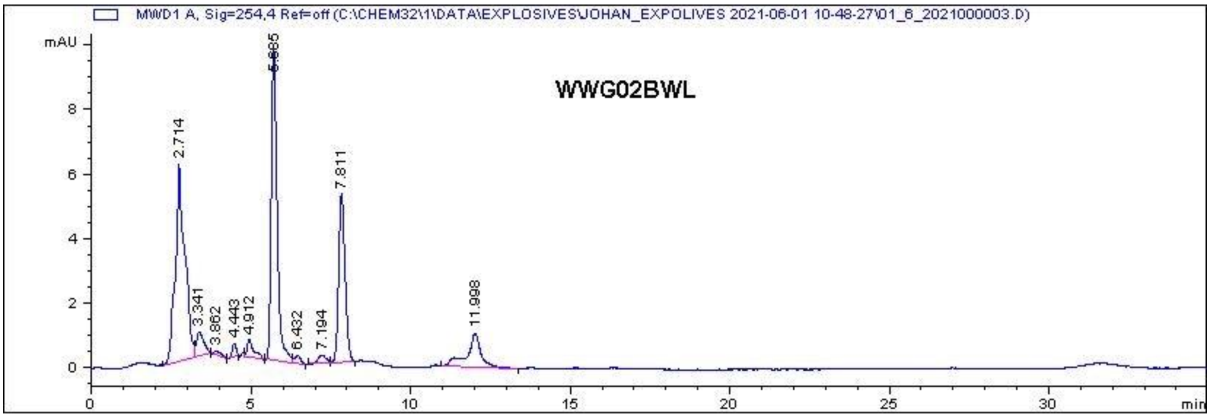
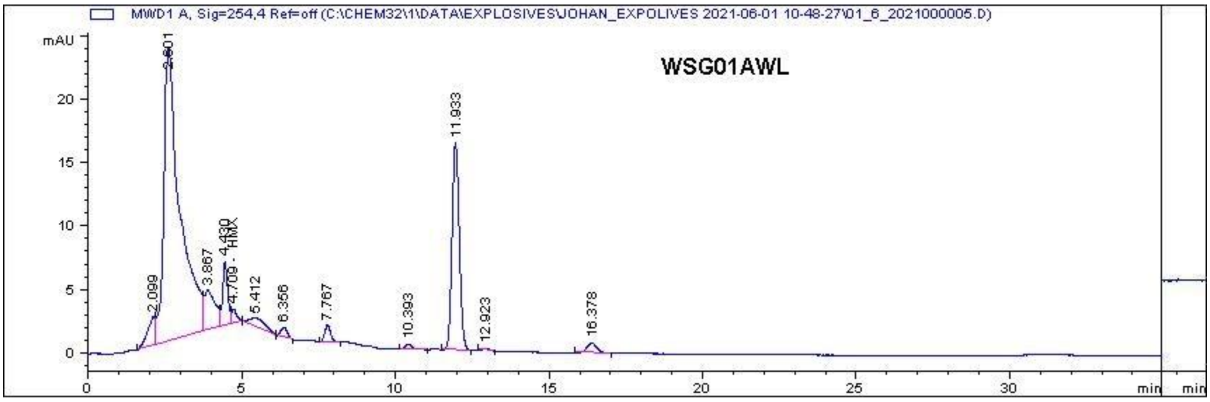
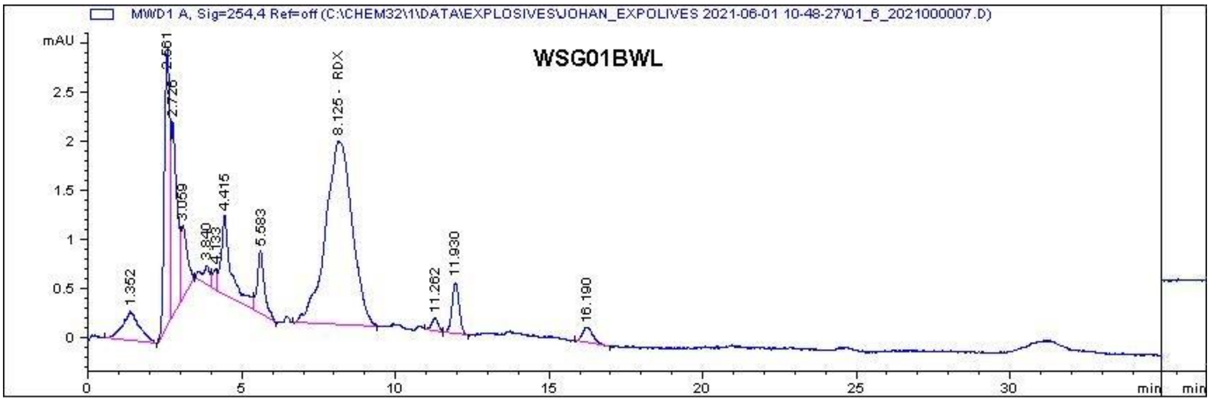
WSG07A
mAU
50
40
30
20
10
0
1.293
2.463
2.896
2.920
4.425
7.977
11.917
0
5
10
15
20
25
30
min









Last Updated: 25 May 2022