Miss Federica Persico

Development of an analytical framework to assess the risks posed to soil by emerging contaminants and chemicals of military concern.

Cranfield Defence and Security
Defence Chemistry

PhD
Academic Year: 2019 – 2022

Supervisor: Dr. Tracey Temple
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ABSTRACT

Soil provides multiple essential functions, such as provision of food and raw materials, a platform for urban development and human wellbeing and as a filtering and transforming medium. Many unregulated contaminants, often termed emerging contaminants, are globally released on soil creating potential risks, especially when undetected leading to significant impact on environmental receptors. The UK ministry of Defence plays an important role in soil protection as the biggest holder of Sites of Special Scientific Interest (SSSI) in the UK as well as being an active polluter in these protected areas through essential training activities. Therefore, there is a need to improve methods for early identification of emerging contamination to avoid long term environmental impacts and costly remediation. The research undertaken for this thesis has contributed to the development of a soil analytical framework to facilitate early identification of the deleterious effects of emerging contaminants and chemicals of military concern on soil. During this research two different scenarios were considered, firstly, when there is a significant body of ecotoxicological data available for a specific contaminant in the literature and secondly, when ecotoxicological data is not available.

A scale based on potential hazards was created for the first scenario, which aims to classify chemicals into three categories - low, medium, and high environmental hazards. This scale serves as an inexpensive method to identify the risk of soil degradation. Results from this research showed that for the contaminants of interest (e.g. 1,3,5-trinitro-1,3,5-triazine - RDX, 2,4,6-Trinitrotoluene - TNT, Perfluorooctanoic Acid - PFOA, Perfluorooctane Sulfonate - PFOS and Cypermethrin) the low-level hazard values were lower than expected. These values were expected to correspond to existing Soil Screening Values (SSVs) and Ecological Soil Screening Levels (Eco-SSL), meaning that the contaminants are likely to have a negative impact on the soil at lower concentrations.

For the second case, when data is not available experiments need to be undertaken to generate primary data. Insensitive High Explosives (IHE) compositions were identified as lacking data and explosive residues were collected and soil mesocosms were carried out to define the long-term consequences on soil. Field experiments were used to quantify IHE residue deposition concentrations from a standard 155 mm artillery shell, which was then used to estimate potential contamination after 100 detonations. These values were used to estimate low, medium and high contaminant concentration for soil mesocosm studies to quantify the impact on soil using indicators identified through literature review. A standardised procedure was developed based on this, which quantifies the consequences of explosives on soil. This procedure revealed that soils that are already degraded are more susceptible to the impact of explosives, which primarily affects the chemical and biological properties of the soil. .

Specifically, this work has shown that the frequent use of IHE filled munitions on training ranges will have an effect on the quality of the soil even when low quantities of energetic residue are deposited. Results for this thesis represent a first step towards a more comprehensive soil analytical framework development providing early identification tools for soil protection.

Keywords: Soil quality, Insensitive High Explosives (IHE), environmental hazard, land degradation, soil assessment

ACKNOWLEDGEMENTS

I would like to start by thanking my supervisors, Dr. Tracey Temple and Professor Frederic Coulon that since the beginning of this journey encouraged me and helped me to perform at my best. Without their guidance none of this would have been possible. They guided me and I am deeply thankful to everything that I have learnt thanks to them*... Grazie*.

A special thank you goes to Dr. Melissa Ladyman, that has been helping me, not only during my PhD project, but has been my mentor since I started my new journey with the Environmental Science Group. She has been encouraging and gave me guidance and support throughout the entire process and I will always be grateful for that*… Grazie*.

None of this would have been literally possible without the lovely Bea Kingdon. She offered me shelter, support, she has been an amazing friend always there for me. Honestly, there are no words to say how deeply grateful I am for everything she has done for me*…Grazie*.

A big thank you goes to my other half, Ernesto, that has always been there for me, even during tough times! Always there to support, listen and comfort me. And a thank you goes also to my family, that has been there for me even from overseas!*...Grazie.*

A thank you to everyone that helped me at one point or another during my project, to friends, colleagues on and off site, PhD researchers, MSc students, the researchers from CENTA. Everyone played an essential role during my journey and has been part of my personal and academic growth.

Grazie a tutti

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LIST OF ABBREVIATIONS

2,4 – ANAN	2-Amino-4-nitroanisole
AF	Assessment Factor
ATO	3- Amino-1,2,4-triazol-5-one
CEC	Cation Exchange Capacity
CEP	Circular Regular Probable
DNAN	2,4-dinitroanisole
DNP	2,4-Dinitrophenol
DU	Decision Units
EC	Electrical Conductivity
ECHA	Environmental Chemical Agency
Eco-SSL	Ecological Soil Screening Level
EQI	Environmental Quality Index
ERAs	Environmental Risk Assessments
HPLC	High Performance Liquid Chromatrography
IHE	Insensitive High Explosives
IM	Insensitive Munitions
MIS	Multi-Increment Sampling
NTO	3-Nitro−1,2,4-triazol−5-one
NEQ	Net Explosive Quantity
PFAS	Per- and polyfluoroalkyl substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonate
PNEC	Predicted Non-Effect Concentration
REACH	Registration, evaluation, authorisation and restriction of chemicals.
RDX	1,3,5-trinitro-1,3,5-triazine
SAC	Special Area of Conservation
SOP	Standard Operating Procedure
SPA	Soil Protection Area
SQI	Soil Quality Index
SSSI	Sites of Special Scientific Interest
SSV	Soil-Screening Levels

TNT	2,4,6-Trinitrotoluene
USEPA	United States Environmental Protection Agency

1 Introduction

Soil protection and management have been featured in policy discussions since the late 1930s (Montanarella, 2015). However, the topic has recently been expanded and there is a greater interest in the development of related policies, particularly with regards to the role of soil as a resource, independent of the functions that it carries out. In Europe, the importance of soil has been highlighted by recent policies resulting in the EU Soil mission “A Soil Deal for Europe” which is focussed on ensuring research funding and help the transition towards healthy soil because “life on earth depends on soil” (European Commission, 2021). The mission aims to ensure that soil does not undergo further degradation, hoping to achieve Land Degradation Neutral (LDN) by 2030. The EU Soil mission further focuses on evaluating environmental pollution and understanding its consequence on soil health and quality through research programmes. This approach is also internationally pledged by 196 countries. Due to the worldwide increase in land degradation, many countries have developed responses to ensure soil safety and protect soil health. The UK have also responded by publishing a 25-year environmental plan (“A Green Future: Our 25 Year Plan”) focussing on how to improve land management and the safeguarding of soil health, not only for the environment, but for the future economy (DEFRA, 2018).

Ministry of Defence (MoD), as a UK wide problem owner, has a responsibility to comply with environmental regulations at both the UK level and devolved administration levels. Devolved administrations, such as the Scottish Government, Welsh Government, and Northern Ireland Executive, have the power to create their own environmental regulations and standards that may differ from those set at the UK level. (DSA01.1, 2016) Therefore to ensure that the UK reaches its objectives and targets set in legislation (DSA01.1, 2016). the MoD has developed policies (such as JSP 418) and frameworks (such as the Ministry of Defence Climate Change and Sustainability Strategic Approach) to address environmental challenges at military level (Ministry of Defence, 2021; *JSP 418 - Management of Environmental Protection in Defence*, 2014) with Site Environmental Protection Officers (SEPOs) responsible for ensuring that land in protected at both UK level and MoD level (*Environmental Protection Act 1990*, 1990). It is important for MOD to understand and comply with these regulations to ensure that its operations and activities do not have a negative impact on the environment in any of the devolved administrations where it operates. Failure to comply with these regulations can result in legal and financial consequences, as well as damage to the environment and the reputation of the MOD.

Moreover, MOD has an opportunity to go beyond compliance and actively engage with devolved administrations to promote sustainable and environmentally responsible practices. By working with local communities and stakeholders, MOD can help to build trust and foster positive relationships while also contributing to a cleaner and healthier environment.

This urgent need of addressing land degradation-related problems is associated with the fact that soil provides multiple important functions such as provision of food and raw materials, a platform for urban development and human wellbeing and a filtering and transforming media for water, nutrients, and carbon (Blume et al., 2016).

The move towards integrated management that has been driving policies for air and water has proven to be a challenge for soil management, mainly due to the multiple functions that soils provide (Teng et al., 2014). This is also true internationally and explained by several drivers for soil protection including among others soil contamination, construction, agriculture, and amenity value (Montanarella, 2015).

The last 70 years of ‘environmental revolution’ in the UK has also helped to establish comprehensive frameworks built around preventing pollution and risk-based management. After various lessons learnt, the UK has now established a set of mature policy frameworks and successful track records of sustainable integrated remediation strategies. The risk-based approach of the UK’s contaminated land legislative regimes has further allowed more innovative cost-effective approaches to be applied than elsewhere in the world. But main challenges are frequently arising due to the increase of new Emerging

Contaminants (ECs) whose behaviour and consequences in the environment are not yet fully understood (Sauvé & Desrosiers, 2014).

This progression is rapid as only in the 1950s, as a result of the book "Silent Spring" by Rachel Carson, the serious problems related to new contaminants emerging from modern and innovative production processes, was firstly recognised (Pereira et al., 2018; Sauvé & Desrosiers, 2014). Every year, around 80,000 new synthetic chemicals, derived from manufacturing processes or industrial waste, are being released into the environment (Naidu et al., 2016). China and the United States of America (USA), where most of the literature regarding case of ECs is found, are the largest producers of new substances (Bao et al., 2015). ECs have broad purposes, from household products to warfare applications. As a matter of fact, military activities have been recognised to be cause of a wide increase of land degradation contributing to negative change in the physical, chemical, and biological section of the soil over the world (Certini et al., 2013).

The UK Ministry of Defence (MOD) are responsible for many protected sites, such as Sites of Special Scientific Interest (SSSI), Special Protected Areas (SPA's) etc in the UK and around the world where they operate. It has been reported that the UK MOD is one of the greatest polluters, across the UK, out of all the governmental bodies (e.g. NHS) (Ministry of Defence, 2021). It is worth noting that the MOD is one of the largest landowners in the UK and operates a significant number of facilities and installations, which have the potential to generate various forms of pollution. For example, military training activities, the use of explosives, and the storage and disposal of hazardous materials are just a few examples of activities that could potentially impact the environment.

In recent years, the MOD has taken steps to improve its environmental performance and reduce its impact on the environment. This has included measures such as implementing waste reduction and recycling programs, increasing the use of renewable energy, and adopting more sustainable practices in its procurement processes.

It is also worth noting that while the MOD may be a significant polluter in some areas, it is not the only source of environmental pollution in the UK. There are many other industries and sectors, such as transportation, energy production, and agriculture, that also contribute to environmental pollution and have their own environmental impact. This is also due to the new developed standards in the UK towards safeguarding soil, as expressed in the UK soil strategy (DEFRA, 2009), a more environmentally conscious approach is now needed within the MOD. This has led to an increase in research on new and supposedly environmentally friendly chemicals, to ensure not only maintenance in capability but also environmental protection (Ministry of Defence, 2021).

As there are many challenges incorporated with assessing soil changes, novel studies need to have a broader view of the consequences on the matrix caused by the release of a wide range of contaminants in the environment (Bussian et al., 2021); to tackle the problems that are happening downstream (e.g. people's health) and it is also important to understand consequences upstream (e.g. soil) as anthropogenic activities are mainly happening on land. Numerous studies have centred around evaluating soil quality, with a focus on assessing soil health. Soil health refers to the soil's capacity to function as a living system, where various soil characteristics work in tandem to maintain the ecosystem.(**Chapter 2**).

Generally, studies that are focussed on understanding the consequences of a contaminant on the soil environment concentrate their efforts in evaluating the toxicity of such contaminants against living organisms, as non-lethal/lethal effects of a chemical compound can be a representation of changes in the matrix in which the entity lives (Environment Agency, 2017). While such data are fit-for-purpose to understand the consequences of different contaminants on soil; they are currently not appropriately used to assess how hazardous the presence of these contaminants are impacting soil health (**Chapter 3**).

Although, challenges arise when EC are considered as not enough data is available to carry out a complete evaluation. This is specifically the case for new Insensitive High Explosive (IHE) compositions, that are currently being used around the world although consequences on the environment are not yet fully understood (Lent, 2019). The deposition of higher quantities of explosive residue resulting from the use of IHE filled munitions can increase accumulation rates, leading to potential environmental consequences. While RDX contamination has previously been a concern, many locations have implemented effective environmental management procedures. However, DNAN and NTO, which have not been used in significant quantities in munitions so far, may require additional environmental monitoring and management in the future. NTO is of particular concern due to its potential to dissolve and transport rapidly into soil and ultimately ground or surface waters, causing discoloration. Its behavior in the environment has not been fully investigated, and there is uncertainty surrounding the chemical and toxicological properties of its degradation products, such as 5-amino-1,2,4-triazol-3-one (ATO), which may be more toxic than NTO toward specific organisms. Although NTO has low toxicity, the potential for significant deposition and its uncertain environmental behaviour make it a particular concern. Therefore, understanding the consequences on soil requires a different approach which involves experimental analyses and evaluation of data to be collected overtime (**Chapter 4 and 5**).

Frameworks developed in chapter 3 and 5, can be both utilised to early identify deleterious effects of a wide range of contaminants pre-empting remediation costs by predicting future consequences of these contaminants in the environment diminishing future land degradation.

1.1 Aim and Objectives

The overall aim of this research is to develop a soil analytical framework to facilitate early identification of the deleterious effects of emerging contaminants and chemicals of military concern on soil (Figure 1-1).

This was achieved through the following objectives:

1. To critically review how environmental risk posed by chemicals, especially for emerging contaminants and chemicals of military concern is conducted and identify research needs and opportunities (Chapter 2);
2. To evaluate the environmental impact of selected defence-related chemicals using an integrated toxicity scale approach based on secondary data (Chapter 3);
3. To assess the dispersion of post detonation residues from full order detonations of a 155mm artillery shell filled with an Insensitive High Explosive (IHE) mixture (Chapter 4);
4. To assess the environmental effects of IHE on diverse soils by measuring changes in soil health and quantifying soil quality using an Environmental Quality Index (Chapter 5).

The PhD story is presented in Fig. 1-1 aligned with chapter titles.

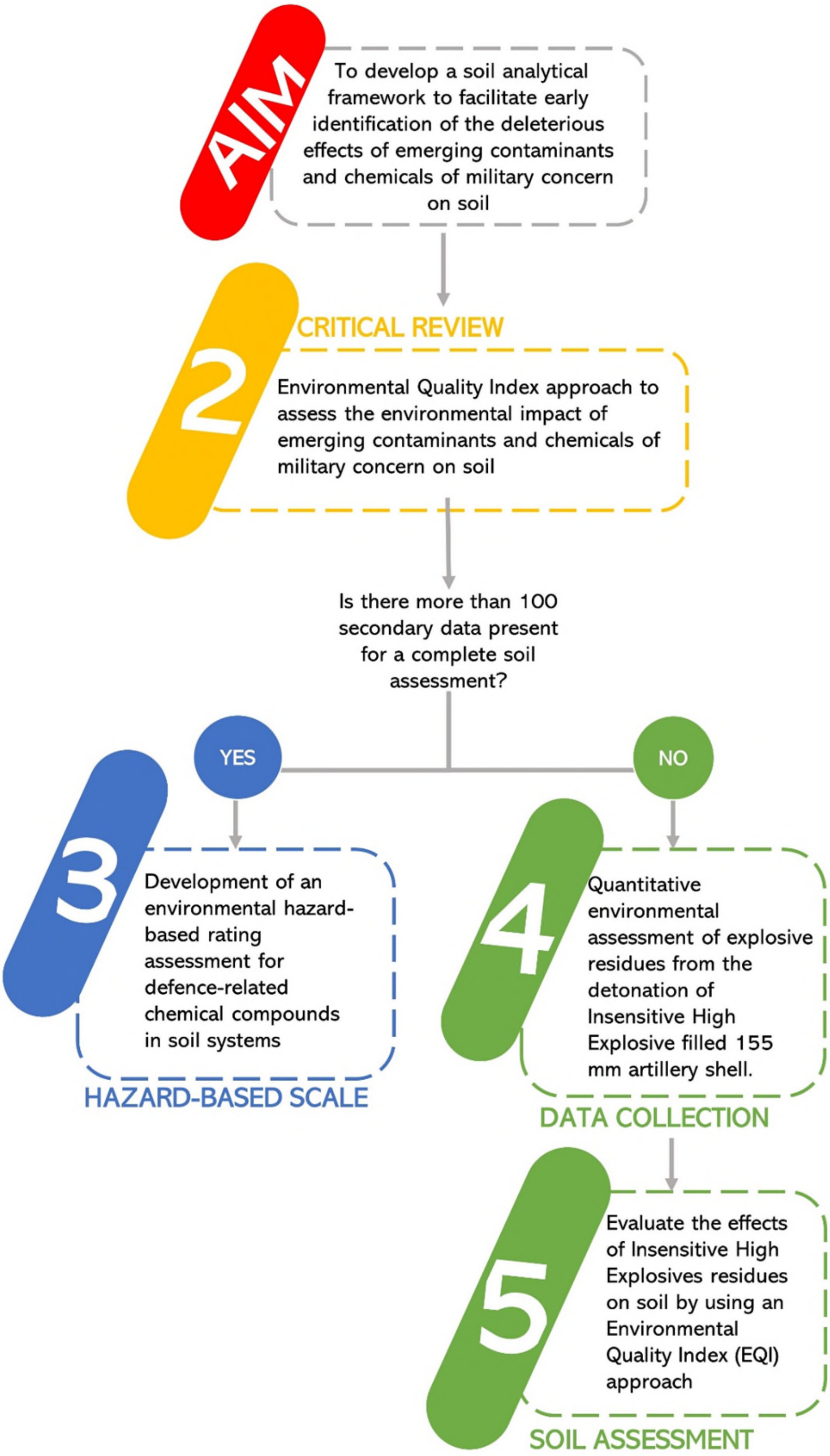


Figure 1-0-1 - Thesis structure aligned to each presented chapter

2 Environmental Quality Index approach to assess the environmental impact of emerging contaminants and chemicals of military concern on soil

2.1 Abstract

Contaminated soil is often evaluated by using toxicity data for specific organisms, which is representative of their environment. The European Union and the United States of America developed different approaches to evaluate the ecotoxicological impact of chemicals and determine soil threshold values, Ecological Soil Screening Levels and Soil Screening Values, respectively. These approaches are typically relying on literature data and are selective based only on contaminants that have been widely studied limiting research for new emerging contaminants. These processes fail in explaining the specific consequences on soil by assuming that no effects are expected under a determine concentration solely based on the organism response. Further research evaluated changes in soil by determining, based on experimental data, alterations in soil indicators, related to the physical, chemical, and biological section of the soil. This was achieved by calculating Soil Quality Indexes and developing soil health assessments. Although, soil indicators selection has only been based on land management and short-term changes in the environment, therefore never analysing full soil changes nor creating comparable results. Therefore, based on previous literature, an Environmental Quality Index (EQI) has been developed to ensure that all the relevant soil indicators, independently from the land management, are included. Having the same indicators means that results from the EQI can be comparable across every type of soil and considering every emerging contaminant even when data is not currently available.

2.2 Introduction

Military training areas represent approximately 2% of the Earth's terrestrial soil surface (Zentelis et al., 2017). These areas are used for several purposes such as non–mechanised training, from so-called ‘low-level’ (up to platoon-size) exercises through to large-scale, many in arduous conditions. Activities may include live firing of artillery rounds, demolition exercises and there is a variety of ranges to accommodate this aspect of skill-at-arms in preparation for higher-level field firing on the principal training areas (Zentelis et al., 2017). The training areas often have restricted access because of their primary purpose and associated safety issues; but it is also the case that where public access restrictions have been imposed, wildlife has found sanctuary – many rare or uncommon species of plants, insects and birds manage to co-exist with the ‘bangs and flashes’ associated with military training activities. Indeed, several training areas are classified as Site of Special Scientific Interest (SSSI) and/or as an EU Special Area of Conservation (SAC), as well as a Special Protection Area (SPA) for birds under the European Birds Directive (Ministry of Defence, 2021).

One of the main risks associated with military activities is the possibility of contamination of drinking water and further consequences on the terrestrial environment. Previously, hundreds of thousands of dollars have been invested to remediate contaminated environments following migration of explosive compounds in the groundwater system (Bortone et al., 2019). Environmental Risk Assessments (ERAs) are used to address these concerns. The purpose of an ERA is to estimate the likelihood, and magnitude of the environmental effects associated with a particular anthropogenic activity to help reduce possible costs related to environmental remediation (Calow, 2009). Risk and likelihood of an activity are measured considering the harm that it can cause against a living organism (e.g. earthworms, birds, humans) using dose-concentration response assessment. Decision-making for ERAs is informed by data collection, although due to the newness of some contaminants and chemical mixtures, not enough information is known to properly assess the risks associated with these chemical compounds (Riva et al., 2019). In general, more than 100,000 different chemicals, military and non-military, are used that represent a threat to the environment, although for only 1% of them there is enough information to carry out a proper assessment (J∅rgensen & Fath, 2011). There is also growing concern associated with Emerging Contaminants (ECs) whose behaviour and consequences in the environment are not yet known (Bao et al., 2015; Naidu et al., 2016; Sauvé & Desrosiers, 2014; Stuart et al., 2012); therefore, there is a need to develop new methods to identify risks associated with their usage when not enough data is available (Naidu et al., 2016)

Since the 1950s many groups of ECs studied were chlorinated paraffins, hexabromocyclodecanes, organic pollutants, pesticides (e.g., DDT), and many others. However, in the past decade, ECs classes are increasing with a focused awareness on pharmaceutical, plastics, microplastics, insensitive high explosives (IHE), care products, flame retardants, perfluoroalkyl substances (PFAS), neonicotinoids, industrial additives, by-products, along with many others (Bao et al., 2015; Naidu et al., 2016; Sauvé & Desrosiers, 2014; Stuart et al., 2012). Military-related ECs comprises of different classes of chemical compounds: IHE formulations, which are designated to detonate on command and not accidentally; permethrin-pesticides, used for protecting military personnel; and PFAS, related to the usage of aqueous film-forming foams (AFFFs).

During the tiered stage process involved in ERA process, risk assessors evaluate risks or hazards by determining toxicity of the chemical of concern against specific organisms because of the lack of understanding of how that toxicity translates into a positive or negative changes to soil biodiversity, health or functioning (Teng et al., 2014). Therefore, there is a missing link between the contaminant's concentration and the actual changes to the soil environment which is now solely based on ecotoxicological data.

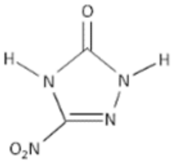
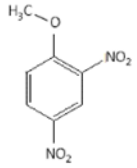
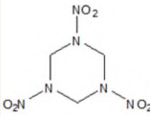
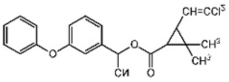
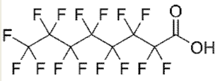
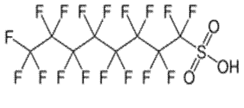
Soil Quality Indexes (SQIs) and soil health assessments, which has been previously defined as the capacity of soil to "function as a living system", where an intricate network of different soil characteristics merge together to sustain the entire ecosystem (Doran & Safley, 1997; Karlen et al., 2003; Lal, 2016; Moebius-Clune et al., 2016; Sintim et al., 2019), are fit for purpose to fill the literature gap, providing insight in the decision-making process. Different characteristics are evaluated to determine the healthiness of soil (Cardoso et al., 2013). These indicators comprise of attributes related to the physical, chemical and biological sections of the soil (Cardoso et al., 2013; Karlen et al., 2019). When evaluating soil changes, chemical indicators such as organic matter content, pH, soil infiltrability, water availability, fraction of water stable aggregates, nutrient content and electrical conductivity are often considered the most sensitive indicators. (Andrews et al., 2002; Arias et al., 2005; Chaves et al., 2017; Idowu et al., 2008; Karlen et al., 2019; Rinot et al., 2019; Schloter et al., 2003; Subbaiah, 2019; Williams et al., 2020; Zvomuya et al., 2008). Incorporating the assessment from soil health and the calculation of the SQIs, will ensure a more thorough assessment because, when in contact with the soil, a contaminant can interfere with most soil properties, determining changes into soil indicators undermining the healthiness of the matrix. Utilising soil evaluations to understand consequences of different contaminants, at specific concentrations, on the soil environment, will establish specific soil tolerability boundaries, which can be translated into a new and broader soil assessment. Consequently, increasing the possibility of thoroughly evaluating the risks and hazards associated with a contaminant, better informing the decision-making process.

Therefore, the aim of this review is to understand how environmental risk posed by chemicals, especially for emerging contaminants and chemicals of military concern is conducted and identify research needs and opportunities. Results from the review will improve the decision-making process by understanding how to evaluate the risks associated with the contaminants′ presence in the soil.

2.3 Emerging contaminants of military concern

A growing body of literature is currently evaluating new defence-related contaminants (Table 2.1) whose behaviour in the environment is not yet well characterised. Different classes belong in this category, and, due to the world development, the number of ECs classes are destinated to continuously increase.

Table 2-1. Properties of different defence-related contaminants with application and possible transport routes.

CONTAMINANT		CHEMICAL NAME	CHEMICAL STRUCTURE	APPLICATIONS	TRANSPORT
IHE formulation	**NTO**	3-Nitro-1,2,4-triazol-5-one		• explosive composition	• Surface run-off • Infiltration to soil
	DNAN	2,4 - Dinitroanisole		• explosive composition • pesticide • propellant	• Surface run-off • Transport to groundwater • Infiltration to soil
	RDX	Hexahydro-1,3,5-trinitro-s-triazine		• explosive composition	• Accumulation • Transport to groundwater
Cypermethrin		Cyano-(3-phenoxyphenyl)methyl]3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate		• insecticide	• Infiltration and persistence in soil
PFOA		pentadecafluorooctanoic acid		• electronics • textile • non-stick cookware	• From landfills during disposal • Release from industries and homes
PFOS		Heptadecafluoro-1-octanesulfonic acid		• protective coating (e.g. carpets, textiles leather) • cleaning products • fire fighting foams • hydraulic fluids	• From landfills during disposal • Release from industries and homes

The Ministry of Defence (MoD) utilises a large number of ECs during both training and in-theatre, although, due to their commitment to ‘governmental greening’ targets, more research has been focussed on how to minimise contamination during training activities (Ministry of Defence, 2021). But while the environmental concerns are growing, there also is an increased demand for safety during explosive transportation and training, therefore, research has seen the development of Insensitive High Explosives (IHEs) formulations. In contrast from traditional explosives, IHE typically comprise up to five constituents including 2,4-dinitroanisle (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and RDX (1,3,5-hexahydro-1,3,5-trinitrotriazine) (Table 2.1). Although RDX is in a different crystallised form (particles have a different morphology) compared to when mixed in traditional explosives compositions. These compounds are mixed in various ratios to achieve a desired performance and have been designed to detonate on command and not accidently (Singh et al., 2010).

These new formulations are utilised as IHE fillings for Insensitive Munitions (IM) which are currently in use in military operations and in training areas around the world (Walsh et al., 2017). There is some literature available on the physiochemical nature of these materials, although the actual consequence of residues being deposited post detonation is still an unexplored area of research (Ladyman et al., 2019; Persico et al., 2022).

Other activities on training ranges involve the use of aqueous film-forming foam (AFFF) utilised in military firefighter training exercises to extinguish intentionally ignited fires (ITRC, 2022). And even though AFFFs have been currently banned in different States (Jordan Gillis, 2020) they are part of the largest and most impactful ECs class ever existed, PFAS is known to cause problems even after years of non-usage (Place & Field, 2012). PFAS are a large group of anthropogenic produced chemicals composed by perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and associated compounds (Atkinson et al., 2008; Gredelj et al., 2020). In the last 60 years, PFAS became a part of everyday life, they have different commercial applications, from fire-fighting foams, non-stick coating, waterproof materials, packaging, and cosmetics. They are known as “forever chemicals” because their carbon-fluorine chain is unbreakable in both the environment and the human body, so they represent persistent compounds in the environment bioaccumulating through the trophic chain (Atkinson et al., 2008; Kahkashan et al., 2019). AFFF substances have often been related to military areas because of the continuous usage during training; as a matter of fact, in the US 75% of the produced AFFF is bought and used on military areas, the remaining 25% is utilised in non-related military activities although, the majority of them, is located near military training ranges (Field et al., 2017). PFOS, and PFOA have been previously found in these areas because of years of AFFF usage, even though they are respectively not in use anymore or not intended to be part of the formulation (Place & Field, 2012; Turner et al., 2021). This problem has been encountered world-wide and currently governments are investing in evaluating problems and determining thresholds levels in drinking water (U.S. EPA, 2016). Legally enforceable federal standards for other matrices, like soil, are not yet determined due to the uncertainty of information because of the newness of this emerging problem (Weber et al., 2019).

Another notable example is the continuous use of pesticides, that are not only widely utilised in agriculture and naturally transferred through the environment leading to major environmental problems and harmful human effects (Birch et al., 2015; Das & Mukherjee, 2003), but have different military applications. Specifically, permethrin-based chemical compounds, are a class of insecticides, used to treat military uniforms and equipment to avoid insects′ bites during military operations (Khoobdel et al., 2005, 2020; Vatandoost et al., 2010). The insecticide is sprayed on the uniforms and equipment to avoid victor-borne diseases spreading throughout the military personnel (Ho et al., 2019). Because of the close contact between skin and uniforms, health effects of permethrin-based compounds have been widely assessed (Army, 1994; Khoobdel et al., 2005, 2020; Vatandoost et al., 2010). Although, there is a growing concern, which has not yet been addressed in literature, to analyse the environmental problems that can cause the use of these pesticides, especially those commonly used (e.g.

Cypermethrin) (Maule et al., 2019), because of their release into the environment through spraying and hand washing of clothing in theatre(Khoobdel et al., 2005).

Assessing the environmental consequences due to the presence of these defence-related contaminants can provide insight during the decision-making process to ensure that ERAs evaluations are properly completed.

2.4 Toxicity and soil evaluation

Soil is a carbon reservoir that represents a key player in the entire ecosystem functionality (Arias et al., 2005). The soil structure includes different characteristics, and it depends on the type of soils that forms the soil matrix (Jahn et al. 2006). The soil matrix consists of an inorganic fraction (e.g. minerals, water, air) and an organic fraction (e.g. microorganisms, organic matter, plants, animals) (Blume et al., 2016). Even though soil is an important ecosystem for food production or recreation, it is the least studied matrix since the relationship between human exposure and soil is not immediate (Teng et al., 2014). Moreover, soil is a sink for pollutants, but an advantage is that contamination in soil can reflect contamination overtime (Kowalska et al., 2018; Teng et al., 2014) making it easier to understand for how long that contaminant has been in soil, when the contamination has occurred, and the environmental consequences. Soil type and its characteristics can affect how a contaminant is stored and can influence degradation processes depending on the contaminant (Sanderson et al., 2012; Smolders et al., 2009). It is also worth noticing that external factors and different evolving environmental issues such as climate change can affect soil contamination by chemicals in several ways. Changes in precipitation patterns can alter soil moisture content and groundwater recharge, which can impact the transport and fate of chemicals. Temperature changes can affect the rate of microbial degradation of contaminants. Extreme weather events can cause soil erosion and damage infrastructure, increasing the transport of contaminants. Changes in plant growth and sea level rise can also impact soil contamination. Overall, climate change can influence the transport, fate, and degradation of contaminants in soil.

A starting point for analysing consequences of different contaminants in the environment is to define the toxicity of that chemical against terrestrial organisms. Projects have evaluated the consequences on earthworms by looking at reproduction, juvenile response, differences in food ingestion and different limits are determined (Castro-Ferreira et al., 2012; Lent, 2019; Stroud, 2018). First signs of death are recorded, and different concentrations are evaluated because of the death of a certain percentage of the studied population. Earthworms are bioindicators of soil quality and contamination due to their sensitivity to changes in soil conditions. Their presence, absence, or behaviour can be essential to indicate the health of the soil. Although, this approach can fail to define the actual consequences on the terrestrial environment, missing a broader picture and possible consequences on the physical, chemical, or biological section of the soil.

Toxicity data has been previously used for the determination of different concentrations above which changes are expected on the soil environment (Environmental Agency, 2020). Different approaches have been developed in different countries to determine the ecotoxicological impact, and predictive thresholds, of different chemical species to soil using literature-base data (Environmental Chemical Agency (ECHA), 2008; USEPA, 2003c). The United States Environmental Protection Agency (USEPA), through a score-grading procedure of the literature data, developed a set of risk-based ecological soil screening levels (Eco-SSLs) based on contaminants that have been proven to be a threat for both flora and fauna (USEPA, 2003c). The European Chemical Agency (ECHA), which developed an effective technique to determine Soil Screening Values (SSVs) based on data collected through the ECHA database under the Regulation (EC) No 1907/2006 introduced in Europe in 2007, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Merrington et al., 2008) and statistical analyses (Environmental Agency, 2020). Although, part of the process involves evaluation of the data by expert's opinion, making the process far from objective, mainly dependant on the researcher completing the assessment.

Soil assessments have traditionally focused on the impact of chemical compounds on soil productivity, rather than the soil itself. This means that assessments have been primarily directed towards crop production and farm activities (Blume et al., 2016). As a result, soil investigations are tailored to the intended use of the soil, and evaluation techniques are selected accordingly. There is however currently no established approach for conducting a soil assessment that is independent of the intended use of the soil.

Click or tap here to enter text.In the 1970s, various studies attempted to develop techniques for evaluating changes in the soil environment. One such approach has been the design of Soil Quality Indexes (SQIs), which aim to mathematically quantify the quality of the soil (Andrews et al., 2002; Chaves et al., 2017; Mukherjee & Lal, 2014)(Andrews et al., 2002; Chaves et al., 2017; Mukherjee & Lal, 2014)(Andrews et al., 2002; Chaves et al., 2017; Mukherjee & Lal, 2014). There are different methodologies for calculating SQIs, but they all typically involve the integration of soil indicators. The choice of these indicators is typically guided by expert opinion based on the intended land management and ultimate purpose of the soil (Andrews et al., 2002a). Choosing appropriate indicators, that are reflective of how the soil can change due to a contamination presence, has been the main challenge during the development of SQIs because not commonly reliant on literature but based on the general external conditions (e.g. land management) (Mukherjee & Lal, 2014). This procedure limited the choice of the indicators solely based on the soil function of interest, focusing exclusively on the physical and chemical changes of the soil.

From the 2000s, research focussed more on how to interpret differently the soil functionality which eventually translated to the development of soil health evaluations. Soil was then seen as an intricate system of different soil characteristics merging to sustain the entire ecosystem (Doran & Safley, 1997; Karlen et al., 2003, 2019; Lal, 2016; Moebius-Clune et al., 2016; Sintim et al., 2019). For the first time, evaluation of soil organisms, representing the biological section of the soil, were discussed and included when looking at soil health. Therefore, evaluating soil health translated into evaluating how the soil functions.

Overtime, various methods for evaluating soil health have been developed (Table 2-2). Doran and Zeiss (2000) were among the first to take a more holistic approach, identifying five key aspects of soil health and incorporating biological indicators and economic benefits into their assessment framework. Arias et al., (2005), reviewed different soil indicators to determine soil health and evaluated relevant soil attributes including physical, chemical, and biological indicators. Meanwhile, Chaves et al., (2017), proposed an index focused on the evaluation of the land management and land use instead of determining the soil properties.

The SQI integrated by Chaves et al., 2017 but originally developed by Karlen et al., 2003, which integrated the biological section of the soil, was a step forward towards understanding how the soil function, although, the soil indicators choice was still driven by the land management practices and experts' opinion. First step was the understanding of the soil indicators to consider, this decision was solely based on the land management and what the landowners needed at the time to ensure that their productions were not affecting the quality of the soil. After the indicators selection Principal Components Analyses (PCA) were carried out to define the indicators that were likely to be mostly impacted within the soil. The highest impacted indicators were the scored through a statistical linear score or based on previous research (Amacher et al., 2007).

Table 2-2 Comparison of different soil assessment with their pros and cons.

Type of study	**Methodology applied**	**Pros**	**Cons**	**Reference**
Soil health assessment	Biological, chemical and physical indicators are separately analysed	• Different indicators can be assessed	• Greater emphasis on biological indicators • No scoring is available	Doran and Zeiss, 2000; Arias et al., 2005

			• Soil health cannot be quantified • Indicators to analysed are based on expert`s opinion	
Soil functionality evaluation	Soil is considered as an intricate system based on eco-system services	• Soil section of the soil can be economically quantified giving a loss in price to environmental degradation	• Some indicators might be missed • No scoring is available	Rinot et al., 2019
Soil Quality Index	Soil indicators based on the physical, chemical and biological section are scored	• Soil quality can be quantified	• Chosen indicators are dependent from land management • The land user together	Andrews et al., 2002; Chaves et al., 2017; Mukherjee & Lal, 2014

			with an expert decides the most appropriate indicators to analyse - Results are incomparable between sites	

The second step integrated the soil indicators ranked from the lowest to the highest based on their means and grouped in sub-indices, one for each soil section:

2-1

$$\boldsymbol{SQI_p = 3T_{p_{i1}} + 2T_{p_{i2}} + T_{p_{i3}}}$$

2-2

$$\boldsymbol{SQI_c = 3T_{c_{i1}} + 2T_{c_{i2}} + T_{c_{i3}}}$$

2-3

$$\boldsymbol{SQI_b = 3T_{b_{i1}} + 2T_{b_{i2}} + T_{b_{i3}}}$$

where: SQIp = physical sub-index; SQIc = chemical sub-index; SQIb = biological sub-index; Tci1 = number of times that the ith treatment had the highest mean in the group of the physical indicators; Tci2 = number of times that the ith treatment had the 2nd highest mean in the group of the physical indicators, Tpi3 = number of times that the ith treatment had the 3rd highest mean in the group of the physical indicators. The same procedure is used for the analysed chemical and biological indicators.

The sum of the physical, chemical and biological sub-indexes is then normalised to calculate the SQI:

2-4

$$\boldsymbol{SQI} = \left(\boldsymbol{SQI}_p / \boldsymbol{I}_p\right) + \left(\boldsymbol{SQI}_c / \boldsymbol{I}_c\right) + \left(\boldsymbol{SQI}_b / \boldsymbol{I}_b\right)$$

Where $I_{p/c/b}$ are how many physical, chemical and biological indicators considered.

Although, this methodology overlooks a series of indicators that might be considered more resilient to short-term consequences, but have, in the long run, more impact on the overall soil quality. This is because the PCA is identifying only those indicators that can quickly change and are considered more “fragile” because of the sudden change that can happen due to a bad land management practice or a specific contaminant presence.

More recently, Williams et al., (2020), utilised the Comprehensive Assessment of Soil Health (CASH) analyses, which tries to relate the land productivity and the environmental impact on an agricultural soil, to determine changes in soil in a farm in Sweden. Similarly, Purakayashta et al., (2019), determined the impact of land management on the soil health status. The researcher developed a Soil Health Card (SHC) where different properties were displayed. The card was distributed among different farmlands to understand characteristics of different soils and how the land management could have been improved to assure a better soil health. Both methodologies choose their indicators based on the experts’ opinion.

Rinot et al., (2019), differentiated his work evaluating soil health by dividing the soil ecosystem in three different sections called Ecosystem Services (ES); each of those sustained a particular role in the soil, which specifically are: provisioning, regulating and supporting the soil environment. An ES confers either direct or indirect benefits to humans. These benefits are delivered and related to the soil functionalities (Faucon et al., 2017). ESs delivered by the soil include a wide range of functionalities, water purification, carbon sequestration, nutrient storage, climate changes (Kihara et al., 2020; Millennium Ecosystem Assessment (MEA),

2005) each of those sections can be directly affected by land management practises which can render the site unusable altering precious functionalities (e.g. provision of food for future generations) (Pereira et al., 2018). High soil disturbances, directly related to land management, can lead to a decrease in Soil Health which can cause ESs degradation and devaluation (Pereira et al., 2018; Van Oudenhoven et al., 2012).

Due to all the different methodologies presented, (Jian et al., 2020), developed a Soil Health Database (SoilHealthDB) where a gathering of values started with the purpose of creating a unique spot where it was possible to understand possible consequences on the soil environment because of certain land management practises.

Although, much of the literature on soil evaluations are all land management-dependent and currently no standardised procedure for soil health evaluations is present making all the previous processes presented not entirely comprehensive for soil health evaluation purposes. By developing a comprehensive soil evaluation process, it will be possible to ensure that the same tool is used to evaluate possible risks associated with the presence of a certain contaminant in the environment.

2.5 A new environmental quality index process

Previous studies developed either SQIx or Soil heath assessments selecting soil indicators based on the experts′ opinion. Whether from landowners or researchers, soil indicators were carefully chosen looking only at immediate changes in the soil. One major drawback of these methodologies is that many slow changing indicators (e.g., physical changes) are eliminated from the analyses because there was no primary concern for landowners.

Therefore, there a is a need to ensure that all the indicators, from the biological, chemical and physical section, are equally considered to ensure a comprehensive assessment of soil changes. By using the SQIx calculations, although avoiding the PCA analyses to select only a few indicators, an

Environmental Quality Index (EQI) which is more comprehensive, considering short- and long-term soil changes, should be developed.

The first step for the development of the EQI is to define the soil indicators that will ensure a comprehensive assessment, unrelated to the land management. Therefore, different studies have been analysed and the most common indicators, for the physical, chemical and biological section of the soil, used for the development of the EQI.

Physical properties are strictly related to the soil structure. The soil structure includes different characteristics, and it mainly depends on the type of soils that forms the soil mixture (Jahn et al., 2006). A good structure ensures a passage of water throughout the soil which improves a transfer of nutrients from the soil to the plants (Subbaiah, 2019). Structural support is based on bulk density, which represent the soil compaction. This measurement has been the main part of different soil evaluations (Arias et al., 2005; Chaves et al., 2017; Purakayastha et al., 2019; Subbaiah, 2019; Williams et al., 2020) since different soil layers can have a different bulk density which can constrain, when too compacted, the movement of both water and air which are two of the main conditions that represent the basis for life in soil (Arias et al., 2005).

The interaction between soil and water benefits plants growth and can be evaluated by looking at the water holding capacity of soil which represent the soil ability to retain water (Subbaiah, 2019). When all the pores are saturated, the moisture represents a perfect carrier of nutrients in the soil ecosystem (Manahan, 2005) making it a perfect measurement of soil changes that can also be a main link to a change in chemical properties of the soil (Arias et al., 2005; Chaves et al., 2017; Purakayastha et al., 2019; Subbaiah, 2019; Williams et al., 2020).

Water stored in soil is influenced by the grain size and their disposition affecting porosity. Bigger pores allow more water storage and directly impacts soil permeability, which is the capacity to be crossed by the water (Brady et al., 2008). Porosity is a parameter that is indispensable to understand the contaminants movement in soil (Yu et al., 2020) helping soil evaluations (Arias et al., 2005; Chaves et al., 2017; Purakayastha et al., 2019; Subbaiah, 2019; Williams et al., 2020). Calculating the water infiltration rate, which represent the velocity of the water to trespass the soil, help understanding the soil structure and the water availability by the plants (USDA, 2019). When this velocity is too high the plant roots are not able to capture the water in time and the nutrients that the moisture transports with it (Brady et al., 2008; Manahan 2005). The water infiltration rate can also influence the movement of both nutrients and contaminants in soil, making it one of the most important physical parameters that needs to be measured to explain changes in soil.

The soil resilience is related to the soil aggregates stability. Aggregates represent several particles bonded together due to the interaction between the biota (microorganisms can produce a type of glue that holds the particles together) and the mineral components of the soil being decisive also for infiltration and root growth. A good soil aggregates stability is representative of a resilient soil that can resist more to external alterations (USDA, 2019).

Chemical properties are representative of the nutrients provision for the ecosystem. Compared to physical properties, chemical properties are more dynamic and more easily influenced by external stimuli (Oliver et al., 2013). The chemical components of the soil affect many reactions and processes occurring in the soil (Brady et al., 2008). pH represents mainly a critical factor in maintaining an ecosystem stability in soil since it controls many factors, from nutrients availability, enzyme activities, cation-exchange capacity (CEC) (Cho et al., 2016; Neina, 2019). Measuring the pH of the soil is also important to understand if a contaminant underwent changes, examples of this behaviour were evaluated by (Zeng et al., 2011), that determined changes in movement and solubility of different Heavy Metals due to pH changes in soil. Soil pH also affects the activity of beneficial microorganisms, which affects nutrient availability. (Bronner & Goss, 2011) evaluated the organic sorption dependence in soil from pH. Moreover, pH is the main chemical property that is measured in every research related to soil evaluation because it can mainly influence the chemical structure or behaviour of all chemical compounds and mixtures (Chaves et al., 2017; Idowu et al., 2008; Purakayastha et al., 2019; Williams et al., 2020).

The soil Electrical Conductivity (EC) represents the ability of soil solution to conduct electric current (Awale et al., 2017). This activity takes place in the water-filled pores, where, through cations (Ca_2^+, Mg_2^+, NH_4^+, Na^+, K^+) and anions (SO_4^{2-} , Cl^- , NO_3^- , and HCO_3^-), dissolved salts, the electricity find its path (Awale et al., 2017; Corwin & Lesch, 2005). EC has become essential for identifying other soil properties from the chemical and physical section (Corwin & Lesch, 2005) since the salt presence can be indicative of different factors. When the salinity increases, the EC rise, although an excess in salt levels can be damaging for the environment (e.g., crop yields reduction, decrease in microorganisms' activity, reduce the ability of the roots to incorporate water) (Awale et al., 2017; Molin & Faulin, 2013). On the other hand, having a low EC can be an indirect indicator of other factors (e.g., clay presence, water holding capacity, nutrients availability) (Awale et al., 2017; Molin & Faulin, 2013; Sintim et al., 2019) making this measurement essential to understand what is happening in the soil ecosystem. On the same line, Cation Exchange Capacity (CEC) can represent the continuous exchange and holding of different salts and contaminants into the soil system and determine the soil biochemistry and plant growth (Chaves et al., 2017; (CUCE), 2007; Ross & Kettering, 1995).

Nutrients′ availability is greatly influenced by different properties, microbial activity, water holding capacity, organic matter presence making this measurement primarily important due to the correlation with different soil sections (Cardoso et al., 2013; Idowu et al., 2008; Subbaiah, 2019). A good assessment is needed because nutrient presence is mainly subjected by anthropogenic activities; fertilizers intake, specifically, is the main cause of nutrients increase or decrease in the environment, therefore, land management can be an important parameter to understanding nutrient presence (Cardoso et al., 2013; Doran, 2002; Subbaiah, 2019)

A growing interest in soil assessments has produced a focus on Soil Organic Matter (SOM) due to the powerful effects that it has on each different functionality of the soil (Magdoff and Weill, 2004). SOM is mainly formed by dead material that went through biological, chemical and physical transformation to produce organic products that can retain nutrients improving the ecosystem functionality (Lehmann & Kleber, 2015). SOM occupy only 5% of the entire soil mixture and it changes overtime due to the microbial activity over the soil profile (Arias et al., 2005). The percentage of SOM present in the soil is an important measurement to evaluate and understand different changes in soil evaluations. SOC is a component of SOM and it can contribute to the nutrients′ availability, water retention and it can help the contaminants degradation and it is the main source of nutrition for microbial activities. Most importantly, when the C is present in low concentration the soil can capture C from the CO2 in the atmosphere helping the reduction of the climate changes. The SOC plays an important role in the ecosystem functionality making it an important parameter to measure. (Andrews et al., 2002).

Biological properties are specifically based on living organisms and their functionality in the terrestrial ecosystem, making it one of the most important sections to study for a complete soil evaluation (Doran & Zeiss, 2000). Microorganisms that are represented in the microbial biomass are smaller than 10 µm and comprises of both bacteria and fungi due to their main role in nutrient transportation (Schloter et al., 2003). They are primarily important because they undergo many roles in the ecosystem: N and C mineralisation and new biomass formation; helping the nutrient cycle; stabilization of the soil structure (Niemeyer et al., 2012); but they can also be influenced by changes in pH, external inputs or C changes. Compared to the other soil properties, microbial biomass is one of the fastest indicators to a change in the environment due to the susceptibility of some microorganisms. Weighting microbial biomass helps to identify changes in the microbial occurrence. Chloroform fumigation and substrate-induced respiration (SIR) techniques are both used as methods to evaluate microbial biomass (Arias et al., 2005; Doran & Zeiss, 2000).

Schloter et al., (2003) evaluated microbial activity as one of the main measurements to determine the soil functionality because of the microbe′s ability to degrade unwanted compounds into useful chemicals for plants and other soil organisms (Schloter et al., 2003). Moreover, by differentiating the microbial communities the processes that are contributing to soil changes can be determined. As well as the microbial community, soil macro-fauna also has a main role in the ecosystem stability; invertebrates, such as, nematodes, earthworm and mites, are mainly studied to understand the ecosystem stability (Pervaiz et al., 2020). These organisms tend to live on the surface, in the soil pores or near the plant roots, and with their movement, excretion and death, they play an important role in the ecosystem (Anitha, 2020).

Ultimately, soil represents an important link between the atmosphere and the soil ecosystem (Wienhold et al., 2005). This interaction is translated into Soil Respiration, which characterises one of the main carbon fluxes in the entire ecosystem (Bond-Lamberty et al. 2018; Shi et al. 2020; Wienhold et al., 2005).

The soil represents an entire ecosystem and as previously explained, each property is related to each other. All these parameters represent a soil measurement that is representative of the system condition and its capability to perform, being useful to understand the soil processes (Doran & Zeiss, 2000; MacEwan, 2007). Therefore, this literature review has drawn together a series of soil parameters, which renders the soil assessment process, evaluated independently from the land management and the type of contaminants present (Table. 2-3).

Table 2-3 Complete range of soil indicators to determine consequences of the ECs presence in the terrestrial environment.

		Indicators	Reference
Physical properties	1	Bulk density	(Williams et al., 2020)
	2	Water Holding capacity	(Williams et al., 2020)
	3	Porosity	(Yu et al., 2020)
	4	Water Infiltration Rate	(USDA, 2019)
	5	Aggregate Stability	(USDA, 2019)
Chemical	1	pH	(Neina, 2019)
	2	Electrical Conductivity	(Awale et al., 2017)

	3	Cation Exchange Capacity	(Chaves et al., 2017)
	4	Nutrient Availability	(Cardoso et al., 2013)
	5	Soil Organic Carbon	(Lehmann & Kleber, 2015)
Biological Properties	1	Microbial Biomass	(Niemeyer et al., 2012)
	2	Microbial Biodiversity	(Schloter et al., 2003)
	3	Microbial Activity	(Schloter et al., 2003)
	4	Soil Respiration	(Cardoso et al., 2013)
	5	Earthworms	(Pervaiz et al., 2020)

2.6 Conclusions on soil assessments: a tool to inform decision-making

Soil has always been overlooked because it is not directly related to the impact that a change in the system might have on people′s health and the entire environment. Therefore, research tends to focus on consequences on soil organisms to explain possible effects on the soil environment (Stroud, 2018). Different research bodies, previously attempted to evaluate, based on the toxicity of different contaminants against soil organisms, threshold values under which no changes in the environment are expected (Environmental Chemical Agency (ECHA), 2008; USEPA, 2003c). Although, data collection is mainly based on the expert’s opinion making the process subject to the amount of information that the researcher retains.

Therefore, during the years, research attempted to define changes in the soil matrix by developing SQIs or Soil Health evaluations (Arias et al., 2005; Chaves et al., 2017; Purakayastha et al., 2019; Rinot et al., 2019). Although, all the research involved is strictly guided by land management practises on site as guidance to determine changes in the soil environment. A database for a global soil health assessment has been developed merging a series of data related to fieldwork activities which analysed the effects of different management practices on the soil environment (Jian et al., 2020). Although, the research, once again, together with the literature, is focussing on different land management practices missing the real linkage between the contaminants that are present in the soil and the consequences on the matrix.

Evaluating the potential risks associated with the presence of a specified contaminant in the environment is essential to ensure that the decision-making process has enough information to make a weighted decision, independently from the land management practises.

As highlighted above, different indicators (Table 2-2) can be used to evaluate values above which problems are expected in the soil environment impacting soil (Environmental Agency, 2020). Soil evaluations can be a new tool to better understand the consequences of different contamination on the soil environment. The need of a quantitative method for the evaluation of different activities to provide insights in the decision-making process is necessary to avoid biased decision (Xu & Liu, 2009), although, environmental data tend to be vague and imprecise (Darbra et al., 2008) and they tend to be site specific (Williams et al., 2020) so a more precise and comprehensive methodology is necessary.

Soil assessment is mainly guided by measuring different indicators for the physical, chemical, and biological section of the soil, to ensure that the system maintain vital cycles in place safeguarding a properly working environment. Bulk density (Williams et al., 2020), WHC (Williams et al., 2020), porosity (Yu et al., 2020), water infiltration rate(USDA, 2019), aggregates stability(USDA, 2019), pH(Neina, 2019), electrical conductivity (Awale et al., 2017), CEC (Chaves et al., 2017), nutrient availability (Cardoso et al., 2013), SOC (Lehmann & Kleber, 2015), microbial biomass(Niemeyer et al., 2012), biodiversity and activity (Schloter et al., 2003), soil respiration (Cardoso et al., 2013) and earthworms (Pervaiz et al., 2020) have been proven to be between the most common indicators used for soil evaluation. By using the same indicators and assessments for the different experiments, a EQI can be calculated following the SQI calculations (equation to 2-1 to 2-4) which ensures that comparable numbers are developed across the studies, making them independent from the land management practises that influenced the choice in the first place.

Possible limitation will involve the amount of fieldwork needed to collect this data, although, this can be overcome by looking at information held in different databases regarding the relationship in between the chemical and the soil environment. Future work requires an in-depth knowledge of defence-related chemicals and their relationship with the environment, because for contaminants, specifically explosives, some analyses might be difficult to organise because of the nature of the samples that can interfere with instruments that are normally used to assess soil indicators. Therefore, future work will involve more research to understand how to work around these problems ensuring that soil is properly assessed.

Future work can help comprehensively understand how soil changes in response to specific contaminants. This understanding will enable research to determine the associated risks of their presence based solely on the contaminant concentration in soil.

3 Development of an environmental hazard-based rating assessment for defence-related chemical compounds in soil systems

3.1 Abstract

Environmental hazard-based methods are commonly used to categorise the severity of chemical contamination to ecological soil systems, although a traffic-light approach (green, amber, red) has never been used to assess these consequences. A traffic light approach is an easy to interpretate data as it has a clear visual display which can provide an early warning approach for stakeholders to identify areas that require further investigation. This approach should be underpinned by extensive research data and systematic methods of development. However, the extent of reliable data available for specific chemicals can be limited and therefore decision making may rely on expert judgement. Therefore, in this study, an environmental hazard-based rating methodology was developed by combining the guidelines from the European Chemical Agency (ECHA) and the USEPA for Predicted Non-effect Concentration (PNEC) and Ecological Soil Screening Levels (Eco-SSL) for defence-related chemicals (2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), cypermethrin, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)). The developed hazard-based rating assessment was design to categorise the chemicals into low, medium and high environmental hazards priority to inform and ease the decision-making process for contaminated areas to ensure that sustainable operations are carried out.

3.2 Introduction

To characterise and manage the ecological hazards posed by chemicals in the soil system a variety of approaches have been developed. Rating systems have been widely utilised to simplify and better visualise consequences across a variety of disciplines (Ei San et al.,2020; Pan et al., 2020) (e.g. low, medium and high rating systems) to enable practitioners to rapidly interpret data and implement mitigation. However, developing the different categories requires a wide and comprehensive body of data.

Risk/hazard-based rating systems have been used across a variety of disciplines from financial to environmental and are usually based on a matrix that categorises the occurrence and the impact of each activity to infer the level of risk or hazard i.e. low, medium or high (Finizio & Villa, 2002; Pickering et al., 2010). However, these processes are frequently reliant on qualitative assessment by subject matter experts and while providing a subjective assessment, cannot provide quantitative assessments (Pickering et al., 2010). In a risk-based assessment, decision-making is typically based on a combination of available data and expert judgment. When data is not available, the decision-making process may rely more heavily on expert judgment. However, the more objective and comprehensive the available data, the more informed and accurate the decision can be. An alternative approach is to use a ranking evaluation, which use 'traffic light' colour coding system e.g. green, amber and red to represent low, medium and high-hazard levels. While these systems are based on quantitative data, multiple variables are used to compile the data, and subject matter expert opinion is still required to make decisions regarding the data used and therefore the system is still heavily subjective (Kovačević et al., 2019). Therefore, an additional system is required to ensure to underpin the hazard-based rating system with a more thorough and comprehensive body of data to enable practitioners to easily define different levels of hazard.

The process of gathering a viable body of data has been presented by different nations although they have not been considered for broader applications such as informing rating systems to define different levels of ecological hazards.

The United States Environmental Protection Agency (USEPA), use a score-grading procedure of the literature data, and calculates a set of Ecological Soil Screening Levels (Eco-SSLs) based on contaminants that have been proven to be a threat for both flora and fauna (USEPA, 2003c). In Europe, a step further has been made by the European Chemical Agency (ECHA) by developing Soil Screening Values (SSVs) based on reliable data in the literature and statistical analyses (Environment Agency, 2017). Unlike the Eco-SSL technique, the gathering of data occurs through the ECHA database under the Regulation (EC) No 1907/2006 introduced in Europe in 2007, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Environment Agency, 2008). The data obtained from this procedure are selected and extrapolated where gaps are identified. However, due to the lack of records related to different chemicals, the researcher must rely on the expert opinion to decide whether or not the data can be used to develop SSVs.

The USEPA methodology develops Eco-SSL values based on experimental data, specifically, to concentrations that produce changes (i.e. reproduction, inhibition of growth) to 10% or 20% of the studied population (EC_{10}, EC_{20}), or the highest effective concentration at which there was not an observed toxic or adverse effect (NOAEC) and the lowest effective concentration at which there was an observed toxic or adverse effect (LOAEC).

In contrast, SSVs are derived from the calculation of the Predicted No Effect Concentration (PNEC) value which is different depending on the ecosystem. The PNEC is a regulatory concentration level under which sufficient protection for the ecosystem considered is ensured (ECHA, 2008; Environment Agency, 2017). The considered ecosystems are characterised by different groups of organisms and since there is more than one set of data for each organism in different soil environments the PNEC calculation is estimated on the values that are most reliable. The reliability of the results are chosen based on the expert's opinion having discrepancies dependent on who is carrying out the procedure. Although, SSVs are typically developed for a limited set of contaminants and exposure scenarios, and may not be applicable to all situations. They do not account for the potential for combined exposure to multiple contaminants or the effects of long-term exposure. They are typically set at a level that is protective of human health and the environment, which can lead to unnecessary remediation or restrictions on land use. This can result in significant economic costs and limit the beneficial reuse of contaminated land. Moreover, SSVs are based on generic data and assumptions, and do not take into account site-specific factors, such as soil properties, site history, and land use. This can lead to inaccuracies in the risk assessment and potential mismanagement of contaminated sites.

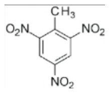
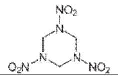
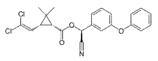
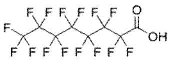
These methodologies have wide applications, particularly in the agricultural sector, although they have also been applied to other sectors (Checkai et al., 2014). This study focussed on military training ranges, which can be exposed to a range of chemical contaminants from the use of explosives, fire-fighting foams and other military equipment.

Regulating and minimising the environmental risks associated with routine operations at military training ranges (e.g. live-fire training, transportation), is necessary to maintain training and to support military capability (Bortone et al., 2019). Historically for both security and safety reasons, military training ranges are almost always situated in remote areas, so that essential training activities can be carried out without interfering with built-up areas (Havlick, 2014). Despite restricted access, many rare or uncommon species of plants, insects and birds thrive in these areas which consequently become classified as Sites of Special Scientific Interest (SSSI) and/or as EU Special Areas of Conservation (SAC), as well as Special Protection Areas (SPA) for birds protected under the European Birds Directive.

Routine operations on site can also lead to contamination of military areas, with consequences to soil and groundwater (Broomandi et al., 2020; Ferreira et al., 2019). This means that the natural environment and military activities coexist, leading to the need to protect these areas while continuing essential training activities (Bortone et al., 2019; Broomandi et al., 2020). To ensure the safe use and sound management of these military areas, Environmental Risk Assessments (ERA) are typically conducted to assess the environmental impact of defence-related chemical substances.

Chemical substances used on military training ranges (Table 3-1) comprise a wide range including among others, traditional explosives (e.g. 2,4,6 – trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX)), which may be a threat to the environment including surface and groundwater, soil and biota (Clausen et al., 2004; Dodard et al., 2003; Gong et al., 2007; Kuperman et al., 2005; Robidoux et al., 2002; Stanley et al., 2015; Vila et al., 2008); Aqueous Film Forming Foam (AFFF) containing per- and polyfluoroalkyl substances (PFAS) which are used for extinguishing inflammable liquid fires which may also be persistent and a threat to the environment (Filipovic et al., 2015; Place & Field, 2012; Turner et al., 2021; Zhao et al., 2011); and the use of pyrethroid insecticides such as cypermethrin and its isomers to treat military uniforms and equipment (e.g. bed nets) so that military personnel are protected from insect bites, such as mosquitos during military operations (Army, 1994; Friedl et al., 2007; Hassan et al., 2010; Khoobdel et al., 2005). During washing of the uniforms, water contaminated with the pesticide can enter soil and water courses (Hassan et al., 2010) and threat soil quality impacting agriculture (Hassan et al., 2010; Khoobdel et al., 2005; Zhou et al., 2008). Moreover, this insecticide has a high affinity to organic matter which can harm non-target organisms such as aquatic invertebrates (e.g. insects and crustaceans) (Birch et al., 2015; Conte et al., 2005; Das & Mukherjee, 2003; Environment Agency, 2019; Zhou et al., 2008). The selection of each contaminant was informed by a comprehensive literature review that assessed the prevalent contaminants associated with military ranges both in the United Kingdom and globally. Furthermore, the study aimed to investigate various contaminants with distinct properties to assess dissimilarities in soil changes as they have different chemical stability in the environment. PFOS and PFOA are both fluorinated organic compounds, which are highly resistant to degradation due to their strong carbon-fluorine bonds. These compounds are classified as persistent organic pollutants (POPs) and have been found to persist in the environment for a long time. RDX and TNT are both nitroaromatic compounds, which are relatively stable in the environment. RDX is more chemically stable than TNT, meaning that it is less prone to decomposition or breakdown in the environment. Cypermethrin is a synthetic pyrethroid insecticide, which is generally considered to be more stable than other organic insecticides. It has a half-life of around 20 days in soil and can persist for several weeks in aquatic environments.

Table 3-1 . The chemical substance name, empiric formula and structure of the five defence related chemicals used for the application phase in this paper.

Chemical name	Empiric Formula	Chemical Structure	pKa	Solubility in water	LogKoW
2,4,6-Trinitrotoluene (TNT)	$C_7H_5N_3O_6$		N/A	130 mg/L[1]	1.86[1]
1,3,5-Trinitroperhydro-1,3,5-triazine (RDX)	$C_3H_6N_6O_6$		5.5[2]	39 mg/L 20°C [1]	0.87[1]
cyano-3-phenoxybenzyl-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (Cypermethrin)	$C_{22}H_{19}Cl_2NO_3$		N/A	0.009 mg/L 20°C [3]	6.60[4]
Pentadecafluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$		2.6[4]	2290 mg/L at 24°C[4]	4.81[4]
Heptadecafluorooctane-1-sulfonic acid (PFOS)	$C_8HF_{17}O_3S$		1.3[4]	3.2X10-3 mg/L 24°C[4]	N/A

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[1] Lingamdinne, L. P., Roh, H., Choi, Y. L., Koduru, J. R., Yang, J. K., & Chang, Y. Y. (2015). Influencing factors on sorption of TNT and RDX using rice husk biochar. Journal of Industrial and Engineering Chemistry, 32, 178-186.

[2] Alizadeh, T., Atashi, F., & Ganjali, M. R. (2019). Molecularly imprinted polymer nano-sphere/multi-walled carbon nanotube coated glassy carbon electrode as an ultra-sensitive voltammetric sensor for picomolar level determination of RDX. Talanta, 194, 415-421.

[3] WHO (1989). Cypermethrin Environmental Health Criteria 82

[4] PubChem Database

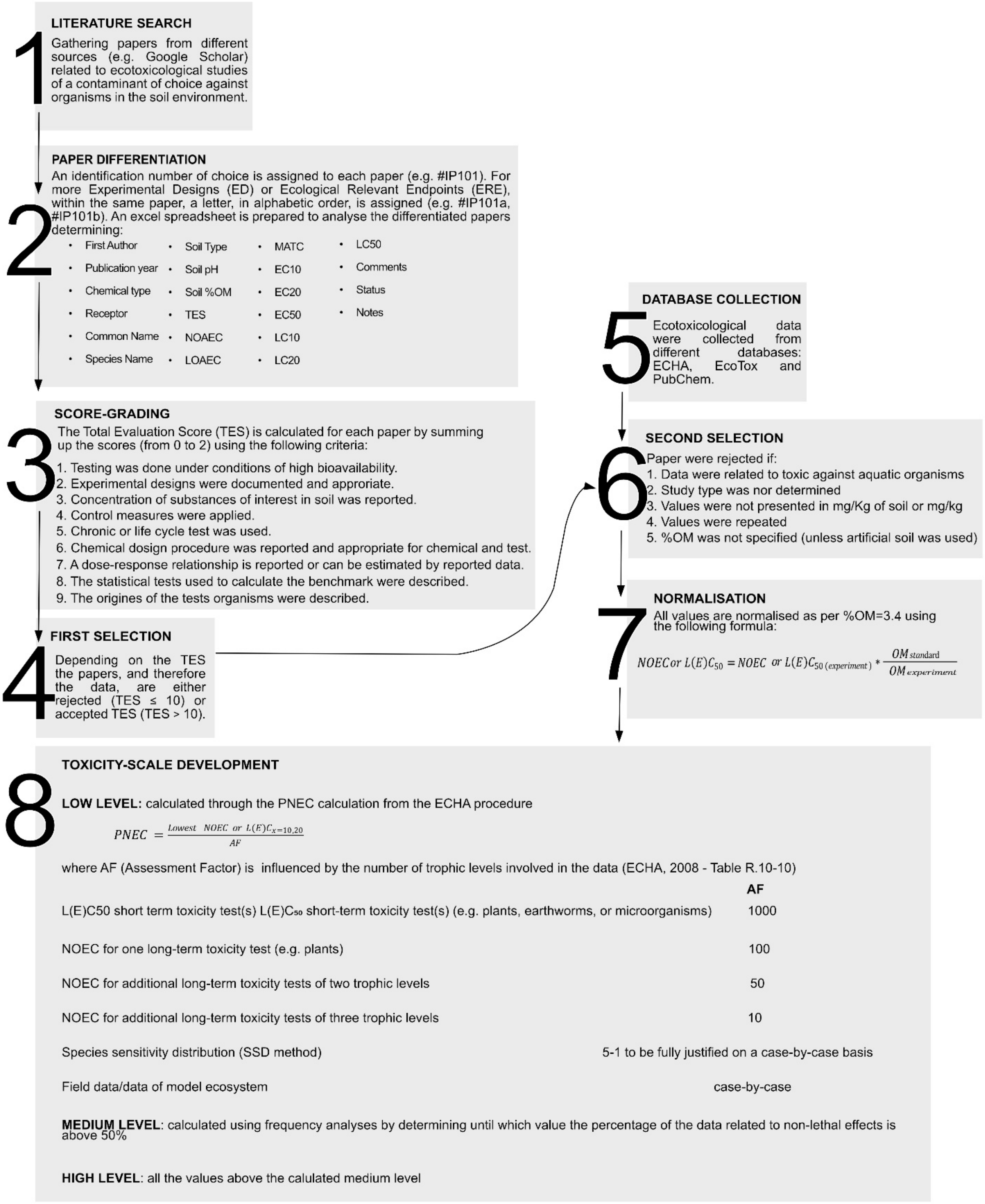
Using a hazard-based ranking system, based on a green, amber and red visual aid, ensures that proper decision making is carried out on training ranges considering the contamination that is already in place. This approach can be applied to different soil types and is not limited by the activity at the site decision

Therefore, the aim of this work was to develop an environmental hazard-based rating assessment which characterises the ecological hazards posed by chemicals (TNT, RDX, cypermethrin, PFOA and PFOS) used in defence-related activities based on a comprehensive body of data objectively selected. This was achieved by combining the USEPA ECO-SSLs and ECHA SSVs methodologies to develop a maximum contaminant concentration in soil that would not require short-term further investigation of the site (low hazard level). In contrast, contaminant concentrations in the medium and high-hazard levels would require further site investigation to ensure that sustainable operations are carried out. This method has been designed to ease the decision-making assessment process for soil such that a threshold value could inform whether further site investigation is required.

3.3 Methodology

3.3.1 The Process

The following section outlines a summary of the methodology undertaken to develop the environmental hazard-based rating assessments by combining the methodologies for soil screening levels from the ECHA and USEPA procedures (Fig. 3-1) to ensure an objective data collection to determine different hazard levels for the ecological soil systems.



LITERATURE SEARCH

Gathering papers from different sources (e.g. Google Scholar) related to ecotoxicological studies of a contaminant of choice against organisms in the soil environment.

PAPER DIFFERENTIATION

An identification number of choice is assigned to each paper (e.g. #IP101). For more Experimental Designs (ED) or Ecological Relevant Endpoints (ERE), within the same paper, a letter, in alphabetic order, is assigned (e.g. #IP101a, #IP101b). An excel spreadsheet is prepared to analyse the differentiated papers determining:

- First Author
- Publication year
- Chemical type
- Receptor
- Common Name
- Species Name
- Soil Type
- Soil pH
- Soil %OM
- TES
- NOAEC
- LOAEC
- MATC
- EC10
- EC20
- EC50
- LC10
- LC20
- LC50
- Comments
- Status
- Notes

SCORE-GRADING

The Total Evaluation Score (TES) is calculated for each paper by summing up the scores (from 0 to 2) using the following criteria:

1. Testing was done under conditions of high bioavailability.
2. Experimental designs were documented and approriate.
3. Concentration of substances of interest in soil was reported.
4. Control measures were applied.
5. Chronic or life cycle test was used.
6. Chemical dosign procedure was reported and appropriate for chemical and test.
7. A dose-response relationship is reported or can be estimated by reported data.
8. The statistical tests used to calculate the benchmark were described.
9. The origines of the tests organisms were described.

FIRST SELECTION

Depending on the TES the papers, and therefore the data, are either rejected (TES ≤ 10) or accepted TES (TES > 10).

DATABASE COLLECTION

Ecotoxicological data were collected from different databases: ECHA, EcoTox and PubChem.

SECOND SELECTION

Paper were rejected if:
1. Data were related to toxic against aquatic organisms
2. Study type was nor determined
3. Values were not presented in mg/Kg of soil or mg/kg
4. Values were repeated
5. %OM was not specified (unless artificial soil was used)

NORMALISATION

All values are normalised as per %OM=3.4 using the following formula:

$$NOEC\,or\;L(E)C_{50} = NOEC\;or\;L(E)C_{50\,(experiment)} * \frac{OM_{standard}}{OM_{experiment}}$$

TOXICITY-SCALE DEVELOPMENT

LOW LEVEL: calculated through the PNEC calculation from the ECHA procedure

$$PNEC = \frac{Lowest\;\;NOEC\;\;or\;\;L(E)C_{x=10,20}}{AF}$$

where AF (Assessment Factor) is influenced by the number of trophic levels involved in the data (ECHA, 2008 - Table R.10-10)

	AF
L(E)C50 short term toxicity test(s) L(E)C₅₀ short-term toxicity test(s) (e.g. plants, earthworms, or microorganisms)	1000
NOEC for one long-term toxicity test (e.g. plants)	100
NOEC for additional long-term toxicity tests of two trophic levels	50
NOEC for additional long-term toxicity tests of three trophic levels	10
Species sensitivity distribution (SSD method)	5-1 to be fully justified on a case-by-case basis
Field data/data of model ecosystem	case-by-case

MEDIUM LEVEL: calculated using frequency analyses by determining until which value the percentage of the data related to non-lethal effects is above 50%

HIGH LEVEL: all the values above the calulated medium level

Figure 3-1. The methodology for developing the toxicity scale, from the gathering of the data to the calculated values for the low, medium and high hazard levels (steps 1 to 8), to determine the possible level of hazard towards the soil systems data against the biota. Differently from the USEPA procedure, in this methodology

all the ERE and experimental designs were considered and all the values were part of the dataset used to develop the environmental hazard-based rating assessment.

A thorough **literature search** has been carried out (Step 1) of available toxicity data, for terrestrial organisms and plants.

The **paper differentiation** (Step 2) and Score-grading (Step 3) was carried out following the Standard Operating Procedure (SOP) #1 and #2, attachment 3.1 and 3.2 for invertebrates, developed by the USEPA(USEPA, 2003b, 2003a).

A **first selection** was carried out (Step 4) and paper were either rejected or accepted depending on the Total Evaluation Score (TES) where scores ≤10 were accepted and >10 were rejected. According to the methodology outlined by the USEPA, low scores indicate a dataset that lacks a sufficient number of variables and where the methodology for collecting the data has not been adequately elucidated, resulting in potentially imprecise values. Consequently, these datasets are not deemed suitable for inclusion in the evaluation process.

In Step 5 ‘**database collection**’ values from different databases (e.g. PubChem, EcoTox were collated to create a body of data, which was added to the papers that scored a TES >10.

The next step was the second selection (Step 6), where a selection of data was rejected based on the following:

- relationship to toxicity against aquatic organisms
- study type was not determined
- values were not presented in mg/kg of soil or mg/kg
- values were repeated
- %OM was not specified (unless artificial soil was used)
- the experimental design scored <10.

Once all data were standardised, the calculation of the PNEC or SSVs values were carried out to determine the upper boundary of the **low-hazard toxicity level** (Step 8) for the different contaminants.

The evaluation of the medium and high level of hazard for the soil environment in the cumulative environmental hazard-based rating assessment was then determined using frequency analysis of all the chosen data, clustering them based on the study type (e.g. reproduction, survival) (Step 8).

3.3.2 Research Strategy

Various sources (e.g. Google Scholar, Web of Science) were utilised for the collection of secondary data through a literature search. A first screening procedure was carried out following the USEPA procedure, considering the literature related to ecotoxicological experiments involving TNT, RDX, PFOA, PFAS and Cypermethrin within the terrestrial environment. Each selected paper was differentiated based on different variables, which translated in different experimental designs (e.g. type of soil, organisms); additionally, unlike the USEPA procedure, each paper was also evaluated separately based on different Ecologically Relevant Endpoints (ERE) (e.g. reproduction, growth) and more data were included in the selection such as: EC_{50}, LC_{20}, LC_{50} or data reported in mg/kg together with the EC_{10}, EC_{20}, NOAC and LOEC and data in mg/kg of soil considered from the USEPA procedure.

Each paper was assigned an identification number (e.g. IP#101) which differentiated not only different research articles but also different ERE and studies distinguished by use of different variables within the same paper (e.g. IP#101a, IP#101b). Each paper associated with an identification number was scored following the nine criteria from the USEPA procedure.

3.3.3 Data Selection

In the USEPA procedure each paper is scored against nine criteria (Table 3-2) from 0 to 2 (with 0 being the lowest). The process is rendered unbiased by the usage of tables and specific instructions contained in the SOP #2 attachment 3.2 (USEPA, 2003b). Using this method, a paper was scored more than once if more than one set of variables were investigated, thus considering them as different studies in within the same paper. For example, if two different soils were used to compare changes in the reproduction of a specific organism this was classified as two different studies. This differentiation was also applied if ERE were recorded. For example, if results from changes in reproduction and growth were presented in the same paper and the soil considered was the same, the paper was again evaluated as two different studies.

The previously presented scoring process differs from the USEPA procedure whereby the differentiation of studies within the papers was not applied when more than one consequence, or ERE, on the biota was recorded. For example, in the USEPA procedure if toxicological data on the same soil were collected and results recorded were related to reproduction and growth of the organism, the paper is considered as one study and the toxicity was selected according to a pre-settled hierarchy for the invertebrates (Reproduction > Population > Growth) or the most sensitive measurement of biomass production for plants.

Table 3-2. Criteria evaluation for each chosen paper for the evaluation of Eco-SSL values (USEPA, 2003c)

Criteria	Evaluation
1	Testing was Done Under Conditions of High Bioavailability
2	Experimental Designs were Documented and Appropriate
3	Concentration of Substance of Interest in Soil was Reported
4	Control Measures were Applied
5	Chronic or Life Cycle Test was Used
6	Chemical Dosing Procedure was Reported and Appropriate for Chemical and Test
7	A Dose-Response Relationship is Reported or can be Estimated from Reported Data

8	The Statistical Tests used to Calculate the Benchmark and the Levels of Significance were Described
9	The Origin of the Test Organisms were Described

For example, following the USEPA methodology, the first criteria analyses whether the experiments were carried out under conditions of high availability, and depending on the pH and the % organic material (OM) in the soil, a different score is selected based on the bioavailability tables given in the SOP #2 (USEPA, 2003c). Although, the scoring of the papers should be completed by more than one researcher to ensure that complete unbiased decisions are achieved. All the scores for each paper were summed to determine the Total Evaluation Score (TES) of each article. Data was accepted, to develop the environmental hazard-based rating assessment, if the TES had more than 10 total points as stated in the USEPA procedure. Once all the gathered information had been organised further data was added from the ECHA database.

The non-confidential toxicity information, that has been submitted to ECHA, and are also available from other databases, such as EcoTox, PubChem, were reported and organised as follows: data related to aquatic organisms was excluded; only values presented in mg/kg of soil or mg/kg was considered; where %OM was not reported the data was not considered (except for artificial soil); data with no study type listed was also excluded from the research.

Since different studies include different soil types, a standardisation of the data to is required (ECHA, 2008; Environment Agency, 2017) and it is applied to all the gathered data using formula (3-1).

3.3.4 Data Standardisation

Different soil characteristics (e.g. pH, %OM) can influence the toxicity and bioavailability of a chemical and the %OM has been defined as one the most influencing parameters, meaning that there is a need for normalisation to ensure that the toxicity of the compound are representative of the bioavailability in soil, meaning that the data needs to be standardised (Step 7) as they are presented in a standard soil (Environment Agency, 2017). A standard soil is defined to have 3.4% of OM (Environment Agency, 2017) and all the values are standardised against this percentage to make the data comparable as follows:

$$\textbf{3-1} \qquad \boldsymbol{NOEC\ or\ L(E)C_{50} = NOEC\ or\ L(E)C_{50(in\ experiment)} * \frac{OM_{standard}}{OM_{in\ experiment}}}$$

where $NOEC\ or\ L(E)C_{50(in\ experiment)}$ represent the values that have been found for each paper in the literature research; $OM_{standard}$ equals 0.038 and $OM_{in\ experiment}$ are the OM values found in the literature for each experiment (ECHA, 2008). The aforementioned equation is utilised in instances where a dataset consisting of over 100 values is gathered to facilitate comparability of the outcomes.

3.3.5 Low-hazard toxicity level calculation

A low-level hazard for the ecological soil system can be defined as the concentration at which no effects were observed. This definition is also representative of the SSVs or the PNEC, meaning that the value that correspond to an SSVs or PNEC of a specific contaminant are utilised as the upper boundary of the low-hazard level.

The PNEC value was calculated using Equation 3-2.

$$\textbf{3-2} \qquad \boldsymbol{PNEC = \frac{Lowest\ NOEC\ or\ L(E)C_{x=10,20}}{AF}}$$

where NOEC or L(E)C_x values represent the lowest value identified from the procedure utilised and AF is the Assessment Factor.

The Assessment Factor (AF) is derived as summarised in Table 3-3.

Table 3-3. Assessment factors (reproduced from ECHA, 2008 Table R.10-10)

Information Available	Assessment Factor
$L(E)C_{50}$ short-term toxicity test(s) (e.g. plants, earthworms, or microorganisms)	1000
NOEC for one long-term toxicity test (e.g. plants)	100
NOEC for additional long-term toxicity tests of two trophic levels	50
NOEC for additional long-term toxicity tests of three trophic levels	10
Species sensitivity distribution (SSD method)	5-1 to be fully justified on a case-by-case basis
Field data/data of model ecosystem	case-by-case

Preferably the NOEC or EC_{10} values should be used (either by calculation or from the literature) because they represent chronic exposures which represent more appropriate and relevant measures for understanding the protection of population and communities, compared to acute toxicity tests. The presented methodology defines the most reliable results as the ones with the highest TES. If, from the most reliable data, values presented from experiments with the same settings and organisms, were less or equal to one magnitude apart, a geometric mean was calculated merging the presented data together (Environment Agency, 2017). PNEC values are considered as SSVs but only if there is enough data to support the calculations; this is usually when the assessment factor is <50 (Environment Agency, 2017), indicating that values from more than one trophic level are presented.

As the SSVs, the low-hazard level is defined as “levels of chemicals in soil below which there is unlikely to be any risk to its health and functions” (Environment Agency, 2017). Once the PNEC value has been calculated, the chemical concentration range in which no deleterious effects on the soil environment are expected can be defined.

3.3.6 Medium and High-hazard toxicity level calculation

Once the upper boundary of the low-hazard level has been defined, an analysis of the frequency is carried out on all the data based on the different study types (e.g. reproductivity, survival). Frequency analysis were used to determine different ranges of values, related to the analysed studies, in which lethal and non-lethal effects are evaluated. The range of concentration that determine the medium-hazard level was determined as the highest value in the set of data where 50% of the studies resulted in non-lethal effects on terrestrial organisms. Values exceeding the calculated boundary were regarded as being associated with a high degree of risk. As such, the medium-hazard level was defined as “levels of chemicals in soil in which it is likely to have deleterious effects on ecological soil functionalities” and the high-hazard level as “levels of chemicals in soil above which it is likely to have irreversible effects on ecological soil functionalities”. All the values above the most frequent values that did not cause a deleterious effect on the biota (death of the organisms) are considered a high-hazard level in, defining the range of concentration of the contaminants in which it is expected to have a lethal effect on the ecological soil system. Similarly, the most likely values in which it is expected to have deleterious effects on the soil environment (because of their consequences on the biota) will represent the medium-hazard level in the environmental hazard-based rating assessment.

3.4 Results and Discussion

3.4.1 Research evaluation

For the application phase of this research five different contaminants from defence related activities were selected: TNT, RDX, Cypermethrin, PFOA and PFOS (Table.3-4). During the first part of the literature search undertaken in accordance with the established USEPA methodology (USEPA, 2005) 30 reports and peer-reviewed papers in total, were identified as suitable for a first data analysis. The papers that were selected evaluated toxicity against a range of invertebrates and plants (Figure 3-2).

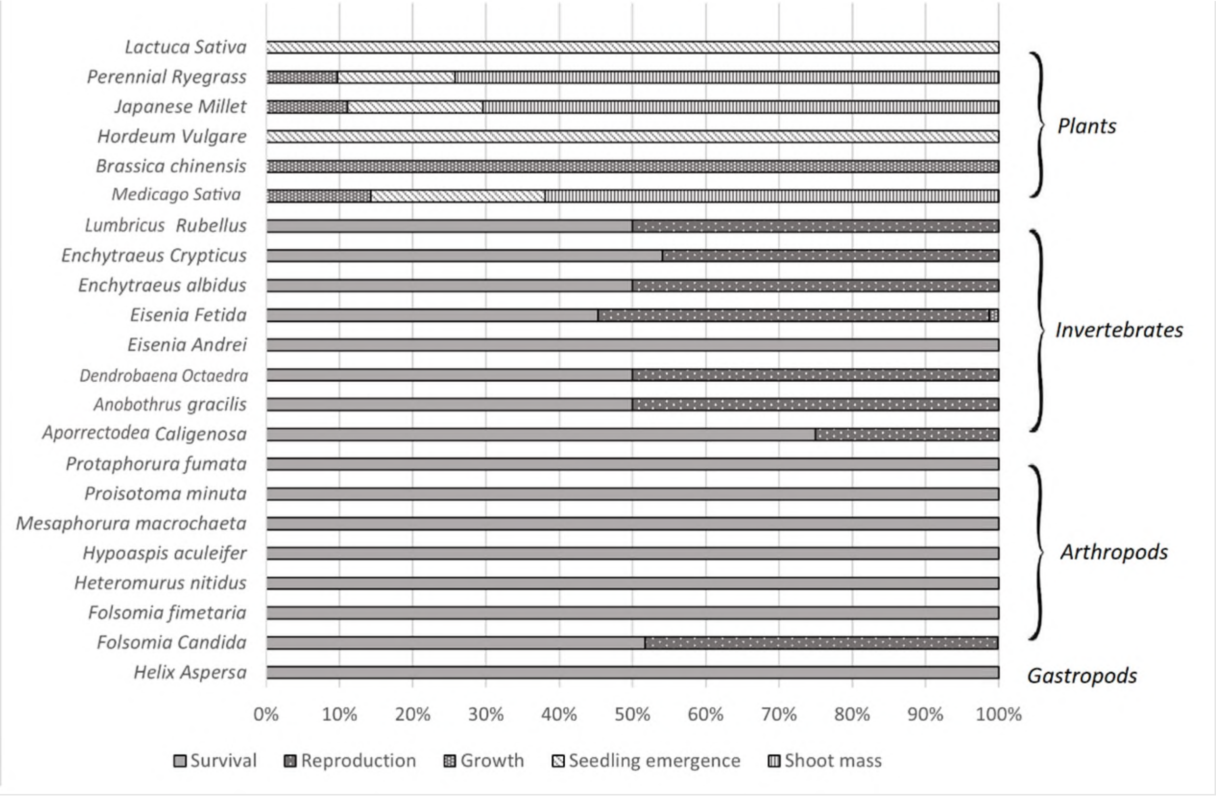


Figure 3-2. Percentages of values for each organism related to different ERE found during the literature search using the USEPA procedure.

During the initial stage of the procedure, a total of 233 papers were examined, resulting in the assessment of 709 values for the environmental hazard-based rating assessment (Supplementary data). The studies, represented by the different changes in variables, were individually scored following the 9 criteria in Table 2, and calculated TES varied from a minimum of 4 to a maximum of 18 points. Because of how the USEPA methodology is developed, PFOA and PFOS related papers have scored the lowest TES values. The reason for the score of 0 for ERE related to heavily stable compounds, such as PFOS or PFOA, is due to the limitations of the first scored criterion, which pertains to testing conducted under conditions of high bioavailability. This criterion is based on the bioavailability of organic compounds and metals in soil with certain pH and organic matter levels. However, it is not suitable for evaluating soil conditions with heavily stable compounds, which remain persistent in the environment. Therefore, the current methodology lacks the necessary sensitivity for assessing the environmental risk associated with these compounds.

In general, the experimental designs that scored ≤10 points were rejected and data related were not used to develop the environmental hazard-based rating assessment because they were considered unreliable. Across all the contaminants, 14 studies were rejected and 205 accepted. Each study contained 1 or more result relating to the percentage of the studied population that was affected by a certain amount of contaminant (e.g EC_{10}, EC_{50}), consequently the total accepted values that have been used, from the USEPA methodology, for determining the environmental hazard-based rating assessment was 546 (230 for TNT, 45 for Cypermethrin, 255 for RDX, 0 for PFOA and 16 for PFOS).

Furthermore, a total of 9208 values were collated from the ECHA, EcoTox and Pubchem databases and only 540 were used in the environmental hazard-based rating assessment (140 for TNT, 21 for Cypermethrin, 155 for RDX, 131 for PFOA and 93 for PFOS) (Supplementary data). This was due to several studies either not reporting results in mg/kg or mg/kg of soil, related to terrestrial organisms, or the study type was not specified. The final body of data that was analysed is shown in Table 3-4.

Table 3-4. Total numbers of values gathered from a selection of sources e.g. from the open literature (USEPA) and the following databases: ECHA, EcoTox, PubChem (ECHA). Within each study, more EREs and EDs were differentiated.

CONTAMINANT	NUMBER OF VALUES GATHERED FROM LITERATURE AND DATABASES					
	TOTAL ERE and E.D.* (USEPA)	ACCEPTED ERE (USEPA)	n. VALUES FROM ACCEPTED ERE (USEPA)	TOTAL DATA FROM DATABASES (ECHA)	ACCEPTED DATA FROM DATABASES (ECHA)	NUMBER OF VALUES FOR THE ENVIRONMENTAL HAZARD-BASED RATING ASSESSMENT
TNT	78	73	230	1976	140	370
RDX	104	104	255	821	155	410
CYPERMETHRIN	37	33	45	2251	21	66
PFOA	4	0	0	1300	131	131
PFOS	10	6	16	2860	93	109

*Experimental Designs

All data were standardised for 3.4% OM (Supplementary data).

3.4.2 Low-hazard level

PNEC values were determined for all the contaminants (Table 3-5) using Equation (3-1) and the AF factor was derived following the criteria listed in Table 3-3.

Table 3-5. Each trophic level that was identified during the literature search and the database collection was listed and the equivalent AF factor was chosen. PNEC calculation was carried out as follows.

CONTAMINANT	PREVIOUS VALUES USING THE ECHA APPROACH		CALCULATED VALUES USING NEW APPROACH			
	AF	PNEC	AF	TROPIC LEVELS	LOWEST NOEC OR EC10	PNEC (or SSV) (mg/Kg)
TNT	50	0.01	10	*Plants* *Earthworms* *Arthropods*	2.61	0.3
RDX	100	1	50	*Plants* *Earthworms*	51.3	0.1
CYPERMETHRIN	100	0.08	10	*Plants* *Earthworms* *Arthropods* *Gastropods*	0.17	0.02
PFOA	N/A	N/A	10	*Plants* *Earthworms* *Arthropods*	8.99	0.9
PFOS	N/A	N/A	50	*Plants* *Earthworms*	40	0.8

These values are representative of the upper boundary of the low-hazard level where adverse effects are unlikely to occur in the biota. Consequently, no changes in soil are expected in the defined range meaning that a concentration within the range of the low-hazard section represent momentarily a safe environment. Although, future considerations are needed as those contaminants are likely to bioaccumulate in the environment causing, potentially, different problems for people and the environment.

PNEC values have been previously defined in the literature (Table 3-5) for TNT, RDX and cypermethrin, as respectively 0.01 mg/kg soil dw (AF of 50), 7.56 mg/kg soil dw (AF of 100), 0.08 mg/kg (AF of 100); although, PNEC values that were calculated using the presented combined methodology included a wider body of data influencing the number of values used to calculate the PNEC showing a difference between data. Data in mg/kg have been included and more trophic levels have been considered, with a recent growing body of data that included a wide range of values for the arthropods class.

The $PNEC_{TNT}$ that has been calculated is currently higher than the literature (ECHA database), where an AF of 10 has been used has previously established. During the data gathering, 2 values reported ecotoxicity data against arthropods, adding a third trophic level, changing the AF to 10 which has been used for the $PNEC_{TNT}$ calculation.

$PNEC_{RDX}$ has been previously calculated using the ECHA procedure using an AF of 100 when only one tropic level was evaluated. Using the presented combined methodology an AF of 50 has been used because, a wider body of data, included more then one trophic level. The $PNEC_{RDX}$ calculated using the presented combined methodology, significantly lowered the previously calculated $PNEC_{RDX}$.

Compared to the $PNEC_{CYP}$ calculated in the ECHA (7.56 mg/kg soil dw) the $PNEC_{CYP}$ determined by this methodology was considerably lower because of the more inclusive body of data which incorporated Cypermethrin isomers and recently published literature. This is despite, compared to the average of data that has been used to calculate the different environmental hazard-based rating for each contaminant (217.2), the number of values used is 70% lower (66).

Furthermore, more trophic levels (plants, earthworms, arthropods, and gastropods) were included in the analysis and an AF of 10 was used unlike the ECHA where an AF of 100 was utilised meaning that the concentration that defined the value under which no changes are expected in the ecological soil system is much lower.

$PNEC_{PFOA}$ and $PNEC_{PFOS}$ were calculated respectively with an AF of 10 and an AF of 50, unexpectedly the number of values collected for the PNEC calculation was more than 100 even though these contaminants are extremely new compared to the other evaluated chemicals.

3.4.3 Medium and High – hazard levels

A frequency analyses of the data were done by determining the occurrences of the values respectively related to survival and different responses (e.g. reproduction, growth) which are not related to death of the organism. The data that had a toxic effect on the biota, without causing death of the organism, were considered to be representative of the medium-hazard level of the toxicity scale because these values are representative of different concentrations of the contaminants that can have a deleterious, but not lethal, effect on the soil environment. All the values above this range were considered high-hazard level.

Different ranges of values were calculated for the chosen chemical compounds. For TNT (Figure 3-3a) the values ranged from 0.03 to 1906.8 mg/kg of soil. Between the range of 100 to 200 mg/kg concentration in soil lethal effects on the organisms were observed in more than 50% of the organisms. Within that range, the highest value with a non-deleterious effect was 194.7 mg/kg (Supplementary data) representing the upper boundary of the medium-hazard level. For RDX has been highlighted (Figure 3b), in the range between 0 – 2000 mg/kg, that 56% of the data is related to lethal effects against organisms, determining upper boundary of the medium-hazard level in between 0 to 1000 mg/kg. For first instance only, 45% of the data represented non-lethal effects against organisms in that range outlining the medium hazard level as between 0.1 – 839.5 mg/kg.

The same process was followed for Cypermethrin, PFOA and PFOS where less data has been recorded compared to TNT and RDX using the combined methodology. The results obtained from the Cypermethrin data analysis showed that 50% of the data were between 20-30 mg/kg (Figure 3-3c) and are related to lethal effects towards organisms. Using frequencies analyses the upper boundary of the medium-hazard level has been established to be 20.4 mg/kg. For PFOA and PFOS lethal effects data exceed 65% (Figure 3-3d) and 89% (Figure 3-3e), respectively between the range of 100-200 mg/kg, compared to data related to lethal effects, defining the upper boundaries at 176.2 mg/kg and 183.2 mg/kg.

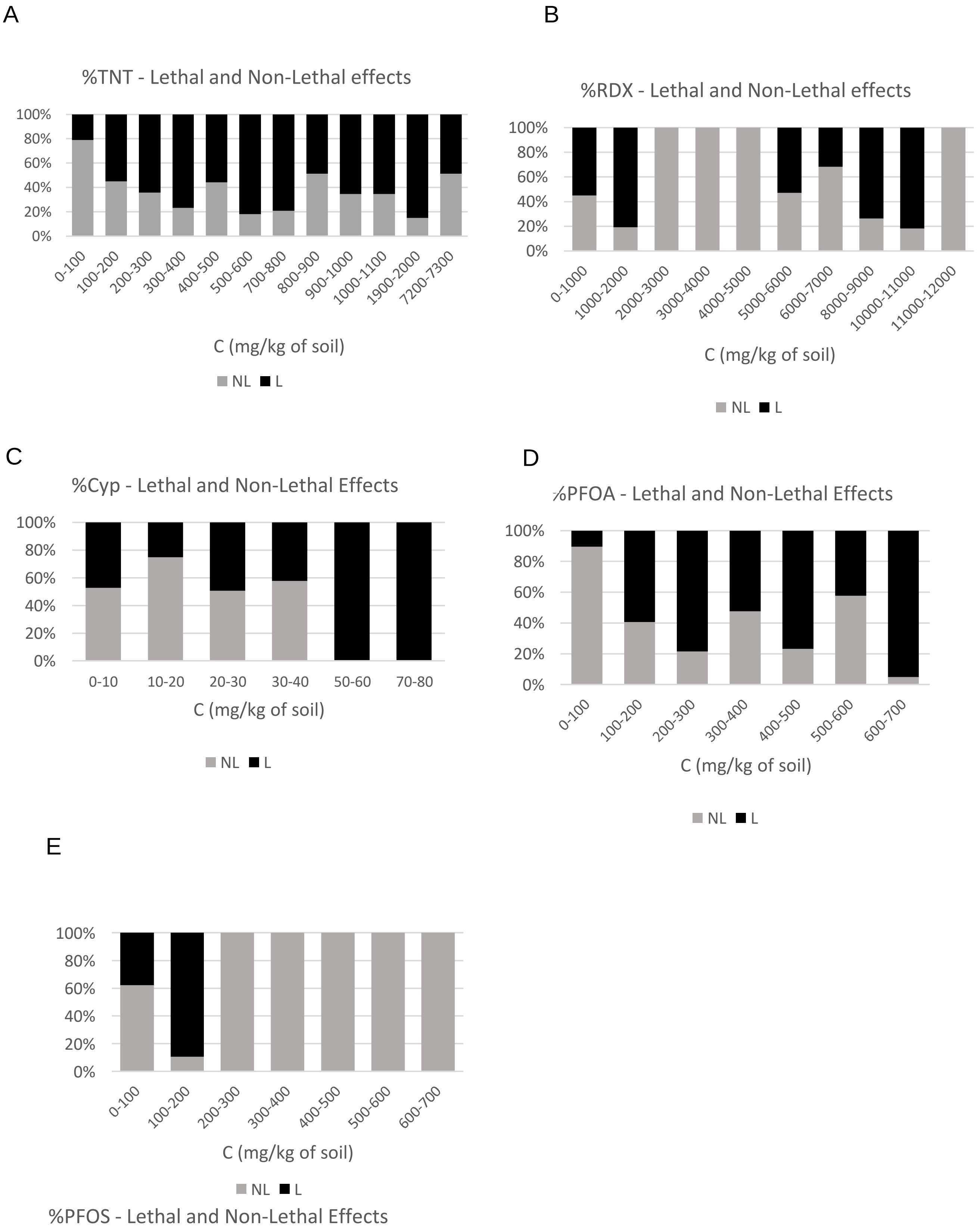


Figure 3-3. Gathering of concentration (C) data in mg/kg using frequency analyses (showed in %) of the studied contaminants whose data are related to deleterious

effects (e.g. reproduction, growth, dry biomass) which did not cause death in the organism (grey) and lethal effects (black).

All the values above the upper boundary of the calculated medium level of hazard must therefore belong to the high-hazard level. It is worth noticing that the current body of literature suggests that the lack of values within specific concentration ranges can be attributed to the dearth of research studies conducted at non-lethal concentrations. Thus, the absence of data in these concentration ranges is indicative of the insufficient scientific inquiry conducted within these bounds. For each contaminant the environmental hazard-based rating assessment has been carried out, and the low, medium and high hazard levels have been evaluated (Table 3-6):

Table 3-6. Environmental hazard-based rating assessment for each contaminant resulting from the presented methodology.

Level of hazard	Value (mg/kg of soil)				
	TNT	RDX	Cypermethrin	PFOA	PFOS
Low	0 – 0.3	0-0.1	0 – 0.02	0 – 0.9	0 – 6.6
Medium	0.3 – 194.7	0.1-839.5	0.02 – 20.4	0.9 – 176.2	6.6 – 183.2
High	> 194.7	> 839.5	> 20.4	> 176.2	> 183.2

The advantage of this new approach is to facilitate the decision-making process with a hazard-based rating system approach. Translating effects on the biota to consequences on the soil environment has been a wide area of research, although, with the toxicity scale, future literature can focus their effort on understanding, at these different concentrations, if the predictions are adequate and the changes that are undermining the soil. Therefore, a completion of this study will evaluate, by knowing the contaminants concentration in the soil environment, the hazard associated with the chemical, decreasing further investigation costs.

3.5 Conclusion

Various chemicals associated with defence-related activities have the potential to impact on ecological soil systems. Therefore, ERAs are used to assess the likelihood of an activity causing harm to the environment, and to understand the consequences of these contaminants on the soil environment.

The purpose of this study was to develop an environmental hazard-based rating assessment that can be used as part of the ERA procedure. It did this by combining ecotoxicological data which have been previously used by USEPA and ECHA to evaluate the consequences of a contaminant in the soil environment. The hereby presented methodology merged these two techniques to ease and inform the decision-making process. The newly developed methodology aims to incorporate a broader range of data points, thus ensuring a more comprehensive consideration of all hazards levels. The objective is to provide informed hazard level assessments, based on reliable and accurate data that has been made available through this improved methodology. Consequently, it was possible to develop an environmental hazard-based rating assessment for different defence-related contaminants. Although, this study is not only limited to a few representative classes of chemicals used in defence related activities and can have much broader implications evaluating only secondary data present in the literature. Moreover, a broader application can be considered for different ecosystems (e.g. aquatic environment) which can be achieved by changes in the procedure specifically to the PNEC value calculations as determined in the ECHA procedure. The understanding and calculation of different levels of hazard can determine a baseline for future human toxicity evaluations related to bioaccumulation process happening through the trophic chain.

Different hazard-levels have been calculated for TNT, RDX, Cypermethrin, PFOA and PFOS as defence-related chemicals based on ecotoxicological secondary data as representation of risks to the matrix in which the entity leaves. At present, no comparative analysis with other methodologies has been conducted.

However, the new calculated results were compared with the SSV values to assess the variation between the original and the updated values. Future work will include validating the developed hazard levels in the environmental hazard-based rating assessment for changes in soil to pre-empt the chemical impact on the environment and to avoid severe consequences on the environment to ensure that sustainable operations are appropriately conducted on military training ranges. The validation process will entail conducting empirical analyses to comprehensively comprehend the influence of the contaminant on soil at the three distinct hazard levels. This is intended to refine the definition of each level and more accurately characterise the environmental impacts arising from such contamination

4 Quantitative environmental assessment of explosive residues from the detonation of Insensitive High Explosive filled 155 mm artillery shell

4.1 Abstract

Insensitive High-Explosive (IHE) typically comprise up to five constituents including 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), which are mixed in various ratios to achieve desired performance and increase insensitivity. Insensitive munitions, which are designated to detonate on command and not accidentally, are currently in use in military operations and in training areas around the world. However, there is minimal literature available on the physiochemical behaviour of these materials in the environment, therefore the actual consequence of residues being deposited post detonation is still an unexplored area of research. Three 155 mm artillery shells filled with an IHE mixture of 53% NTO, 32% DNAN and 15% RDX were detonated in an inert sand arena to collect and quantify residues. Post detonation, approximately 0.02% NTO and 0.07% DNAN are deposited in the environment which may rapidly accumulate dependent on the number of rounds fired. This is of concern due to the toxicity of DNAN and its degradation products, and the potential for increased acidity of soil and discoloration of watercourses from NTO contamination.

4.2 Introduction

Energetic compounds are regularly deposited on military ranges following live-fire training activities (Zentelis et al., 2017). The use of traditional explosives in various training areas has led to the contamination of soil and groundwater with recalcitrant and persistent hazardous chemicals which can render the sites unusable, therefore adversely affecting military readiness due to accumulation over time (Clausen et al., 2004; Jenkins et al., 2005; Walsh et al., 2012, 2014). New generation Insensitive High Explosive (IHE) formulations consisting of 3-nitro-1,2,4-triazol-5-one (NTO) (53%), 2,4-dinitroanilisole (DNAN) (32%) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) (15%), are increasingly being introduced into military service due to their improved safety profile (Singh et al., 2010). For example, the United States (US) Department of Defence have investigated the use of 61 mm and 80 mm mortars filled with PAX-21 (RDX, DNAN and Ammonium Perchlorate) and Insensitive Munitions Explosive (IMX)-104 (DNAN, NTO, RDX) to replace legacy explosive fills (Walsh et al., 2014, 2017). However, IHE's contain chemical compounds and formulations not previously used in munitions e.g. NTO, and therefore their environmental consequences are not fully understood.

There have been limited studies into the deposition of explosives residues from munitions due to the challenges in efficiently sampling an area post-detonation. However, quantification of explosive residue deposition has been achieved using the Multi Increment Sampling (MIS) method on snow covered ranges (Jenkins et al., 2005). MIS has been proven to be reproduceable and representative, particularly for a non-homogeneous contamination (Jenkins et al., 2005; Walsh et al., 2008). This method has been used to investigate residue deposition from munitions containing traditional explosive fills such as mortars, artillery rounds and grenades containing Composition B, and has shown that very small quantities of explosive residues are deposited from first order detonations (~0.00003% RDX from Comp B filled 61 mm mortar).

Multi-increment sampling (MIS) is a method used to collect representative samples of contaminated soil or other media, such as sediment or water. MIS is a proprietary term and was developed by the Danish company, COWI A/S, in the 1980s.

The MIS method involves collecting multiple small samples, or increments, from a specific location within a sampling area. These increments are then combined to create a composite sample, which is representative of the area being sampled. By collecting multiple small samples, the MIS method reduces the likelihood of sampling errors and ensures that the composite sample accurately reflects the variability of contamination within the sampling area.

Compared to other sampling methods, such as grab sampling or composite sampling, MIS provides a more representative sample that can be used to estimate the average concentration of contamination in a specific area. Additionally, MIS can be used to estimate the variability of contamination within a sampling area, which is important for determining the appropriate remediation strategy. While the most significant source of contamination is likely to be from blow-in-place disposals or partial detonations (Hewitt et al., 2005; Walsh et al., 2005, 2008), residue from first order detonations may accumulate over time depending on the number of rounds fired (Hewitt et al., 2003, 2005). For some live-fire ranges this may be tens of thousands of rounds per year resulting in significant accumulation of explosive residue, and the potential for soil and water contamination. However, research suggests that IHE filled munitions may deposit more explosive residue compared to conventional munitions. For example, RDX/HMX residues from IMX-104 filled 60 and 81 mm mortars may be as high as 0.006% and 0.001% respectively (Walsh et al., 2014). This equates to tens of milligrams per round. The percentage of DNAN residue deposited from the two IMX-104 filled rounds is comparable to the percentage of RDX (0.005% and 0.001% respectively), though this equates to a higher mass of DNAN per round due to the higher DNAN percentage in the formulation (Walsh et al., 2014). However, it is the percentage of NTO deposition that is most cause for concern (1.2% and 0.4% respectively), resulting in thousands of milligrams deposited per round. The tested rounds have relatively small explosive load (360 g and 831 g) compared to the 155 mm artillery shell which has a Net Explosive Quantity (NEQ) of 11.2 kg and therefore may deposit significant quantities of DNAN and NTO if used frequently at military training ranges (Walsh et al., 2014).

The deposition of increased quantities of explosive residue from IHE filled munitions may increase accumulation rates, and therefore increase the likelihood of environmental consequences. RDX contamination has previously been of concern, however in many locations effective environmental management procedures have been implemented (Ryu et al., 2007). In addition, due to the low quantity of RDX in the IMX-104 formulation (13%) RDX is not the main contaminant of concern. Conversely, DNAN and NTO have not been used in significant quantities in munitions to date and environments where they are in use may require additional environmental monitoring and management in the future.

NTO is of particular concern due to the potentially large quantities that may be deposited, as well as its acidity (pKa 3.76) and solubility (16.6 g/L at 25°C) (Arthur et al., 2018; Nandi et al., 2013) which means it may rapidly dissolve and transport into soil and ultimately to ground or surface waters where it may cause discoloration (Mark, 2014; Mark et al., 2017; Temple et al., 2018). The behavior of NTO in the environment has not been fully investigated with uncertainty surrounding the chemical and toxicological properties of degradation products such as 5-amino-1,2,4-triazol-3-one (ATO) (Krzmarzick et al., 2015; le Campion et al., 1998; Madeira et al., 2018; Mark et al., 2016). However, early indications suggest that ATO may be more toxic than NTO toward specific organisms (Le Campion et al., 1998). While NTO has particularly low toxicity (LD50 5 g/kg in rats), and sublethal toxicity (oligospermia), the uncertainty of its environmental behavior and the potential for deposition of significant quantities make it a particular concern (Crouse et al., 2015; Lent et al., 2016).

Understanding of the environmental fate of DNAN is more comprehensive than that of NTO. While DNAN is a nitrobenzene similar in structure to TNT, it is slightly more soluble (198.1 mg/L) and more toxic (LD50 199 mg kg-1) and therefore may present a comparatively greater risk to the environment (Dilley et al., 1982; Hawari et al., 2015; Lent et al., 2012; Ro et al., 1996; Taylor et al., 2013). In addition, several of the ammino degradation products, such as 2-amino-4-nitroanisole (2-ANAN), have similar toxicity and may also present a risk to groundwater and local human and animal receptors (Dodard et al., 2013; Lent et al., 2016; Taylor, Walsh, et al., 2017). The chemico-physical properties of DNAN, NTO, RDX and TNT are summarized in Table 4-1.

Table 4-1. Summary of the physicochemical and environmentally relevant properties of RDX, NTO and DNAN compared to TNT.

Name	Formula[1]	Solubility[2] mg L^{-1}	Log K_{oc}[3]	pKa	Toxicity LD_{50} mg kg-^{1}
TNT	$C_6H_3CH_3$	100	1.10 [36]	NA	607-767 [5]
RDX	$C_3H_6N_6O_6$	60	0.88-2.4	NA	119 [6]
NTO	$C_2H_2N_4O_3$	16,642	2.1 0.60-1.79	3.76[4]	5000 [6]
DNAN	$C_7H_6N_2O_5$	276	1.79-1.92 1.62 1.58	NA	199 [6f]

[1](Akhavan, 2004); [2](Taylor et al., 2013); [3](Arthur et al., 2017); [4](Nandi et al., 2013); [5](Reddy et al., 2000); [6](Arthur et al., 2018).

The fate of explosive compounds is highly dependent on the local environment, however, to inform environmental assessment it is essential to understand the potential for accumulation of explosive residues from commonly used munitions such as the 155 mm artillery shell. In addition, understanding the potential for contamination may enable a more proactive approach to environmental management ensuring that live-fire training with new generation munitions does not result in significant contamination incidents as has already occurred with legacy explosives (Bordeleau et al., 2008; Clausen et al., 2004; Racine et al., 1992). Therefore, the aim of this work was to quantify the percentage of DNAN, NTO and RDX residue remaining on the soil surface after detonation of an IMX-104 filled 155 mm artillery shell to determine the potential accumulation rate at military training areas.

4.3 Experimental Section

4.3.1 Explosive residue collection

4.3.1.1 Preparation of sampling arena

A sampling arena was created by levelling 11,900 Kg of inert fine particle sand to a depth of 5 cm in a semi-circular area (radius 10 m) on top of an impermeable plastic groundsheet (Appendix B). The arena was contained with flexible wooden edging panels around the external circumference (62 m). A 155 mm IMX-104 filled artillery shell was placed at the centre of the arena, at a hight of 1 m, and detonated by a simulation fuze that closely approximated the live-firing initiation mechanism. A total of three detonations were carried out, two with the artillery shell in horizontal orientation and one with the artillery shell in a vertical orientation to comprehensively assess the residue distribution. Following each detonation, the sand was cleared away and fresh sand (11,900 kg) was levelled on top of new clean groundsheets.

4.3.1.2 Explosive residue sampling

After the detonation, residue was collected from the 5 cm layer of sand that had been prepared prior to the detonation. The Multi-Increment Sampling (MIS) method was used to collect the residue. This involved collecting approximately 100 small samples of sand (100 x 10 g) in triplicate from discrete Decision Units (DU) within the sampling arena using a metal scoop." (Jenkins et al., 2005). Two different DU layouts were used for the two horizontal orientation detonations, an arc layout and a radial layout (Figure 4-1a-b). For the vertical orientation detonation, the arc pattern was repeated (Figure 4-1a). All collected samples were double bagged and stored in a freezer at (-18°C) until analysis (~3 months). In addition, the entire arena was sampled after each detonation as one DU to ensure comprehensive coverage.

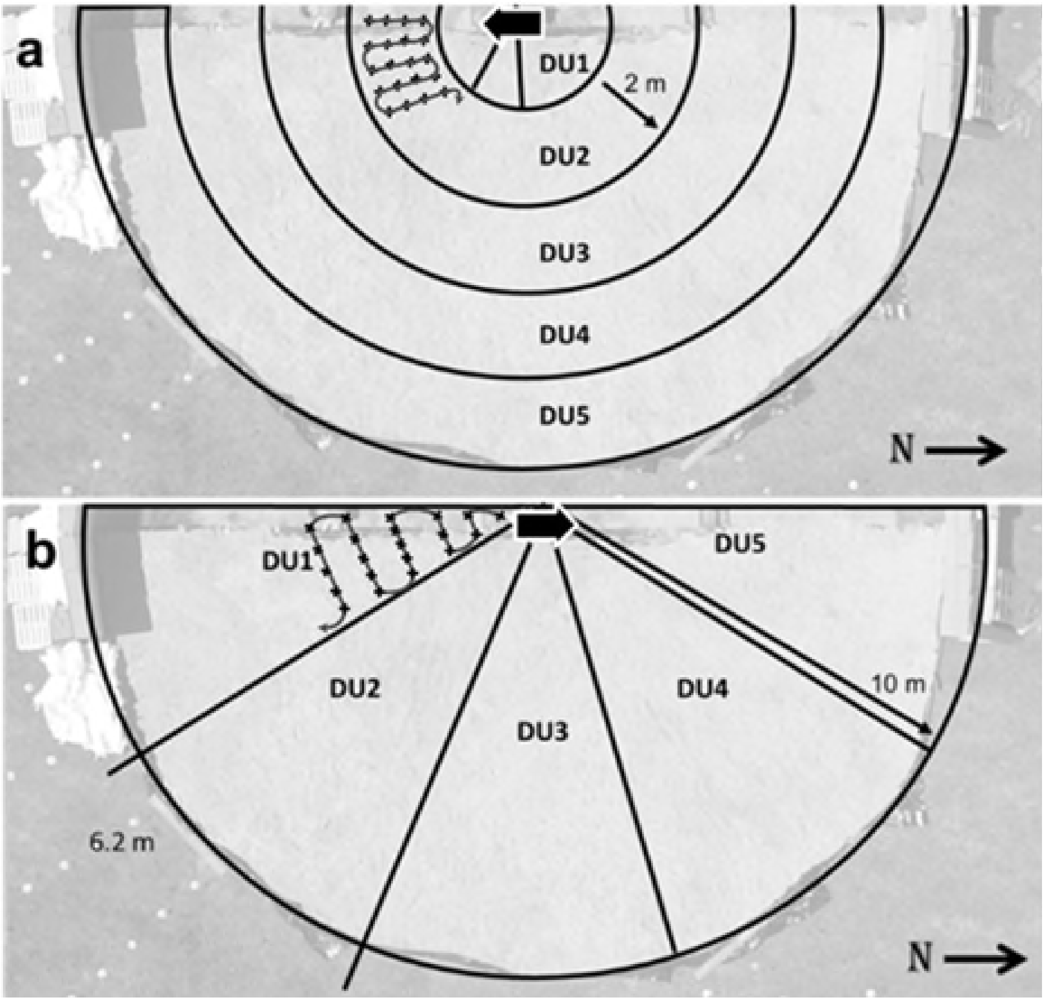


Figure 4-1 Decision Units (DU) for each detonation a) Detonation 1 and 3: arc DU's; b) detonation 2: radial DU's. Black arrows with white outline denotes orientation of the 155 mm shell for horizonal detonations (arrow point = nose). An example of how increments were collected (X`s) is shown by the location of crosses on a sampling route, repeated three times on different routes for each DU.

4.3.1.3 Field controls

Control samples of the inert sand were taken prior to preparing the sampling area to ensure the sand used during the experimental phase was free from explosive contamination. Control samples were also taken from the soil underneath the groundsheet to baseline for cross-contamination and random samples within the DU's were collected as positive controls (PC) to validate the sampling method and reproducibility of the results (Supplementary data). Additional controls samples were collected from outside the immediate sampling area prior to and post-detonation to ensure no DNAN, NTO or RDX residues were missed during analysis and to detect any potential cross-contamination from outside of the sampling area. This area was extended by 6 m from the boundary of the sampling area. All control samples were collected by using MIS in triplicate, with sand samples collected using a metal scoop and soil collected using a coring tool.

4.3.2 Laboratory Sample analysis

4.3.2.1 Sample processing

Collected samples were defrosted and air dried over 5-7 days before being passed through a 2.00 mm sieve to remove any foliage or large fragments. Samples were mechanically mixed and sub-sampled in triplicate by taking increments (~0.5 g) from a 5 by 5 grid to a mass of ~20 g.

4.3.2.2 Sample extraction

Sub-samples were extracted with acetonitrile/water (1:1) (40 mL) by shaking for 18 hours at 180 rpm in amber glass vials (Temple et al., 2019). Samples were left to stand for 30 minutes before filtration through a 0.2 µm PES filter and analysed by HPLC. To confirm very low levels of NTO, DNAN and RDX residue the bulk liquid (5 mL) from a sub-selection of extractions was concentrated 5 times by evaporation at 35°C and quantified by HPLC. Resulting concentrations were used to determine the mass deposited. HPLC analysis

Samples were analysed and separated by High Pressure Liquid Chromatography (HPLC) using a 150 x 4.6mm (3.5 particle size) Agilent Zorbax Eclipse Plus C18 column in a Waters Alliance 2695 with a Waters 996 photodiode array detector (Fawcett-Hirst et al., 2020). The mobile phase was a 40:60 acetonitrile/water mix at a flow rate of 1.5 mL min-1 with an injection volume of 10 µL and a constant temperature of 30oC. Residue concentration (NTO – 315nm, DNAN – 296nm, RDX – 235nm and common degradation products ATO - 315, DNP - 296 nm, 2-ANAN – 308 nm, 4-ANAN – 330 nm and 2,4-ANAN - 308) was determined by calibration to an IMX-104 standard calibration curve. Limit of Detection (LOD) and Limit of Quantification (LOQ) are presented in Table 4-2. To determine LOQ and LOD, 7 standards of IMX-104 have been used (from 296 ppm to 0.09 ppm)

(Tab. 4-2) to define the calibration curve for each component of the composition; the wide range was decided based on the unknown results that would have been expected from the detonations. In the soil samples collected, the identification of peaks was carried out by comparing the retention time and UV characteristics of the compounds with those of the standard compounds.

Table 4-2 HPLC calculated LOD and LOQ values based on standards

Compound	Linearity R^2	LOD (µL)	LOQ (mL)
NTO	0.9996	0.48	1.44
DNAN	0.9996	0.46	1.40
RDX	0.9994	0.41	12.6

4.3.2.3 Quality controls

Play sand was artificially spiked with NTO, DNAN and RDX (12.5 ppm) and extracted after 24h, 48h and 6 days with 100% efficiency. Previous work has shown that in sand at ambient temperature (18 °C) NTO, DNAN and RDX remain stable for up to four months in the absence of light, and no degradation was detected in samples stored in the freezer for 3 months.

4.4 Results and Discussion

4.4.1 Determination of mass of explosive residue from detonation of 155 mm artillery shell

To quantify the explosive residues from detonation of the 155 mm artillery shells the detonation area was sampled using the MIS method. The published protocols for MIS were followed, with the exception of mechanical grinding of the samples due to the potential for initiation caused by friction between the sand and explosive residue (Jenkins et al., 2006). Therefore, the sand was manually mixed prior to analysis to maximise homogeneity. As it has been shown that improved mixing (grinding) increases representativeness of samples, an increased error was accepted (Walsh et al., 2012). Analysis of control samples taken prior to the detonations confirmed that the groundsheet and 5 cm sand layer was sufficient to prevent cross-contamination from the surrounding and underlying soil.

There was concern that the detonation may significantly disrupt the sand and render it impossible to sample, however after the first detonation it was clear that only the centre of the arena was disrupted (Supplementary data). Therefore, the entire arena was sampled after each detonation by MIS. No explosive residues were detected in the entire arena samples for either detonation in the horizontal plane, nor for the detonation in the vertical plane. Samples concentrated by a factor of five also resulted in non-detect of any NTO, DNAN or RDX, suggesting that as expected the total residue deposition from a single 155 mm artillery shell was below the limit of detection (0.5 µl) due to the mass of sand diluting the explosive residue. However, quantifiable concentrations of DNAN were detected in several of the smaller DU’s for all detonations (Table 4-3). The errors reported reflect the heterogeneity of results wherein some samples had significantly higher concentration of DNAN, and in other samples no DNAN was detected. Therefore, the results have been used as a broad estimate of potential residue deposition.

NTO was only detected in quantifiable concentrations in detonation 2, DU2, although characteristic NTO peaks were observed in samples from all DU’s from all three detonations, suggesting that NTO was concentrations were below the limit of quantification of NTO (1.4 mg L-1) (Temple et al., 2018). This was confirmed by concentrating select sample extracts i.e. in one of the replicates for detonation 3, decision unit 3 0.002 mg kg-1 NTO was detected. Evaporating samples was considered to be too time consuming to achieve for all samples, and therefore unquantifiable concentrations of NTO have been reported as ‘trace’ (Table 4-3).

RDX was detected in the ‘area control’ sample i.e. the soil directly beneath the sampling area, but was not detected in the sampling area, including in the concentrated samples. Previous work in the literature suggests it is likely that RDX is deposited, but the concentrations were too low to be detected by the methods used (Table 4-2). This was expected due to the low percentage of RDX in the IMX-104 composition (13%), other compositions have much higher concentrations of RDX (> 60%) making deposition of detectable concentrations much more likely (Taylor et al., 2006).

Table 4-33 Summary of results from IMX-104 filled 155 mm artillery shell detonations. Standard deviation reported.

Decision Unit	**Horizontal orientation- DU Arcs**			**Horizontal orientation- DU Radial**			**Vertical orientation- DU Arcs**		
	NTO mg kg^{-1}	**DNAN mg kg^{-1}**	**RDX mg kg^{-1}**	**NTO mg kg^{-1}**	**DNAN mg kg^{-1}**	**RDX mg kg^{-1}**	**NTO mg kg^{-1}**	**DNAN mg kg^{-1}**	**RDX mg kg^{-1}**
Blank (sand)	0	0	0	0	0	0	0	0	0
Area control	0	0	Detect	0	0	Detect	0	0	Detect
DU1	Detect	0.23 ± 0.9	0	Detect	0	0	Detect	0	0
DU2	Detect	0.0009 ± 0.004	0	Detect	0.055± 0.2	0	Detect	0.0008 ±0.004	0
DU3	Detect	0.11 ± 0.57	0	Detect	0	0	Detect [a]	0	0
DU4	Detect	0	0	Detect	0	0	0	0	0
DU5	Detect	0.24 ± 1.2	0	0.16 ± 0.27	0	0	0	0.16 ±0.8	0
PC1	Detect	0.002 ± 0.001	0	Detect	0.17 ± 0.9	0	Detect	0	0
PC2	Detect	0	0	Detect	0	0	0	0	0
PC3	Detect	0.0008 ± 0.003	0	Detect	0	0	Detect	0	0
Whole area	0	0	0	0	0	0	0	0	0

[a] Upon concentrating replicate 2, concentration of NTO was quantified as 0.002 mg kg-1.

4.4.2 Mass of DNAN residue deposition

Concentrations of DNAN were detected in four of the five DU's for detonation 1 (arcs), confirmed by trace detection of DNAN in the positive controls in DU 1 (PC3) and DU 5 (PC1), and the non-detect in the positive control within DU4 (PC2). Conversely, in the second detonation DNAN was only detected in DU2 (radial), confirmed by detection of DNAN in the random positive control. It is interesting to note that DNAN was only detected in the second radial DU in detonation 2 (South-Easterly) (Appendix D) and it is likely that DNAN identified in detonation 1 was concentrated in a North-Easterly direction corresponding to DU2 in detonation 2, and the rear of the 155 mm shell (Figure 4-1). To ensure all explosive residues were accounted for, samples were also analysed for DNAN degradation products 2-ANAN, 4-ANAN, 2,4-ANAN and DNP, but these were not detected in any samples.

From the results of the horizontal detonations, it was expected that DNAN deposition from the third detonation would be similar, but possibly more uniformly distributed due to the vertical orientation. This is because in the vertical position, the shell was positioned nose-up meaning any increased DNAN deposition at the rear-end of the shell would be evenly distributed in the sampling area. While DNAN was detected in DU5 (furthest from the detonation centre), and very low levels detected in DU2, DNAN was not detected in any other DU's. In the vertical position, it is possible that residues were deposited beyond the sampling area, although no DNAN was detected in these control samples, very low concentrations may have been masked in the HPLC trace by the noise from soil organic matter.

The constructed sampling arena was semi-circular as it was assumed that the deposition would be symmetrical about the long axis of the projectile (nose to tail) and estimates of mass of residue deposited could be doubled to account for both halves. In reality, doubling the mass is unlikely to give a perfect estimate as deposition could be affected by slight variations in weather conditions and slight misalignments of the 155 mm artillery shell. A number of other assumptions were also made to enable estimation of the deposited mass of DNAN per kilogram of soil. For example, the mass of soil was determined by assuming

DNAN would be deposited on the soil surface and no deeper than the sampling depth of 5 cm, and that the density of soil is similar to that of sand. As the concentration of DNAN recovered from the three detonations was significantly different, the mass of DNAN deposited was calculated from a) the combined concentrations from all DU's in detonation 1; b) DU5 in detonation 2; and c) DU5 in detonation 3 to provide upper and lower estimates. The total estimated mass of DNAN from each detonation was calculated by multiplying the concentration (mg kg-1) by double the mass of sand in the DU's where DNAN was found (Equation 4-1).

4-1 $$\boldsymbol{Estimated\ mass\ of\ DNAN\ in\ DU = C_{residue} \times M_{sand}}$$

Where C is the concentration in soil (mg kg-1) and M is the mass of sand in the decision unit.

From the data obtained from Equation 1, the total estimated mass of DNAN from the three detonations accounted for between 0.006% and 0.07% of the total DNAN content in the 155 mm shell (Table 4-4). The upper estimate is slightly higher than previously published literature on the residue from 60 mm and 81 mm IMX-104 shells which found 0.006% and 0.001% DNAN deposited respectively(Walsh et al., 2014). An increase in deposited residue may be due to the significant increase in the Net Explosive Quantity between the three shell sizes (approximately 11 kg (155 mm) vs 339 g (61 mm) and 807 g (81 mm)).

Table 4-44 Mass DNAN deposited from detonation of 155 mm artillery shell.

Detonation	Concentration mg kg^{-1}	Total Mass g	% Mass
1	0.22 +0.0009 + 0.11 +0.24	2.8±0.46	0.1
2	0.049	0.23±0.08	0.008
3	0.16	1.23±0.48	0.05

As expected from previously published literature, the mass of DNAN deposited from detonation of an IMX-104 filled 155 mm artillery shell is higher than for commensurate legacy munitions, such as TNT from Comp B filled 155 mm shells (Walsh et al., 2012, 2013, 2014). This is of note, as DNAN is a nitrobenzene with similar properties to TNT, although it is slightly more toxic (199 mg kg-1 vs 607-767 mg kg-1). DNAN's environmental behaviour may therefore be similar to TNT i.e. mineralisation by photo and bio-degradation before significant exposure to environmental receptors. However, this may not be true of all environments as it is highly dependent on soil type and weather conditions, and it may be possible for residues to accumulate to potentially hazardous levels. This is unlikely to be a problem for operational use as the incident rate is low, and in localised areas i.e. DNAN is likely to be diluted through environmental action such as infiltration with rainwater, surface run off and degradation. Therefore, in the absence of additional incident DNAN the concentration of this compound in the environment will rapidly decrease. However, the accumulation of DNAN may need to be considered for training with IMX-104 filled 155 mm artillery shells.

4.4.3 Mass of NTO deposition

One sample from the detonation 2, DU5, contained detectable quantities of NTO (0.16 ± 0.17 mg kg-1). and detection of NTO was consistent in all DU samples, suggesting that during the detonation NTO was evenly distributed across the arena. Using Equation 1 and assuming a) the highest level of deposition (0.16 mg kg-1) in detonation 2, DU5 and b) assuming an average deposition of 0.03 mg kg-1 across the entire area, the mass deposited from a single detonation was between 71 mg and 762 mg (Table 4-5). This equates to between 0.001% and 0.01% of the mass of NTO in the 155 mm shell. This is significantly lower than the estimated deposition mass in the published literature from the detonation of 60 mm and 81 mm munitions on snow (0.4 - 1.2 %), suggesting that the mass of NTO deposited is lower for the 155 mm artillery shell (Walsh et al., 2014).

Whilst NTO is significantly less toxic than DNAN (5000 mg kg-1 vs 199 mg kg-1), there is limited research into its wider environmental impact. One potential issue is that NTO may be acidic when solubilised i.e. after rainfall, which may increase leaching of nutrients and metals from the existing contamination in soil (Mark, 2014). For example, many explosive test and impact areas are contaminated with lead, which is known to leach more rapidly in soils with pH lower than 4 (Walsh et al., 2012). In addition, NTO discolours water at low concentrations (10 ppm), which would be considered pollution under multiple UK and European regulations, even if there were no associated toxicity (Tennant et al., 2019).

Table 4-55 Mass NTO deposited from detonation of 155 mm artillery shell.

Detonation	Concentration mg kg^{-1}	Total Mass g	% Mass
2	0.16	0.76±0.006	0.05
1&3	0.003	0.07±0.17	0.004

4.4.4 Potential environmental impact of IMX-104 155 mm artillery shells

As RDX was not detected in appreciable concentrations the accumulation rate of hazardous concentrations of IMX-104 residues in the environment was based on the deposition of DNAN and NTO. Therefore, assuming the masses of DNAN and NTO residue per detonation as calculated above (Table 4-4 and Table 4-5) the estimated rate of accumulation during training was calculated using the Circular Error Probable (CEP) i.e. the radius of the area in which 50% of the rounds are likely to land. For the 155 mm artillery shell the CEP is 94 m - 267 m depending on the distance fired (15-30 km). The calculation takes into account that only 50% of rounds are likely to land within the CEP, with the remaining 50% distributed in an even larger area of diminishing soil concentration. The area increases with increasing distance. Using this calculation, after 1000 detonations the concentration of DNAN on the surface soil could be as high as 2.37 mg kg-1 (assuming lower CEP and higher mass deposited) but is more likely to fall between 0.21 and 2.37 mg kg-1. Table 4-6 outlines the potential maximum concentration of DNAN and NTO in soil at CEP 94 m and CEP 267 m for detonation of 1000 and 10,000 IMX-104 filled 155 mm shells in the absence of other environmental processes such as adsorption, degradation and surface run off.

Table 4-66 The potential accumulation of DNAN and NTO in soil for 1000 and 10,000 firings for CEP 94 m and 267 m.

Explosive re sidue deposited from 155 mm shell	Estimated soil concentration 1000 detonations (mg kg^{-1})		Estimated soil concentration 10,000 detonations (mg kg^{-1})	
	CEP 94 m	**CEP 267 m**	**CEP 94 m**	**CEP 267 m**
DNAN 0.008%	0.0001±7.8*10^{-5}	1.37*10^{-5}±9.7*10^{-6}	0.001±0.0007	0.0001± 9.7*10^{-5}
DNAN 0.05%	0 0006±0.0004	8.1*10^{-5}±5.4*10^{-5}	0.006±0.004	0.$^{-6}$008±0.0005
DNAN 0.1%	0.001±0.0004	0.0001±5.7*10^{-5}	0.01±0.004	0.002±0.0005
NTO 0.004%	3.2*10^{-5}±5.7*10^{-6}	3.6*10^{-6}±7.1*10^{-7}	0.0003±5.7*10^{-5}	4.03*10^{-5}±7.09*10
NTO 0.05%	0.0003±0.0001	3.5*10^{-5}±1.9*10^{-5}	0.003±0.001	0.0004±0.0002

Unfortunately, there are no current legal Soil Screening Level (SSL) for DNAN or NTO in soil although health-based environmental screening levels are in development (Lent et al., 2021). However, for the US EPA has given a residential and industrial SSL of 19 and 79 mg kg-1 respectively for TNT, which has similar properties to DNAN (United States Environmental Protection Agency, 2014). Although it is unlikely that the SSL for DNAN would be the same as for TNT, as DNAN is more toxic, it does give a guideline figure for concentrations of concern which are potentially exceeded at localised areas of soil on training ranges within more than 10,000 firings. In addition, this figure does not consider the number of partially detonated or non-functioning ordnance which may be disposed by blow-in-place or left in the environment. Both methods known to deposit significant concentrations of explosives in the environment therefore contributing to the accumulation of residues (Lent et al., 2021; Walsh et al., 2014).

The results in Table 4-6 suggest that the concentration of DNAN in soil could increase rapidly at training areas where 155 mm shells are in use. However, this calculation assumes that there is no transport beyond the first 5 cm of soil and that the training targets do not change. In reality, training is likely to take place over a much larger area further reducing the accumulation rate, and over a significant period of time. For example, if 10,000 155 mm shells are fired within a year, it is likely that a significant quantity of deposited DNAN will be dissolved by incident rainfall and transported into soil where it may to be rapidly degraded, especially in high organic content soils (50% within 3 months) (Temple et al., 2018). While some degradation products are equally as toxic as DNAN, these are also likely to be further degraded to mineralised products such as nitrates and nitrites before exposure to a receptor. Therefore, while the contamination of soil is a concern, it may be managed by rotating training areas and avoiding areas with sensitive groundwater resources.

Accumulation of NTO is also of concern as the behaviour of NTO in the environment is still under investigation. For example, whilst some NTO degradation products have been speculated, such as ATO, they have not yet been identified in environmentally representative samples such as soil studies (Moores et al., 2020). In addition, there are limited toxicity studies on NTO and its degradation/decomposition products making it difficult to assess its environmental impact. From the findings in this work, and previous work indicating the rapid degradation of NTO in the environment, it is likely that NTO will be deposited in the environment from the use of IMX-104 filled 155 mm artillery shells, therefore, further investigation into the degradation products and their toxicity is required (Krzmarzick et al., 2015; Temple et al., 2018).

4.5 Conclusion

It is clear that DNAN and NTO residues were deposited from the detonation of an IMX-104 filled 155 mm artillery shell in slightly higher concentrations than has been recorded for legacy (RDX/TNT) filled munitions. While the deposited concentrations may not be of immediate concern after a single detonation, care must be taken if large quantities of IMX-104 filled munitions are to be used for training to manage accumulation and minimise environmental impact. The training environment is particularly relevant as the accumulation of DNAN and NTO will be highly dependent on rate of infiltration into soil with rainfall, and the rate of degradation and therefore environmental management techniques must be chosen for their suitability to the local environment. Finally, it must be noted that this residue deposition investigation was relatively small scale, with only three detonations for comparison. To increase confidence in results, additional studies should be undertaken such as an accumulation study wherein samples are collected after 5 to 10 detonations.

5 Evaluate the effects of Insensitive High Explosives residues on soil by using an Environmental Quality Index approach

5.1 Abstract

The environmental impact of Insensitive High Explosive (IHE) detonation residues to soil quality was assessed using a series of outdoor soil mesocosms. Two different soils were used including a pristine sandy soil and a land-degraded soil collected from a training range. Both soils were spiked with an IHE mixture comprised of 53% NTO, 32% DNAN and 15% RDX at three different concentrations 15, 146 and 367 mg/kg respectively. The concentration levels were derived from approximate residues from 100 detonations over a 2-week training period. A set of five physico-chemical and biological indicators representative of the two soils were selected to develop environmental quality indexes (EQI). It was found that none of the concentrations tested for the pristine soil affected the chemical, biological and physical indicators, suggesting no decrease in soil quality. In contrast, the EQI for the degraded soil was reduced by 24%, mainly due to a decrease in the chemical and biological components of the soil. Therefore, it is concluded that depending on the soil health status, IHE residues can have different consequences on soil health. Further studies are needed to determine the environmental impact of IHE on soil and water especially in the case where a larger number of detonations are more likely to be carried out on a training range.

5.2 Introduction

Environmental contamination of live-fire military trainings areas used for live firing has been recognised as a worldwide problem and being ranked as the second-largest anthropogenic source of environmental pollution after mining activities (Jenkins et al., 2006; Pichtel, 2012; Tauqeer et al., 2020; Walsh et al., 2005). In addition, new generation of explosives, such as the Insensitive High Explosives (IHE), are of increasing concern due to their toxicity and early indications that increased quantities will be deposited on soil compared to legacy explosives (Johnson et al., 2017; Krnj, 2021; Taylor, Dontsova, et al., 2017). IHE formulations

consist of combinations of legacy explosives such as 2,4-dinitroanisole (DNAN) and previously unused energetic materials such as 3-nitro-1,2,4-triazol-5-one (NTO) (Lent, 2019). This mixture is replacing the use of Comp B as it less sensitive to unintentional shock with DNANs replacing TNT as it safer during the manufacturing processes (Braida et al., 2012; Singh et al., 2010).

(Lent, 2019)(Braida et al., 2012; Singh et al., 2010)Deposition and accumulation of energetic chemical compounds in soil are due to repeated field detonation of Insensitive Munitions (IM) on training ranges (Hewitt et al., 2005; Walsh et al., 2012; Zentelis et al., 2017). In a previous study, we quantified the residual concentration of explosive compounds in soil after three full-order detonations of a 155 mm filled with a melt-cast mixture of 53% NTO, 32% DNAN and 15% RDX (Persico et al., 2022). The residual concentrations were then extrapolated to predict the highest residual concentration from 100 detonations, which has been estimated to be 370 mg/kg. In comparison, the three components characterising the explosive mixture, NTO, DNAN and RDX, have a calculated acute LD_{50} of respectively >5000 mg/kg, 199 mg/kg and 59 mg/kg (Lent, 2019), Justifying the need to pre-evaluate any explosive residue in soil to pre-empt any potential impact and avoid severe consequences to environmental receptors.

Previous studies have demonstrated the environmental impacts of traditional explosives, such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) on soil and water ecosystems functioning and biodiversity (Chatterjee et al., 2017; Stanley et al., 2015; Tauqeer et al., 2020; Travis et al., 2008) In contrast, environmental impact studies for IHE remain scarce. Missing ecotoxicological values and limited understanding of the mechanisms effective for evaluating soil changes in the environment has left a gap in research, and a suitable standardised procedure has not yet been developed.

The consequence of contamination on the soil environment is usually evaluated by assessing soil quality, although currently procedures focus on crop production for agricultural land purposes rather than environmental impact(Moebius-Clune et al., 2016; Purakayastha et al., 2019; USDA, 2019). Soil, is defined as "*as a vital living system within ecosystem and land-use boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and promote plant and animal health*" (Doran & Zeiss, 2000) where the physical, chemical and biological properties are ensuring that the system properly functions. Soil Quality Indexes (SQIs) assess and apply weighting to the physical, chemical, and biological parameters that are essential to maintain soil integrity for its intended purpose I.e., agriculture, storage etc... (Amacher et al., 2007; Chaves et al., 2017). SQIs use a selection of indicators currently designed to evaluate soil health for land management (Chaves et al., 2017). Each indicator is scored using principal component analysis (PCA); the indicators that are given higher weighing are then scored and used to calculate the SQI (Mukherjee & Lal, 2014). Therefore, SQI values calculated for different landscapes are not comparable because the indicators are chosen based on the different land management. Therefore, the aim of this work was to evaluate the consequences of IHE residue deposition on soil environmental status using a series of soil mesocosms exposed to outdoor conditions, evaluating soil changes by using an EQI approach. For this work a specific set of soil indicators representing the physical, chemical, and biological parameters of the soil were scored by giving the same relevance to each parameter and avoiding PCA analysis. Ultimately, a new Environmental Quality Index (EQI) approach was developed where all the indicators are scored and considered to quantify the quality of soil to enable comparison between sites to ensure a more comprehensive assessment when different areas are evaluated. Moreover, military training exercises may require different types of soils depending on the specific training objectives. For example, sandy soils may be preferred for training in desert environments, while clay soils may be more appropriate for training in wet and muddy, therefore sandy loam and a loamy sand soil have been chosen for the experiments. (Amacher et al., 2007; Chaves et al., 2017)(Chaves et al., 2017)(Mukherjee & Lal, 2014)Methodology

5.2.1 Soil Characterisation and soil preparation

To ensure a comparison between a synthetic and a representative soil (Tab. 5-1), a pristine sandy loam soil (Soil A) purchased from SureGreen and a loamy sand soil from an active military training area in the UK (Soil B) were used. Both soils were homogenised by screening through a 2-mm sieve and air dried for 2 weeks at ambient room temperature. Soil B was collected using the multi-increment sampling methodology as it is, to date, the most representative collection technique for a non-homogeneous contamination (ITRC, 2012).

Both soils were characterised (Supplementary material - S1) using particle size distribution according to STM D 2487-11, soil pH and Electrical Conductivity were measured on a Jenway 3540, Carbon (organic and total) (BS 7755-3.8:1995, ISO 10694:1995, total hydrogen and total nitrogen (BS EN 16168:2012) were measured on an Elementar vario EL cube (Temple et al., 2019).

Table 5-1 Soil Characteristics.

	Units	Soil A	Soil B
Dry matter content[1]	% (m/m)	82.6	95.9
Water content[2]	% (m/m)	21.1	4.3
600µm - 2mm	%	7.99	3.73
212µm - 600µm	%	34.59	48.91
106µm - 212µm	%	25.18	14.46
63µm - 106µm	%	17.69	9.78
2µm – 63µm	%	14.55	23.11
pH$_{(1:5)\text{ in water (approx. 2 hours)}}$[3]		8.7	6.5
Carbon$_{\text{total}}$[2]	%	7.08	4.81
Nitrogen$_{\text{total}}$[2]	%	0.54	0.43
Hydrogen$_{\text{total}}$[2]	%	1.04	1.30
Carbon$_{\text{organic}}$[2]	%	7.04	4.63
Electrical conductivity (1:5 soil:water extract) [3]	µS/cm	70.08	12.14
K availability	ppm	151.3	27.2
Loss of ignition[4]	%	10	11.3

[1] air-dried soil; [2] reported on an oven-dry basis; [3] reported on an air-dry basis; [4] reported as a percentage of the dehydrated sample.

5.2.2 Preparation of soil

Both air dried soils were spiked with an IHE solution at either low, medium, or high concentration as determined by the residue collection in Chapter 4 (Persico et al., 2022) (Tab. 5-2). Briefly, IHE flakes (12.5 mg (low), 1250 mg (medium) and 3375 mg (high)) were dissolved in 5.8 L of distilled water at pH 7 for 2 weeks using a Heidolph MR3002 agitator with a magnetic bar. The volume of water for dissolving the IHE flakes was determined by the solubility of RDX (66 mg L^{-1}) at the maximum concentration of the experiments, being the compound with the lowest solubility (Lent, 2019). The soil (8 kg) was then added to the IHE solution and frequently mixed over 3 weeks under a fume cupboard in black containers until excess water had evaporated. The soil mixture was prepared in black containers away from direct sunlight to limit any photodegradation of the explosive mixture. (Blume et al., 2016, Lent, 2019)

Table 5-2 Spiked levels used for the soil mesocosms

	Soil A			**Soil B**		
	Low	**Medium**	**High**	**Low**	**Medium**	**High**
53% NTO (mg/kg)	8.1	82	194.9	8.1	81.1	196.7
32% DNAN (mg/kg)	4.9	49.5	117.7	4.2	49	118.8
15% RDX (mg/kg)	2.3	23.2	55.2	2.3	23	55.7
IHE total concentration in soil (mg/kg)	15.3	154.6	367.7	14.6	153.1	371.2

5.2.3 Mesocosm experiments

To prepare the mesocosms, closed buckets with sealed lids were utilized. The lids were cut and shaped (2) to fit commercially available black plastic seed trays (3) (20.5 × 15.4 × 5.0 cm) that were lined with silicon (Appendix D) to ensure rainwater would first pass through the soil, allowing for observation of changes in soil health. To prevent direct contact between the soil and the bottom of the tray and minimize soil loss, each tray (36 total) was initially filled with 0.5 cm of damp inert quartz sand. Subsequently, spiked soil (8 kg) was placed into each tray to a depth of 5 cm (Appendix D), with the final weight recorded. The depth of soil was determined based on the top layer of soil (5 cm), where any changes to soil properties due to surface contamination are expected to occur (Blume et al., 2016). To account for low, medium, and high levels of contamination, 5 contaminated samples and 3 positive controls (clean soil) were prepared.

Samples were sacrificed at day 0, 1, 7, 14, and 36 and prepared for analysis. Leachate volume was collected in triplicates using 50 mL amber glass tubes to avoid photodegradation of the IHE. For biological analysis, soil (5 g) was collected from each mesocosm in triplicate using a 5mL sterile vials and 20 µL of glycerol was added to preserve the soil for biological analysis. Soil samples were stored at -70°C until biological analyses were carried out. The remaining soil was stored at -18 °C for physical and chemical properties analyses and leachate were collected and stored at 4 °C until chemical analysis was carried out.

5.2.4 Weather condition data collection

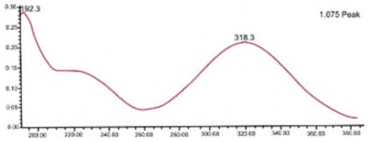
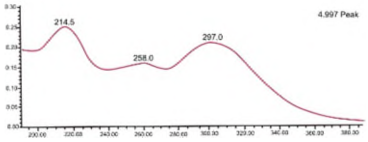
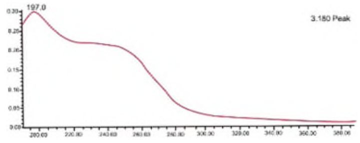
The mesocosms were set up during the UK summer months (July-August) and weather conditions data was recorded during this time from the closest weather station (Marlborough, 22 km from the samples collection area). The data was recorded daily and included minimum and maximum air temperatures, rainfall in mm, wind strength and direction, evapotranspiration, solar energy, direct sunshine, humidity, and temperature of the first 5 cm of the soil. The data is publicly available at https://www.windrushweather.co.uk/station/.

The experiments were run during summer time as the decreased rainfall during this periods can result in an increased retention of the explosive within the soil matrix, leading to a greater likelihood of chemical interactions occurring between the explosive and the soil. This contrast withperiods of higher precipitation, such as during winter, when the explosive is more prone to dissolving in rainwater and leaching into the groundwater system.Soil analyses

5.2.5 Explosive extraction and analysis

Soil collected from the mesocosm was air dried. Triplicate soil samples (10 g) were collected at the onset and day 1, 7, 14 and 36. The explosive was extracted from the soil using the Temple et al., (2019) method. Briefly, a mixture of acetonitrile/water (1:1) (20 mL) was added to the soil (10 gr) and shaken for 18 hours at 180 rpm in 50 mL amber glass tubes. Samples were filtered using 0.2 µm polyether sulfone (PES) filter and analysed by High Pressure Liquid Chromatography (HPLC). Water samples (50 mL) were collected in triplicates, filtered using nylon filters (0.2 µm) and analysed by HPLC as described by (Temple et al., 2019). Quantification of NTO, DNAN and RDX was carried out using a calibration curve. The Limit of detection and limit of quantification are reported in Table 5-3 columns and conditions are the same used in Chapter 4 in the methodology section. Although DNAN, NTO, and RDX are typically introduced to the soil as a mixture, they exhibit distinct behaviours, and therefore, their individual impacts have been evaluated separately. .

Table 5-3 Linearity, HPLC accuracy: Limit of Detection (LOD) and Limit of Quantification (LOQ) for the IHE composition

IHE composition	**Linearity (R)**	**LOD (μg/mL)**	**LOQ (μg/mL)**	**Wavelength (nm)**	**Chromatogram**
NTO	0.9997	0.48	1.44	315	
DNAN	0.9997	0.46	1.40	295	
RDX	0.9992	0.41	12.6	235	

5.2.6 Soil physical properties determination

Due to the nature of the sample, qualification but not quantification of changes of the physical properties could have been determined. Therefore, variations were evaluated on air-dried samples.

First physical property determined was the bulk density (ρ_b) (kg/m³) which was calculated following the formula (5-1):

5-1
$$\boldsymbol{\rho_b} = {}^{\boldsymbol{M_s}}/_{\boldsymbol{V_s}}$$

where M_s is the mass in mg of the soil sample, which is calculated by weighting the dry soil sample. V_s is calculated as the volume of the dry soil sample in m³ (Han et al., 2016).

Soil Particle density (mg/m³) (SPD) was instead determined according to STM standards (D854 – 14) although, due to the nature of the samples, the soil has been air dried instead of oven dried, therefore results are showing variability in SPD. Those calculations were necessary for the soil porosity variation (%) which was derived from the soil bulk density and the soil particle density. Soil porosity was calculated as follows:

5-2

$$\boldsymbol{f = \frac{1-\rho_b}{\rho_s}\ x\ 100}$$

With ρ_b as the bulk density in g/cm3 and ρ_s as the specific gravity of soil solids (or soil particle density) (Hazelton, 2016).

5.2.7 Soil chemical properties determination

pH was recorded from soils (1:5) and leachate water using HI-98100 Checker Plus pH Tester. Electrical Conductivity (EC) was measured (mS/cm) in soil using HI-98331 Groline Direct Soil Conductivity & Temperature Tester. Soil nutrients were analysed using hatch test kits (Hanna Instruments - HI-3895) for qualitative evaluation of P, N and K variability. A colorimetric (P, N) and turbidimetric (K) evaluation was used to measure trace, low, medium, and high levels of nutrients concentration to determine their variability. Distilled water (30 mL) was added to soil samples (10 g) together with the additive powder from the kit, stirred and allowed to settle for 30 min. Potassium Availability (K^+) was measured in ppm following the procedure from (Motsara & Roy, 2008). Potassium Chloride (KCl) (1.907 g) was dissolved in Ammonium Acetate/Acetic Acid solution (50 mL) and standards were prepared ranging from 10 to 100 ppm. The acetate/Acetic Acid solution (50 mL) was added to soil (10 g), and. the samples shaken for 30 min. The solution was than filtered using a Whatman No.30 filter paper and the leachate analysed using a Flame Photometer (Motsara & Roy, 2008).

5.2.8 Soil biological properties determination

The Viable Plate Count technique (Jett et al., 1997) has been used to evaluate the number of bacteria present in the original soil samples to observe the variability at different IHE concentrations. 23 g of nutrient agar were added to 1L of distilled water and autoclaved at 121°C for 1.30 hour. The warm agar was added to sterile polystyrene plastic petri dishes (55 x 15 mm) and left to dry in a sterile environment. 1 mg of soil was added to 100 µL of PBS, the samples were diluted up to 9 times to ensure visual counting of the bacteria colonies. The diluted solutions (up to 10^{-10}) were spread on the petri dishes which were then left in an incubator at 37°C overnight. The standard deviation calculated for all results was found ≤ 9.7% for CFU estimation.

5.3 Environmental Quality Index (EQI)

Each of the soil indicators were scored following the procedure for the SQIs (Andrews et al., 2002; Chaves et al., 2017) although avoiding the PCA selection to ensure that all the values are considered. This is because SQIs between different sites are not directly comparable as the soil indicators of a particular site/area tend to be site- or area-specific. Therefore, weighted soil parameters might preclude a comparison between sites (Qi et al., 2009; B. J. Wienhold et al., 2004), being SQIs incomparable when different sites are analysed.

Based on previous research the most common set of indicators to assess the impact of different contaminant on soil has been highlighted (Table 2-2).

The average value from the six indicators used for each IHE concentration and day of collection was scored based on Amacher et al. (2007) that provided a list of scorings for SQIs based on the calculated experimental values (Supplementary Material). For the values where a score was not provided the “low is better” and “more is better” function was used (Lenka et al., 2022). This approach, by using the same set of indicators as of equal importance, ensures comparison between different sites.

Following the scoring from each physical, chemical, and biological indicator (Supplementary material), separately, the EQI of each parameter were summed:

5-3

$$\boldsymbol{EQI_{p/c/b} = S_1 + S_2 + S_3 + S_4 + S_5}$$

Where S represent the score for each parameter. If one of the previous indicators from Table 5-4 was not analysed, 0 was the score given.

The EQI was calculated and normalised as follows:

$$EQI = \left({EQI_p}/{I_p} \right) + \left({EQI_c}/{I_c} \right) + \left({EQI_b}/{I_b} \right) \qquad \text{5-4}$$

Where EQI is the Environmental Quality Index for the physical, chemical, and biological properties, $I_{p/c/b}$ are the numbers of physical, chemical, and biological indicators considered. The EQI has been calculated for the control, low, medium, and high concentrations for both soils for each day (0-1-7-14-36).

5.3.1 Statistical Analysis

Regression analysis were carried out on data related to the physical, chemical, and biological properties analysed using Excel (MS Office) to evaluate the relationship between each variable and their dependencies. Results are shown using draftsman plot (Fig. 1) to understand and display the distribution and patterns of the data. Moreover, using SPSS (IBM, USA), two-way ANOVA tests were carried out to analyse the dependency of each variable on the explosive concentration that was spiked on the soil mesocosms.

5.4 Results

5.4.1 Physical properties

Bulk density and soil particle density (SPD) were measured at day 1 and 36 for the control and the highest contaminated samples. For both soils, both the SPD and the Bulk Density were higher at day 36 for the highest contaminated samples compared to the controls, with a difference of 29% for Soil A and 42% for Soil B. All the calculated values, with an exception for the control sample of Soil B, were higher than 1.8 g/cm³ which is the critical value for sandy loam soils representing an extremely compact soil where root penetration is restricted (Hazelton & Murphy, 2016).

5.4.2 Chemical properties

In Soil A (Fig. 5-1), on average, the control soil had a 62% lower EC value compared to the high contaminated sample (1.83 mS/cm), indicating that the presence of IHE influenced the soil matrix. This was confirmed by the difference in EC detected in soil B (Fig. 5-1) which sees the highest contaminated samples 39% higher compared to the controls. Overall, for both soils, EC characterised the matrices as non-saline. The EC values were also influenced from the amount of water that was found in the soil, therefore, after the 15 days of non-registered rainfall, for all samples the EC registered was 0 mS/cm.

Although the r^2 values are not high enough to indicate a strong correlation, the data suggest a trend between the medium IHE soil contamination levels and the potassium ion concentration in Soil A and B. In contrast, there is a poor correlation between the potassium ion concentration and the high IHE levels spiked into the soil. This suggests that the interaction between K+ and the IHE molecule is less likely to occur when a higher nitrogen content is present in the soil.

A clear correlation was observed between the different IHE concentrations and the soil pH in both soils ($r^2 = 0.74$ for Soil A at the Highest contaminated sample). This correlation was expected as it has been shown that pH influences IHE behaviour in soil (Mark et al., 2016; Temple et al., 2019; Wallace et al., 2011). The pH of the leachate from Soil A remained stable during the experiment. While the pH of the leachate from Soil B increased by 1%, this increase was recorded for all samples including the controls and therefore cannot be attributed to the IHE content.(Mark et al., 2016; Temple et al., 2019; Wallace et al., 2011)

Qualitative assessment of nutrients (Tab. 5-4) has shown a greater change in N and P for Soil B. Soil A had a consistent decrease across all samples in Nitrogen, compared to Soil B where the N behaviour was more variable. For the high and medium concentration samples Nitrogen decreased after day 1, although an increase of N across all samples resulted in a high N concentration at day 7. Soil A and B were also lacking in Phosphorus, which was mostly non detected across both soils.

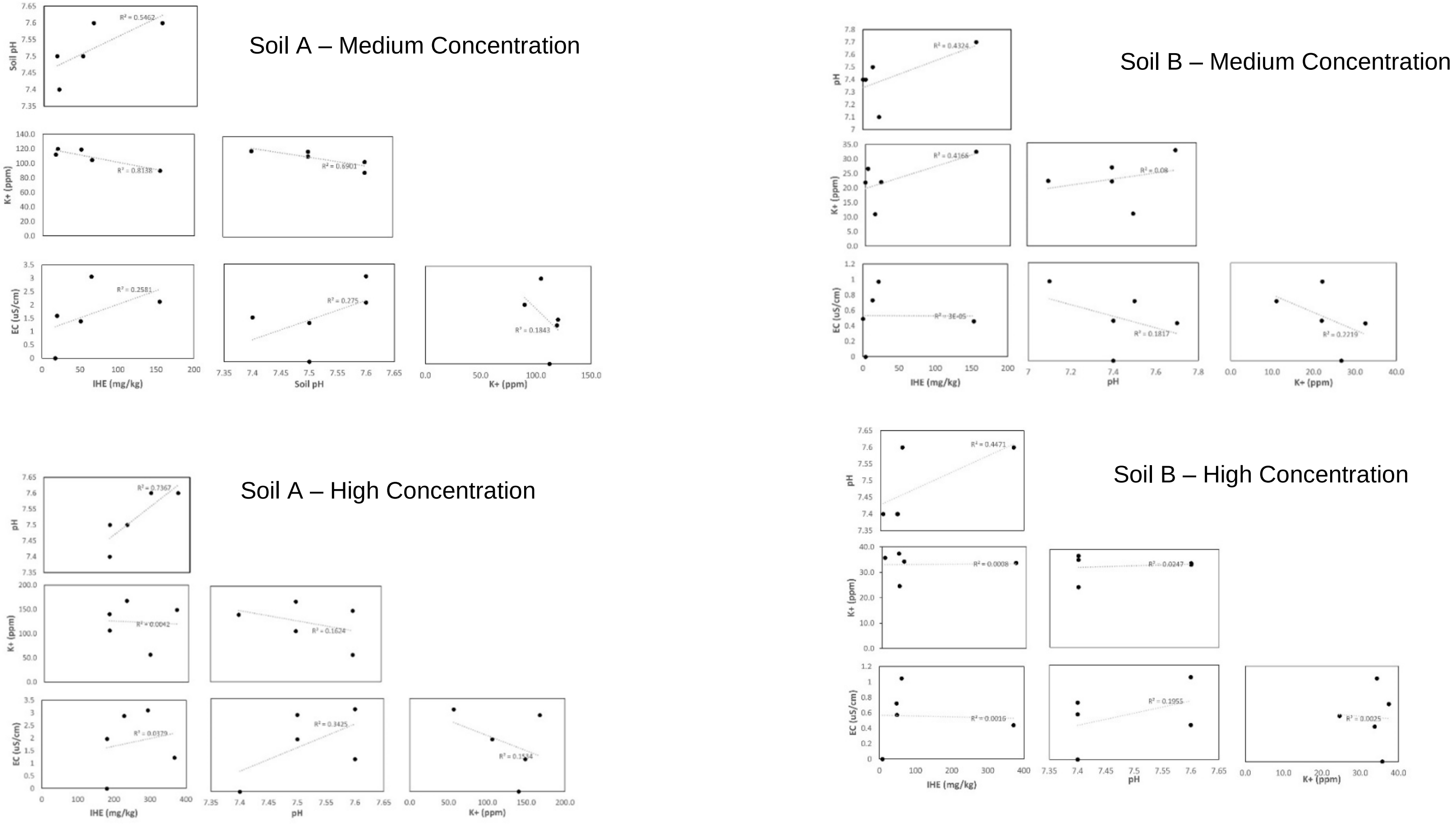


Figure 5-1 Chemical properties and relationships between pH, EC, IHE and K⁺ in Soil A and Soil B in presence of medium and high IHE concentrations

As confirmed from the K^+ availability experiments, total potassium was significantly higher in Soil A compared to Soil B. Total K was also more stable in Soil A, differently from Soil B where an increase in K was determined after day 1 following a regular decrease in all analysed samples.

Table 5-4 Qualitative assessment of N, K and P from the control, low, medium, and high IHE contaminated soil samples.

	IHE Contamination	Nutrient	Day 0	Day 1	Day 7	Day 14	Day 36
Soil A	**Control**	**N**	Low	Medium	Trace	Trace	Trace
		K	High	High	High	High	High
		P	Trace	ND	Low	ND	ND
	Low	**N**	Low	Trace	Low	Trace	Trace
		K	High	High	High	High	Medium
		P	Trace	ND	ND	Low	Low
	Medium	**N**	High	Low	Trace	Trace	Trace
		K	High	High	High	Medium	High
		P	Trace	ND	Low	ND	Trace
	High	**N**	Medium	Low	Medium	Low	Medium
		K	High	Medium	High	High	High
		P	Trace	ND	Low	ND	Trace
Soil B	**Control**	**N**	Low	Medium	High	Medium	Trace
		K	Trace	Medium	Trace	Trace	Trace
		P	ND	ND	ND	ND	ND
	Low	**N**	Low	Low	Medium	Trace	Trace
		K	Medium	High	Medium	Trace	Trace
		P	ND	Trace	ND	ND	ND
	Medium	**N**	High	ND	Medium	Trace	Trace
		K	Trace	Medium	Medium	Trace	Trace
		P	ND	ND	ND	ND	ND
	High	**N**	Low	ND	Medium	Trace	Medium

		K	Trace	Low	Trace	Trace	Trace
		P	ND	ND	ND	ND	ND

5.4.3 Biological properties

Based on CFU analysis, there appears to be a trend in Soil A between the IMX IHE concentration over time and the CFU (Fig. 5-2), with a significant relationship observed ($p<0.05$). After 7 days, Soil A showed an increase in CFU, followed by a subsequent decrease from day 7 to 36. The decrease was more pronounced for low and high IHE concentrations. Furthermore, a two-way ANOVA demonstrated that there was a stronger statistical trend between IMX IHE concentration, soil pH and CFU ($p<0.05$). .

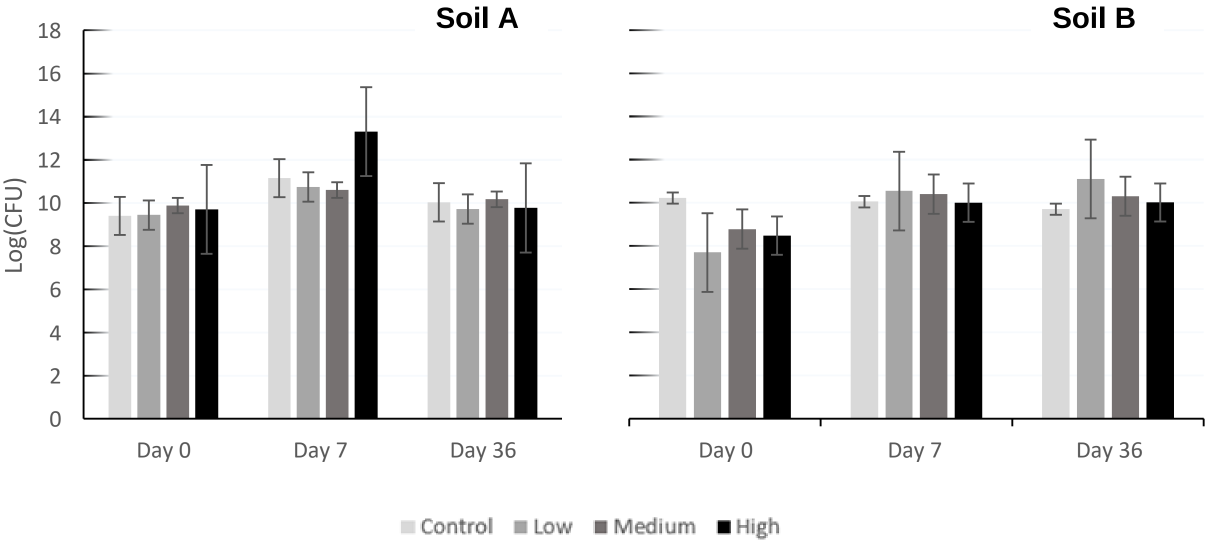


Figure 5-2 CFU/mL at day 0 – 7 – 36 presented in a log$_{10}$(CFU) scale and standard error for each series of calculations.

The same correlation has been found between the rainfall and the CFU in Soil B even though there is a difference in behaviour for the highest contaminated sample. Conversely to Soil A, no significant relationship has been found between the IHE mixture concentration and the CFU counted. Instead, this relationship was found between the soil pH and the CFU (ANOVA $p<0.05$).

5.4.4 Weathering and IHE concentration effect on soil

The experiments were conducted during the summer season in the UK with an average temperature expected to be around 15.6°C, based on the 1981-2010 average (Kendon et al., 2020). the recorded average temperature was 16.6°C with soil temperature recorded, within the first 5 cm, to be 15.3°C. Unexpectedly, during the experiments, rainfall was not registered for 19 days, of which 15 were consecutives (from day 21 to 36). The highest rainfall was registered on day 19 (17.7 mm) with an average rainfall throughout the experiment of 1.6 mm.

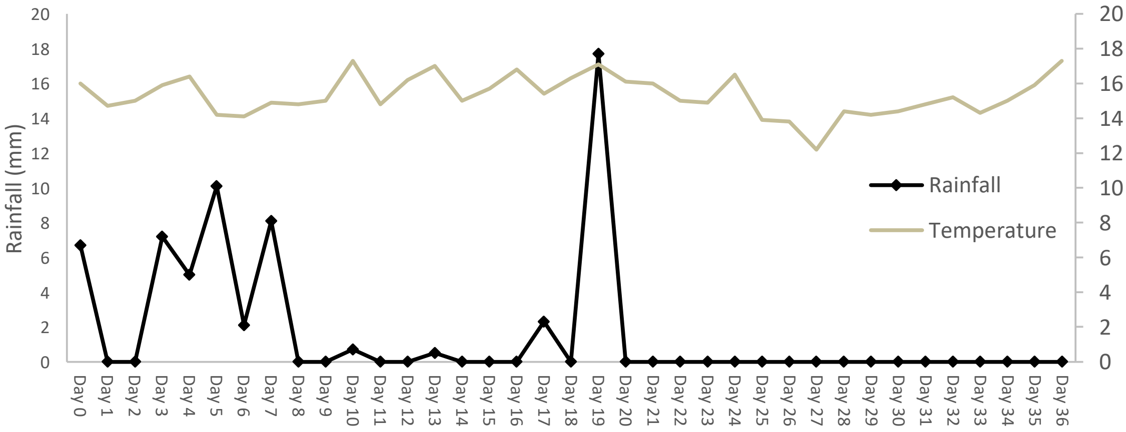
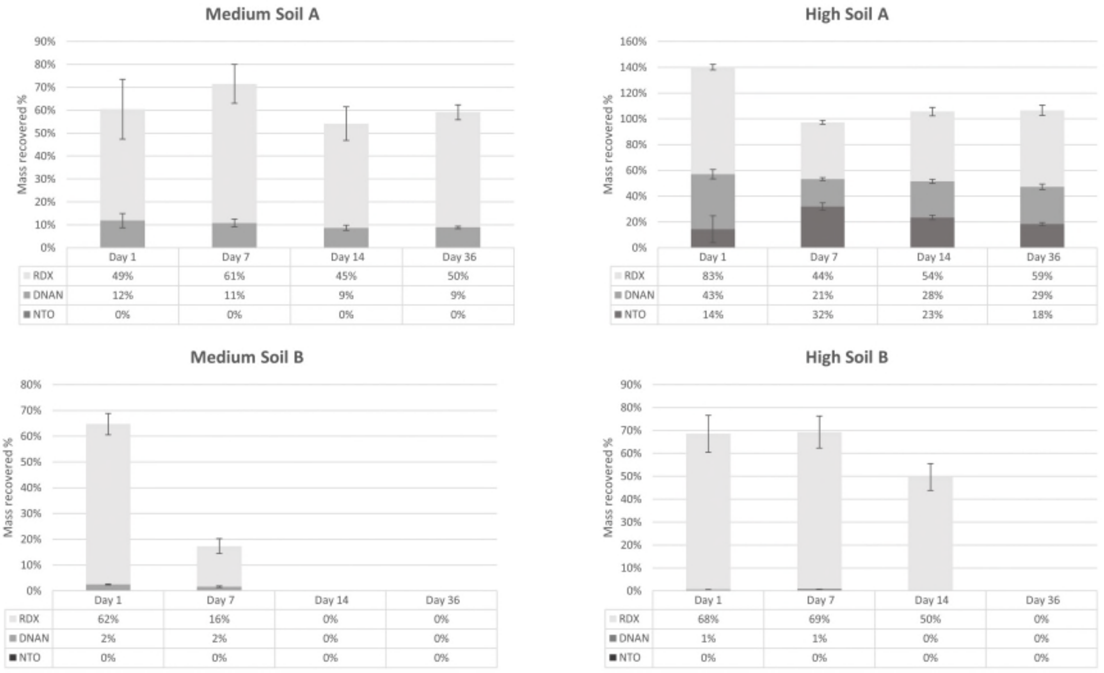


Figure 5-3 Rainfall in mm and soil Temperature (°C) for the first 5 cm, from day 0 to day 36 from the Marlborough weather station.

Rainfall influenced the transport of chemicals within the matrix, with a rise in leachate when the rainfall was at high levels which could increase the transport of the chemicals from soils to groundwater systems (Zhang et al., 2019). As the rainfall was higher in the first part of the experiments (from day 0 to day 20) (Fig. 5-3), a higher dissolution and transport of the IHE mixture was expected during this time. Due to the differences in solubility of the three IHE constituents NTO: 17200 mg/l; DNAN: 216 mg/l, and RDX: 59.7 mg/l (Lent, 2019), it was expected that a higher there would be higher concentrations of NTO and DNAN in the leachate during rainy periods compared to RDX.(Lent, 2019)

Moreover, the amount of rainfall is also associated with a decrease or increase in microbial activity which sees a decline in microbial communities when rainfall is lower (Wu et al., 2020). The CFU calculated in this experiment highlighted the dependencies of the microbes on rainfall, with a strong relationship determined in Soil A ($r^2=0.8$). Consequently, due to the rainfall, which was not registered in the second part of the experiments, a decrease is CFU has been detected in all samples.

From day 0 to 36, the IHE composition was extracted and NTO, DNAN and RDX separately assessed. In the controls (non-contaminated soil), no IHE concentration were found for both Soil A and B. The concentration at day 0 represents the day in which the experiments have been set up and therefore used as the baseline for comparison. Due to the three-week preparation time to enable evaporation of excess water, the concentration of IHE detected was lower at Day 0 than the initial spiked concentration. Therefore, in all the samples contaminated with the lower concentration of IHE (15.34 mg/kg) only 38% and 6% of the concentration, respectively for Soil A and B, has been recovered after 1 day of experiment with the concentration falling to 0 mg/kg at day 7.



Medium Soil A

	Day 1	Day 7	Day 14	Day 36
RDX	49%	61%	45%	50%
DNAN	12%	11%	9%	9%
NTO	0%	0%	0%	0%

High Soil A

	Day 1	Day 7	Day 14	Day 36
RDX	83%	44%	54%	59%
DNAN	43%	21%	28%	29%
NTO	14%	32%	23%	18%

Medium Soil B

	Day 1	Day 7	Day 14	Day 36
RDX	62%	16%	0%	0%
DNAN	2%	2%	0%	0%
NTO	0%	0%	0%	0%

High Soil B

	Day 1	Day 7	Day 14	Day 36
RDX	68%	69%	50%	0%
DNAN	1%	1%	0%	0%
NTO	0%	0%	0%	0%

Figure 5-4 Recovered Mass (%) from soil at each day of collection. The recovery percentages for each component were calculated with respect to the initial concentration of 100% of each component on day zero.

In Soil A, at the medium concentration, 23% of the IHE mixture has been recovered on day 0 of experiment, with a decrease and then a stabilisation of the IHE mixture in the soil which has been recovered with an average of 48 ± 5% from day 1 to day 36 compared to day 0. NTO, being the most soluble of the three compounds, was not recovered in soil (Fig. 5-4), although it has been found in its original form in the leachate at day 1 (44.7 mg/l) and day 14 (33.5 mg/l). DNAN was recovered in all samples with an average concentration detected of 4.6 ± 1.1 mg/kg in soil A. As expected, RDX was the most stable molecule with a concentration that varied from 31.8 mg/kg at day 0 to 11.7 mg/kg at day 36 where almost 50% was regularly found in the soil throughout the experiments. RDX was also recovered in water at each day of experiment ranging from 2.6 to 0.5 mg/l.

At high concentration in Soil A (Fig. 5-4), a higher percentage of the explosive mixture was recovered at day 0 (117.6 mg/kg) with no degradation, during the three weeks of preparation, of the RDX compound and low degradation of NTO and DNAN being mostly recovered in the leachate at day 1. The total degradation in soil from day 0 to day 1 was negligible with a recovery of 5% higher compared to the beginning of the experiment. This recovery is highlighting the difficulties in analysing explosive compounds, with NTO being the most difficult to detect, therefore an error was expected has highlighted in previous work (Temple et al., 2019) due to the heterogeneous nature of the soil matrix. NTO was recovered in high quantities in the water leachate ranging from 163.7 mg/l at day 1 to 73.2 mg/l at day 36, emphasizing its rapid transport through soil due to the diminishing leachate concentration over time. Figure 5-5 depicts a reduction in the concentration of the explosive, indicating the potential degradation of the substance in aqueous environments. This observation suggests the likelihood of the dissolution of the explosive in the event of precipitation. DNAN was not significantly detected in water (0.6 mg/l at day 1) remaining mostly stable during the experiments with only 37% decrease in recovery from day 0 to day 36. 55% and 68% of the total RDX was recovered, respectively at the medium and high concentration after 36 days (12.8 mg/kg; 36.7 mg/kg). It should be noted that several factors can impact the concentration of the explosive in the leachate, including the quantity of rainfall experienced during a given period, the potential interaction between the individual components of the explosive and the soil matrix, and the solubility of each of the explosive's constituents.

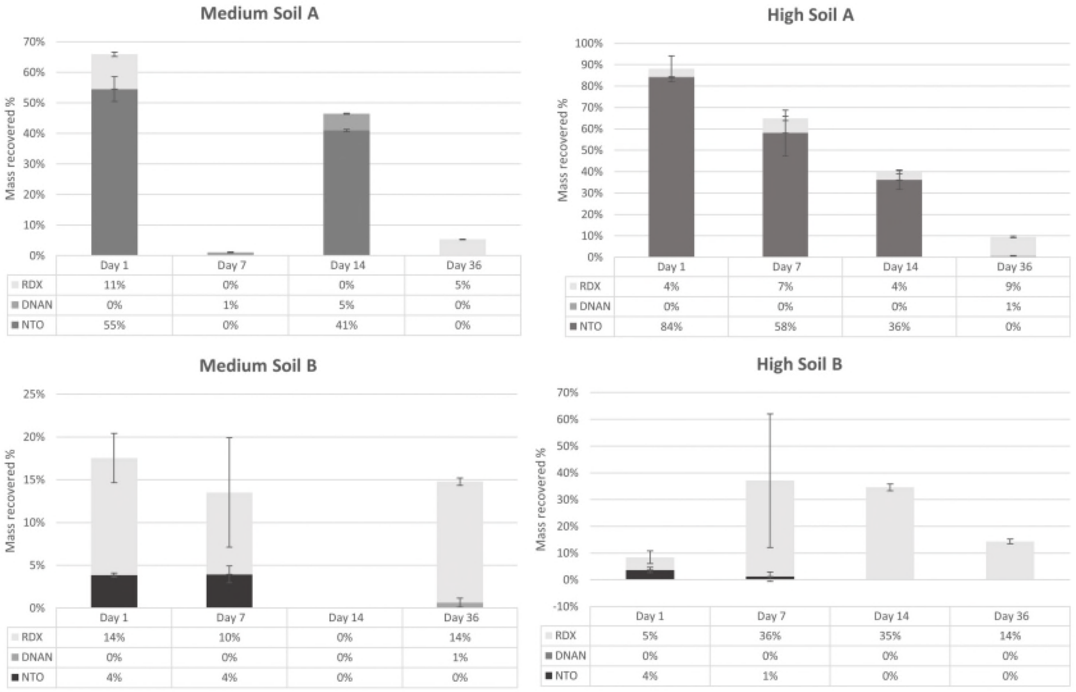


Figure 5-5 – Mass of explosives recovered in the leachate water (%) considering the explosive spiked on day 0.

In Soil B at the medium concentration only 18% of the IHE mixture was recovered at Day 0 with a further decrease in soil of 42% from the start of the experiment to day 1 (15 mg/kg) and 71% at day 7 (8 mg/kg). NTO, DNAN and RDX were also detected in the collected leachate for the medium concentrated sample. NTO was not recovered in soil, but it was detected in water at day 1 (3.1 mg/l) and day 7 (3.0 mg/l) showing the low adsorption to Soil. DNAN, decreased in concentration from day 0 to day 1 of 77%. DNAN was not detected in water leachate until day

36 when a small amount (0.3 mg/l) has been recovered. RDX decreased by 35% on day 1 and 67% on day 7, compared to the concentration detected at day 0 (22 mg/kg). From day 14 to day 36 RDX was not recovered in soil, although 3.3 mg/l was detected in water leachate at day 36. The increased rate of transport of RDX in soil B compared to Soil A can be attributed to the decreased organic content in the matrix. No NTO was recovered from the high concentration samples of Soil B, although some explosive was recovered in water at day 1 (7.2 mg/l) and day 7 (2.3 mg/l). This suggested that NTO underwent chemical changes, as it was not found in either soil and only 6 water samples in its original form. . DNAN recovery was lower at day 1 and similar at day 7, compared to the medium contaminated samples of Soil B. likely that degradation was more rapid in Soil B compared to soil A as DNAN was recovered in much lower quantities in its original form. A higher recovery of RDX from Soil B compared to the medium concentration was detected, which remained stable until day14, with 31% of the explosive recovered compared to day 0. Although, no RDX was detected at day 36 in soil. RDX was regularly recovered in the water leachate with an average of 12.5 mg/l.

As indicated in Figure 5-4 and 5-5, the recovery of NTO in Soil A was significantly higher than in Soil B, particularly at medium and high concentrations. This can be attributed to the higher organic content in Soil A, which facilitates the retention of polar compounds through interactions with soil particles. The recovery of NTO in Soil A was found to be highest in the first 7 days of the experiment, with almost 95% of the explosive being recovered in total between the water and the leachate. However, from day 14 to day 36, there was a considerable decrease in NTO recovery, with the majority of the explosive being retained in the soil due to the absence of rainfall in the later stages of the experiment.

On the other hand, RDX was found to be the most stable explosive component, with recoveries as high as 100% in Soil B at day 7, indicating its resistance to degradation by microorganisms, even in soils with high microbial content. In Soil B, the recovery of RDX was consistent throughout the experiment, being regularly recovered in both water and soil. In Soil A, however, the recovery of RDX was lower compared to Soil B, despite having higher organic content, suggesting that the organic content alone cannot protect the explosive from degradation. In contrast, DNAN displayed a high affinity for soils with higher organic content, showing a higher recovery rate and remaining mostly in its original form. The recovery of DNAN was found to be regular throughout the experiment, with recoveries of 12% and 31% at medium and high concentrations, respectively, in Soil A. In a soil with low organic matter and high microbial activity, it is more likely that DNAN will be broken down into its degradation products. In conclusion, the organic content of soil plays a significant role in the retention and degradation of explosive components, with polar compounds being retained more efficiently in soils with higher organic content. The stability of the explosive component to microbial degradation is also an important factor to consider, with RDX being the most stable and NTO and DNAN being the most susceptible.

It is worth noticing that even though IHE was not detected in some of the samples the concentration may be lower than the limit of detection (<0.004).

5.4.5 Preliminary Environmental Quality Index (EQI) calculation

Each parameter has been scored following Amacher et al. (2007) to provide a list of SQIs based on the calculated experimental values and theoretical values taken from Lenka et al., 2022 when scores could not be derived (Table 5-6).

Table 5-6 Example of chemical properties, for Soil A at medium concentration, scored for the calculation of the EQIc. A value of “0” was selected when missing data were present.

Soil A chemical properties		Value obtained from experimental analyses					Scored values					Reference/Technique used
		Day 0	**Day 1**	**Day 7**	**Day 14**	**Day 36**	**Day 0**	**Day 1**	**Day 7**	**Day 14**	**Day 36**	
pH		7.6	7.6	7.4	7.5	7.5	1	1	1	1	1	Amacher et al. (2007)
EC		2.1	3.01	1.6	1.4	0	3	3	3	3	0	Amacher et al. (2007)
CEC		0	0	0	0	0	0	0	0	0	0	Missing analyses
K^+	**Nutrients**	90	105	120	119	112	0	1	1	1	1	Amacher et al. (2007)
N		4	2	1	1	1	4	2	1	1	1	“More is better”
P		1	0	2	0	1	1	0	2	0	1	“More is better”
SOC		0	0	0	0	0	0	0	0	0	0	Missing analyses

Nutrient values obtained were then averaged. SOC values were scored as “0” (Tab. 5-6) as soils could not be oven dried due to the explosive nature of the samples. DNAN degrades at approximately 200C therefore the procedure could have impacted the nature of samples giving false results. Therefore SOC values were not fit-for-purpose for the EQI although more research is needed for application of SOC calculation methodologies to ensure that quantitative analyses are carried out.

The biological, chemical, and physical scores were summed according to formula (5-2) (Table 5-7). Following the scoring, data were added up and adjusted based on the number of indicators that have been experimentally analysed. The adjusted scores were summed up following equation (5-3) and an EQI was obtained for each day of experiment at each concentration (Supplementary material).

Table 5-7 Example of calculation of EQIc for Soil A at medium concentration.

Soil A – Medium contamination chemical properties	Total Score	N Indicators	EQIc
Day 0	5.7	5	1.14
Day 1	5	5	1
Day 7	5.3	5	1.06
Day 14	4.7	5	0.94
Day 36	2	5	0.4

Due to the limitation of the analyses of the explosive contaminated sample, the chemical indicators were the most influential parameters in EQI as chemical parameters were mostly analysed for the preliminary EQI, respectively 60% and 76% on average for Soil A and Soil B, followed by the biological section (23% for Soil A and 20% for Soil B) and the physical indicators (1% for both Soil A and B). Therefore, because further studies are needed to understand how to overcome the explosive contaminants issues for some analyses, the EQI obtained are preliminary values. Although, these values will provide insight on possible influences of explosives on soil determining a baseline until further analyses can be done to have more comprehensive values.

In both soils (Fig. 5-5), the EQIs had similar variation, ranging from 0.63 to 1.87 for Soil A and 0.60 to 1.80 for Soil B. The EQI calculated for the non-contaminated samples was, as expected, lower for Soil B, compared to Soil A, as Soil B is a land degraded matrix. Although, the EQIs for Soil A and B did not decrease overtime having only a 1% difference between the first to the last day of collection. As expected, as the contamination in the samples increased so did the differences in EQI between the soils. At the low, medium, and high concentration Soil B average values were 6%, 20% and 24% lower respectively compared to

Soil A at the same concentrations. In fact, the difference between the highest affected sample in Soil A (with the lowest EQI on average – low contaminated samples) and the control, differed by only 1% compared to Soil B where this difference was 24%. Overall, the EQI increased for all the samples at Day 7, again highlighting the importance of the weather conditions as a main influential factor for the analysed properties.

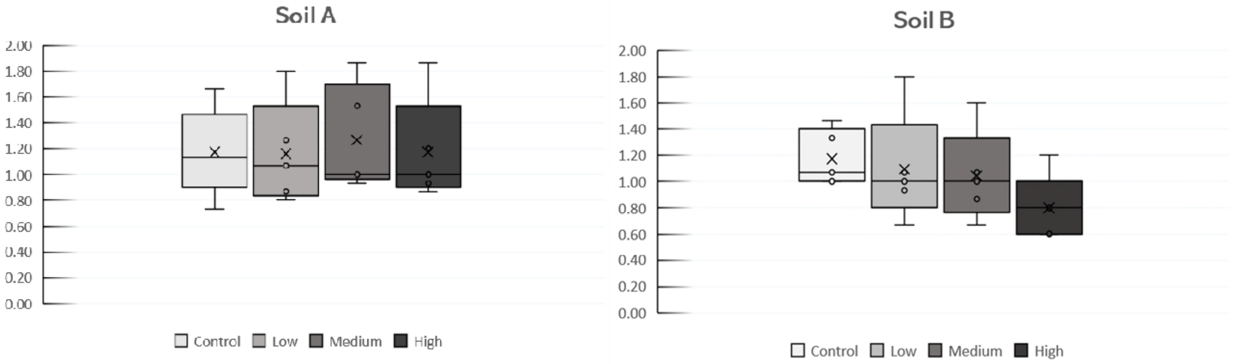


Figure 5-6 Environmental Quality Index (EQI) calculated across all the samples for the control, lowest, medium, and highest concentration.

Chemical properties, which were the most studied in this work, significantly affected the outcome of the EQI and further work is needed to increase the amount of data available for the physical and biological values. However, these preliminary results have shown how Soil B was increasingly affected by the IHE contamination, subsequently increasing the rate of degradation. In Soil A, this difference could not be determined, meaning that the explosive components are not currently affecting the soil properties at the studied concentrations

5.5 Discussion

The increase interest in understanding soil changes due to IHE exposure, has been led by a rise in usage of these new explosive mixtures and further discoveries of soil surface and groundwater contaminations (Jenkins et al., 2006; Morley et al., 2006; Temple et al., 2018b). The fate and transport of the IHE compounds is guided by the soil composition (Monteil-Rivera et al., 2021; Taylor, Dontsova, et al., 2017; Temple et al., 2018b) is influenced by the soil properties.

Sandy Loam and Loamy Sand, which have been named Soil A and B, have many physical similarities but were characterised by more significant chemical differences. Soil A, had on average the highest K+ content, pH, and EC. Moreover, because Soil B was collected from a training range, degradation of the matrix has led to a different relationship with the chemical compounds (Tetteh, 2015) which were spiked for the evaluations.

Because of the relationship between K and N components (Johnston & Milford, 2012), which increases N adsorption as K availability rise, Soil A retained NTO, DNAN and RDX more compared to Soil B,, due to an increase in adsorption processes which has been also consistently reported for DNAN in the literature (Linker et al., 2015). This retention was strengthened by the high pH (8.7) increases the interaction between the NTO and the soil matrix (Mark et al., 2016). This interaction can also lead to changes in the NTO molecule increasing degradation due to polar interactions.. This study did not analyse for degradation products, as out of scope, although, because of the high organic content in Soil A it was expected to not find NTO in its original form, because of the increased likelihood of NTO degradation products. Conversely a high concentration of NTO was recovered in the leachate from Soil B suggesting that when soil is more prone to degradation, it is less likely for the explosive to accumulate in the soil system. This suggests that there is a higher likelihood of the chemical contaminating groundwater systems. RDX, was recovered in both soils, with highest retention in Soil A due to the affinity between the molecule and the organic content, which was higher compared to Soil B (Lent, 2019). RDX is known to be the most stable compound in the IHE (Lent, 2019; Temple et al., 2019), and therefore as expected was generally recovered at high concentration in both soils in the medium and high contaminated samples. Moreover, compared to NTO and DNAN, RDX was highly resistant to microbial degradation (Lent, 2019), confirmed by the low degradation rate reported for Soil B, which had the highest microbial content.

Therefore, the IHE are less likely to transport to sub-soil and groundwater systems in Soil A, although there is an increased likelihood of degradation products and subsequently an increased contact with the soil matrix. It may be expected that in soils with increased contact time with IHE, there would be an increased likelihood of negative impacts, however in this work the opposite was observed with Soil B being more effected by the IHE.

Similar physical changes were observed in the soil matrix for both the control samples and the contaminated samples. These changes cannot to be attributed to the presence of IHE, so must be attributed to the method in which the mesocosm were set up and the weather conditions.

There greater variation in the chemical properties in Soil B compared to Soil A. In general, the EC was most significantly influenced in both soils, which was expected as increase in EC has been previously used as an indicator of pollution (Edwin-Wosu & Nkang, 2019; Gevao et al., 2000). Contaminants can increase the concentration of ions in the soil, which increases the soil's ability to conduct electricity, therefore it can be a cause for concern as certain contaminants can be harmful to plants and animals. The controls had a 60% and 40% lower EC for Soil A and B respectively compared to the contaminated samples of the same soil. This change is likely de to the increase in nutrient content (Othaman et al., 2020) provided by the nitrogen rich IHE. As expected, the difference was more significant (60%) in Soil A due to the greater retention of IHE constituents. In Soil A, this was confirmed by the increase in nitrogen content compared to the control. pH slightly decreased overtime in all samples, including the controls, therefore those changes were not attributed to the presence of IHE, although, as highlighted above, pH can alter the retention of IHE in soil and therefore is a key parameter to observe.

(Edwin-Wosu & Nkang, 2019; Gevao et al., 2000)(Othaman et al., 2020)Biological changes were evaluated by the microbial abundance which was, at the beginning of the experiment, 85% higher in Soil B compared to Soil A. Although, the microbial abundance was mostly subject to the weather conditions with an increase in microbial abundance during the first 7 days when the highest level of rainfall was recorded.. Further studies are needed to investigate the relationship between potential degradation product formation and the CFU in the soil. For the same reason, a decrease in CFU was recorded all samples at day

36 due to the unexpected 20 day dry spell prior to completion of the experiments. It is worth noticing that at day 36 the microbial abundance was highest in the high concentration sample of Soil B, in contrast to Soil A where the highest microbial abundance was found in the control. More studies are needed to analyse if this difference is due to the high explosive content. Due to the low IHE concentration in soil, the biological parameters were not affected by the IHE components at the concentrations investigated, which was expected due to the concentrations being were lower compared to the latest ecotoxicological data (Dodard et al., 2013; Monteil-Rivera et al., 2021).

The EQI value was calculated based on the scoring of different soil parameters. Although, because of the challenges faced when explosive contaminated samples further studies are needed to create a more comprehensive visualisation of the environmental challenges. Therefore, based on the current analyses a preliminary EQI was calculated, and values determined for both soils. For Soil A, the EQI value suggest that at the studied concentrations the IHE are not negatively impacting the soil health. However, this cannot be said for Soil B where a significant decrease in EQI has was recorded between the low and high concentration samples. A reasonable number of live rounds fired annually is up to 10,000 (Galante et al., 2017), however this work has shown that with contamination levels from as few as 100 detonations soil quality can deteriorate. For large live-fire ranges 100 detonations can occur within two weeks, which would correlate to a major decrease in soil quality over 1 year for Soil B. This highlights the importance of continuing research into the threat that IHE pose to some soils, such as Soil B, a naturally degraded soil likely to be found on training ranges, as the investigated contamination levels are all below reported LD_{50} values suggesting that soil health begins to deteriorate long before accepted toxic concentrations are reached (Dodard et al., 2013; Monteil-Rivera et al., 2021).

5.6 Conclusion

In this work, the impact of the IHE mixture has been assessed on two different soils, a pristine sandy loam and a degraded soil collected from a military training range. It has been found that IHE behaviour in the environment is dependent on the soil matrix, such as whether the soil is initially degraded or non-degraded. The pristine soil (Soil A) was found to have more chemical interactions with the IHE constituents, which appeared to reduce the consequences on the soil matrix. The degraded soil (Soil B) was more sensitive to the presence of IHE, with significant changes to nutrients and EC observed, suggesting that potentially IHE has a great impact on degraded soil. Therefore future research is needed to investigate the cumulative impact of IHE on degraded soils as it is more likely to be affected by the explosive components. Although, it is worth highlighting that soil composition and external weather conditions play a key role on the transport and fate of explosive residues. Therefore, further studies are needed to quantify the consequences after an increased number of detonations (>10,000), as 100 detonations, the equivalent in this study, is not representative of actual training activities. Currently, SQIs are not comparable between different sites, this is because the SQI has a different value depending on the chosen indicators and the different areas. The EQI, developed here is based on the same concept but enables comparison and therefore should start generating comparable data between sites enabling a standardise soil quality scale. It is concluded that compared to traditional explosives IHE compositions are unlikely to have the same major impact on the environment at the studied concentrations for pristine soil, although further studies are needed to determine at what point the IHE concentration can cause a major stress on the environment and potentially have an impact on the biota and people`s health especially on degraded soils.

6 Overall conclusion, research implications and recommendation for future work

Protecting the soil environment has become one of the biggest concerns of the last two decades, with an emerging increase of dedicated research and legislation around the world to ensure safety of soils and a decrease in soil degradation (DEFRA, 2018; European Commission, 2021; Ministry of Defence, 2021; UNCCD, 2017). Soil provides multiple important functions, such as provision of food and raw materials, a platform for urban development and human wellbeing and filtering and transforming media for water, nutrients, and carbon, although, because of the indirect relationship between soil and possible consequences on people's health, is currently still one of the least studied matrices (Teng et al., 2014). The relationship between a contaminant and soil, is scarcely investigated, leaving big gaps in understanding especially when brand-new contaminants, whose behaviour and consequences are unknown, called Emerging Contaminants (ECs) are released in the environment (Sauvé & Desrosiers, 2014). This category comprises also of contaminants that have been in the environment for a long period of time but only now there are environmental concerns about their behaviour. ECs have broad applications, from household products to military weapons, rendering this a major reason of concern for the MoD, as the biggest holder of Sites of Special Scientific Interest (SSSI) in the UK (Ministry of Defence, 2021). For this research military related ECs have been considered:

- Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS): used previously in the production of Teflon, food packaging, Aqueous Film Forming Foam (AFFF) used for fire-fighting training (Place & Field, 2012; Turner et al., 2021);
- Cypermethrin: widely used insecticides, applied on military clothing for protection of military personnel overseas (Environment Agency, 2019; Vatandoost et al., 2010);
- Insensitive High Explosives (IHE): currently in military operations and in training areas around the world in different combinations of constituents including 2,4-dinitroanisle (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and

1,3,5-Trinitroperhydro-1,3,5-triazine (RDX) (Arthur et al., 2018; Singh et al., 2010);

Data availability for these contaminants varies, depending on the amount of research that has been done on the specific chemicals (Das & Mukherjee, 2003; Lent, 2019; Scher et al., 2018). Therefore, there is a need to explore more the impact of these ECs on the soil environment.

The aim of this PhD research was to develop an analytical framework for soil to facilitate early identification of the deleterious effects of emerging contaminants and chemicals of military concern. During this research the literature review (**Chapter 2**) identified that to date, there is no wide fit-for-purpose procedure to evaluate the impact of contaminants in soil, independently from the land management, because research tend to focus on soil assessment for crop management purposes.

Different attempts have been made using ecotoxicological data as a representation of the environment in which the entity lives to understand, which can be used to understand potential consequences on soil of different contaminants. Although, different developed procedures to relate this data to change in soil basing part of the judgments on expert's opinion (ECHA, 2008; USEPA, 2003c) with tedious processes rendering the system biased. Moreover, the problem increased when data is not available, this being the case for most ECs. The research in this thesis was therefore designing and developing a soil analytical framework for two main scenarios: (1) when there is wide eco-toxicological data availability; (2) when data on the EC are not available.

6.1 **Overview of the key findings and contribution to knowledge**

To address the knowledge gap identified above, the first phase of the work described in **Chapter 3** was to determine a soil assessment framework for contaminants when a wide body of secondary ecotoxicological data are present.

Different procedures that are currently in place to evaluate threshold values (values under which no changes are expected in the environment) in soil were assessed, which based their decision-making on secondary data availability. The United States Environmental Protection Agency (USEPA) and the Environmental Chemical Agency (ECHA) developed procedures for the calculation of Soil Screening Values (SSVs) and Ecological Soil Screening Values (Eco-SSL), respectively (USEPA, 2003; ECHA, 2008). However, these two methodologies are relying on researchers and experts in undertaking the task therefore making the process subject to bias. To minimise the impact of bias decisions, these two methodologies have been merged to develop a hazard-based rating assessment, focus, but not limited to, different defence-related contaminants, using a traffic light (red for warning and the activity should stop, amber for further investigation and green for a safe environment) system. A traffic light approach is an easy to interpretate data as it has a clear visual display which can provide an early warning approach for stakeholders to identify areas that require further investigation. The developed hazard-based rating assessment was designed to categorise the chemicals into low, medium and high environmental hazards priority to inform and ease the decision-making process for contaminated areas to ensure that sustainable operations are carried out.

The merged proposed methodology procedure has 8 different steps. The first 4 steps used the USEPA procedure from the analyses and scoring of values gathered from a literature search. Differently from the USEPA procedure, more values were considered (e.g., EC_{10}, EC_{20}, EC_{50}), rendering the body of data wider for the evaluation of the hazard-scale. From step 6 to 8, the ECHA procedure was used, and based on the USEPA criteria, values were considered from different databases (e.g., PubChem, EcoTox). Using frequency analysis and mathematical calculation of the PNEC value, a low, medium, and high hazard level were determined for each considered contaminant. The understanding and calculation of different levels of hazard can define a baseline for future human toxicity evaluations as pre-empting possible consequences by just calculating the amount of contamination detected in soil. Different hazard-levels have been calculated for TNT, RDX, Cypermethrin, PFOA and PFOS as defence-related chemicals based on ecotoxicological secondary data as representation of risks to the matrix in which the entity leaves.

Although, there are cases in which the procedure developed in **Chapter 3** cannot be applied because of missing information and ecotoxicological data for the contaminants. This is the case for Insensitive High Explosives (IHE), where there is missing data related to the potential consequences of these contaminants on the soil environment(Arthur et al., 2018; Lent, 2019). Thus, the first step for carrying out a proper soil assessment evaluation, was to understand the actual quantities that can be discharged on soil during military training activities. In that respect, **Chapter 4** focussed on calculating the potential of a IHE mixture (3-nitro-1,2,4-triazol-5-one (NTO) (53%), 2,4-dinitroanilisole (DNAN) (32%) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) (15%)) to be deposited on soil after a full-order detonation of a 155 mm Insensitive Munition (IM), as currently increasingly used around the world. Therefore, an experiment was set up on a live-fire training area where a sampling arena was created by levelling 12 tonnes of inert fine particle sand to a depth of 5 cm in a semi-circular area (radius 10 m) on top of an impermeable plastic groundsheet for the collection of the post-detonation residues. This set-up avoided cross-contamination from the already contaminated area to ensure that the residue collected was only from the experimental detonations. Three detonations were carried out with the munition positioned in different directions (vertical and horizontal) each time, to ensure a complete assessment of the dispersed residue deposition. Moreover, multi-Incremental Sampling methodology (ISM) was carried out as currently proven to characterise large areas and is reproduceable and representative, particularly for non-homogeneous contamination (Jenkins et al., 2005). The explosive residues collected from the 155mm detonation were slightly higher compared to the values recorded for traditional explosives (RDX/TNT) filled munitions (Hewitt et al., 2005). The potential accumulation of DNAN was specifically higher compared to previous research where 0.04% of DNAN was deposited, on average, from the original composition. This value is higher than previously collected residues from a 61mm and 80mm filled with IHE, with respectively 0.006% and 0.001% recovered (Walsh et al., 2014). This deposition is a cause for concern as DNAN, compared to the traditional explosive TNT, has a higher toxicity. Trace NTO was recovered, where on average 0.01% of NTO mass was identified, in lower amount compared to residues from the 60 mm and 81 mm artillery shell, which were respectively 0.4% and 1.2%. Even though NTO is less toxic compared to the other explosive components, a concentration of just 10 mg/L can discolour water, which is considered, under multiple UK and European regulation, pollution (Tennant et al., 2019). RDX was not detectable following the detonations, as being just 15% of the entire IHE composition, although, being RDX a stable chemical compound it is expected that after several detonations, accumulation of RDX can be of concern. Therefore, results from **Chapter 3**, while the deposited concentrations may not be of immediate concern after a single detonation, care must be taken if large quantities of IMX-104 filled munitions are to be used for training to manage accumulation and minimise environmental impacts. The training environment is particularly relevant as the accumulation of DNAN and NTO is dependent on the weather conditions and therefore environmental management techniques must be chosen for their suitability to the local environment.

To understand the environmental impact of the explosive residues collected in **Chapter 3**, experimental analyses have been carried out in **Chapter 4** using soil mesocosms to understand the consequences of the IHE on different types of soil. Two soils with similar physio-chemical characteristics were chosen, although for comparison purposes, one was a pristine soil and the other a land degraded soil collected from a training range where regular activities are ongoing. Both soils were spiked with the IHE composition at a low, medium, and high concentration using data from **Chapter 3**. Soil indicators analysed, were based on the literature review (**Chapter 2**) in which a series of parameters, to ensure a complete evaluation of the biological, chemical, and physical section of the soil, were selected. Analyses confirmed that the IHE fate and transport is influenced by soil properties as well as weathering processes. NTO, DNAN and RDX were mostly influenced by parameters such as the amount of rainfall, soil pH, soil organic content and microbial abundance. The pristine soil, with a higher organic content, electrical conductivity (EC) and potassium salt (K+) availability, compared to the land-degraded soil, retained the IHE mixture more. This relationship was not solely based on the organic content, which was higher for the pristine soil, but also based on the high likelihood of interaction between the soil nitrogen and the high potassium content, and the high pH (8.7) which renders the negatively charged molecule, NTO, is more likely to interact with the soil matrix. It was further concluded that the likelihood of the IHE mixture to accumulate in the pristine soil was 50% higher than the degraded soil. This finding suggests that IHE residues on training range are more likely to reach groundwater systems and ultimately impacting people’s health.

A problem encountered in **Chapter 2** was there is currently not a quantifiable way to understand soil changes independently from land management. Therefore, using the results collected in **Chapter 5** and the analyses from **Chapter 2**, a novel set of Environmental Quality Index (EQI) has been developed and calculated.

In **Chapter 2** it has been defined that currently Soil Quality Indexes (SQI) and Soil Health evaluations (Andrews et al., 2002; Cardoso et al., 2013; Chaves et al., 2017; Doran & Doran, 2002; Maikhuri, 2012), are used for quantification of the healthiness of soil. Although most of the research focussed their analyses on crop production, influencing the soil parameters choice, as guided by the ultimate purpose of the land.

Moreover, once the parameters were analysed, Principal Component Analyses (PCA) was carried out to evaluate the most influential parameters. Each parameter was then scored, using literature data or the “low is better” “more is better” analyses and summed up to quantify the quality of soil. Although, different are the problems with this approach. Firstly, the choice of the indicators is only based on the experts’ opinion which is related to the land management purposes; secondly, a PCA analyses eliminates soil indicators that might be essential for long term evaluations; thirdly, results within different areas are not comparable as the parameters analysed. Therefore, the EQI start with the premises that a fair comparison is only achievable if the same parameters are analysed, and the selected parameters which have been analysed and **Chapter 5** are the results of the literature review undertaken in **Chapter 2**. Moreover, each parameter should have the same weight, therefore, no value is excluded for the analyses, rendering the process comparable within different sites.

In **Chapter 5**, the first analysis with the EQI has been carried out, as a first step for a future, completer and more comparable, soil analytical framework. Preliminary results for the EQI in **Chapter 5**, showed that, for IHE that was utilised during the experiments (comparable to 100 detonations on a training range, equivalent to 4 days of training in the US) is not currently of concern when a pristine soil is considered because the EQI value did not vary from the clean samples to the highest contaminated samples. Cumulative deposition over a full year of training would equal to level of up to 4000 mg/kg, although, deposition and accumulation will be highly dependent on rate of infiltration into soil with rainfall, and the rate of degradation of the explosive composition. In a worst-case scenario, such levels would then pose a risk to both environmental and human health.

A different result for the EQI of the land-degraded soil showed that there is a higher likelihood for the IHE to have major consequences on a degraded soil. This assumption is based on two main reasons: the EQI was 32% lower for the highest contaminated samples to the clean samples, after a concentration comparable to 100 detonations; on average, on a training range 10000 detonations are carried out in 1 year of activity (Galante et al., 2017).

Overall, results from this thesis have suggested a novel approach for standardising for soil evaluation for emerging contaminants that will contribute to the development of a. soil analytical framework. The key research outputs provide solutions to two scenarios, 1 – where literature data is available and 2 – where data literature is unavailable to proactively identify potentially hazardous contaminations in soil. The positive aspects of this are early warning signs providing a cost-effective approach to eliminate the need for remediation as management procedures are already in place. Moreover, when this approach is routinely carried out results will contribute to the improvement of improving decision-making processes for Environmental Risk Assessments (ERAs).

6.2 **Further Work**

The developed analytical frameworks are providing a starting point to have a more independent soil evaluation which is not guided by the land management but has a much broader application. However, further work needs to focus on proving these methodologies as a wider proof of application. Future work might include:

- Further mesocosm experiments evaluating the impact of IHE on a wider range of soils can provide more insight on the influence that the IHE can have on the wider environment;
- Longer experimental analyses with larger scaled soil mesocosms increasing the depth of the soil, to evaluate differences at different depths;
- Experimental analyses with an increased concentration of IHE;
- Further experimental analyses to better define the significance of the medium and high hazard levels developed in **Chapter 3**
- Integration of the tools provided in the ERAs decision-making process

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APPENDICES

Appendix A Published papers, Conferences and Outputs

A.1 Published Papers and Book Chapters:

In addition to the work reported as thesis chapters, the following work was also published during the PhD from the PhD work and other collaborations:

Persico, F., Temple, T., Ladyman, M., Gilroy-Hirst, W., Guiterrez-Carazo, E., & Coulon, F. (2022). Quantitative Environmental Assessment of Explosive Residues from the Detonation of Insensitive High Explosive Filled 155 mm Artillery Shell. *Propellants, Explosives, Pyrotechnics*, *47*(3), e202100220. https://doi.org/10.1002/prep.202100220

Persico, F., Coulon, F., Ladyman, M., & Temple, T. (2022). Development of an environmental hazard-based rating assessment for defence-related chemical compounds in ecological soil systems. *Environment International*, 166, 107392. https://doi.org/10.1016/j.envint.2022.107392

Ladyman, M., Gutierrez-Carazo, E., **Persico, F.**, Temple, T., & Coulon, F. (2022). Assessing the performance of environmental management in academic research laboratories. *Heliyon*, *8*(3), e09135. https://doi.org/10.1016/j.heliyon.2022.e09135

Persico, F., Gutierrez-Carazo, E., (2022). An introduction to risk analysis for scientists and engineers. In T. Temple and M. Ladyman (Eds.), *Challenges in Risk Analysis for Science and Engineering: Development of a common language*. IOP Publishing.

Gutierrez-Carazo, E., **Persico, F.**, Ladyman, M., Temple, T., Coulon F., (2022). Minimising the risks to decision-making by selecting representative experimental methods for environmental science research. In T. Temple and M. Ladyman (Eds.), *Challenges in Risk Analysis for Science and Engineering: Development of a common language.* IOP Publishing.

Persico, F., Coulon, F., Ladyman, M., Lopez, C.F. & Temple, T. (2023) Evaluate the effects of Insensitive High Explosives residues on soil by using an Environmental Quality Index (EQI) approach. Science of the Total Environment, 896, 161797. https://doi.org/10.1016/j.scitotenv.2023.161797

A.2 Conferences Attended

During the course of the PhD I had the opportunity to attend and present, either a talk or a poster to different conferences:

RAS/19 - Risk Assessment Symposium, 2-3 December 2019, Cranfield Defence and Security, Cranfield University, UK.

DSDS20 - Defence and Security Doctoral Symposium, 10-11 November 2020, Cranfield Defence and Security, Cranfield University, UK.

C/21 - CENTA 2020 – 2-4 September 2020, Online Event.

RAS/20 - Risk Assessment Symposium, 18-19 November 2020, Online Event.

DN/20 – Doctoral Network, 3 December 2020, Online Event

ACS/21 – AquaConSoil, 15-17 May 2021, Online Event.

C/21 - CENTA 2021 – 9-10 September 2021 - University of Birmingham (UoB)

DSDS22 - Defence and Security Doctoral Symposium, 9-10 November 2022, Cranfield Defence and Security, Cranfield University, UK.

I also had the opportunity to help and develop an online student conference for Cranfield University:

Cop26 - Cranfield Conference – 27-28 October 2021 – Online Event.

A.3 Other Outputs

During the course of this PhD I was able to provide Laboratory support to the following Explosives Ordnance Engineering Master Level (EOE MSc) projects:

Grimes, A. (2020). *Enhanced conceptional site models for environmental risk assessments in military training areas.* Explosives Ordnance Engineering MSc, Centre for Defence Chemistry, Cranfield University, UK.

Christian, O. (2021). *Evaluating Insensitive High Explosive degradation processes in soil on military training areas in the UK.* Explosives Ordnance Engineering MSc, Centre for Defence Chemistry, Cranfield University, UK.

Dodds, C (2021). *Surface Modification of Wheat Straw and Rice Husk biochars for selective adsorption of NTO from wastewater*. Explosives Ordnance Engineering MSc, Centre for Defence Chemistry, Cranfield University, UK.

Spencer, M. (2021). *Development of an environmentally preferable method for the efficient disposal of insensitive high explosive through the reaction of a thermite composition.* Explosives Ordnance Engineering MSc, Centre for Defence Chemistry, Cranfield University, UK.

Fuentealba, H. (2022). *Development of a method to capture and detect emissions from open burning of explosives.* Explosives Ordnance Engineering MSc, Centre for Defence Chemistry, Cranfield University, UK.

Myhill, J. (2022). Biodegradability of shot gun ammunition wadding. Explosives Ordnance Engineering MSc, Centre for Defence Chemistry, Cranfield University, UK.

Appendix B Pictures of pre- and post-detonation of a 155mm filled with IHE related to chapter 3

B.1 Pre-detonation – Arena set up

Figure B.1 1– Arena set up. On the left the black plastic groundsheet to avoid cross-contamination from the soil underneath. On the right the laying out of the sand.

Figure B.1 2 – Arena completed with the sand for the environmental collection and the fragment arena for fragments collection

B.2 Post-detonation pictures

Figure B.2 1 - Post-detonation residues after detonation 1 with munition in horizontal position

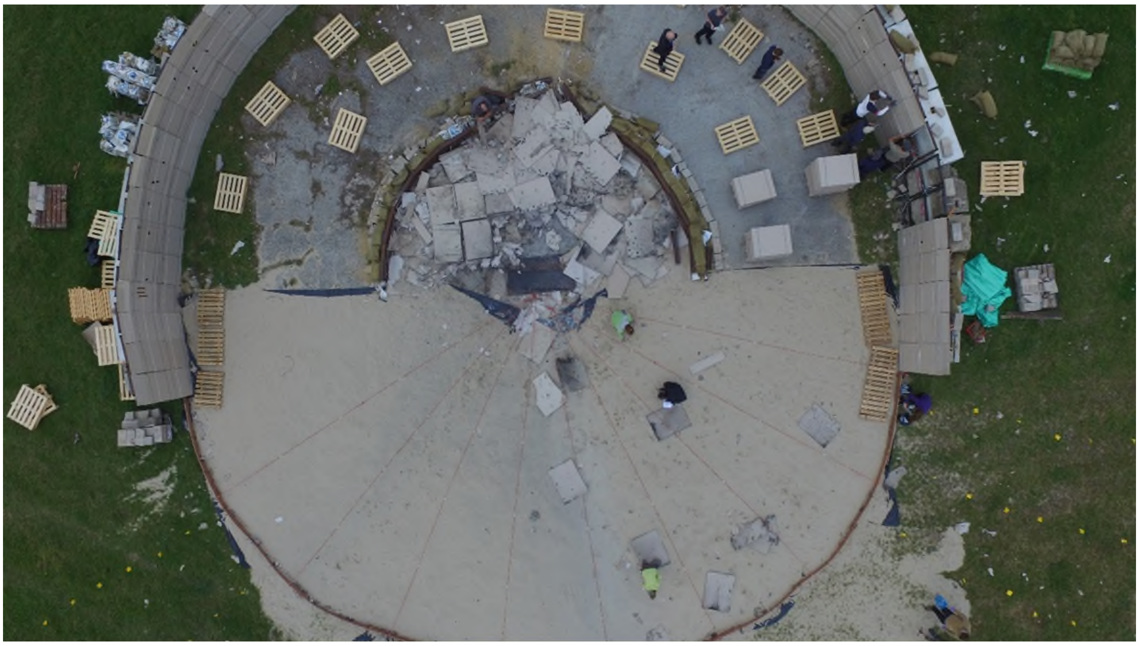

Figure B.2 2 – Post-detonation residues after detonation 2 with munition facing horizontal position

Figure B.2 3 – Post-detonation residues after detonation 3 with the munition in vertical position

Appendix C DNAN residue distribution for the three detonations

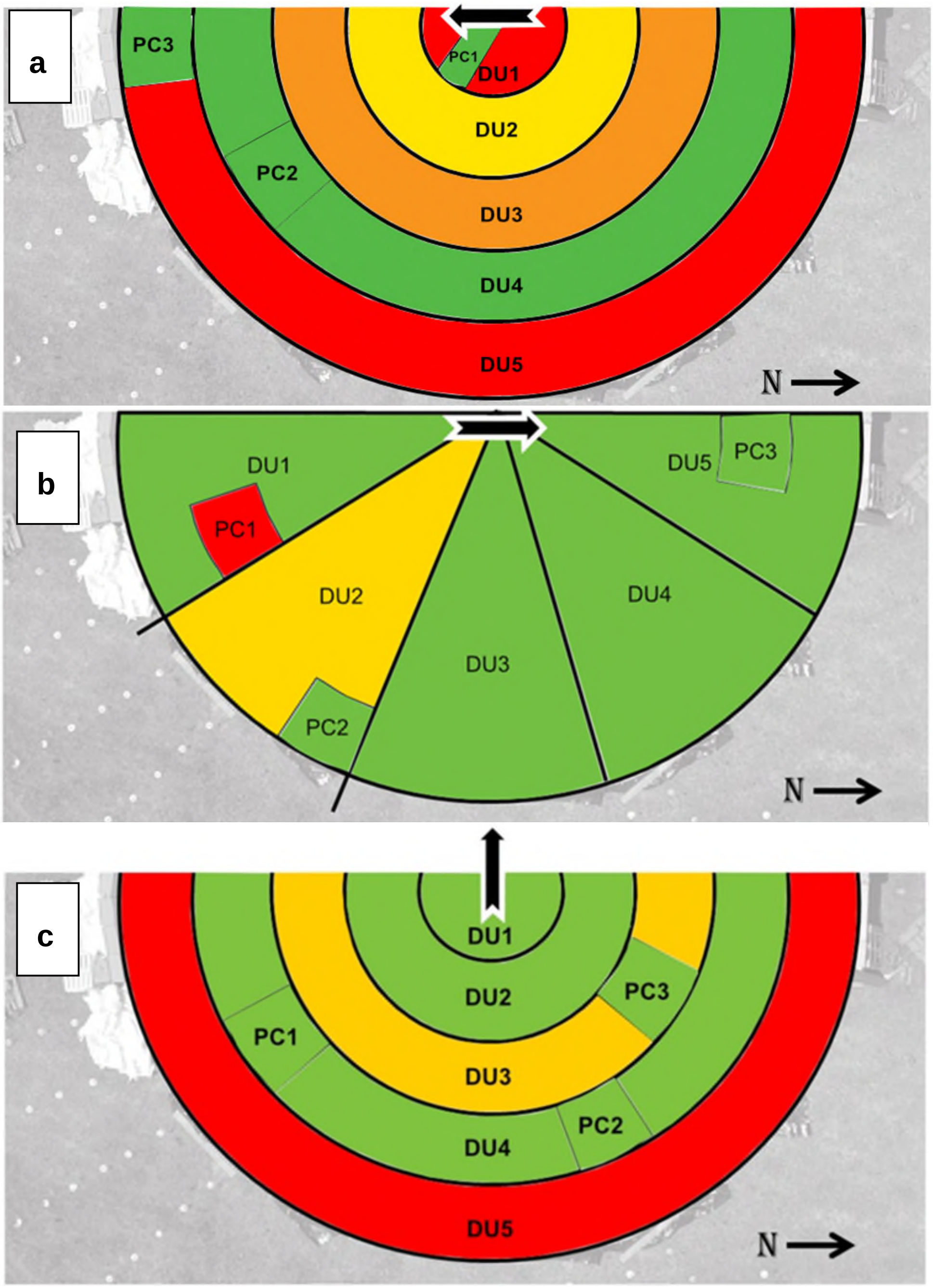

Figure C.1 1 a. First detonation DNAN residue deposition; b. Second detonation DNAN residue deposition; c. Third detonation residue deposition. PC are the random areas chosen as quality controls.

Appendix D Picture from soil assessment experiments mesocosm set up from chapter 4

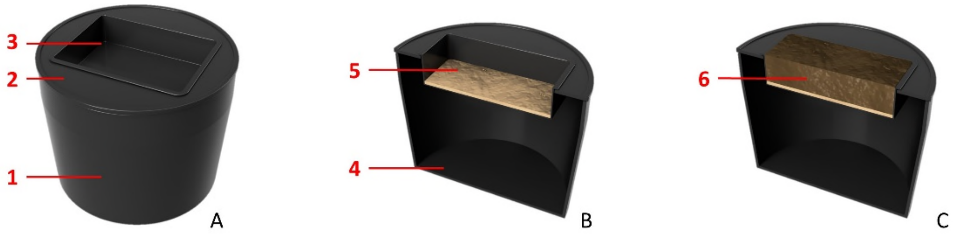

Figure D 1 Mesocosm set up. The empty set up: A) the bucket (1) with sealed lid (2) and the plastic heavy duty seeds tray (3); B) The mesocosms were filled 0.5 cm of damp inert sand (4) on the empty bucket (4) where water leachate was collected; C) And contaminated soil (6) was added on the dump inert sand.

Risk - level	Control	Low	Medium	High
IMX-104 Concentration (ppm)	0	0.215	215.5	581
IMX-104 Weight (mg)	0	125	1250	3375

Figure D 2– Mesocosms set-up. On the far left the contamination of the soil. On the left side the pristine soil and on the right the land degraded soil, both contaminated with the different IHE concentrations.

Appendix E Published Paper: Quantitative environmental assessment of explosive residues from the detonation of Insensitive High Explosive filled 155 mm artillery shell

Federica Persico[1], Melissa Ladyman[1], Tracey Temple[1], William Gilroy-Hirst[1], Encina Guiterrez-Carazo[1] and Frederic Coulon[2].

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Research Article

Propellants, Explosives, Pyrotechnics

doi.org/10.1002/prep.202100220

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Quantitative Environmental Assessment of Explosive Residues from the Detonation of Insensitive High Explosive Filled 155 mm Artillery Shell

Federica Persico,[a] Tracey Temple,*[a] Melissa Ladyman,[a] William Gilroy-Hirst,[a] Encina Guiterrez-Carazo,[a] and Frederic Coulon[b]

Abstract: Insensitive High-Explosive (IHE) typically comprises up to five constituents including 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), which are mixed in various ratios to achieve desired performance and increase insensitivity. Insensitive munitions, which are designed to detonate on command and not accidentally, are currently in use in military operations and training areas around the world. However, there is minimal literature available on the physiochemical behavior of these materials in the environment, therefore the actual consequence of residues being deposited post-detonation is still an unexplored area of research. Three 155 mm artillery shells filled with an IHE mixture of 53 % NTO, 32 % DNAN, and 15 % RDX were detonated in an inert sand arena to collect and quantify residues. Post detonation, approximately 0.02 % NTO, and 0.07 % DNAN were deposited in the environment which may rapidly accumulate dependent on the number of rounds fired. This is of concern due to the toxicity of DNAN and its degradation products, and the potential for increased acidity of soil and discoloration of watercourses from NTO contamination.

Keywords: 3-nitro-1,2,4-triazol-5-one (NTO) · 2,4-dinitroanilisole (DNAN) · 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) · Explosive residue · Multi-Increment sampling

1 Introduction

Energetic compounds are regularly deposited on military ranges following live-fire training activities [1]. The use of traditional explosives in various training areas has led to the contamination of soil and groundwater with recalcitrant and persistent hazardous chemicals which can render the sites unusable, therefore adversely affecting military readiness due to accumulation over time [2–5]. New generation Insensitive High Explosive (IHE) formulations consisting of 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanilisole (DNAN) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), are increasingly being introduced into military service due to their improved safety profile [6]. For example, the United States (US) Department of Defence have investigated the use of 61 mm and 80 mm mortars filled with PAX-21 (RDX, DNAN, and Ammonium Perchlorate) and Insensitive Munitions Explosive (IMX)-104 (DNAN, NTO, RDX) to replace legacy explosive fills [5,7]. However, IHE's contain chemical compounds and formulations not previously used in munitions e.g. NTO, and therefore their environmental consequences are not fully understood.

There have been limited studies into the deposition of explosive residues from munitions due to the challenges in efficiently sampling an area post-detonation. However, quantification of explosive residue deposition has been achieved using the Multi Increment Sampling (MIS) method on snow-covered ranges [8]. MIS has been proven to be reproducible and representative, particularly for non-homogeneous contamination [8,9]. This method has been used to investigate residue deposition from munitions containing traditional explosive fills such as mortars, artillery rounds, and grenadescontainingComposition B, and has shown that a very small quantity of explosive residues are deposited from first-order detonations (~0.00003 % RDX from Comp B filled 61 mm mortar). While the most significant source of contamination is likely to be from blow-in-place disposals or partial detonations [3,10,11], residue from first-order detonations may accumulate over time de-

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.202100220 pending on the number of rounds fired [3,12]. For some live-fire ranges, this may be tens of thousands of rounds per year resulting in significant accumulation of explosive residue, and the potential for soil and water contamination. However, research suggests that IHE filled munitions may deposit more explosive residue compared to conventional munitions. For example, RDX/HMX residues from IHE filled 60 and 81 mm mortars may be as high as 0.006 % and 0.001 % respectively [13]. This equates to tens of milligrams per round. The percentage of DNAN residue deposited from the two IHE filled rounds is comparable to the percentage of RDX (0.005 % and 0.001 % respectively), though this equates to a higher mass of DNAN per round due to the higher DNAN percentage in the formulation [13]. However, it is the percentage of NTO deposition that is most cause for concern (1.2 % and 0.4 % respectively), resulting in thousands of milligrams deposited per round. The IHE filled tested rounds have a relatively small explosive load (360 g and 831 g) compared to the 155 mm artillery shell which has a Net Explosive Quantity (NEQ) of 11.2 kg and therefore may deposit significant quantities of DNAN and NTO if used frequently at military training ranges [13].

The deposition of increased quantities of explosive residue from IHE filled munitions may increase accumulation rates, and therefore increase the likelihood of environmental consequences. RDX contamination has previously been of concern, however, in many locations effective environmental management procedures have been implemented [14]. In addition, due to the low quantity of RDX in IHE formulations (< 15 %), RDX is not the main contaminant of concern. Conversely, DNAN and NTO have not been used in significant quantities in munitions to date, and environments, where they are in use, may require additional environmental monitoring and management in the future. NTO is of particular concern due to the potentially large quantities that may be deposited, as well as its acidity (pKa 3.76) and solubility (16.6 $\mathrm{g\,L^{-1}}$ at 25 °C) [15,16], which means it may rapidly dissolve and transport into the soil and ultimately to ground or surface waters where it may cause discoloration [17–19]. The behavior of NTO in the environment has not been fully investigated with uncertainty surrounding the chemical and toxicological properties of degradation products such as 5-amino-1,2,4-triazol-3-one (ATO) [20–23]. However, early indications suggest that ATO may be more toxic than NTO toward specific organisms [24]. While NTO has particularly low toxicity (LD_{50} 5 $\mathrm{g\,kg^{-1}}$ in rats), and sublethal toxicity (oligospermia), the uncertainty of its environmental behavior and the potential for deposition of significant quantities make it a particular concern [25,26].

Understanding of the environmental fate of DNAN is more comprehensive than that of NTO, although DNAN is a nitrobenzene and is similar in structure to TNT, it is slightly more soluble (198 $\mathrm{mg\,L^{-1}}$) and more toxic (LD_{50} 199 $\mathrm{mg\,kg^{-1}}$) and therefore may present a comparatively greater risk to the environment [27–31]. In addition, several of the amino degradation products, such as 2-amino-4-nitro anisole (2-ANAN), have similar toxicity and may also present a risk to groundwater and local human and animal receptors [26,32,33]. The chemical-physical properties of DNAN, NTO, RDX, and TNT are summarized in Table 1.

The fate of explosive compounds is highly dependent on the local environment, however to inform environmental assessment it is essential to understand the potential for accumulation of explosive residues from commonly used munitions such as the 155 mm artillery shell. In addition, understanding the potential for contamination may enable a more proactive approach to environmental management ensuring that live-fire training with new generation munitions does not result in significant contamination incidents as has already occurred with legacy explosives [2,39,40]. Therefore, this work aimed to quantify the percentage of DNAN, NTO and RDX residue remaining on the soil surface after the detonation of an IHE filled (53 % NTO, 32 % DNAN, and 15 % RDX) 155 mm artillery shell to determine the potential accumulation rate at military training areas.

Table 1. Summary of the physicochemical and environmentally relevant properties of RDX, NTO, and DNAN compared to TNT.

Name	Formula [34]	Solubility [29] $\mathrm{mg\,L^{-1}}$	Log Koc [35]	pKa	Toxicity LD50 $\mathrm{mg\,kg^{-1}}$
TNT	$C_6H_3CH_3$	100	1.10 [36]	NA	607–767 [37]
RDX	$C_3H_6N_6O_6$	60	0.88-2.4	NA	119 [38]
NTO	$C_2H_2N_4O_3$	16,642	2.1 0.60–1.79	3.76 [16]	5000 [38]
DNAN	$C_7H_6N_2O_5$	276	1.79–1.92 1.62 1.58	NA	199 [38]

2 Experimental Section

2.1 Explosive Residue Collection

2.1.1 Preparation of Sampling Arena

A sampling arena was created by leveling 11,900 kg of inert fine particle sand to a depth of 5 cm in a semi-circular area (radius 10 m) on top of an impermeable plastic groundsheet. The arena was contained with flexible wooden edging panels around the external circumference (62 m). A 155 mm IHE filled artillery shell was placed at the center of the arena, at a height of 1 m, and detonated by a simulation fuze that closely approximated the live-firing initiation mechanism. A total of three detonations were carried out, two with the artillery shell in a horizontal orientation and one with the artillery shell in a vertical orientation to comprehensively assess the residue distribution. Following each detonation, the sand was cleared away and fresh sand (11,900 kg) was leveled on top of new clean groundsheets.

2.1.2 Explosive Residue Sampling

The residue was collected post-detonation using the Multi-Increment Sampling (MIS) method. In brief, approximately 100 increments of sand (100×10 g) were collected in triplicate from discrete Decision Units (DU) within the sampling arena using a metal scoop [8]. Two different DU layouts were used for the two horizontal orientation detonations, an arc layout and a radial layout (Figure 1a-b). For the vertical orientation detonation, the arc pattern was repeated (Figure 1a). All collected samples were double bagged and stored in a freezer at (−18 °C) until analysis (~3 months). In addition, the entire arena was sampled after each detonation as one DU to ensure comprehensive coverage.

2.1.3 Field Controls

Control samples of the inert sand were taken prior to preparing the sampling area to ensure the sand used during the experimental phase was free from explosive contamination. Control samples were also taken from the soil underneath the groundsheet to baseline for cross-contamination and random samples within the DU's were collected as positive controls (PC) to validate the sampling method and reproducibility of the results (Supplementary data). Additional controls samples were collected from outside the immediate sampling area before and post-detonation to ensure no DNAN, NTO or RDX residues were missed during analysis and to detect any potential cross-contamination from outside of the sampling area. This area was extended by 6 m from the boundary of the sampling area. All control samples were collected by using MIS in triplicate, with sand samples collected using a metal scoop and soil collected using a coring tool.

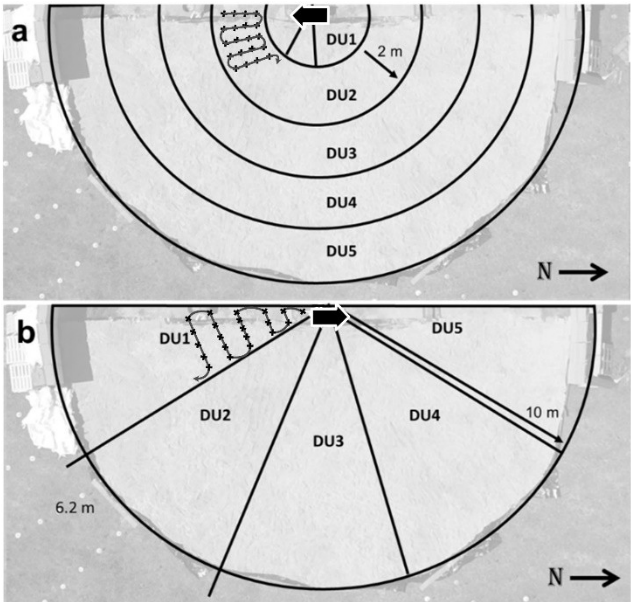

Figure 1. Decision Units (DU) for each detonation a) Detonation 1 and 3: arc DU's; b) detonation 2: radial DU's. Black arrows with a white outline denote the orientation of the 155 mm shell for horizontal detonations (arrow point = nose). An example of how increments were collected is shown by the location of crosses on a sampling route, repeated three times on different routes for each DU.

2.2 Laboratory Sample Analysis

2.2.1 Sample Processing

Collected samples were defrosted and air-dried over 5–7 days before being passed through a 2.00 mm sieve to remove any foliage or large fragments. Samples were mechanically mixed and sub-sampled in triplicate by taking increments (~0.5 g) from a 5 by 5 grid to a mass of ~20 g.

2.2.2 Sample Extraction

Sub-samples were extracted with acetonitrile/water (1 : 1) (40 mL) by shaking for 18 hours at 180 rpm in amber glass vials [41]. Samples were left to stand for 30 minutes before filtration through a 0.2 μm PES filter and analyzed by HPLC. To confirm very low levels of NTO, DNAN, and RDX residue the bulk liquid (5 mL) from a sub-selection of extractions was concentrated 5 times by evaporation at 35 °C and quantified by HPLC. The resulting concentrations were used to determine the mass deposited.

2.3 HPLC Analysis

Samples were analyzed by High Pressure Liquid Chromatography (HPLC) using a 150×4.6 mm Agilent Zorbax Eclipse Plus C18 column in a Waters Alliance 2695 with a Waters 996 photodiode array detector [42]. The mobile phase was a 40:60 acetonitrile/water mix at a flow rate of $1.5\ \mathrm{mL\,min^{-1}}$ and a constant temperature of 30 °C. Residue concentration (NTO, DNAN, RDX, and common degradation products ATO, DNP, 2-ANAN, 4-ANAN, and 2,4-ANAN) was determined by calibration to an IHE standard calibration curve.

2.4 Quality Controls

Play sand was artificially spiked with NTO, DNAN, and RDX (12.5 ppm) and extracted after 24 h, 48 h, and 6 days with 100 % efficiency. Previous work has shown that in the sand at ambient temperature (18 °C) NTO, DNAN and RDX remain stable for up to four months in the absence of light, and no degradation was detected in samples stored in the freezer for 3 months.

3 Results and Discussion

3.1 Determination of Mass of Explosive Residue from Detonation of 155 mm Artillery Shell

To quantify the explosive residues from the detonation of the 155 mm artillery shells the detonation area was sampled using the MIS method. The published protocols for MIS were followed, except for mechanical grinding of the samples due to the potential for initiation caused by friction between the sand and explosive residue [8]. Therefore, the sand was manually mixed before analysis to maximise homogeneity. As it has been shown that improved mixing (grinding) increases the representativeness of samples, an increased error was accepted [9]. Analysis of control samples taken before the detonations confirmed that the groundsheet and 5 cm sand layer was sufficient to prevent cross-contamination from the surrounding and underlying soil.

There was concern that the detonation may significantly disrupt the sand and render it impossible to sample, however after the first detonation it was clear that only the center of the arena was disrupted (Supplementary data). Therefore, the entire arena was sampled after each detonation by MIS. No explosive residues were detected in the entire arena samples for either detonation in the horizontal plane or the detonation in the vertical plane. Samples concentrated by a factor of five also resulted in non-detect of any NTO, DNAN, or RDX, suggesting that, as expected, the total residue deposition from a single 155 mm artillery shell was below the limit of detection ($0.5\ \mu\mathrm{l\,ml^{-1}}$) due to the mass of sand diluting the explosive residue. However, quantifiable concentrations of DNAN were detected in several of the smaller DU's for all detonations (Table 2). The errors reported reflecting the heterogeneity of results wherein some samples had a significantly higher concentration of DNAN, and in other samples, no DNAN was detected. Therefore, the results have been used as a broad estimate of potential residue deposition.

NTO was only detected in quantifiable concentrations in detonation 2, DU2, although characteristic NTO peaks were observed in samples from all DU's from all three detonations, suggesting that NTO concentrations were below the limit of quantification of NTO ($1.4\ \mathrm{mg\,L^{-1}}$) [17]. This was confirmed by concentrating select sample extracts i.e. in one of the replicates for detonation 3, decision unit 3 $0.002\ \mathrm{mg\,kg^{-1}}$, NTO was detected. Evaporating samples was considered to be too time-consuming to achieve for all samples, and therefore unquantifiable concentrations of NTO have been reported as 'trace' (Table 2).

Table 2. Summary of results from IHE filled 155 mm artillery shell detonations. Standard deviation reported.

Decision Unit	Horizontal orientation- DU Arcs			Horizontal orientation- DU Radial			Vertical orientation- DU Arcs		
	NTO $\mathrm{mg\,kg^{-1}}$	DNAN $\mathrm{mg\,kg^{-1}}$	RDX $\mathrm{mg\,kg^{-1}}$	NTO $\mathrm{mg\,kg^{-1}}$	DNAN $\mathrm{mg\,kg^{-1}}$	RDX $\mathrm{mg\,kg^{-1}}$	NTO $\mathrm{mg\,kg^{-1}}$	DNAN $\mathrm{mg\,kg^{-1}}$	RDX $\mathrm{mg\,kg^{-1}}$
Blank (sand)	0	0	0	0	0	0	0	0	0
Area control	0	0	Detect	0	0	Detect	0	0	Detect
DU1	Trace	0.24 ± 0.39	0	Trace	0	0	Trace	0	0
DU2	Trace	0.0009 ± 0.002	0	Trace	0.055 ± 0.1	0	Trace	0.0008 ± 0.002	0
DU3	Trace	0.11 ± 0.2	0	Trace	0	0	Trace[a]	0	0
DU4	Trace	0	0	Trace	0	0	0	0	0
DU5	Trace	0.24 ± 0.42	0	0.16 ± 0.27	0	0	0	0.16 ± 0.27	0
PC1	Trace	0.002 ± 0.001	0	Trace	0.17 ± 0.31	0	Trace	0	0
PC2	Trace	0	0	Trace	0	0	0	0	0
PC3	Trace	0.0008 ± 0.003	0	Trace	0	0	Trace	0	0
Whole area	0	0	0	0	0	0	0	0	0

[a] Upon concentrating replicate 2, concentration of NTO was quantified as $0.002\ \mathrm{mg\,kg^{-1}}$.

RDX was detected in the 'area control' sample i.e. the soil directly beneath the sampling area, but was not detected in the sampling area, including in the concentrated samples. Previous work in the literature suggests it is likely that RDX is deposited, but the concentrations were too low to be detected by the methods used (Table 2). This was expected due to the low percentage of RDX in the IHE composition (15%), other compositions have much higher concentrations of RDX (>60%) making deposition of detectable concentrations much more likely [43].

3.1.1 Mass of DNAN Residue Deposition

Concentrations of DNAN were detected in four of the five DU's for detonation 1 (arcs), confirmed by trace detection of DNAN in the positive controls in DU 1 (PC3) and DU 5 (PC1), and the non-detect in the positive control within DU4 (PC2). Conversely, in the second detonation DNAN was only detected in DU2 (radial), confirmed by detection of DNAN in the random positive control. It is interesting to note that DNAN was only detected in the second radial DU in detonation 2 (South-Easterly) and it is likely that DNAN identified in detonation 1 was concentrated in a North-Easterly direction corresponding to DU2 in detonation 2, and the rear of the 155 mm shell (Figure 1). To ensure all explosive residues were accounted for, samples were also analyzed for DNAN degradation products 2-ANAN, 4-ANAN, 2,4-ANAN, and 2,4-dinitrophenol, but these were not detected in any samples.

From the results of the horizontal detonations, it was expected that DNAN deposition from the third detonation would be similar, but possibly more uniformly distributed due to the vertical orientation. This is because in the vertical position, the shell was positioned nose-up meaning any increased DNAN deposition at the rear-end of the shell would be evenly distributed in the sampling area. While DNAN was detected in DU5 (furthest from the detonation center), and very low levels were detected in DU2, DNAN was not detected in any other DU's. In the vertical position, it is possible that residues were deposited beyond the sampling area, although no DNAN was detected in these control samples, very low concentrations may have been masked in the HPLC trace by the noise from soil organic matter.

The constructed sampling arena was semi-circular as it was assumed that the deposition would be symmetrical about the long axis of the projectile (nose to tail) and estimates of the mass of residue deposited could be doubled to account for both halves. In reality, doubling the mass is unlikely to give a perfect estimate as deposition could be affected by slight variations in weather conditions and slight misalignments of the 155 mm artillery shell. Several other assumptions were also made to enable the estimation of the deposited mass of DNAN per kilogram of soil. For example, the mass of soil was determined by assuming DNAN would be deposited on the soil surface and no deeper than the sampling depth of 5 cm, and that the density of soil is similar to that of sand. As the concentration of DNAN recovered from the three detonations was significantly different, the mass of DNAN deposited was calculated from a) the combined concentrations from all DU's in detonation 1; b) DU5 in detonation 2; and c) DU5 in detonation 3 to provide upper and lower estimates. The total estimated mass of DNAN from each detonation was calculated by multiplying the concentration ($mg\,kg^{-1}$) by double the mass of sand in the DU's where DNAN was found (Equation 1).

$$\textit{Estimated mass of DNAN in DU} = C_{residue} \times M_{sand} \qquad (1)$$

Where C is the concentration in soil ($mg\,kg^{-1}$) and M is the mass of sand in the decision unit.

From the data obtained from Equation 1, the total estimated mass of DNAN from the three detonations accounted for between 0.006% and 0.07% of the total DNAN content in the 155 mm shell (Table 3). The upper estimate is slightly higher than previously published literature on the residue from 60 mm and 81 mm IHE shells which found 0.006% and 0.001% DNAN deposited respectively [13]. An increase in deposited residue may be due to the significant increase in the Net Explosive Quantity between the three shell sizes (approximately 11 kg (155 mm) vs 339 g (61 mm) and 807 g (81 mm)).

As expected from previously published literature, the mass of DNAN deposited from the detonation of an IHE filled 155 mm artillery shell is higher than for commensurate legacy munitions, such as TNT from Comp B filled 155 mm shells [13,44,45]. This is of note, as DNAN is a nitrobenzene with similar properties to TNT, although it is slightly more toxic (199 $mg\,kg^{-1}$ vs 607–767 $mg\,kg^{-1}$). DNAN's environmental behaviour may therefore be similar to TNT i.e. mineralization by photo and bio-degradation before significant exposure to environmental receptors. However, this may not be true of all environments as it is highly dependent on soil type and weather conditions, and it may be possible for residues to accumulate to potentially hazardous levels. This is unlikely to be a problem for operational use as the incident rate is low and in localized areas i.e. DNAN is likely to be diluted through environmental action such as infiltration with rainwater, surface runoff, and degradation. Therefore, in the absence of additional incident DNAN, the concentration of this compound in the environment will rapidly

Table 3. Mass DNAN deposited from detonation of 155 mm artillery shell.

Detonation	Concentration $mg\,kg^{-1}$	Total Mass g	% Mass
1	0.22 + 0.0009 + 0.11 + 0.24	2.63	0.07
2	0.049	0.23	0.006
3	0.16	1.23	0.03

decrease. However, the accumulation of DNAN may need to be considered for training with IHE filled 155 mm artillery shells.

3.1.2 Mass of NTO Deposition

One sample from detonation 2, DU5, contained detectable quantities of NTO (0.16 ± 0.17 $mg\,kg^{-1}$) and detection of NTO was consistent in all DU samples, suggesting that during the detonation NTO was evenly distributed across the arena. Using Equation 1 and assuming a) the highest level of deposition (0.16 $mg\,kg^{-1}$) in detonation 2, DU5 and b) assuming an average deposition of 0.03 $mg\,kg^{-1}$ across the entire area, the mass deposited from a single detonation was between 71 mg and 762 mg (Table 4). This equates to between 0.001 % and 0.01 % of the mass of NTO in the 155 mm shell. This is significantly lower than the estimated deposition mass in the published literature from the detonation of 60 mm and 81 mm munitions on snow (0.4–1.2 %), suggesting that the mass of NTO deposited is lower for the 155 mm artillery shell [5].

Whilst NTO is significantly less toxic than DNAN (5000 $mg\,kg^{-1}$ vs 199 $mg\,kg^{-1}$), there is limited research into its wider environmental impact. One potential issue is that NTO may be acidic when solubilised i.e. after rainfall, which may increase leaching of nutrients and metals from the existing contamination in soil [18]. For example, many explosive test and impact areas are contaminated with lead, which is known to leach more rapidly in soils with pH lower than 4 [44]. In addition, NTO discolors water at low concentrations (10 ppm), which would be considered pollution under multiple UK and European regulations, even if there were no associated toxicity [46].

3.2 Potential Environmental Impact of IHE Filled 155 mm Artillery Shells

As RDX was not detected in appreciable concentrations the accumulation rate of hazardous concentrations of IHE residues in the environment was based on the deposition of DNAN and NTO. Therefore, assuming the masses of DNAN and NTO residue per detonation as calculated above (Table 3 and Table 4) the estimated rate of accumulation during training was calculated using the Circular Error Probable (CEP) i.e. the radius of the area in which 50 % of the rounds are likely to land. For the 155 mm artillery shell, the CEP is 94 m–267 m depending on the distance fired (15–30 km). The calculation takes into account that only 50 % of rounds are likely to land within the CEP, with the remaining 50 % distributed in an even larger area of diminishing soil concentration. The area increases with increasing distance. Using this calculation, after 1000 detonations the concentration of DNAN on the surface soil could be as high as 2.37 $mg\,kg^{-1}$ (assuming lower CEP and higher mass deposited) but is more likely to fall between 0.21 and 2.37 $mg\,kg^{-1}$. Table 5 outlines the potential maximum concentration of DNAN and NTO in the soil at CEP 94 m and CEP 267 m for the detonation of 1000 and 10,000 IHE filled 155 mm shells in the absence of other environmental processes such as adsorption, degradation, and surface runoff.

Unfortunately, there are no current legal Soil Screening Level (SSL) for DNAN or NTO in the soil although health-based environmental screening levels are in development [47]. However for the US EPA has given a residential and industrial SSL of 19 and 79 $mg\,kg^{-1}$ respectively for TNT, which has similar properties to DNAN (United States Environmental Protection Agency, 2014). Although it is unlikely that the SSL for DNAN would be the same as for TNT, as DNAN is more toxic, it does give a guideline figure for concentrations of concern which are potentially exceeded at localized areas of soil on training ranges within as few as 10,000 firings. In addition, this figure does not consider the number of partially detonated or non-functioning ordnance which may be disposed of by blow-in-place or may be left in the environment. Both methods are known to deposit significant concentrations of explosives in the environment, therefore contributing to the accumulation of residues [13,47].

The results in Table 5 suggest that the concentration of DNAN in soil could increase rapidly at training areas where 155 mm shells are in use. However, this calculation assumes that there is no transport beyond the first 5 cm of soil and that the training targets do not change. In reality, training is likely to take place over a much larger area further reducing the accumulation rate, and over a significant period. For ex-

Table 4. Mass NTO deposited from detonation of 155 mm artillery shell.

Detonation	Concentration $mg\,kg^{-1}$	Total Mass g	% Mass
2	0.16	762	0.01
1&3	0.003	71	0.001

Table 5. The potential accumulation of DNAN and NTO in soil for 1000 and 10,000 firings for CEP 94 m and 267 m.

Explosive residue deposited from 155 mm shell	Estimated soil concentration 1000 detonations ($mg\,kg^{-1}$)		Estimated soil concentration 10,000 detonations ($mg\,kg^{-1}$)	
	CEP 94 m	CEP 267 m	CEP 94 m	CEP 267 m
DNAN 0.006 %	0.21	0.03	2.10	0.26
DNAN 0.02 %	0.72	0.09	7.24	0.90
DNAN 0.07 %	2.37	0.29	23.68	2.93
NTO 0.001 %	0.06	0.00	0.64	0.08
NTO 0.01 %	0.69	0.09	6.86	0.85
DNAN 0.006 %	0.21	0.03	2.10	0.26

ample, if 10,000 155 mm shells are fired within a year, a significant quantity of deposited DNAN will likely be dissolved by incident rainfall and transported into the soil where it may be rapidly degraded, especially in high organic content soils (50% within 3 months) [17]. While some degradation products are equally as toxic as DNAN, these are also likely to be further degraded to mineralised products such as nitrates and nitrites before exposure to a receptor. Therefore, while the contamination of soil is a concern, it may be managed by rotating training areas and avoiding areas with sensitive groundwater resources.

Accumulation of NTO is also of concern as the behavior of NTO in the environment is still under investigation. For example, whilst some NTO degradation products have been speculated, such as ATO, they have not yet been identified in environmentally representative samples such as soil studies [48]. In addition, there are limited toxicity studies on NTO and its degradation/decomposition products making it difficult to assess its environmental impact. From the findings in this work, and previous work indicating the rapid degradation of NTO in the environment, it is likely that NTO will be deposited in the environment from the use of IHE filled 155 mm artillery shells, therefore, further investigation into the degradation products and their toxicity is required [17,49].

4 Conclusion

DNAN and NTO residues were deposited from the detonation of an IHE filled 155 mm artillery shell in slightly higher concentrations than has been recorded for legacy (RDX/TNT) filled munitions. While the deposited concentrations may not be of immediate concern after a single detonation, care must be taken if large quantities of IHE filled munitions are to be used for training to manage accumulation and minimise environmental impact. The training environment is particularly relevant as the accumulation of DNAN and NTO will be highly dependent on the rate of infiltration into the soil with rainfall, and the rate of degradation, and therefore environmental management techniques must be chosen for their suitability to the local environment. Finally, it must be noted that this residue deposition investigation was relatively small scale, with only three detonations for comparison. To increase confidence in results, additional studies should be undertaken such as an accumulation study wherein samples are collected after 5 to 10 detonations.

Acknowledgements

The authors would like to thank Antony Grimes, Bonny Thawani, Charich Chuenta, Ana Paula Lopes, Jacopo Bonifacio, Lara Temple, Cait Gilroy-Hirst, and Ruben Moya for their help with setting up the detonation arena and collecting samples. In addition, the authors thank BJ Clarke and Trevor Lawrence for their support during the practical phase of the work, and Karl Norris for making the surrounding barrier and pegs. With thanks to RWM Italia for funding.

Data Availability Statement

Research data can be found in the Cranfield University data repository (CORD).

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Manuscript received: July 28, 2021
Revised manuscript received: October 29, 2021
Version of record online: ■■■, ■■■■

Appendix F Published Paper: Development of an environmental hazard-based rating assessment for defence-related chemical compounds in ecological soil systems

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Environment International 166 (2022) 107392

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Full length article

Development of an environmental hazard-based rating assessment for defence-related chemical compounds in ecological soil systems

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ARTICLE INFO

Handling Editor: Adrian Covaci

Keywords:
Toxicity
Ecotoxicity
Soil contamination
Hazard
Soil

ABSTRACT

Environmental hazard-based methods are commonly used to categorise the severity of chemical contamination to ecological soil systems, although a traffic-light approach (green, amber, red) has never been used to assess these consequences. A traffic light approach is an easy to interpretate data as it has a clear visual display which can provide an early warning approach for stakeholders to identify areas that require further investigation. This approach should be underpinned by extensive research data and systematic methods of development. However, the extent of reliable data available for specific chemicals can be limited and therefore decision making may rely on expert judgement. Therefore, in this study, an environmental hazard-based rating methodology was developed by combining the guidelines from the European Chemical Agency (ECHA) and the USEPA for Predicted Non-effect Concentration (PNEC) and Ecological Soil Screening Levels (Eco-SSL) for defence-related chemicals (2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), cypermethrin, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)). The developed hazard-based rating assessment was design to categorise the chemicals into low, medium and high environmental hazards priority to inform and ease the decision-making process for contaminated areas to ensure that sustainable operations are carried out.

1. Introduction

To characterise and manage the ecological hazards posed by chemicals in the soil system a variety of approaches have been developed. Rating systems have been widely utilised to simplify and better visualise consequences across a variety of disciplines (San et al., 2020; Pan et al., 2020) (e.g. low, medium and high rating systems) to enable practitioners to rapidly interpret data and implement mitigation. However, developing the different categories requires a wide and comprehensive body of data.

Risk/hazard based rating systems have been used across a variety of disciplines from financial to environmental and are usually based on a matrix that categorises the occurrence and the impact of each activity to infer the level of risk or hazard i.e. low, medium or high (Finizio and Villa, 2002;Murray et al., 2011; Pickering and Cowley, 2010). However, these processes are frequently reliant on qualitative assessment by subject matter experts and while providing a subjective assessment, cannot provide quantitative assessments (Pickering and Cowley, 2010). An alternative approach is to use a ranking evaluation, which use 'traffic light' colour coding system e.g. green, amber and red to represent low, medium and high-hazard levels. While these systems are based on quantitative data, multiple variables are used to compile the data, and subject matter expert opinion is still required to make decisions regarding the data used and therefore the system is still heavily subjective (Kovačević et al., 2019). Therefore, an additional system is required to ensure to underpin the hazard-based rating system with a more thorough and comprehensive body of data to enable practitioners to easily define different levels of hazard.

The process of gathering a viable body of data has been presented by different nations although they have not been considered for broader applications such as informing rating systems to define different levels of ecological hazards.

The United States Environmental Protection Agency (USEPA), use a score-grading procedure of the literature data, and calculates a set of Ecological Soil Screening Levels (Eco-SSLs) based on contaminants that have been proven to be a threat for both flora and fauna (USEPA, 2005). In Europe, a step further has been made by the European Chemical Agency (ECHA) by developing Soil Screening Values (SSVs) based on reliable data in the literature and statistical analyses (Environment Agency, 2017). Unlike the Eco-SSL technique, the gathering of data

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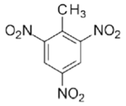
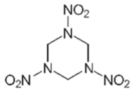
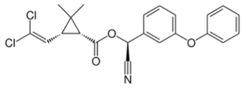
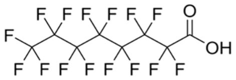
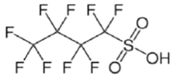
https://doi.org/10.1016/j.envint.2022.107392
Received 5 November 2021; Received in revised form 29 June 2022; Accepted 1 July 2022

Table 1
The chemical substance name, empiric formula and structure of the five defence related chemicals used for the application phase in this paper.

Chemical name	Empiric Formula	Chemical Structure
2,4,6-Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	
1,3,5-Trinitroperhydro-1,3,5-triazine (RDX)	$C_3H_6N_6O_6$	
cyano-3-phenoxybenzyl-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (Cypermethrin)	$C_{22}H_{19}Cl_2NO_3$	
Pentadecafluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$	
Heptadecafluorooctane-1-sulfonic acid (PFOS)	$C_8HF_{17}O_3S$	

occurs through the ECHA database under the Regulation (EC) No 1907/2006 introduced in Europe in 2007, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Merrington et al., 2008). The data obtained from this procedure are selected and extrapolated where gaps are identified. However, due to the lack of records related to different chemicals, the researcher must rely on the expert opinion to decide whether or not the data can be used to develop SSVs.

The USEPA methodology develops Eco-SSL values based on experimental data, specifically, to concentrations that produce changes (i.e. reproduction, inhibition of growth) to 10% or 20% of the studied population (EC_{10}, EC_{20}), or the highest effective concentration at which there was not an observed toxic or adverse effect (NOAEC) and the lowest effective concentration at which there was an observed toxic or adverse effect (LOAEC).

In contrast, SSVs are derived from the calculation of the Predicted No Effect Concentration (PNEC) value which is different depending on the ecosystem. The PNEC is a regulatory concentration level under which sufficient protection for the ecosystem considered is ensured (ECHA, 2008, Environment agency, 2017). The considered ecosystems are characterised by different groups of organisms and since there is more than one set of data for each organism in different soil environments the PNEC calculation is estimated on the values that are most reliable. The reliability of the results are chosen based on the expert's opinion having discrepancies dependent on who is carrying out the procedure.

These methodologies have wide applications, particularly in the agricultural sector, although they have also been applied to other sectors (Checkai et al., 2014). This study focussed on military training ranges, which can be exposed to a range of chemical contaminants from the use of explosives, fire-fighting foams and other military equipment.

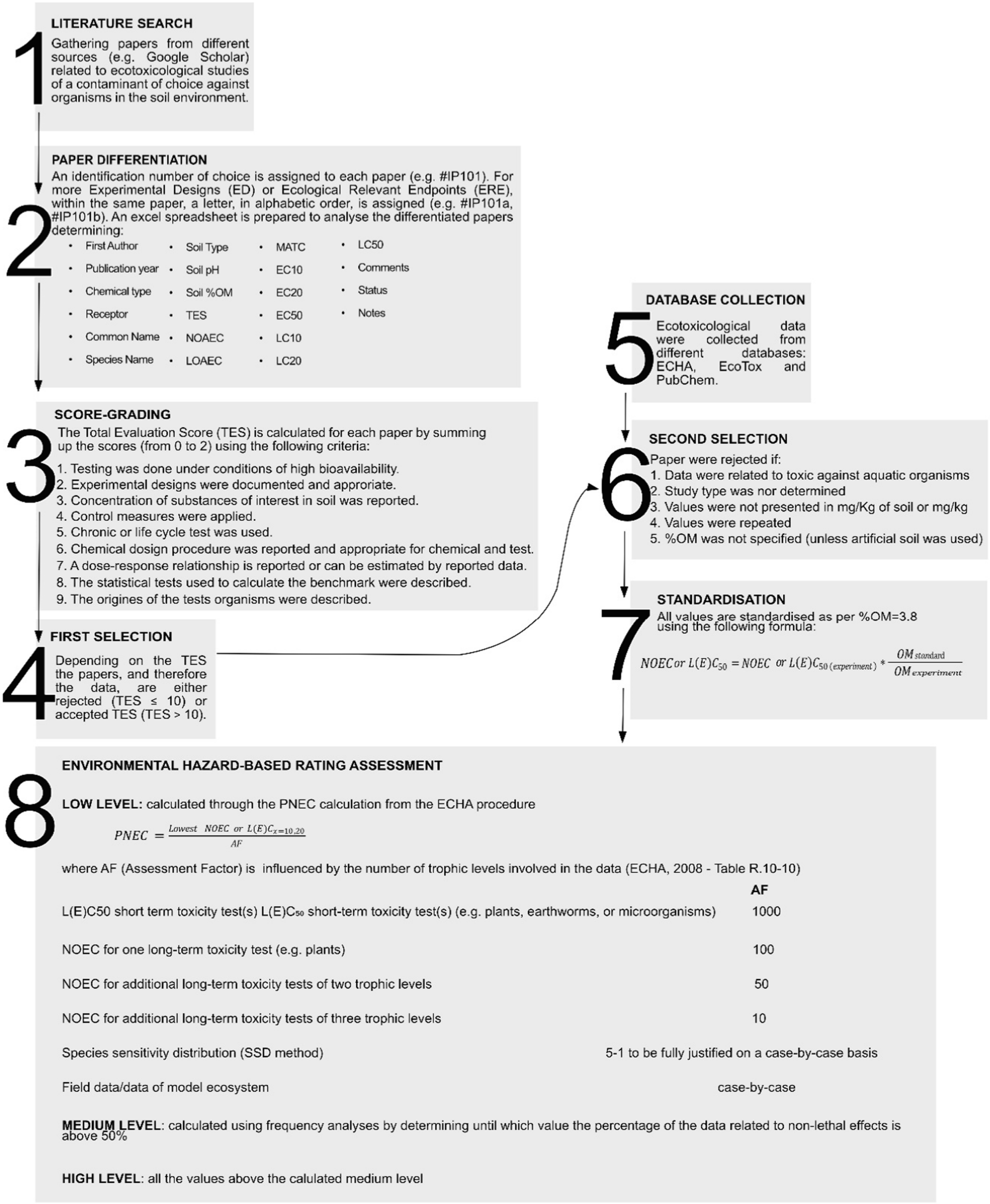
Regulating and minimising the environmental risks associated with routine operations at military training ranges (e.g. live-fire training, transportation), is necessary to maintain training and to support military capability (Bortone et al., 2020). Historically for both security and safety reasons, military training ranges are almost always situated in remote areas, so that essential training activities can be carried out without interfering with built-up areas (Havlíček et al., 2018). Despite restricted access, many rare or uncommon species of plants, insects and birds thrive in these areas which consequently become classified as Sites of Special Scientific Interest (SSSI) and/or as EU Special Areas of Conservation (SAC), as well as Special Protection Areas (SPA) for birds protected under the European Birds Directive.

Routine operations on site can also lead to contamination of military areas, with consequences to soil and groundwater (Broomandi et al., 2020; Ferreira et al., 2020). This means that the natural environment and military activities coexist, leading to the need to protect these areas while continuing essential training activities (Bortone et al., 2020; Broomandi et al., 2020). To ensure the safe use and sound management of these military areas, Environmental Risk Assessments (ERA) are typically conducted to assess the environmental impact of defence-related chemical substances.

Chemical substances used on military training ranges (Table 1) comprise a wide range including among others, traditional explosives (e.g. 2,4,6 – trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX)), which may be a threat to the environment including surface and groundwater, soil and biota (Clausen et al., 2004; Dodard et al., 2003; Gong et al., 2007; Kuperman et al., 2005; Lotufo, 2017; Robidoux et al., 2002; Vila et al., 2008). Aqueous Film Forming Foam (AFFF) containing per- and polyfluoroalkyl substances (PFAS) which are used for extinguishing inflammable liquid fires which may also be persistent and a threat to the environment (Filipovic et al., 2015; Place and Field, 2012; Turner et al., 2021; Zhao et al., 2011); and the use of pyrethroid insecticides such as cypermethrin and its isomers to treat military uniforms and equipment (e.g. bed nets) so that military personnel are protected from insect bites, such as mosquitos during military operations (Army, 1994; Friedl et al., 2007; Hassan et al., 2010; Khoobdel et al., 2005). During washing of the uniforms, water contaminated with the pesticide can enter soil and water courses (Hassan et al., 2010) and threat soil quality impacting agriculture (Shiping et al., 2008; Hassan et al., 2010; Khoobdel et al., 2005). Moreover, this insecticide has a high affinity to organic matter which can harm both soil invertebrates (Zhou et al., 2008, 2011; Zortéa et al., 2015) non-target organisms such as aquatic invertebrates (e.g.insects and crustaceans) (Conte et al., 2005; Environmental Agency, 2019; Birch et al., 2015; Das and Mukherjee, 2003; Shiping et al., 2008).

Using a hazard-based ranking system, based on a green, amber and red visual aid, ensures that proper decision making is carried out on training ranges considering the contamination that is already in place. This approach can be applied to varying soil types and is not limited by the activity at the site.decision

Therefore, the aim of this work was to develop an environmental hazard-based rating assessment which characterises the ecological hazards posed by chemicals (TNT, RDX, cypermethrin, PFOA and PFOS) used in defence-related activities based on a comprehensive body of data objectively selected. This was achieved by combining the USEPA ECO-SSLs and ECHA SSVs methodologies to develop a maximum contaminant concentration in soil that would not require short-term further investigation of the site (low hazard level). In contrast, contaminant concentrations in the medium and high-hazard levels would require further site investigation to ensure that sustainable operations are carried out. This method has been designed to ease the decision-making



LITERATURE SEARCH

Gathering papers from different sources (e.g. Google Scholar) related to ecotoxicological studies of a contaminant of choice against organisms in the soil environment.

PAPER DIFFERENTIATION

An identification number of choice is assigned to each paper (e.g. #IP101). For more Experimental Designs (ED) or Ecological Relevant Endpoints (ERE), within the same paper, a letter, in alphabetic order, is assigned (e.g. #IP101a, #IP101b). An excel spreadsheet is prepared to analyse the differentiated papers determining:

- First Author
- Publication year
- Chemical type
- Receptor
- Common Name
- Species Name
- Soil Type
- Soil pH
- Soil %OM
- TES
- NOAEC
- LOAEC
- MATC
- EC10
- EC20
- EC50
- LC10
- LC20
- LC50
- Comments
- Status
- Notes

SCORE-GRADING

The Total Evaluation Score (TES) is calculated for each paper by summing up the scores (from 0 to 2) using the following criteria:

1. Testing was done under conditions of high bioavailability.
2. Experimental designs were documented and approriate.
3. Concentration of substances of interest in soil was reported.
4. Control measures were applied.
5. Chronic or life cycle test was used.
6. Chemical dosign procedure was reported and appropriate for chemical and test.
7. A dose-response relationship is reported or can be estimated by reported data.
8. The statistical tests used to calculate the benchmark were described.
9. The origines of the tests organisms were described.

FIRST SELECTION

Depending on the TES the papers, and therefore the data, are either rejected (TES ≤ 10) or accepted TES (TES > 10).

DATABASE COLLECTION

Ecotoxicological data were collected from different databases: ECHA, EcoTox and PubChem.

SECOND SELECTION

Paper were rejected if:

1. Data were related to toxic against aquatic organisms
2. Study type was nor determined
3. Values were not presented in mg/Kg of soil or mg/kg
4. Values were repeated
5. %OM was not specified (unless artificial soil was used)

STANDARDISATION

All values are standardised as per %OM=3.8 using the following formula:

$$NOEC \text{ or } L(E)C_{50} = NOEC \text{ or } L(E)C_{50\,(experiment)} * \frac{OM_{standard}}{OM_{experiment}}$$

ENVIRONMENTAL HAZARD-BASED RATING ASSESSMENT

LOW LEVEL: calculated through the PNEC calculation from the ECHA procedure

$$PNEC = \frac{Lowest\ \ NOEC\ \ or\ \ L(E)C_{x=10,20}}{AF}$$

where AF (Assessment Factor) is influenced by the number of trophic levels involved in the data (ECHA, 2008 - Table R.10-10)

	AF
L(E)C50 short term toxicity test(s) L(E)C$_{50}$ short-term toxicity test(s) (e.g. plants, earthworms, or microorganisms)	1000
NOEC for one long-term toxicity test (e.g. plants)	100
NOEC for additional long-term toxicity tests of two trophic levels	50
NOEC for additional long-term toxicity tests of three trophic levels	10
Species sensitivity distribution (SSD method)	5-1 to be fully justified on a case-by-case basis
Field data/data of model ecosystem	case-by-case

MEDIUM LEVEL: calculated using frequency analyses by determining until which value the percentage of the data related to non-lethal effects is above 50%

HIGH LEVEL: all the values above the calulated medium level

Fig. 1. The methodology for developing the toxicity scale, from the gathering of the data to the calculated values for the low, medium and high hazard levels (steps 1 to 8), to determine the possible level of hazard towards the ecological soil systems data against the biota. Differently from the USEPA procedure, in this methodology all the ERE and experimental designs were considered and all the values were part of the dataset used to develop the environmental hazard-based rating assessment.

assessment process for soil such that a threshold value could inform whether further site investigation is required.

2. Methodology

2.1. The process

The following section outlines a summary of the methodology

Table 2
Criteria evaluation for each chosen paper for the evaluation of Eco-SSL values (USEPA, 2005).

Criteria	Evaluation
1	Testing was Done Under Conditions of High Bioavailability
2	Experimental Designs were Documented and Appropriate
3	Concentration of Substance of Interest in Soil was Reported
4	Control Measures were Applied
5	Chronic or Life Cycle Test was Used
6	Chemical Dosing Procedure was Reported and Appropriate for Chemical and Test
7	A Dose-Response Relationship is Reported or can be Estimated from Reported Data
8	The Statistical Tests used to Calculate the Benchmark and the Levels of Significance were Described
9	The Origin of the Test Organisms were Described

undertaken to develop the environmental hazard-based rating assessments by combining the methodologies for soil screening levels from the ECHA and USEPA procedures (Fig. 1) to ensure an objective data collection to determine different hazard levels for the ecological soil systems.

A thorough **literature search** has been carried out (Step 1) of available toxicity data, for terrestrial organisms and plants.

The **paper differentiation** (Step 2) and **Score-grading** (Step 3) was carried out following the Standard Operating Procedure (SOP) #1 and #2, attachment 3.1 and 3.2 for invertebrates, developed by the USEPA.

A **first selection** was carried out (Step 4) and paper were either rejected or accepted depending on the Total Evaluation Score (TES) where scores ≤ 10 were accepted and >10 were rejected.

In Step 5 '**database collection**' values from different databases (e.g. PubChem, EcoToxwere collated to create a body of data, which was added to the papers that scored a TES > 10.

The next step was the **second selection** (Step 6), where a selection of data was rejected based on the following:

- relationship to toxicity against aquatic organisms
- study type was not determined
- values were not presented in mg/kg of soil or mg/kg
- values were repeated
- %OM was not specified (unless artificial soil was used)
- the experimental design scored < 10.

Once all data were standardised, the calculation of the PNEC or SSVs values were carried out to determine the upper boundary of the low-hazard toxicity level (Step 8) for the different contaminants.

The evaluation of the medium and high level of hazard for the soil environment in the cumulative environmental hazard-based rating assessment was then determined using frequency analysis of all the chosen data, clustering them based on the study type (e.g. reproduction, survival) (Step 8).

2.2. *Research strategy*

Various sources (e.g. Google Scholar, Web of Science) were utilised for the collection of secondary data through a literature search. A first screening procedure was carried out following the USEPA procedure, considering the literature related to ecotoxicological experiments involving TNT, RDX, PFOA, PFAS and Cypermethrin within the terrestrial environment. Each selected paper was differentiated based on different variables, which translated in different experimental designs (e.g. type of soil, organisms); additionally, unlike the USEPA procedure, each paper was also evaluated separately based on different Ecologically Relevant Endpoints (ERE) (e.g. reproduction, growth) and more data were included in the selection such as: EC_{50}, LC_{20}, LC_{50} or data reported in mg/kg together with the EC_{10}, EC_{20}, NOAC and LOEC and data in mg/kg of soil considered from the USEPA procedure.

Each paper was assigned an identification number (e.g. IP#101) which differentiated not only different research articles but also different ERE and studies distinguished by use of different variables within the same paper (e.g. IP#101a, IP#101b). Each paper associated with an identification number was scored following the nine criteria from the USEPA procedure.

2.3. *Data selection*

In the USEPA procedure each paper is scored against nine criteria (Table 2) from 0 to 2 (with 0 being the lowest). The process is rendered unbiased by the usage of tables and specific instructions contained in the SOP #2 attachment 3.2 (USEPA, 2005). Using this method, a paper was scored more than once if more than one set of variables were investigated, thus considering them as different studies in within the same paper. For example, if two different soils were used to compare changes in the reproduction of a specific organism this was classified as two different studies. This differentiation was also applied if ERE were recorded. For example, if results from changes in reproduction and growth were presented in the same paper and the soil considered was the same, the paper was again evaluated as two different studies.

The previously presented scoring process differs from the USEPA procedure whereby the differentiation of studies within the papers was not applied when more than one consequence, or ERE, on the biota was recorded. For example, in the USEPA procedure if toxicological data on the same soil were collected and results recorded were related to reproduction and growth of the organism, the paper is considered as one study and the toxicity was selected according to a pre-settled hierarchy for the invertebrates (Reproduction > Population > Growth) or the most sensitive measurement of biomass production for plants.

For example, following the USEPA methodology, the first criteria analyses whether the experiments were carried out under conditions of high availability, and depending on the pH and the % organic material (OM) in the soil, a different score is selected based on the bioavailability tables given in the SOP #2 (USEPA, 2005). Although, the scoring of the papers should be completed by more than one researcher to ensure that complete unbiased decisions are achieved. All the scores for each paper were summed to determine the Total Evaluation Score (TES) of each article. Data was accepted, to develop the environmental hazard-based rating assessment, if the TES had more than 10 total points as stated in the USEPA procedure. Once all the gathered information had been organised further data was added from the ECHA database.

The non-confidential toxicity information, that has been submitted to ECHA, and are also available from other databases, such as EcoTox, PubChem, were reported and organised as follows: data related to aquatic organisms was excluded; only values presented in mg/kg of soil or mg/kg was considered; where %OM was not reported the data was not considered (except for artificial soil); data with no study type listed was also excluded from the research.

Since different studies include different soil types, a standardisation of the data to is required (ECHA, 2008; Environment Agency, 2017) and it is applied to all the gathered data using formula (1).

2.4. *Data standardisation*

Different soil characteristics (e.g. pH, %OM) can influence the toxicity and bioavailability of a chemical and the %OM has been defined as one the most influencing parameters, meaning that there is a need for normalisation to ensure that the toxicity of the compound are representative of the bioavailability in soil, meaning that the data needs to be standardised (Step 7) as they are presented in a standard soil (Environment Agency, 2017). For OECD guidelines, a standard soil has 3.8% of OM and all the values are standardised against this percentage to make the data comparable as follows:

Table 3
Assessment factors (reproduced from ECHA, 2008 Table R.10–10).

Information Available	Assessment Factor
$L(E)C_{50}$ short-term toxicity test(s) (e.g. plants, earthworms, or microorganisms)	1000
NOEC for one long-term toxicity test (e.g. plants)	100
NOEC for additional long-term toxicity tests of two trophic levels	50
NOEC for additional long-term toxicity tests of three trophic levels	10
Species sensitivity distribution (SSD method)	5–1 to be fully justified on a case-by-case basis
Field data/data of model ecosystem	case-by-case

$$NOECorL(E)C_{50} = NOECorL(E)C_{50(inexperiment)} * \frac{OM_{standard}}{OM_{inexperiment}} \qquad (1)$$

where $NOECorL(E)C_{50(inexperiment)}$ represent the values that have been found for each paper in the literature research; $OM_{standard}$ equals 0.038 and $OM_{inexperiment}$ are the OM values found in the literature for each experiment (ECHA, 2008).

2.5. Low-hazard toxicity level calculation

A low-level hazard for the ecological soil system can be defined as the concentration at which no effects were observed. This definition is also representative of the SSVs or the PNEC, meaning that the value that correspond to an SSVs or PNEC of a specific contaminant are utilised as the upper boundary of the low-hazard level.

The PNEC value was calculated using Eq. (2).

$$PNEC = \frac{LowestNOECorL(E)C_{x=10,20}}{AF} \qquad (2)$$

where NOEC or L(E)CX values represent the lowest value identified from the procedure utilised and AF is the Assessment Factor.

The Assessment Factor (AF) is derived as summarised in Table 3.

Preferably the NOEC or EC_{10} values should be used (either by calculation or from the literature) because they represent chronic exposures which represent more appropriate and relevant measures for understanding the protection of population and communities, compared to acute toxicity tests. The presented methodology defines the most reliable results as the ones with the highest TES. If, from the most reliable data, values presented from experiments with the same settings and organisms, were less or equal to one magnitude apart, a geometric mean was calculated merging the presented data together (Environment Agency, 2017). PNEC values are considered as SSVs but only if there is enough data to support the calculations; this is usually when the assessment factor is <50 (Environment Agency, 2017), indicating that values from more than one trophic level are presented.

As the SSVs, the low-hazard level is defined as "levels of chemicals in soil below which there is unlikely to be any risk to its health and functions" (Environment Agency, 2017). Once the PNEC value has been calculated, the chemical concentration range in which no deleterious effects on the soil environment are expected can be defined.

2.6. Medium and High-hazard toxicity level calculation

Once the upper boundary of the low-hazard level has been defined, an analysis of the frequency is carried out on all the data based on the different study types (e.g. reproductivity, survival). Frequency analysis were used to determine different ranges of values, related to the analysed studies, in which lethal and non-lethal effects are evaluated. The range of concentration that determine the medium-hazard level was determined as the highest value in the set of data where 50% of the studies resulted in non-lethal effects on terrestrial organisms. All the values above the calculated boundary were considered to be related to a high-hazard level. As such, the medium-hazard level was defined as "levels of chemicals in soil in which it is likely to have deleterious effects on ecological soil functionalities" and the high-hazard level as "levels of chemicals in soil above which it is likely to have irreversible effects on ecological soil functionalities". All the values above the most frequent values that did not cause a deleterious effect on the biota (death of the organisms) are considered a high-hazard level in, defining the range of concentration of the contaminants in which it is expected to have a lethal effect on the ecological soil system. Similarly, the most likely values

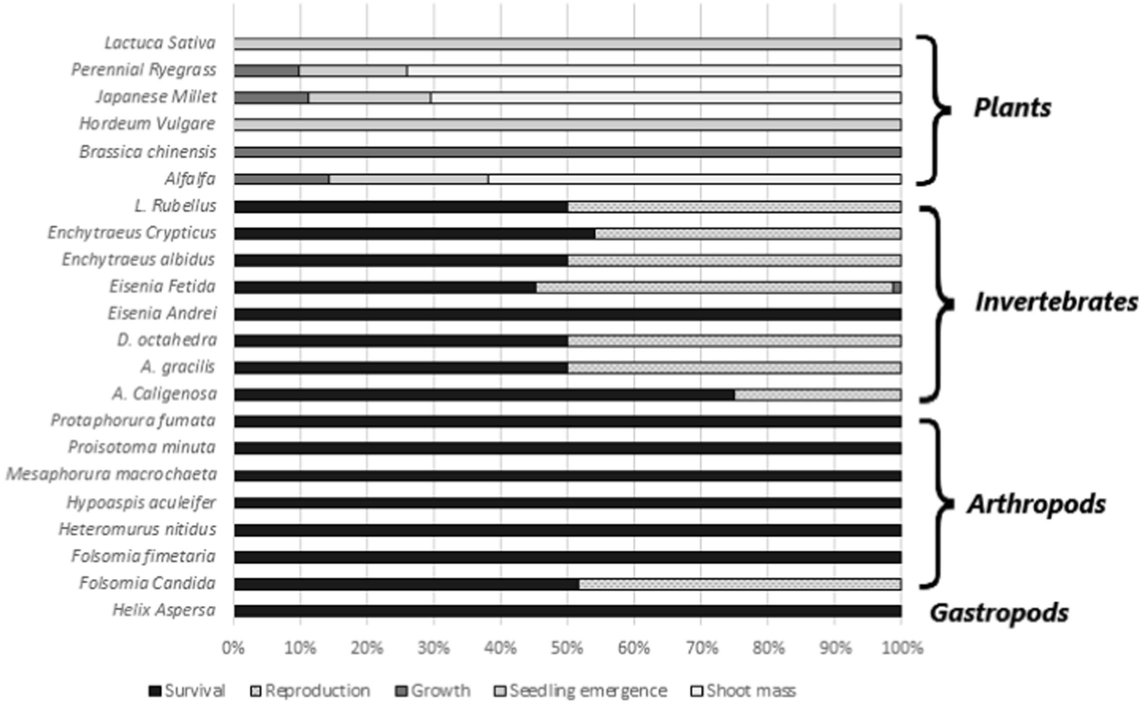


Fig. 2. Percentages of values for each organism related to different ERE found during the literature search using the USEPA procedure.

Table 4
Total numbers of values gathered from a selection of sources e.g. from the open literature (USEPA) and the following databases: ECHA, EcoTox, PubChem (ECHA). Within each study, more EREs and EDs were differentiated.

Contaminant	Number of values gathered from literature and databases					
	Total ERE and E. D.* (USEPA)	Accepted ERE (USEPA)	n. Values from accepted ERE (USEPA)	Total data from databases (ECHA)	Accepted data from databases (ECHA)	Number of values for the environmental hazard-based rating assessment
TNT	78	73	230	1976	140	370
RDX	104	104	255	821	155	410
CYPERMETHRIN	37	33	45	2251	21	66
PFOA	4	0	0	1300	131	131
PFOS	10	6	16	2860	93	109

*Experimental Designs.

Table 5
Each trophic level that was identified during the literature search and the database collection was listed and the equivalent AF factor was chosen. PNEC calculation was carried out as follows.

Contaminant	Previous values using the ECHA approach		Calculated values using new approach			
	AF	PNEC	AF	Tropic levels	Lowest NOEC or EC10	PNEC (or SSV) (MG/KG)
TNT	50	0.01	10	*Plants* *Earthworms* *Arthropods*	2.61	0.3
RDX	100	7.56	50	*Plants* *Earthworms*	51.3	0.1
CYPERMETHRIN	100	0.08	10	*Plants* *Earthworms* *Arthropods* *Gastropods*	0.17	0.02
PFOA	N/A	N/A	10	*Plants* *Earthworms* *Arthropods*	8.99	0.9
PFOS	N/A	N/A	50	*Plants* *Earthworms*	40	0.8

in which it is expected to have deleterious effects on the soil environment (because of their consequences on the biota) will represent the medium-hazard level in the environmental hazard-based rating assessment.

3. Results and discussion

3.1. Research evaluation

For the application phase of this research five different contaminants from defence related activities were selected: TNT, RDX, Cypermethrin, PFOA and PFOS (Table.1). During the first part of the literature search undertaken in accordance with the established USEPA methodology (USEPA, 2005) 30 reports and peer-reviewed papers in total, were identified as suitable for a first data analysis. The papers that were selected evaluated toxicity against a range of invertebrates and plants (Fig. 2).

From these papers 233 studies were identified, which led to the evaluation of 709 values for the environmental hazard-based rating assessment during the first part of the procedure (Supplementary data). The studies, represented by the different changes in variables, were individually scored following the 9 criteria in Table 2, and calculated TES varied from a minimum of 4 to a maximum of 18 points. Because of how the USEPA methodology is developed, PFOA and PFOS related papers have scored the lowest TES values. This is because the first scored criteria “Testing was done under conditions of High Bioavailability” is not adequate for evaluating soil conditions with synthetic contaminants, therefore, a score of 0 has been selected for all the ERE that were PFOS or PFOA related.

In general, the experimental designs that scored $\leq$ 10 points were rejected and data related were not used to develop the environmental hazard-based rating assessment because they were considered unreliable. Across all the contaminants, 14 studies were rejected and 205 accepted. Each study contained 1 or more result relating to the percentage of the studied population that was affected by a certain amount of contaminant (e.g EC10, EC50), consequently the total accepted values that have been used, from the USEPA methodology, for determining the environmental hazard-based rating assessment was 546 (230 for TNT, 45 for Cypermethrin, 255 for RDX, 0 for PFOA and 16 for PFOS).

Furthermore, a total of 9208 values were collated from the ECHA, EcoTox and Pubchem databases and only 540 were used in the environmental hazard-based rating assessment (140 for TNT, 21 for Cypermethrin, 155 for RDX, 131 for PFOA and 93 for PFOS) (Supplementary data). This was due to several studies either not reporting results in mg/kg or mg/kg of soil, related to terrestrial organisms, or the study type was not specified. The final body of data that was analysed is shown in Table 4.

All data were standardised for 3.8% OM (Supplementary data).

3.2. Low-hazard level

PNEC values were determined for all the contaminants (Table 5) using Equation (1) and the AF factor was derived following the criteria listed in Table 3.

These values are representative of the upper boundary of the low-hazard level where adverse effects are unlikely to occur in the biota. Consequently, no changes in soil are expected in the defined range meaning that a concentration within the range of the low-hazard section represent momentarily a safe environment. Although, future considerations are needed as those contaminants are likely to bioaccumulate in the environment causing, potentially, different problems for people and the environment.

PNEC values have been previously defined in the literature (Table 5) for TNT, RDX and cypermethrin, as respectively 0.01 mg/kg soil dw (AF of 50), 7.56 mg/kg soil dw (AF of 100), 0.08 mg/kg (AF of 100) (ECHA database); although, PNEC values that were calculated using the presented combined methodology included a wider body of data influencing the number of values used to calculate the PNEC showing a difference between data. Data in mg/kg have been included and more trophic levels have been considered, with a recent growing body of data that included a wide range of values for the arthropods class.

The PNECTNT that has been calculated is currently higher than the literature, where an AF of 10 has been used has previously established. During the data gathering, 2 values reported ecotoxicity data against arthropods, adding a third trophic level, changing the AF to 10 which has been used for the PNECTNT calculation.

PNECRDX has been previously calculated using the ECHA procedure using an AF of 100 when only one tropic level was evaluated. Using the

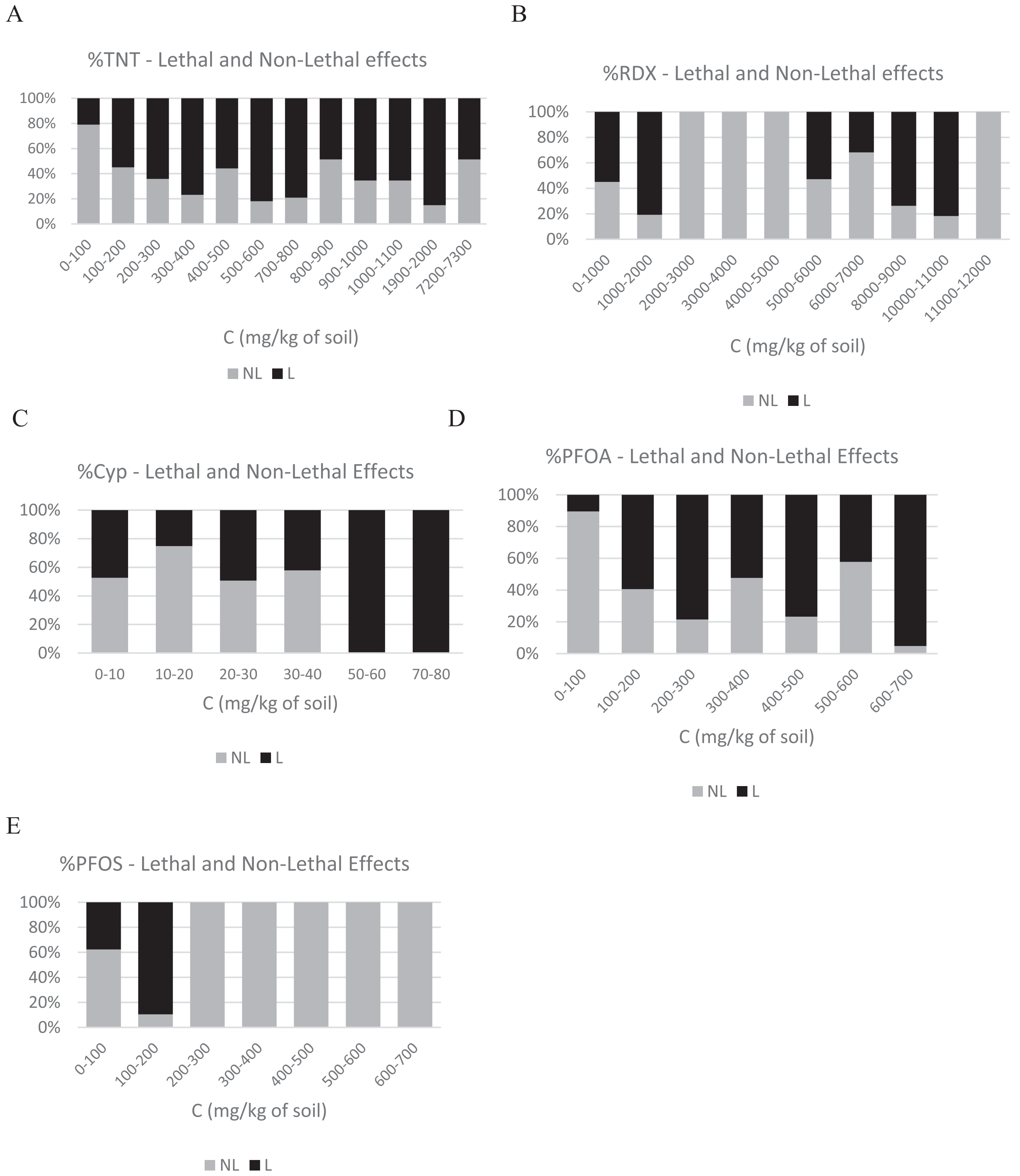


Fig. 3. Gathering of concentration (C) data in mg/kg using frequency analyses (showed in %) of the studied contaminants whose data are related to deleterious effects (e.g. reproduction, growth, dry biomass) which did not cause death in the organism (grey) and lethal effects (black).

presented combined methodology an AF of 50 has been used because, a wider body of data, included more then one trophic level. The PNECRDX calculated using the presented combined methodology, significantly lowered the previously calculated PNECRDX.

Compared to the PNECCYP calculated in the ECHA (7.56 mg/kg soil dw) the PNECCYP determined by this methodology was considerably lower because of the more inclusive body of data which incorporated Cypermethrin isomers and recently published literature. This is despite, compared to the average of data that has been used to calculate the different environmental hazard-based rating for each contaminant (217.2), the number of values used is 70% lower (66). Furthermore, more trophic levels (plants, earthworms, arthropods, and gastropods) were included in the analysis and an AF of 10 was used unlike the ECHA where an AF of 100 was utilised meaning that the concentration that defined the value under which no changes are expected in the ecological soil system is much lower.

Table 6
Environmental hazard-based rating assessment for each contaminant resulting from the presented methodology.

Level of hazard	Value (mg/kg of soil)				
	TNT	RDX	Cypermethrin	PFOA	PFOS
Low	0–0.3	0–0.1	0–0.02	0–0.9	0–6.6
Medium	0.3–194.7	0.1–839.5	0.02–20.4	0.9–176.2	6.6–183.2
High	>194.7	>839.5	>20.4	>176.2	>183.2

PNECPFOA and PNECPFOS were calculated respectively with an AF of 10 and an AF of 50, unexpectedly the number of values collected for the PNEC calculation was more than 100 even though these contaminants are extremely new compared to the other evaluated chemicals.

3.3. *Medium and high – Hazard levels*

A frequency analyses of the data were done by determining the occurrences of the values respectively related to survival and different responses (e.g. reproduction, growth) which are not related to death of the organism. The data that had a toxic effect on the biota, without causing death of the organism, were considered to be representative of the medium-hazard level of the toxicity scale because these values are representative of different concentrations of the contaminants that can have a deleterious, but not lethal, effect on the soil environment. All the values above this range were considered high-hazard level.

Different ranges of values were calculated for the chosen chemical compounds. For TNT (Fig. 3a) the values ranged from 0.03 to 1906.8 mg/kg of soil. Between the range of 100 to 200 mg/kg concentration in soil lethal effects on the organisms were observed in more than 50% of the organisms. Within that range, the highest value with a non-deleterious effect was 194.7 mg/kg (Supplementary data) representing the upper boundary of the medium-hazard level. For RDX has been highlighted (Fig. 3b), in the range between 0 and 2000 mg/kg, that 56% of the data is related to lethal effects against organisms, determining upper boundary of the medium-hazard level in between 0 and 1000 mg/kg. For first instance only, 45% of the data represented non-lethal effects against organisms in that range outlining the medium hazard level as between 0.1 and 839.5 mg/kg.

The same process was followed for Cypermethrin, PFOA and PFOS where less data has been recorded compared to TNT and RDX using the combined methodology. The results obtained from the Cypermethrin data analysis showed that 50% of the data were between 20 and 30 mg/kg (Fig. 3c) and are related to lethal effects towards organisms. Using frequencies analyses the upper boundary of the medium-hazard level has been established to be 20.4 mg/kg. For PFOA and PFOS lethal effects data exceed 65% (Fig. 3d) and 89% (Fig. 3e), respectively between the range of 100–200 mg/kg, compared to data related to lethal effects, defining the upper boundaries at 176.2 mg/kg and 183.2 mg/kg.

All the values above the upper boundary of the calculated medium level of hazard must therefore belong to the high-hazard level. For each contaminant the environmental hazard-based rating assessment has been carried out, and the low, medium and high hazard levels have been evaluated (Table 6):

The advantage of this new approach is to facilitate the decision-making process with a hazard-based rating system approach. Translating effects on the biota to consequences on the soil environment has been a wide area of research, although, with the toxicity scale, future literature can focus their effort on understanding, at these different concentrations, if the predictions are adequate and the changes that are undermining the soil. Therefore, a completion of this study will evaluate, by knowing the contaminants concentration in the soil environment, the hazard associated with the chemical, decreasing further investigation costs.

4. Conclusion

Various chemicals associated with defence-related activities have the potential to impact on ecological soil systems. Therefore, ERAs are used to assess the likelihood of an activity causing harm to the environment, and to understand the consequences of these contaminants on the soil environment.

The purpose of this study was to develop an environmental hazard-based rating assessment that can be used as part of the ERA procedure. It did this by combining ecotoxicological data which have been previously used by USEPA and ECHA to evaluate the consequences of a contaminant in the soil environment. The hereby presented methodology merged these two techniques to ease and inform the decision-making process. Consequently, it was possible to develop an environmental hazard-based rating assessment for different defence-related contaminants. Although, this study is not only limited to a few representative classes of chemicals used in defence related activities and can have much broader implications evaluating only secondary data present in the literature. Moreover, a broader application can be considered for different ecosystems (e.g. aquatic environment) which can be achieved by changes in the procedure specifically to the PNEC value calculations as determined in the ECHA procedure. The understanding and calculation of different levels of hazard can determine a baseline for future human toxicity evaluations related to bioaccumulation process happening through the trophic chain.

Different hazard-levels have been calculated for TNT, RDX, Cypermethrin, PFOA and PFOS as defence-related chemicals based on ecotoxicological secondary data as representation of risks to the matrix in which the entity leaves. Future work will include validating the developed hazard levels in the environmental hazard-based rating assessment for changes in soil to pre-empt the chemical impact on the environment and to avoid severe consequences on the environment to ensure that sustainable operations are appropriately conducted on military training ranges.

Funding

This work was supported by The Natural Environment Research Council (NERC).

CRediT authorship contribution statement

Federica Persico: Conceptualization, Data curation, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Frederic Coulon:** Conceptualization, Funding acquisition, Resources, Supervision, Writing – original draft, Writing – review & editing. **Melissa Ladyman:** Conceptualization, Resources, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing. **Tracey Temple:** Conceptualization, Resources, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2022.107392.

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Appendix G Published Paper: Evaluating the effect of insensitive high explosive residues on soil using an environmental quality index (EQI) approach

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Science of the Total Environment 869 (2023) 161797

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evaluating the effect of insensitive high explosive residues on soil using an environmental quality index (EQI) approach

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HIGHLIGHTS

- Environmental Quality Indexes developed for Insensitive High Explosives (IHE).
- Impacts of IHE mixture residues on soil environmental status established.
- EQI of the training range soil was reduced by >24 % after 1 month.

GRAPHICAL ABSTRACT

ARTICLE INFO

Editor: Jose Julio Ortega-Calvo

Keywords:
Soil quality
Soil assessment
DNAN
NTO
RDX

ABSTRACT

The environmental impact of Insensitive High Explosive (IHE) detonation residues to soil quality was assessed using a series of outdoor soil mesocosms. Two different soils were used including a pristine sandy soil and a land-degraded soil collected from a training range. Both soils were spiked with an IHE mixture comprised of 53 % NTO, 32 % DNAN and 15 % RDX at three different concentrations 15, 146 and 367 mg/kg respectively. The concentration levels were derived from approximate residues from 100 detonations over a 2 week training period. A set of five physico-chemical and biological indicators representative of the two soils were selected to develop environmental quality indexes (EQI). It was found that none of the concentrations tested for the pristine soil affected the chemical, biological and physical indicators, suggesting no decrease in soil quality. In contrast, the EQI for the degraded soil was reduced by 24 %, mainly due to a decrease in the chemical and biological components of the soil. Therefore, it is concluded that depending on the soil health status, IHE residues can have minor or severe consequences on soil health. Further studies are needed to determine the environmental impact of IHE on soil and water especially in the case where a larger number of detonations are more likely to be carried out on a training range.

1. Introduction

Environmental contamination of live-fire military trainings areas has been recognised as a worldwide problem, ranked as the second-largest anthropogenic source of environmental pollution after mining activities (Jenkins et al., 2006; Pichtel, 2012; Tauqeer et al., 2020; Walsh et al., 2005). In addition, new generation explosives, such as Insensitive High Explosives (IHE), are of increasing concern due to their toxicity and early indications that increased quantities will be deposited on soil compared to legacy explosives (Johnson et al., 2017; Taylor et al., 2017). IHE formulations consist of combinations of legacy explosives such as 2,4-dinitroanisole (DNAN) and previously unused energetic materials such as 3-nitro-1,2,4-triazol-5-one (NTO) (Lent, 2019). This mixture is replacing

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http://dx.doi.org/10.1016/j.scitotenv.2023.161797
Received 11 November 2022; Received in revised form 19 January 2023; Accepted 19 January 2023

the use of Comp B as it less sensitive to unintentional shock with DNANs replacing TNT as it safer during the manufacturing processes (Braida et al., 2012; Singh et al., 2010).

Deposition and accumulation of energetic chemical compounds in soil can occur at live fire training ranges due to repeated field detonation of Insensitive Munitions (IM) (Hewitt et al., 2005; Walsh et al., 2012; Zentelis et al., 2017). In a previous study, we quantified the residual concentration of explosive compounds in soil after three full-order detonations of a 155 mm shell filled with a melt-cast mixture of 53 % NTO, 32 % DNAN and 15 % RDX (Persico et al., 2022). The residual concentrations were then extrapolated to predict the highest residual concentration from 100 detonations, which was estimated to be 370 mg/kg. The three components characterising the explosive mixture, NTO, DNAN and RDX, have a calculated acute LD_{50} (lethal dose estimated to kill 50 % of the population) of respectively >5000 mg/kg, 199 mg/kg and 59 mg/kg respectively (Lent, 2019), Justifying the need to pre-evaluate any explosive residue in soil to pre-empt any potential impact and avoid severe consequences to environmental receptors.

Previous studies have demonstrated the environmental impacts of traditional explosives, such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) on soil and water ecosystem functioning and biodiversity (Chatterjee et al., 2017; Stanley et al., 2015; Tauqeer et al., 2020; Travis et al., 2008). In contrast, environmental impact studies for IHE remain scarce. Missing ecotoxicological values and limited understanding of the mechanisms effective for evaluating soil changes in the environment has left a gap in research, and a suitable standardised procedure has not yet been developed.

The consequence of contaminantion on the soil environment is usually evaluated by assessing soil quality, although currently procedures focus on crop production for agricultural land purposes rather than environmental impact (Moebius-Clune et al., 2016; Purakayastha et al., 2019; USDA, 2019). Soil, "*represents the difference between survival and extinction of most land-based life*" and is a "*vital living system*" (Doran and Zeiss, 2000) where the physical, chemical, and biological properties ensure that the system properly functions. Soil Quality Indexes (SQIs) have been developed specifically for this purpose to score the 'healthiness' of the soil (Amacher et al., 2007; Andrews et al., 2002; Chaves et al., 2017). Soil Quality Indexes (SQIs) assess and apply weighting to the physical, chemical, and biological parameters that are essentialto maintain soil integrity for its intended purpose I.e., agriculture, storage etc… (Amacher et al., 2007; Chaves et al., 2017). SQIs use a selection of indicators currently designed to evaluate soil health for land management (Chaves et al., 2017). Each indicator is scored using principal component analysis (PCA); the indicators that are given higher weighing are then scored and used to calculatate the SQI (Mukherjee and Lal, 2014). Therefore, SQI values calculated for different landscapes are not comparable because the indicators are chosen based on the different land management. Therefore, the aim of this work was to evaluate the consequences of IHE residue deposition on soil environmental status using a series of soil mesocosms exposed to outdoor conditions, evaluating soil changes by using an EQI approach. For this work a specific set of soil indicators representing the physical, chemical, and biological parameters of the soil were scored by giving the same relevance to each parameter and avoiding PCA analysis. Ultimately, a new Environmental Quality Index (EQI) approach was developed where all the indicators are scored and considered to quantify the quality of soil to enable comparison between sites to ensure a more comprehensive assessment when different areas are evaluated.

2. Methodology

2.1. Soil characterization and soil preparation

To ensure a comparison between a pristine and a representative soil, a sandy loam soil (Soil A) purchased from SureGreen and a loamy sand soil from an active military training area in the UK (Soil B) were used. Both soils were homogenised by screening through a 2-mm sieve and air dried for 2 weeks at ambient room temperature. Soil B was collected using the multi-increment sampling methodology as it is, to date, the most representative collection technique for a non-homogeneous contamination (ITRC, 2012). Both soils were characterised (Supplementary material 2 - S1) using particle size distribution according to STM D 2487-11, soil pH and Electrical Conductivity were measured on a Jenway 3540, Carbon (organic and total) (BS 7755-3.8:1995, ISO 10694:1995), total hydrogen and total nitrogen (BS EN 16168:2012) were measured on an Elementar vario EL cube (Temple et al., 2019).

2.2. Preparation of soil

Both air dried soils were spiked with an IHE solution at either low, medium, or high concentration as determined in Persico et al., 2022 (Table 1). Briefly, IHE flakes (12.5 mg (low), 1250 mg (medium) and 3375 mg (high)) were dissolved in 5.8 L of distilled water at pH 7 for 2 weeks using a Heidolph MR3002 agitator with a magnetic bar. The volume of water for dissolving the IHE flakes was determined by the solubility of RDX (66 mg L^{-1}) at the maximum concentration of the experiments, being the compound with the lowest solubility (Lent, 2019). The soil (8 kg) was then added to the IHE solution and frequently mixed over 3 weeks under a fume cupboard in black containers until excess water had evaporated. The soil mixture was prepared in black containers away from direct sunlight to limit any photodegradation of the explosive mixture.

2.3. Mesocosm experiments

Sealed buckets were used to prepare the mesocosms by cutting a hole in the lid (20.5 × 15.4 × 5.0 cm) to accommodate commercially available black plastic seed trays, which were sealed with silicon to ensure any collected rainwater first passed through the soil (Supplementary material 1).

Each tray (36 in total) was first filled with 0.5 cm of damp inert quartz sand to avoid contact between the soil and the bottom of the tray and minimise any soil loss through the holes at the bottom of the trays. Spiked soil (8 kg) was then poured into each tray to a depth of 5 cm (Supplementary material 1) and final weight recorded. The depth of soil was determined by the depth of the top layer of soil (5 cm), as this is where any change to soil properties due to surface contamination is expected to be observed (Blume et al., 2016). For low, medium and high contamination 5 contaminated samples, and 3 positive controls (clean soil) were prepared.

Samples were sacrificed at day 0, 1, 7, 14, and 36 and prepared for analysis. Leachate volume was collected in triplicate using 50 mL amber glass tubes to avoid photodegradation of the IHE. For biological analysis, soil (5 g) was collected from each mesocosm in triplicate using a 5 mL sterile vials and 20 μL of glycerol was added to preserve the soil for biological analysis. Soil samples were stored at −70 °C until biological analyses were carried out. The remaining soil (1 Kg for each mesocosm) was stored at −18 °C for physical and chemical property analysis and leachate was collected and stored at 4 °C until chemical analysis was carried out.

2.4. Weather condition data collection

The mesocosms were set up during the UK summer months (July–August) and weather data was recorded during this time from the closest

Table 1
Measured spiked concentration of low, medium and high concentrations used for the soil mesocosms.

	Soil A			Soil B		
	Low	Medium	High	Low	Medium	High
53 % NTO (mg/kg)	8.1	82	194.9	8.1	81.1	196.7
32 % DNAN (mg/kg)	4.9	49.5	117.7	4.2	49	118.8
15 % RDX (mg/kg)	2.3	23.2	55.2	2.3	23	55.7
IHE total concentration in soil (mg/kg)	15.3	154.6	367.7	15.3	153.1	371.2

weather station (Marlborough, 22 km from the sample collection area). The data was recorded daily and included minimum and maximum air temperatures, rainfall in mm, wind speed and direction, evapotranspiration, solar energy, direct sunshine, humidity, and temperature of the first 5 cm of the soil. The data is publicly available at https://www.windrushweather.co.uk/station/.

2.5. Soil analyses

2.5.1. Explosive extraction and analysis

Soil collected from the mesocosm was air dried. From each collected mesocosms triplicate soil samples (10 g) were collected using multi-increment sampling. The explosive was extracted from the soil using the Temple et al. (2019) method. Briefly, a mixture of acetonitrile/water (1,1) (20 mL) was added to soil (10 g) and shaken for 18 h at 180 rpm in 50 mL amber glass tubes. Samples were filtered using 0.2 μm polyether sulfone (PES) filter and analysed by High Performance Liquid Chromatography (HPLC). Water samples (50 mL) were collected in triplicates, filtered using nylon filters (0.2 μm) and analysed by HPLC as described by (Temple et al., 2019). Quantification of NTO, DNAN and RDX was carried out using a calibration curve. The Limit of detection and limit of quantification are reported in Table S2 (Supplementary material 2).

2.5.2. Soil physical properties determination

Due to the nature of the sample, qualification but not quantification of changes of the physical properties was determined. Therefore, variations were evaluated on air-dried samples.

Bulk density (ρ_b) (kg/m^3) was calculated following the formula (1):

$$\rho_b = {}^{M_s}\!/_{V_s} \tag{1}$$

where M_s is the mass in mg of the soil sample, which was calculated by weighing the dry soil sample. V_s was calculated as the volume of the dry soil sample in m^3 (Han et al., 2016). Soil Particle density (mg/m^3) (SPD) was instead determined according to STM standards (D854 – 14) although, due to the nature of the samples, the soil was air dried instead of oven dried, therefore results have variability in SPD. Those calculations were necessary for the soil porosity variation (%) which was derived from the soil bulk density and the soil particle density. Soil porosity was calculated as follows:

$$f = \frac{1-\rho_b}{\rho_s}\, x\, 100 \tag{2}$$

with ρ_b as the bulk density in g/cm3 and ρ_s as the specific gravity of soil solids (or soil particle density) (Hazelton and Murphy, 2016).

2.5.3. Soil chemical properties determination

pH was recorded from soils (1:5) and leachate water using HI-98100 Checker Plus pH Tester. Electrical Conductivity (EC) was measured (mS/cm) in soil using HI-98331 Groline Direct Soil Conductivity & Temperature Tester. Soil nutrients were analysed using hatch test kits (Hanna Instruments - HI-3895) for qualitative evaluation of P, N and K variability. A colorimetric (P, N) and turbidimetric (K) evaluation was used to measure trace, low, medium, and high levels of nutrients concentration to determine their variability. Distilled water (30 mL) was added to soil samples (10 g) together with the additive powder from the kit, stirred and allowed to settle for 30 min. Potassium Availability (K^+) was measured in ppm following the procedure from (Motsara and Roy, 2008). Potassium Chloride (KCl) (1.907 g) was dissolved in Ammonium Acetate/Acetic Acid solution (50 mL) and standards were prepared ranging from 10 to 100 ppm. The acetate/Acetic Acid solution (50 mL) was added to soil (10 g), and. The samples shaken for 30 min. The solution was than filtered using a Whatman No.30 filter paper and the leachate analysed using a Flame Photometer.

2.5.4. Soil biological properties determination

The Viable Plate Count technique (Jett et al., 1997) was used to evaluate the number of bacteria present in the original soil samples to observe the variability at different IHE concentrations. Nutrient agar (23 g) was added to distilled water (1 L) and autoclaved at 121 °C for 1.30 h. The warm agar was added to sterile polystyrene plastic petri dishes (55 × 15 mm) and left to dry in a sterile environment. Soil (1 mg) was added to Phosphate Buffered Saline (PBS) (100 μL), the samples were diluted up to 9 times to enable visual counting of the bacteria colonies. The diluted solutions (up to 10^{-10}) were spread on the petri dishes which were then left in an incubator at 37 °C overnight. The standard deviation calculated for all results was found to be ≤9.7 % for colony forming units (CFU) estimation.

2.6. Environmental quality index (EQI)

Each of the soil indicators were scored following the procedure for the SQIs (Andrews et al., 2002; Chaves et al., 2017) although avoiding the PCA selection to ensure that all the values were considered. This is because SQIs between different sites are not directly comparable as the soil indicators of a particular site/area tend to be site- or area-specific. Therefore, weighted soil parameters might preclude a comparison between sites (Qi et al., 2009; Wienhold et al., 2004).

Based on previous research the most common set of indicators used to assess the impact of different contaminant on soil are listed in the indicators column in Table 2.

The average value from the six indicators used for each IHE concentration and day of collection was scored based on Amacher et al. (2007). This provided a list of scorings for SQIs based on the calculated experimental values (Supplementary Material 1). For the values where a score was not provided the "low is better" and "more is better" function was used (Lenka et al., 2022). This approach, by using the same set of indicators as of equal importance, ensures comparison between different sites.

Following the scoring from each physical, chemical, and biological indicator (Supplementary material 1), separately, the EQI of each parameter were summed:

$$EQI_{p/c/b} = S_1 + S_2 + S_3 + S_4 + S_5 \tag{3}$$

where S represents the score for each parameter. If one of the previous indicators from Table 4 was not analysed, 0 was the score given.

The EQI was calculated and normalised as follows:

$$EQI = \left({}^{EQI_p}\!/_{I_p}\right) + \left({}^{EQI_c}\!/_{I_c}\right) + \left({}^{EQI_b}\!/_{I_b}\right) \tag{4}$$

Table 2

Commonly used soil indicators to assess the effects of contamination and/or land use management on soil. The highlighted indicators were used for scoring the physical chemical and biological parameters in the EQI.

		Indicators	Reference
Physical properties	1	**Bulk density**	Williams et al. (2020)
	2	Water holding capacity	Williams et al. (2020)
	3	Porosity	Yu et al. (2020)
	4	Water infiltration rate	USDA, (2019)
	5	Aggregate stability	USDA, (2019)
Chemical properties	1	**pH**	Neina (2019)
	2	**Electrical conductivity**	Awale et al. (2017)
	3	**Cation exchange capacity**	Chaves et al. (2017)
	4	**Nutrient availability**	Cardoso et al. (2013)
	5	Soil organic carbon	Lehmann and Kleber (2015)
Biological properties	1	**Microbial biomass**	Niemeyer et al. (2012)
	2	Microbial biodiversity	Schloter et al. (2003)
	3	Microbial activity	Schloter et al. (2003)
	4	Soil respiration	Cardoso et al. (2013)
	5	Earthworms	Pervaiz et al. (2020)

where EQI is the Environmental Quality Index for the physical, chemical, and biological properties, $I_p/c/b$ are the numbers of physical, chemical, and biological indicators considered. The EQI was calculated for the control, low, medium, and high concentrations for both soils for each day of collection (0-1-7-14-36).

2.7. Statistical analyses

Regression analysis were carried out on data related to the physical, chemical, and biological properties analysed using Excel (MS Office) to evaluate the relationship between each variable and their dependencies. Results are shown using draftsman plot (Fig. 1) to understand and display the distribution and patterns of the data. Moreover, using SPSS (IBM, USA), two-way ANOVA tests were carried out to analyse the dependency of each variable on the explosive concentration that was spiked on the soil mesocosms.

3. Results

3.1. Physical properties

Bulk density and soil particle density (SPD) were measured at day 1 and 36 for the control and the high contaminated samples as these parameters are least affected by the presence of IHE in a mesocosm study. For both soils, the SPD and the Bulk Density were higher at day 36 for the high contaminated samples compared to the controls, with a difference of 29 % for Soil A and 42 % for Soil B. All the calculated values, with the exception of the control sample for Soil B, were higher than 1.8 g/cm^3 which is a critical value for sandy loam soils as it suggests an extremely compact soil where root penetration would be restricted (Hazelton and Murphy, 2016).

3.2. Chemical properties

In Soil A (Fig. 1), on average, the control soil had a 62 % lower EC value compared to the high contaminated sample (1.83 mS/cm), indicating that the presence of IHE influenced the soil matrix. This was confirmed by the difference in EC detected in soil B (Fig. 1), in which the high contaminated samples had an EC 39 % higher compared to the controls. Overall, for both soils, EC characterised the matrices as non-saline. EC is also influenced by the amount of water in the soil, therefore after 15 days of non-registered rainfall the EC was 0 mS/cm for all samples.

Potassium ion concentration had a stronger correlation with the medium IHE soil contamination levels with r^2 of 0.81 and 0.57 for Soil A and B, respectively. In contrast, a poor correlation was found for the soils spiked with high IHE levels ($r^2 = 0.005$ and 0.0008 for Soil A and B) suggesting that when a higher nitrogen content is spiked into the soil $K+$ is less likely to interact with the IHE molecule.

A clear correlation was observed between the different IHE concentrations and the soil pH in both soils ($r^2 = 0.74$ for Soil A at the high contaminated sample). This correlation was expected as it has been shown that pH influences IHE behaviour in soil (Mark et al., 2016; Temple et al., 2019; Wallace et al., 2011). The pH of the leachate from Soil A remained stable during the experiment. While the pH of the leachate from Soil B increased by 1 %, this increase was recorded for all samples including the controls and therefore cannot be attributed to the IHE content.

Qualitative assessment of nutrients (Table 3) showed a greater change in N and P for Soil B. Soil A had a consistent decrease across all samples in Nitrogen, compared to Soil B where the N behaviour was more variable. For the high and medium concentration samples Nitrogen decreased after day 1, although an increase of N across all samples resulted in a high N concentration at day 7. Soil A and B were also lacking in Phosphorus, which was mostly non detected across both soils.

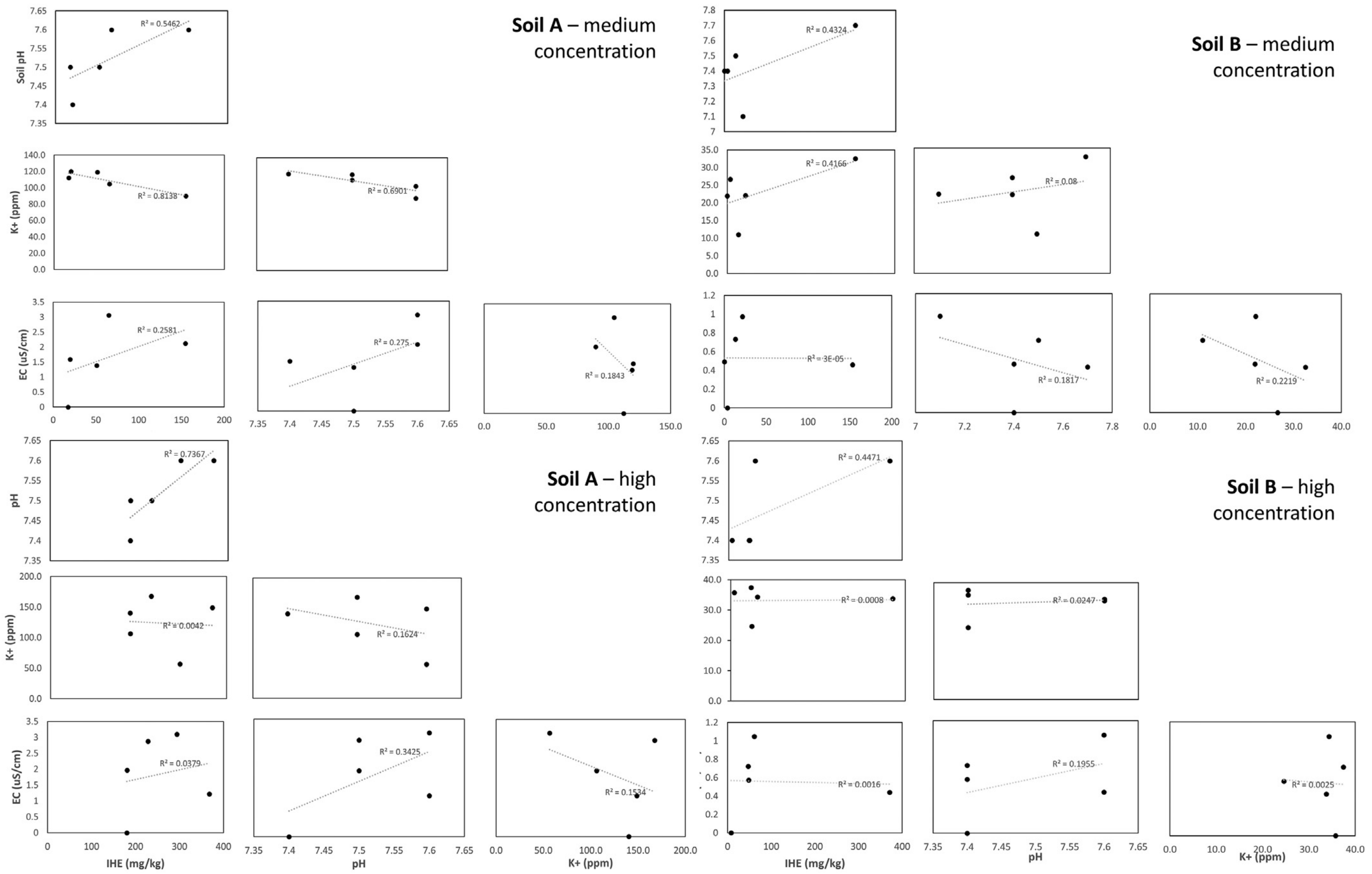

Fig. 1. Chemical properties and relationships between pH, EC, IHE and K^+ in Soil A and Soil B in presence of medium and high IHE concentrations ($n = 56$ per soil).

Table 3
Qualitative assessment of N, K and P from the control, low, medium, and high IHE contaminated soil samples.

	IHE contamination	Nutrient	Day 0	Day 1	Day 7	Day 14	Day 36
Soil A	Control	N	Low	Medium	Trace	Trace	Trace
		K	High	High	High	High	High
		P	Trace	ND	Low	ND	ND
	Low	N	Low	Trace	Low	Trace	Trace
		K	High	High	High	High	Medium
		P	Trace	ND	ND	Low	Low
	Medium	N	High	Low	Trace	Trace	Trace
		K	High	High	High	Medium	High
		P	Trace	ND	Low	ND	Trace
	High	N	Medium	Low	Medium	Low	Medium
		K	High	Medium	High	High	High
		P	Trace	ND	Low	ND	Trace
Soil B	Control	N	Low	Medium	High	Medium	Trace
		K	Trace	Medium	Trace	Trace	Trace
		P	ND	ND	ND	ND	ND
	Low	N	Low	Low	Medium	Trace	Trace
		K	Medium	High	Medium	Trace	Trace
		P	ND	Trace	ND	ND	ND
	Medium	N	High	ND	Medium	Trace	Trace
		K	Trace	Medium	Medium	Trace	Trace
		P	ND	ND	ND	ND	ND
	High	N	Low	ND	Medium	Trace	Medium
		K	Trace	Low	Trace	Trace	Trace
		P	ND	ND	ND	ND	ND

As confirmed from the K^+ availability experiments, total potassium was significantly higher in Soil A compared to Soil B. Total K was also more stable in Soil A (Table 3), differently from Soil B where an increase in K was determined after day 1 following a regular decrease in all analysed samples.

3.3. Biological properties

Soil microbial abundance based on CFU analysis indicated a significant relationship in Soil A between the IHE concentration over time and the CFU ($p < 0.05$). Soil A CFU increased after 7 days and a decrease from day 7 to 36 (Fig. 2). The decrease was more significant for low and high concentration samples. A two-way ANOVA also demonstrated that there was a stronger statistical significance between IHE concentration, soil pH and CFU ($p < 0.05$).

The same correlation has been found between the rainfall and the CFU in Soil B even though there is a difference in behaviour for the high contaminated sample. Conversely to Soil A, no significant relationship has been found between the IHE mixture concentration and the CFU counted. Instead, this relationship was found between the soil pH and the CFU (ANOVA $p < 0.05$) (Supplementary material 1).

3.4. Weathering and IHE concentration effect on soil

The experiments were conducted during the summer season in the UK with an average temperature expected to be around 15.6 °C, based on the 1981–2010 average. The recorded average temperature was 16.6 °C with soil temperature recorded, within the first 5 cm, to be 15.3 °C. Unexpectedly, during the experiments, rainfall was not registered for 19 days, of which 15 were consecutive (from day 21 to 36). The highest rainfall was registered on day 19 (17.7 mm) with an average rainfall throughout the experiment of 1.6 mm (Fig. S1).

Rainfall influenced the transport of chemicals within the matrix, with a rise in leachate when the rainfall was at high levels which could increase the transport of the chemicals from soils to groundwater systems (Zhang et al., 2019). As the rainfall was higher in the first part of the experiment (from day 0 to day 20), a higher dissolution and transport of the IHE mixture was expected during this time. Due to the differences in solubility of the three IHE constituents NTO: 17200 mg/L; DNAN: 216 mg/L, and RDX: 59.7 mg/L (Lent, 2019), it was expected that a higher there would be higher concentrations of NTO and DNAN in the leachate during rainy periods compared to RDX.

Moreover, the amount of rainfall was also associated with a decrease or increase in microbial activity which sees a decline in microbial communities when rainfall is lower (Wu et al., 2020). The CFU calculated in this experiment highlighted the dependencies of the microbes on rainfall, with a strong relationship determined in Soil A ($r^2 = 0.8$). Consequently, due to the rainfall, which was not registered in the second part of the experiments, a decrease is CFU was detected in all samples.

From day 0 to 36, the IHE composition was extracted and NTO, DNAN and RDX independently assessed (Fig. 3). In the controls (non-contaminated soil), no IHE concentration were found for both Soil A and B. The concentration at day 0 was the day on which the experiments were set up and therefore used as the baseline for comparison. Due to the three-week preparation time to enable evaporation of excess water, the concentration of IHE detected was lower at Day 0 than the initial spiked concentration. Therefore, in all the samples contaminated with the lower concentration of IHE (15.34 mg/kg) only 38 % and 6 % of the concentration, respectively for Soil A and B, was recovered after 1 day of experiment with the concentration falling to 0 mg/kg at day 7.

In Soil A, at the medium concentration (Fig. 3), 23 % of the IHE mixture was recovered on day 0 of experiment, with a decrease and then a stabilisation of the IHE mixture in the soil which was recovered with an

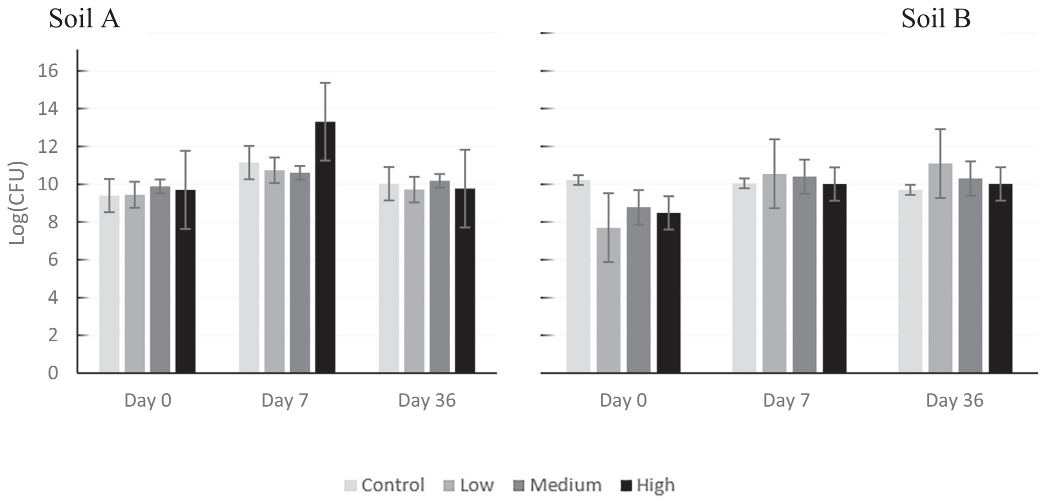

Fig. 2. CFU/mL at day 0–7–36 presented in a $\log_{10}$(CFU) scale ($n = 54$ per soil).

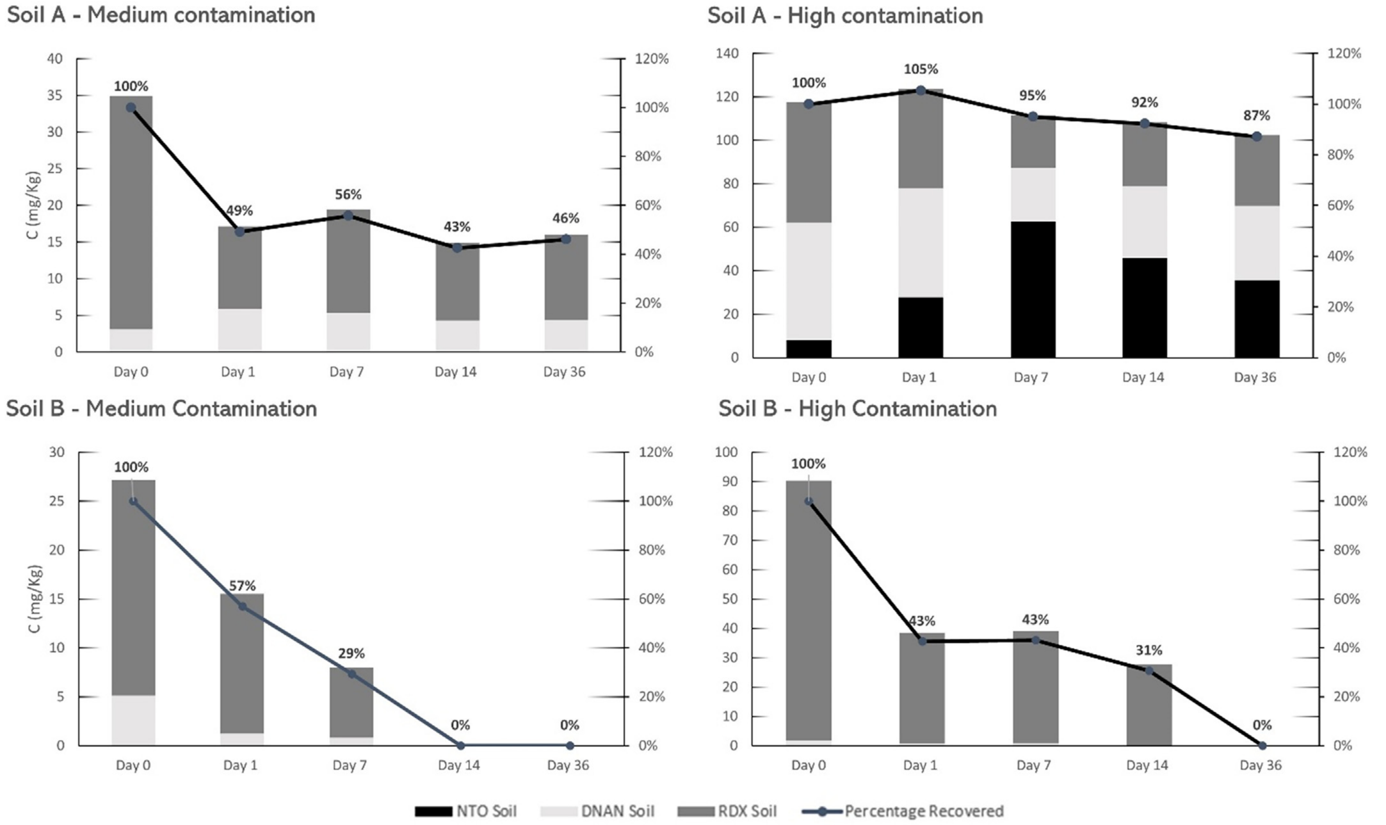

Fig. 3. The concentrations in mg/kg of NTO, DNAN and RDX recovered soil for Soil A and B at the medium and high concentration. The percentages on the graph represent the total % of the IHE formulation recovered from day 0 to 36.

average of 48 ± 5 % from day 1 to day 36 compared to day 0. NTO, being the most soluble of the three compounds, was not recovered in soil, although it was found in its original form in the leachate at day 1 (44.7 mg/L) and day 14 (33.5 mg/L). DNAN was recovered in all samples with an average concentration detected of 4.6 ± 1.1 mg/kg in soil A. As expected, RDX was the most stable with a concentration that varied from 31.8 mg/kg at day 0 to 11.7 mg/kg at day 36. RDX was also recovered in water at each day of experiment ranging from 2.6 to 0.5 mg/L.

At high concentration in Soil A, a higher percentage of the explosive mixture was recovered at day 0 (117.6 mg/kg) with no degradation during the three weeks of preparation of the RDX compound and low degradation of NTO and DNAN, which was recovered in the leachate at day 1 (Table 4). The total degradation in soil from day 0 to day 1 was negligible with a recovery of 5 % higher than at the beginning of the experiment. This recovery highlights the difficulty in analysing IHE compounds, with NTO being the most difficult to detect, therefore an error was expected as highlighted in previous work (Temple et al., 2019) due to the heterogeneous nature of the soil matrix. NTO was recovered in high quantities in the water leachate ranging from 163.7 mg/L at day 1 to 73.2 mg/L at day 36, emphasizing its rapid transport through soil due to the diminishing leachate concentration over time. DNAN was not significantly detected in water (0.6 mg/L at day 1) with only 37 % decrease in recovery from day 0 to day 36. 55 % and 68 % of the total RDX was recovered respectively at the medium and high concentration after 36 days (12.8 mg/kg; 36.7 mg/kg).

Table 4
IHE recovered from the collected leachate for the medium and high concentration in mg/L.

	Soil A			Soil B		
	NTO	DNAN	RDX	NTO	DNAN	RDX
Medium concentration						
Day 1	44.7 ± 3.3	N.D.	2.6 ± 0.2	3.1 ± 0.2	N.D.	3.14 ± 0.66
Day 7	N.D.	N.D.	0.5 ± 0.07	3.0 ± 0.8	N.D.	2.2 ± 1.46
Day 14	33.5 ± 0.3	N.D.	2.7 ± 0.07	N.D.	N.D.	N.D.
Day 36	N.D.	N.D.	1.2 ± 0.02	N.D.	0.3 ± 0.3	3.3 ± 0.09
High concentration						
Day 1	54.7 ± 94.4	0.4 ± 0.1	2.1 ± 3.3	7.1 ± 1.9	N.D.	2.7 ± 1.3
Day 7	75.5 ± 20.8	N.D.	3.7 ± 0.6	2.3 ± 3.5	N.D.	20 ± 13.9
Day 14	70.4 ± 8.5	N.D.	2.1 ± 0.02	N.D.	N.D.	19.2 ± 0.7
Day 36	73.2 ± 15.9	0.7 ± 0.2	4.9 ± 0.2	N.D.	N.D.	8 ± 0.5

In Soil B at the medium concentration only 18 % of the IHE mixture was recovered at Day 0 with a further decrease in soil of 42 % from the start of the experiment to day 1 (15 mg/kg) and 71 % at day 7 (8 mg/kg). NTO, DNAN and RDX were also detected in the collected leachate for the medium concentration samples. NTO was not recovered in soil but was detected in water at day 1 (3.1 mg/L) and day 7 (3.0 mg/L) demonstrating it low adsorption to Soil. DNAN decreased in concentration from day 0 to day 1 by 77 %. DNAN was not detected in water leachate until day 36 when a small amount (0.3 mg/L) was recovered. RDX decreased by 35 % on day 1 and 67 % on day 7, compared to the concentration detected at day 0 (22 mg/kg). From day 14 to day 36 RDX was not recovered from soil, although 3.3 mg/L was detected in water leachate at day 36. The increased rate of transport of RDX in soil B compared to Soil A can be attributed to the decreased organic content in the matrix.

No NTO was recovered from the high concentration samples of Soil B, although some explosive was recovered in water at day 1 (7.2 mg/L) and day 7 (2.3 mg/L). This suggested that NTO underwent chemical changes, as it was not found in either soil and only 6 water samples in its original form. DNAN recovery was lower at day 1 and similar at day 7, compared to the medium contaminated samples of Soil B. It is likely that degradation was more rapid in Soil B compared to soil A as DNAN was recovered in much lower quantities in its original form. A higher recovery of RDX from Soil B compared to the medium concentration was detected, which remained stable until day 14, with 31 % of the explosive recovered compared to day 0. Although, no RDX was detected at day 36 in soil. RDX was regularly recovered in the water leachate with an average of 12.5 mg/L.

It is worth noticing that even though IHE has was not detected in some of the samples, the concentration may have been lower than the limit of detection (<0.004).

3.5. Preliminary environmental quality index (EQI) calculation

Each parameter was scored following Amacher et al. (2007) to provide a list of SQIs based on the calculated experimental values and theoretical values taken from Lenka et al., 2022 when scores could not be derived (Table 5).

Nutrient values obtained were then averaged. SOC values were scored as "0" (Table 5) as soils could not be oven dried due to the explosive nature of the samples. DNAN degrades at approximately 200C therefore the procedure could have impacted the nature of samples giving false results., Therefore SOC values were not fit-for-purpose for the EQI although more research is needed for application of SOC calculation methodologies to ensure that quantitative analyses are carried out.

The biological, chemical, and physical scores were summed according to formula (2) (Supplementary material 2 - Table S3). Following the scoring, data were added up and normalised based on the number of indicators that were analysed experimentally. The normalised scores were summed up following formula (3) and an EQI was obtained for each concentration and day of experiment (Supplementary material 1).

Due to the limitations of analysis of the explosive contaminated samples the chemical indicators were the most influential parameters in the EQI as chemical parameters were mostly analysed for the preliminary EQI, respectively 60 % and 76 % on average for Soil A and Soil B, followed by the biological section (23 % for Soil A and 20 % for Soil B) and the physical indicators (1 % for both Soil A and B). Therefore, because further studies are needed to understand how to overcome the explosive contaminants issues for some analyses, the EQI obtained are preliminary values. Although, these values will provide insight on possible influences of explosives on soil determining a baseline until further analyses can be done to have more comprehensive values.

In both soils (Fig. 4), the EQIs had similar variation, ranging from 0.63 to 1.87 for Soil A and 0.60 to 1.80 for Soil B. The EQI calculated for the non-contaminated samples was, as expected, lower for Soil B, compared to Soil A, as Soil B is a land degraded matrix. Although, the EQIs for Soil A and B did not decrease overtime having only a 1 % difference between the first to the last day of collection. As expected, as the contamination in the samples increased so did the differences in EQI between the soils. At the low, medium, and high concentration Soil B average values were 6 %, 20 % and 24 % lower respectively compared to Soil A at the same concentrations. In fact, the difference between the highest affected sample in Soil A (with the lowest EQI on average – low contaminated samples) and the control, differed by only 1 % compared to Soil B where this difference was 24 %. Overall, the EQI increased for all the samples at Day 7, again highlighting the importance of the weather conditions as a main influential factor for the analysed properties.

Chemical properties, which were the most studied in this work, significantly affected the outcome of the EQI and further work is needed to increase the amount of data available for the physical and biological values. However, these preliminary results have shown how Soil B was increasingly affected by the IHE contamination, subsequently increasing the rate of degradation. In Soil A, this difference could not be determined, meaning that the explosive components are not currently affecting the soil properties at the studied concentrations.

4. Discussion

The increased interest in understanding soil changes due to IHE exposure has been led by a rise in usage of these new explosive mixtures and further discoveries of soil surface and groundwater contaminations (Jenkins et al., 2006; Morley et al., 2006; Temple et al., 2018). The fate and transport of the IHE compounds is guided by the soil composition (Monteil-Rivera et al., 2021; Taylor et al., 2017; Temple et al., 2018) is influenced by the soil properties. Sandy Loam and Loamy Sand, which have been named Soil A and B in this research, have many physical similarities but were characterised by more significant chemical differences. Soil A had on average the highest K+ content, pH, and EC. Moreover, because Soil B was collected from a training range, degradation of the matrix led to a different relationship with the chemical compounds (Tetteh, 2015) which were spiked for the evaluations.

Because of the dependent relationship between K and N components in soils (Johnston and Milford, 2012), which increases N adsorption as K availability rise, Soil A retained NTO, DNAN and RDX more compared to Soil B, due to an increase in adsorption processes which has been also consistently reported for DNAN in the literature (Linker et al., 2015). This retention was strengthened by the high pH (8.7) which increases the interaction between the NTO and the soil matrix (Mark et al., 2016). This interaction can also lead to changes in the NTO molecule, increasing degradation due to polar interactions. This study did not analyse for degradation products, although, because of the high organic content in Soil A it was expected to not find NTO in its original form, because of the increased likelihood of NTO degradation products. Conversely a high concentration of NTO was recovered in the leachate from Soil B suggesting that when soil is more prone to degradation, it is less likely for the explosive to accumulate in the soil system. This suggests that there is a higher likelihood of the chemical contaminating groundwater systems. RDX, was recovered in both soils, with highest retention in Soil A due to the affinity between the molecule and the organic content, which was higher compared to Soil B (Lent, 2019). RDX is known to be the most stable compound in the IHE (Lent, 2019; Temple et al., 2019), and therefore as expected was generally recovered at high concentration in both soils in the medium and high contaminated samples. Moreover, compared to NTO, RDX was highly resistant to microbial degradation (Lent, 2019), confirmed by the low degradation rate reported for Soil B, which had the highest microbial content. Therefore, the IHE are less likely to transport to sub-soil and groundwater systems in Soil A, although there is an increased likelihood of degradation products and subsequently an increased contact with the soil matrix. It may be expected that in soils with increased contact time with IHE, there would be an increased likelihood of negative impacts, however in this work the opposite was observed with Soil B being more effected by the IHE.

Table 5
Example of chemical properties scored for the calculation of the EQI. A value of "0" was selected when missing data were present.

Soil A – medium contamination chemical properties		Value obtained from experimental analyses					Scored values					Reference/Technique used
		Day 0	Day 1	Day 7	Day 14	Day 36	Day 0	Day 1	Day 7	Day 14	Day 36	
pH		7.6	7.6	7.4	7.5	7.5	1	1	1	1	1	Amacher et al. (2007)
EC		2.1	3.01	1.6	1.4	0	3	3	3	3	0	Amacher et al. (2007)
CEC		0	0	0	0	0	0	0	0	0	0	Missing analyses
K +	Nutrients	90	105	120	119	112	0	1	1	1	1	Amacher et al. (2007)
N		4	2	1	1	1	4	2	1	1	1	"More is better"
P		1	0	2	0	1	1	0	2	0	1	"More is better"
SOC		0	0	0	0	0	0	0	0	0	0	Missing analyses

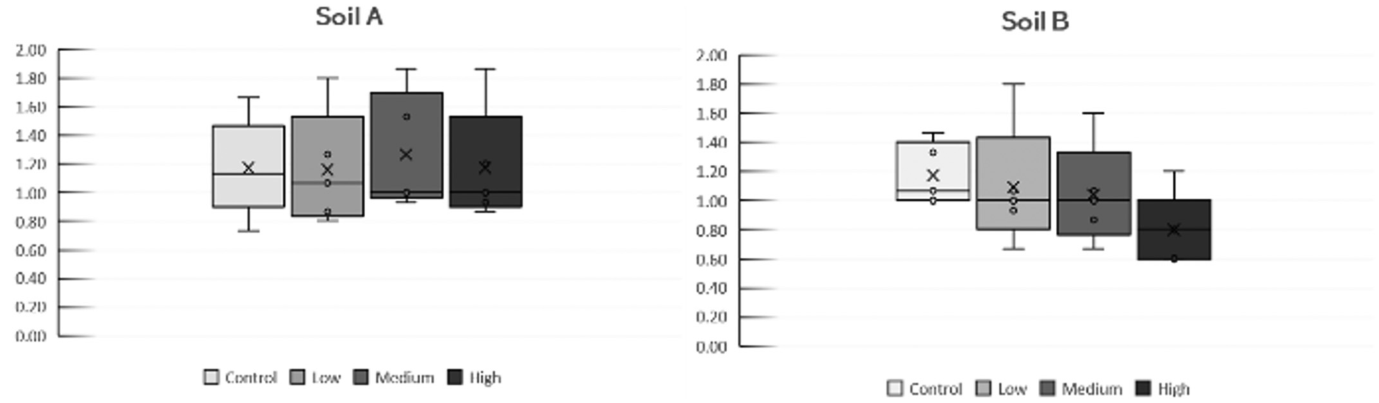

Fig. 4. Environmental Quality Index (EQI) calculated across all the samples for the control, low, medium, and high concentration.

Similar physical changes were observed in the soil matrix for both the control samples and the contaminated samples. These changes cannot to be attributed to the presence of IHE, so must be attributed to the method in which the mesocosm were set up and the weather conditions.

There greater variation in the chemical properties in Soil B compared to Soil A. In general, the EC was most significantly influenced in both soils, which was expected as increase in EC has been previously used as an indicator of pollution (Edwin-Wosu and Nkang, 2019; Gevao et al., 2000). Contaminants can increase the concentration of ions in the soil, which increases the soil's ability to conduct electricity, therefore it can be a cause for concern as certain contaminants can be harmful to plants and animals. The controls had a 60 % and 40 % lower EC for Soil A and B respectively compared to the contaminated samples of the same soil. This change is likely due to the increase in nutrient content (Othaman et al., 2020) provided by the nitrogen rich IHE. As expected, the difference was more significant (60 %) in Soil A due to the greater retention of IHE constituents. In Soil A, this was confirmed by the increase in nitrogen content compared to the control. pH slightly decreased overtime in all samples, including the controls, therefore those changes were not attributed to the presence of IHE, although, as highlighted above, pH can alter the retention of IHE in soil and therefore is a key parameter to observe.

Biological changes were evaluated by microbial abundance which was, at the beginning of the experiment, 85 % higher in Soil B compared to Soil A. Although, the microbial abundance was mostly subject to the weather conditions with an increase in microbial abundance during the first 7 days when the highest level of rainfall was recorded. Further studies are needed to investigate the relationship between potential degradation product formation and the CFU in the soil. For the same reason, a decrease in CFU was recorded all samples at day 36 due to the unexpected 20 day dry spell prior to completion of the experiments. It is worth noticing that at day 36 the microbial abundance was highest in the high concentration sample of Soil B, in contrast to Soil A where the highest microbial abundance was found in the control. More studies are needed to analyse if this difference is due to the high explosive content. Due to the low IHE concentration in soil, the biological parameters were not affected by the IHE components at the concentrations investigated, which was expected due to the concentrations being were lower compared to the latest ecotoxicological data (Dodard et al., 2013; Monteil-Rivera et al., 2021).

The EQI value was calculated based on the scoring of different soil parameters. Although, because of the challenges faced when explosive contaminated samples further studies are needed to create a more comprehensive visualization of the environmental challenges. Therefore, based on the current analyses a preliminary EQI was calculated and values determined for both soils. For Soil A, the EQI value suggests that at the studied concentrations the IHE are not negatively impacting the soil health. However, this cannot be said for Soil B where a significant decrease in EQI has was recorded between the low and high concentration samples. A reasonable number of live rounds fired annually is up to 10,000 (Galante et al., 2017), however this work has shown that with contamination levels from as few as 100 detonations soil quality can deteriorate. For large live-fire ranges 100 detonations can occur within two weeks, which would correlate to a major decrease in soil quality over 1 year for Soil B. This highlights the importance of continuing research into the threat that IHE pose to some soils, such as Soil B, a naturally degraded soil likely to be found on training ranges, as the investigated contamination levels are all below reported LD_{50} values suggesting that soil health begins to deteriorate long before accepted toxic concentrations are reached (Dodard et al., 2013; Monteil-Rivera et al., 2021).

5. Conclusions

In this work, the impact of the IHE mixture has been assessed on two different soils, a pristine sandy loam and a degraded soil collected from a military training range. It has been found that IHE behaviour in the environment is dependent on the soil matrix, such as whether the soil is initially degraded or non-degraded. The pristine soil (Soil A) was found to have more chemical interactions with the IHE constituents, which appeared to reduce the consequences on the soil matrix. The degraded soil (Soil B) was more sensitive to the presence of IHE, with significant changes to nutrients and EC observed, suggesting that potentially IHE has a great impact on degraded soil. Therefore future research is needed to investigate the cumulative impact of IHE on degraded soils as it is more likely to be affected by the explosive components. Although, it is worth highlighting that soil composition and external weather conditions play a key role on the transport and fate of explosive residues. Therefore, further studies are needed to quantify the consequences after an increased number of detonations (>10,000), as 100 detonations, the equivalent in this study, is not representative of actual training activities. Currently, SQIs are not comparable between different sites, this is because the SQI has a different value depending on the chosen indicators and the different areas. The EQI, developed here is based on the same concept but enables comparison and therefore should start generating comparable data between sites enabling a standardise soil quality scale. It is concluded that compared to traditional explosives IHE compositions are unlikely to have the same major impact on the environment at the studied concentrations for pristine soil, although further studies are needed to determine at what point the IHE concentration can cause a major stress on the environment and potentially have an impact on the biota and people's health especially on degraded soils.

CRediT authorship contribution statement

Federica Persico: conceptualization, methodology, writing - original draft, investigation, visualization. Frederic Coulon: conceptualization, methodology, writing - review & editing, visualization, supervision. Melissa Ladyman: conceptualization, methodology, writing - review & editing. Carmen Fernández López: experimental analyses, writing - review

& editing, investigation. Tracey Temple: conceptualization, methodology, writing - review & editing, visualization, supervision.

Data availability

Research data can be found in the Cranfield University data repository (CORD). Data supporting this study are openly available from CORD at https://doi.org/10.17862/cranfield.rd.21501063.v1.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank the Spanish Ministry of Science and Innovation (PID2019-109700RB-C21) for supporting the stay at the Cranfield University of Dr. Carmen Fernández-López. In addition, thanks to Eng. Ernesto De Gregorio for developing the 3D image for the mesocosm design and Karl Norris for making the soil mesocosms.

Funding

This work has been funded by The Central England NERC Training Alliance (CENTA), UKRI Grant number NE/L002493/1.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.161797.

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