CRANFIELD UNIVERSITY

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Fate and transport of Insensitive High Explosives in the environment

Centre for Defence Chemistry

PhD
Academic Year: 2015–2018

Supervisor: Professor Frederic Coulon
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ABSTRACT

The research undertaken for this thesis has contributed to better understanding of the fate and transport of insensitive high explosives (IHE) formulations and suitable extraction methods from soil. Investigations into the dissolution behaviour of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) from Polymer Bonded Explosives (PBX) showed that the polymer retained almost 97% of the explosive filling. This indicates that these formulations release their contents slowly although consistently suggesting that cumulative contamination may occur in the environment. Due to low release of RDX from the polymer it was necessary to validate the findings by ensuring all explosives were accounted for. As there was no existing extraction methods for PBX a novel Accelerated Solvent Extraction (ASE) method was successfully developed and optimised. To further understand IHE behaviours in the environment, fate and transport of IHE in soil was then considered. However, as RDX behaviour is well understood attention was then turned to IMX formulations in soil. Again, suitable extraction for IHE in soil had not been reported, therefore a comparison of suitable extraction methods for IHE constituents in soil was undertaken. Results showed extraction of IHE is dependent on soil types, which highlighted the need to pre-determine extraction efficiency for soil type and targeted contamination. Therefore, pre-testing extraction with known concentrations is recommended. This research was then applied to understanding the behaviour of the mixed constituents in soil, following column transportation studies. Results contributed to and supported work from the literature on the behaviour of individual IHE constituents suggesting that these explosives in combination did not adversely interact with each other when in soil. The novelty of this work was the investigation of IHE as mixtures rather than individually. This work has provided valuable insights into the behaviour of two different IHE (PBX and IMX) in the environment, and has communicated suitable extraction procedures to enable full quantification of contaminant concentrations.

Keywords: Insensitive High Explosives (IHE) formulation; Polymer Bonded Explosives (PBX), explosive soil extraction, PBX extraction, environmental transport

ACKNOWLEDGEMENTS

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μ	Micro
2-ANAN	2-Amino-4-nitroanisole
4-ANAN	4-Amino-2-nitroanisole
ACN	Acetonitrile
ASE	Accelerated Solvent Extraction
ATO	3- Amino-1,2,4-triazol-5-one
Comp-B	Composition B
DAAN	2,4-Diaminoanisole
DI	Deionised water
DNAN	2,4-Dinitroanisole
DNP	2,4-Dinitrophenol
DNX	Hexahydro-1,3-nitroso-5-dinitro-1,3,5-triazine
DOA	Di-(2-ethylhexyl)-adipate
H_2O	Water
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HO-NAN	Hydroxy-nitroanisole
HPLC	High performance liquid chromatography
HTPB	Hydroxyl-terminated polybutadiene
IHE	Insensitive High Explosives
IM	Insensitive Munitions
IMX	Insensitive Munitions Explosive
K_{OC}	Organic carbon partitioning coefficient
MeOH	Methanol
MNX	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
NQ	1-Nitroguanidine
NTO	Nitrotriazolone
PBX	Polymer Bonded Explosives
PCA	Principal Component Analysis
PDA	Photodiode Array
ppm	Parts per million
PSE	Pressurised Solvent Extraction
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
TNT	2,4,6-Tri-nitrotoluene
TNX	Hexahydro-1,3,5-nitroso-1,3,5-triazine
TO	Triazolone
US	United States
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
μg	Micro grams

Chapter 1   Introduction

Training with live munitions is necessary to maintain the combat readiness of military forces. When munitions containing energetic materials are fired continuously in the same locations trace explosive residues are deposited on the soil surface, leading over time to the contamination of land and water (Clausen et al., 2004; Rasmussen and Voie, 2016; Walsh et al., 2014a). Further contamination arises from the inefficient detonation (low-order detonations) or non-functioning of munitions and in consequence, substantial amounts of the explosive materials are deposited on the ground (Chatterjee et al., 2017; Walsh et al., 2013, 2017).

The chemicals that make up these explosive materials have been found at most weapon-firing points and impact areas, on the soil surface and down to 30 cm below (Arthur et al., 2018). They have the potential to cause contamination in both the immediate vicinity and the surrounding area (Pennington et al., 2006). Changes in the law and growing public awareness have increased the pressure on military organisations to ensure their operations are environmentally sustainable (Fisher, Scarlett and Stott, 1997; NATO, 2006; Poulin, 2010; Reeder and Kling, 2010; USEPA Federal Facilities Restoration, 2014). However, military capability must be maintained, and this means continuing live-fire training on training ranges.

Conventional explosives such as 2,4,6-tri-nitrotoluene (TNT) and hexahydro-1,3,5-trinitro1,3,5-triazine (RDX) are known to be toxic and pose a risk to the environment (Burton, Turley and Peters, 1994; Pennington and Brannon, 2002; Thomas et al., 2018), but less is known about insensitive high explosives (IHE), which are now coming into service to replace legacy explosive materials in Insensitive Munitions (IM) (Walsh et al., 2014b). IM are being brought into military service for safety reasons, primarily to avoid the accidental detonation of munitions during storage or transport (Baker and Stasio, 2015). IM can be designed by following one or more of three approaches (Cumming, 2009). First, the munition can be covered with an external protective structure such as an intumescent coating containing char that expands when exposed to fire (Baker and Stasio, 2015). Another example is provided by shipping containers, which are used to protect against thermal and mechanical insults (Baker and Stasio, 2015). Second, the munition can be insulated but also vented, allowing the release of excess pressure to prevent fires (Baker and Stasio, 2015).

Finally, the chemistry of the IHE filling can be selected to improve insensitiveness, for example by using polymer bonded explosives (PBX) or Insensitive Munitions Explosives (IMX) (Ministry of Defence, 2014).

PBX are explosive materials in which the explosive filling is bound together in a matrix using small quantities (typically 5–10% by weight) of a synthetic polymer (RWM Italia, 2011). PBX formulations are often used for explosive materials that cannot be prepared by melt casting or are otherwise difficult to form into the desired shape (Akhavan, 2011). In contrast, IMX compositions are melt-castable, and use 2,4-dinitroanisole (DNAN) as a binder for other insensitive or traditional explosives such as 3-Nitro-1,2,4-triazole-5-one (NTO) and RDX (Lee et al., 2010; Singh et al., 2010).

IHE formulations such as PBXN-109, IMX-104 and IMX-101 (**Table 1-1**) have replaced legacy explosives such as Composition B (Comp B), a mixture of RDX and TNT, due to the improved safety profile. For example, IMX-101, which was approved by the US Army in 1999, has the "same lethality as traditional TNT, but is far less likely to explode if dropped, shot at or hit by a roadside bomb during transport" (Maharrey et al., 2014). Although the environmental behaviour of legacy explosives has been investigated in detail, the fate and transport of IHE has not received the same attention. It is therefore unclear whether IHE pose a risk to the environment during normal use when detonation causes their residues to travel through the open air and come into contact with multiple receptors in the soil.

Table 1-1: Examples of insensitive replacements for traditional explosives.

Name	PBXN-109	IMX-104	IMX-101
Chemical Composition	RDX: 65% Aluminium powder: 20% HTPB (isocyanate cured): 7% Plasticiser 8%	NTO: 51–55% DNAN: 30–34% RDX: 14–17%	DNAN: 43% NTO: 37% NQ: 20%
Type	Cast-cure polymer bonded secondary explosive	Melt-castable secondary explosive	Melt-castable secondary explosive
Main Use	General purpose explosive (Comp B replacement) in air-dropped bombs	Artillery and other large-calibre munitions (replacement for Comp B-filled munitions)	Artillery and other large-calibre munitions (replacement for TNT-filled munitions).

There is increasing interest in the fate and transport of individual IHE constituents in the environment as identified during the literature search (Chapter 2). However, there is still insufficient research to determine the risk associated with these materials in natural environments. In particular, their dissolution and transport behaviour in UK soil and local climatic conditions, especially in their formulated mixtures. In addition to this research gap, it was also evident that efficient, standardised methods for the extraction of IHE constituents had not been developed. This is important to ensure that complete quantification of environmental contamination is accurate, precise and reliable.

.

1.1 Aim and Objectives

The overall aim of the work presented in this thesis was to investigate the fate, transport and persistence of IHE compositions in the environment (**Figure 1-1**). This was achieved by focusing on the following objectives:

1. Critically review the literature covering the environmental fate and transport of IHE under consideration for use in munitions, including the specific ingredients (DNAN, NTO, RDX and NQ) and the formulations (PBX and IMX) (**Chapter 2**).
2. Investigate the weathering mechanisms and dissolution rates of IHE (PBX) (**Chapter 3/ Appendix 1**).
3. Optimise a method to extract the explosive constituents from PBX (**Chapter 4**).
4. Compare current analytical techniques for the extraction of IHE from soils (**Chapter 5**).
5. Assess the influence of soil characteristics such as pH, organic content, porosity and particle size on the environmental distribution and persistence of IHE residues and their degradation products in soil **(Chapter 6/ Appendix 3**).

Figure 1-1: Thesis structure aligned to chapter titles.
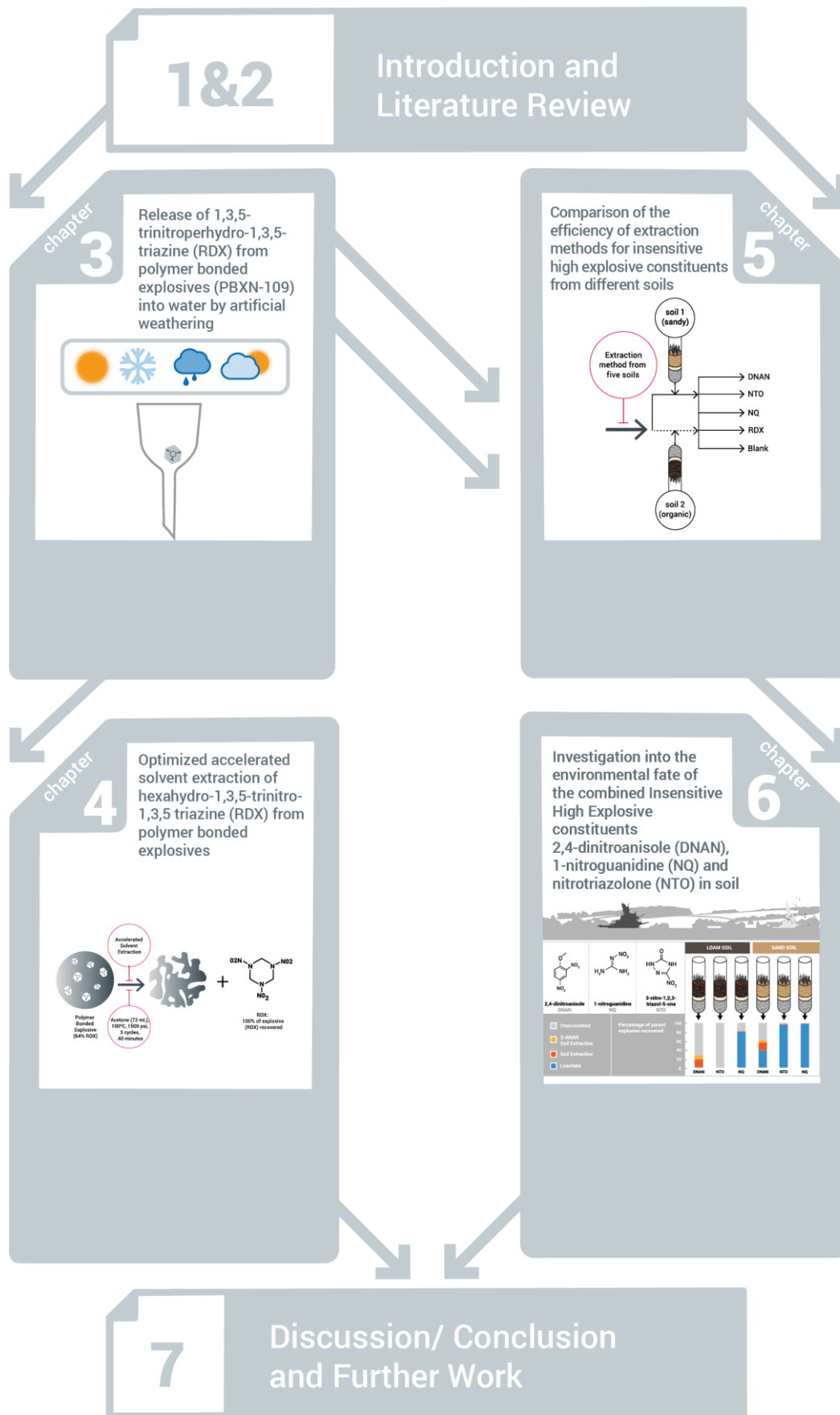
Chapter 2   Literature Review

The environmental impact of traditional and legacy explosives such as TNT, RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is well understood (Juhasz and Naidu, 2007). However, there is little information concerning the behaviour of IHE in specific environmental compartments, such as soil and groundwater. This literature review begins with a brief introduction to the use of IHE in military service, and describes their physicochemical properties, the factors that influence their fate and transport in the environment, how they make their way into the environment, and the challenges presented by the analysis of IHE compared to traditional explosives.

2.1 Insensitive munitions

Defence organisations around the world are increasingly concerned about the vulnerability of munitions stockpiles, specifically the risks of accidental detonation and degradation, and are committed to the replacement of traditional munitions with IM that are safer to handle and transport (Krzmarzick et al., 2015; Rao et al., 2013). The North Atlantic Treaty Organisation (NATO) standardisation agreement (STANAG) 4439 defines insensitive munitions as:

"*Munitions which reliably fulfil their performance, readiness and operational requirements on demand, but which minimize the probability of inadvertent initiation and severity of subsequent collateral damage to weapon platforms, logistic systems and personnel when subjected to selected accidental and combat threats* (NATO, 2006)."

Traditional energetic materials are designed to decompose rapidly on command. This can lead to unplanned initiation when exposed to external stimuli such as high temperatures or accidental insult (Aydemir and Ulas, 2011). Munitions containing traditional explosives can be made insensitive by adapting the packaging or casing to ensure that unexpected stimuli are absorbed, or through the use of barriers and shielding. However, once unpacked, these munitions again become vulnerable. IM can also be created by filling with IHE because these materials are designed to be intrinsically resistant to accidental detonation (Baker and Stasio, 2015). Among the various types of IHE that have been developed, the work described in this thesis concerns PBX and IMX.

PBX formulations are homogeneous mixtures of a solid explosive bound by a polymer matrix such as hydroxyl terminated polybutadiene (HTPB). The polymer matrix improves the mechanical properties of the mixture and ensures insensitivity. PBX formulations have been designed to replace legacy high-explosive formulations because PBX is less sensitive to unintended detonation and external fragment impact (Kumar et al., 2010). PBX formulations typically consist of RDX or HMX (**Figure 2-1**) entrapped in a polymer. They may also contain ammonium perchlorate or reactive metals such as aluminium.

RDX

HMX

Figure 2-1: Chemical structures of the nitramine explosives RDX and HMX.

In contrast, IMX formulations include compounds such as 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO), which are themselves less sensitive to shock and heat than conventional explosives (Taylor et al., 2013). For example, the formulation IMX-104 is an insensitive, melt-cast explosive containing NTO (51–55%), DNAN (29.7–33.7%) and RDX (13.3–17.3%), whereas IMX-101 consists of NTO (43%), DNAN (37%) and 1-nitroguanidine (NQ) (20%) (**Figure 2-2**). DNAN melts at 94.5°C and acts as the binder for NTO and RDX.

NTO

DNAN

NQ

Figure 2-2: Chemical structures of NTO, DNAN and NQ.

2.1.1 Physicochemical properties of IHE constituents

IHE typically comprise up to five constituents including RDX, HMX, DNAN, NTO and NQ (**Table 1-1**), which are mixed in various ratios to achieve the desired performance (Richard and Weidhaas, 2014a).

RDX is a white, crystalline solid with a high melting point (204–206°C), low vapour pressure and a density of 1.806 g/cm^3 at 20°C. RDX is sparingly soluble in water (0.06 mg/L at 20°C) and is stable under ambient conditions. HMX is also a white crystalline solid, with similar properties to RDX, and is a by-product of the RDX manufacturing process (Howa et al., 2014). HMX has a high melting point (275–280°C) and density (1.78–1.96 g/cm^3 at 20°C) and is has limited solubility in water (Pichtel, 2012). PBX formulations containing HMX are more sensitive than those containing RDX (Akhavan, 2011).

DNAN is a pale-yellow nitro-aromatic flammable compound, which is slightly soluble in water (0.28 g/L) (Pichtel, 2012). NTO is a yellow powdered energetic compound that was first used in explosive formulations in 1987 (Lee, Arnot and Mattia, 2010). NTO has a very similar velocity of detonation to RDX (7100 m/s for NTO compared to 7900 m/s for RDX) but is much less sensitive to shock (Vijayalakshmi et al., 2015). NQ is a nitrogen-rich, high-energy material, with good thermal stability and a decomposition temperature of 180°C (Akhavan, 2011). NQ is mainly used in triple-based propellant formulations and more recently in IHE compositions. A summary of the physicochemical properties of IHE constituents is given in **Table 2-1**.

Table 2-1: Summary of the physicochemical properties of explosives

Material	Empirical Formula[1]	Physical form[1]	Molecular Weight	Melting point[1]	Boiling point[1]	Density[1]	Solubility (25 °C)	Temperature of decomposition[1]	Temperature of ignition[1]
			g/mol	(°C)	(°C)	(g/cm^3)	g/L	(°C)	(°C)
DNAN	$C_7H_6N_2O_5$	Tan to yellow crystalline solid	198.1	94.5	315	1.44	Ethanol; ether; acetone; benzene; pyridine[6]	295[2]	347
NTO	$C_2H_2N_4O_3$	White crystalline solid	130.1	273	295	1.91 1.93	16.8 (acetone)[5]	273	258–280
NQ	$CH_4N_4O_2$	Pale yellow crystalline solid	104.1	239	250	1.55	Low solubility in organic solvent[4]	232	NA
RDX	$C_3H_6N_6O_6$	White crystalline solid	222.1	205.5	234	1.82	410 (DMSO)[3]; 82 (acetone)[3]; 55 (acetonitrile)[3]	213	210
HMX	$C_4H_8N_8O_8$	White crystalline solid	296.2	276	286	1.91	570 (DMSO)[3]; 28 (acetone)[3]; 20 (acetonitrile)[3]	280	335

1. Akhavan J. 2011. The Royal Society of Chemistry; 2. Xing et al. 2012. Propellants, Explosives and Pyrotechnic, 37, p179; 3. Sitzmann et al. 1973. White Oak, Silver Spring; 4. PubChem, 2,4,-dinitroanisole, available at: https://pubchem.ncbi.nlm.nih.gov/compound/8385 (date accessed: 14/06/2018); 5. Smith et al., 1999. Report: DSTO-TR-0796; 6. Davies and Provatas 2006. Characterisation of 2,4-Dinitroanisole: An Ingredient for use in Low Sensitivity Melt Cast Formulations.

2.1.2 The behaviour and fate of IHE constituents

Many factors influence the fate and effects of IHE in the environment, including the chemical composition and the quantity of IHE, the location settings and the local climate (Brannon and Pennington, 2002). In the environment, contaminants may remain on the soil surface where they are susceptible to photodegradation, they may dissolve and be transported through soil and water, and they may undergo chemical or biological degradation. In some soils, contaminants may not be degraded and instead transported directly to groundwater. The mobility of a contaminant usually reflects the organic content of the soil, i.e. soils with a high content of organic material are more likely to adsorb or degrade the contaminant than predominantly mineral soils. Soil mobility can be described by the organic carbon partitioning coefficient (K_{OC}), which is defined as the ratio of the mass of a chemical adsorbed by soil per unit mass of organic carbon as per the equilibrium chemical concentration in solution (Batu, 2006).

2.1.2.1 RDX and HMX

RDX and HMX have very low solubility in water (0.06 g/L) and therefore may take some time to dissolve and disperse in soil. However, due to their low K_{OC} values (0.88 and 0.54 for RDX and HMX, respectively), they can also be highly mobile in some low organic matter (1.7%) and low pH soils (4.6), which is evident in incidents of groundwater contamination beneath military training ranges in the USA, e.g. Camp Edwards, Massachusetts (Clausen et al., 2004; Lever et al., 2005; Morley et al., 2006). However, in soils with higher organic matter content (e.g. >5%) and neutral pH, which are more likely to be microbe-rich, RDX and HMX are susceptible to biodegradation (Clausen et al., 2004).

RDX degrades slowly in soil environments to form methanol, hydrazine and dimethylhydrazine via anaerobic transformation (Brannon and Pennington, 2002; Hawari et al., 2000; Pennington and Brannon, 2002). RDX has two proposed degradation routes as investigated in municipal anaerobic sludge. The first is initial reduction of the nitro groups to nitroso groups to form hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-nitroso-5-dinitro-1,3,5-triazine (DNX) and hexahydro-1,3,5-nitroso-1,3,5-triazine (TNX) followed by ring cleavage (Figure 2-3). The second mechanism is initial ring-cleavage to give methylenedinitramine and

bis(hydroxylmethyl)nitramine followed by further degradation into carbon dioxide, methane and water. The nitroso derivatives of RDX have been detected in soil and water samples, suggesting that the reductive pathway may be preferred under environmental conditions, or that these compounds may be stable in solution for environmentally significant periods of time i.e. long enough to impact a receptor (Halasz et al., 2012; Pennington et al., 2006; Sheremata et al., 2001). HMX is more stable than RDX in the environment, and no HMX degradation products have been detected in environmental samples. However, in laboratory studies, the nitro groups of HMX can be reduced to nitroso groups under anaerobic conditions (Brannon and Pennington, 2002).
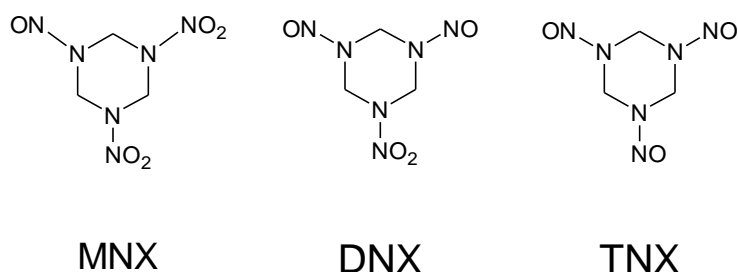
Figure 2-3: Chemical structures of the first stage RDX degradation products MNX, DNX and TNX.

RDX and HMX have been associated with a number of health conditions in humans, such as bone marrow, liver poisoning and convulsions (Kaplan and Kaplan, 1985; Lynch, Brannon and Delfino, 2002). RDX has a median lethal dose (LD_{50}) of 100 mg/kg in rats (Meyer et al., 2005). Consequently, the US Environmental Protection Agency (USEPA) has specified a chronic oral reference dose of 0.003 mg/kg/day (United States Environmental Protection Agency, 2014a). If RDX remains in soil, it can be taken up by plants and can have a detrimental effect on their growth at concentrations greater than 1.5 mg/L (Best et al., 1999). In addition, RDX accumulates in some edible plant species such as lettuce, corn and tomato, even at approved post-remediation concentrations of ≤ 5.8 mg/kg (Price, Richard et al., 1997).

2.1.2.2 NTO

NTO is the most soluble of the IMX constituents (16 g/L) and dissolves in direct correlation with the volume of incident water. Soil lysimeter experiments (D: 20 cm x H: 25 cm) have shown that rate of transport through soil can be significantly reduced

at lower volumes of water, with breakthrough times increasing from 1 - 18 days to 39 days (Braida et al., 2012). In addition, NTO has a low K_{OC} (0.6 - 1.79, depending on the soil type), which means it is unlikely to sorb to soil and therefore has the potential to be highly mobile (USEPA Federal Facilities Restoration, 2014). In batch adsorption experiments NTO showed very low adsorption to a variety of soils within the pH range 4.4 - 8.2, organic matter contents of 0.34 - 5.25% and specific surface areas of 1.7 - 38.3 m^2/g (Mark et al., 2016). There was also a very slight preference for adsorption to soils with low pH, probably due to the dissociation of NTO at soil pH values ranging between 6 and 8 which results in a negative charge on the molecule. Because most organic and mineral soil surfaces tend to have a net negative charge, NTO is more likely to sorb to soil in its neutral form, which is more likely to exist in soils with low pH (Mark, 2014).

Although NTO does not sorb to soils, it is susceptible to biodegradation in aerobic soil cultures, first losing nitrate followed by transformation to 1,2-dihydro-3H-1,2,4-triazol-3-one (ATO) (Richard and Weidhaas, 2014a) (Figure 2-4). NTO is degraded to ATO more quickly by anaerobic degradation, but ATO was found to be resistant to further biodegradation, although under aerobic conditions ATO degraded very slowly to nitrites and nitrates (Krzmarzick et al., 2015). Despite the generation of ATO in NTO soil cultures, NTO degradation by-products have yet to be detected in real soil environments, although ATO is probably the main intermediate before complete mineralisation (Arthur et al., 2018).

NTO   HTO   ATO

Figure 2-4: Chemical structures of the products of biodegradation of NTO.

NTO is one of the least toxic explosives, with an oral LD_{50} of >5000 mg/kg in rats (London and Smith, 1985). Rats exposed to 184 µg/L for 4 h exhibited no adverse effects, which is a good indicator of low chronic toxicity in humans (Crouse, Lent and Leach, 2015). However, both NTO and ATO have anomalous effects on the development of zebrafish embryos, which have neurodevelopment processes homologous to those in humans, suggesting that NTO may cause reproductive toxicity

(Madeira et al., 2017). NTO exposure to skin causes mild, short-term irritation (London and Smith, 1985), and can penetrate skin at 332 µg/cm^2/h (McCain, Williams and Grunda, 2013). Although considered less toxic than TNT, NTO is much more soluble in water (16.64 g/L) than other explosive compounds and may cause discoloration, even at low concentrations.

2.1.2.3 DNAN

DNAN adsorbs rapidly to soil in proportion to the organic content (Arthur et al., 2017). Far less adsorption was observed on the same soils sterilised by autoclaving, suggesting that most of the mass loss was due to biodegradation rather than irreversible binding to soil particles (Arthur et al., 2017). DNAN undergoes rapid aerobic biodegradation with complete mineralisation to nitrites observed within 100 h in culture (Karthikeyan and Spain, 2016). Under anaerobic conditions, DNAN is reductively transformed first to 2-amino-4-nitroanisole (2-ANAN), then to 2,4-diaminoanisole (DAAN). In soil column studies, 2-ANAN was the most common degradation product, with trace amounts of dinitrophenol (DNP) also detected (Arthur et al., 2017, 2018) (Figure 2-5). DNP is a common photodegradation product of DNAN, and is more likely to be produced in solid IMX-104 residues on the soil surface, or in surface waters than in soil (Taylor et al., 2017).
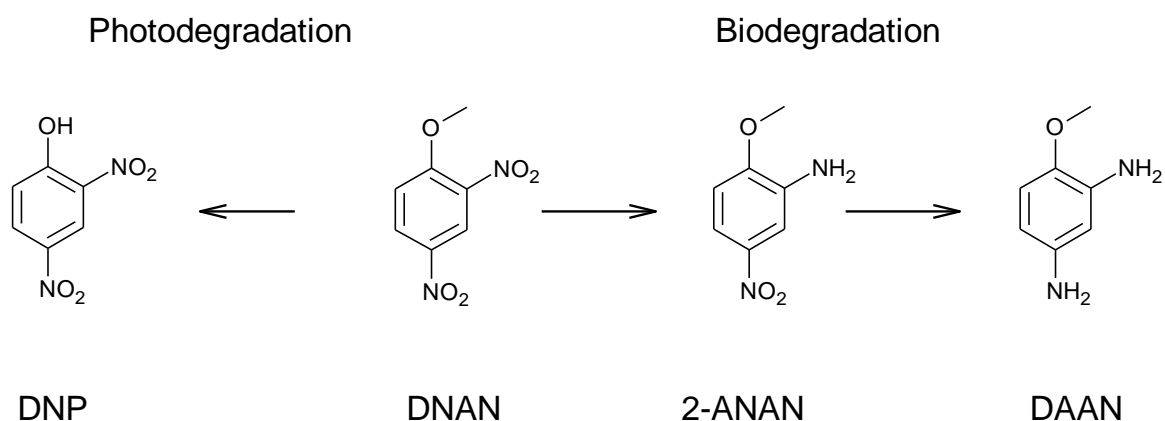
Figure 2-5: Photo- and bio-degradation products of DNAN.

DNAN and its degradation products are toxic in aquatic environments, with an effective concentration (EC$_{50}$) of 60.3 mg/L as determined by the Microtox® test with *Aliivibrio fischeri* (Dodard et al., 2013). Although studies were limited to model species, the repeated evidence of toxicity suggests that DNAN presents a significant risk to freshwater aquatic microbes and animals (Kennedy et al., 2017; Lotufo et al., 2013).

DNAN has an oral LD_{50} of 199 mg/kg and a sub-chronic oral toxicity of 300 mg/kg in rats, suggesting that it is also toxic to humans (Lent et al., 2012; Williams, Eck and Johnson, 2014). The common degradation products 2-ANAN and DAAN are slightly less toxic than DNAN, but may still present an environmental risk (Liang et al., 2013).

2.1.2.4 NQ

NQ is more soluble than DNAN (3.8 g/L) and does not adsorb significantly to soil, so it is expected to be transported quickly to groundwater (Mirecki, Porter and Weiss, 2006). NQ undergoes biodegradation in some soils (yielding ammonia and nitrous oxide), particularly soils with a high organic content, but it may migrate too quickly through soil for any significant degradation to occur before reaching groundwater (Mulherin, Jenkins and Walsh, 2005). NQ is susceptible to photodegradation forming mineralised products such as nitrourea (a highly explosive compound) and ammonia (Kaplan and Kaplan, 1985; Richard and Weidhaas, 2014a).

2.1.2.5   IHE formulations

Most current research focusses on the fate, transport and toxicity of the individual components of IHE (**Table 2-2**), but there is little research on the formulations, which would be encountered in the environment more frequently than the individual ingredients. When energetic materials are mixed in various ratios to achieve the desired performance, the environmental fate of the resulting IHE formulations is dependent on their rate of dissolution from the solid (Dontsova et al., 2014; Lever et al., 2005; Taylor et al., 2013, 2015a). In RDX/TNT compositions such as Comp B, the dissolution of the least-soluble component (RDX) controls the dissolution of the formulation (Lever et al., 2005). This is in contrast to IMX-104 and IMX-101, in which the most soluble component (NTO) is the first and fastest to dissolve, leaving a DNAN/RDX or DNAN/NQ matrix on the surface (Lewis et al., 2009; Taylor et al., 2015a). Once the explosives are solubilised and transported to the environment they appear to act independently, i.e. no interactions between the individual constituents have been observed in laboratory experiments (Arthur et al., 2017; Indest et al., 2017).

Table 2-2: Summary of the environmental properties of IHE

IHE constituent	Solubility[1] (water) g/l	K_{OC}[1]	pKa[1]	Acute oral toxicity (LD_{50}) (mg/kg)
DNAN	0.276	1.93-2.56	NA	199[2]
NTO	16.6	0.60-2.1	3.7	>5000[2]
NQ	3	Unknown	NA	3850[2]
RDX	0.06	0.88-2.4	NA	100[3]
HMX	N/A	0.54-2.8	NA	>7.2

1. Dontsova et al. 2014, Cold Regions Research and Engineering Laboratory. 2014; 2. Johnson et al. 2016. Propellants, Explosives, Pyrotechnics, 42, 9–16; 3. Crouse, L.C.B., Lent, E.M. and Leach, G.J. 2015. 34, p. 55.

PBX formulations are highly resistant to leaching of the energetic material because the insoluble and degradation-resistant binder protects the explosive filling. However, polymers expand as the temperature increases, and they degrade when exposed to sunlight (UV), which may release the explosive (Adeniyi and Kolawole, 1984).

2.2   Investigating the fate and transport of IHE constituents and mixtures

To understand the fate and transport of IHE, laboratory methods are used to simulate environmental conditions to ensure the generation of robust, representative and reproducible data. Often, the dissolution, transport and fate of explosives (i.e. degradation and toxicity) are investigated independently to isolate and control environmental variables such as rainfall, UV exposure, soil types, temperature, physical degradation and biodegradation. Dissolution studies are used to determine the mechanism and rate of dissolution from the formulation matrix under environmental conditions by simulating rainfall (Taylor et al., 2015a). Soil columns are vertical columns deigned to mimic the flow paths of contaminants in soil, and are often used to simulate the transport of IHE in different soil types and climates (Lewis and Sjöstrom, 2010). Finally, photodegradation and biodegradation can be investigated in aqueous solutions and soil suspensions to isolate the effect of UV, biodegradation and adsorption, making it possible to identify associated breakdown products (William and Mark, 2016). Studies tend to focus on individual IHE rather than formulations and mixtures because it is easier to identify individual behaviours. However, to fully understand the impact of these formulations in the environment, the behaviour of mixtures must also be investigated.

2.2.1 Dissolution studies

The primary mechanism by which explosives migrate into the environment is by dissolution during precipitation (Lynch, Brannon and Delfino, 2002). However, only a limited number of standardised methods are available to determine the dissolution rate of explosives in the environment, and these have been applied in studies using different experimental approaches, which makes it difficult to compare the results directly. For example, methods used in the pharmaceutical industry, where dissolution rates are determined by introducing a solid to a large volume of agitated water and then measuring the time taken to achieve dissolution by sub-sampling at frequent intervals have been used to investigate the effect of variable temperatures (10°C, 20°C and 30°C) on the dissolution rate of RDX and TNT (Lynch, Brannon and Delfino, 2002). However, explosives in the environment are unlikely to be submerged continually in agitated water, and are more likely to be dissolved through the action of sporadic rainfall. Further studies to determine changes to the three-dimensional structure of explosive formulations during dissolution by precipitation have been undertaken by submerging samples in water without agitation (Taylor et al., 2013). The samples were submerged in deionised water (DI), which is not representative of natural rainfall because the pH of the water is controlled (pH 7) and submerging the sample does not simulate the mechanical action of rainfall. This approach allowed the samples to be imaged by digital microscopy, which measured the dimensions of the samples as they dissolved.

To simulate the mechanical action of rainfall, indoor dripping tests have been carried out using glass frits holding pieces of explosive underneath the simulated water flow (Dontsova et al., 2014). Water can be delivered using a gravity-fed system (Richard and Weidhaas, 2014a), or by rate-controlled systems such as peristaltic or syringe pumps (Lever et al., 2005; Taylor et al., 2015b). The dripping is designed to mimic rainfall, although the rate of delivery is averaged against real weather conditions e.g. to a consistent time and droplet size. However, artificial droplets were generally larger than natural rain falling at the same rate, highlighting the difficulties of simulating rainfall precisely (Taylor et al., 2009a). Indoor rainfall simulations may be continuous or may include pauses for drying time, which increases the mechanical stress on the sample and is more representative of natural weather (Taylor et al., 2015b). For example, drying the sample introduces cracks which allow the ingress of water, and

may increase the rate of dissolution, but it is difficult to isolate and measure the effect of this variable in the laboratory. In addition, these indoor experiments only investigate the relationship between rainfall and dissolution, and do not consider other environmental variables such as temperature and sunlight. To account for all variables, similar experiments have been undertaken outside and have shown similar dissolution rates, but significant differences were observed in the mass of explosive recovered (Taylor et al., 2009b, 2015b). This suggests that the dissolution rate may be largely dependent on water volume, but the explosives may be degraded through other mechanisms such as photodegradation when exposed on the soil surface, which cannot be determined by laboratory-based dripping experiments.

2.2.2 Soil columns

Soil columns have been used as a standard method to evaluate the fate and transport of various chemicals and contaminants, ranging from pesticides to landfill waste (Barry, 2009; Bergström, 1990; Krüger et al., 2012; Lewis and Sjöstrom, 2010; López Meza et al., 2010; Di Palma and Mecozzi, 2010; Paluch et al., 2018; Schoen, Gaudet and Elrick, 1999). Soil columns are usually vertical tubes containing soil packed at a specific density, allowing the soil to be spiked with a contaminant. There is no standardised format, but the literature suggests best practice for building soil columns with different lengths and diameters, with the largest column weighing up to 50 tonnes (Lewis and Sjöstrom, 2010). There are two main types of column: monolithic and homogeneous.

Monolithic columns are usually soil sections that are extracted from the ground, thus retaining the natural flow path characteristics such as micropores, root cavities and cracks. The method used to extract the monolithic column affects its performance, especially if there is any deformation or compression during extraction. Homogeneous columns are assembled manually from well-characterized soil samples, and preparation involves full soil categorisation, sieving the soil before filling, and tamping the soil in the column to ensure a homogeneous mix without voids or inclusions. This method does not simulate the soil structure found naturally, but it standardises the soil structure and makes the experiment more reproducible allowing comparisons to be drawn between different soil types (Wefer-Roehl and Kübeck, 2014).

Although homogeneous soil columns are useful, if the diameter is less than 7.59 cm it can affect the dispersity and therefore the fluid transport characteristics of the column (Wefer-Roehl and Kübeck, 2014). In addition, to ensure uniform porosity the representative elementary volume (REV) should be at least 100 for flow experiments where REV is the ratio between column diameter and average soil particle diameter (Gibert et al., 2012; Martel and Gélinas, 1996). Sidewall flow is also a concern because it leads to preferential flow paths and unwanted interactions with the side of the column, although this can be minimised by using columns that have a diameter to length ratio of 1:4. The effect can also be mitigated by introducing a membrane, annular rings and even by gluing sand to the inside of the column wall.

Soil columns have been used to investigate the fate and transport of explosives in different soils and environments, although there are no standardised methods (Arthur et al., 2017, 2018; Boopathy, Widrig and Manning, 1997; Morley et al., 2006). For example, soil column experiments were undertaken to measure the transport of NTO through eight soil types with differing levels of organic matter (Arthur et al., 2017). The columns were 7 cm in length and 1.18 cm in diameter which is surprisingly narrow considering the potential sidewall issues discussed above (Bergström, 1990). The columns were packed with 12 g of soil and then covered with glass wool to ensure even distribution of water and fitted with PTFE lids. The columns were saturated from the bottom to avoid air gaps, even though there is no evidence in the literature to indicate this has the desired effect, then leachate was collected under steady state and interrupted flow conditions. At the end of the experiment, the columns were broken down enabling the full calculation of the mass balance accounting for all spiked materials and their transport pathways. This would not be possible in the real environment as contamination concentrations are unknown, and the soil is uncontained allowing far greater sideways transport. Although soil columns are not fully representative of the real environment they provide a controlled, reproducible system that can be used to predict contaminant transport rates and pathways.

2.2.3 Degradation

Explosives are designed to decompose violently when detonated. This also means that explosives are likely to break down due to other mechanisms, particularly in soil which may be rich with minerals, organic compounds and microbes (Spark and Swift,

2002). Degradation in the soil can occur via physical mechanisms (e.g. metal ions as catalysts) or due to biodegradation. The latter can be investigated by exposing specific strains of bacteria to explosive materials at low concentrations for hours or days (Hawari et al., 2015). This is not representative of a real soil environment, therefore soil microcosms have been used where spiked soils are suspended in a basal medium to encourage bacterial growth (Krzmarzick et al., 2015; Olivares et al., 2016). This highlights the effect of different soil types on degradation, specifically looking at characteristics such as organic carbon content, iron availability, and soil texture. However, under these conditions it is difficult to separate the effect of biodegradation from physical degradation and adsorption. One way to eliminate the effect of biodegradation is to sterilise the soils. Autoclaving at 120°C or irradiating with gamma rays destroys bacteria, but keeps the organic carbon content the same, isolating its effect (Hawari et al., 2015; Mark et al., 2017). More destructive methods, such as incineration at 400°C, remove both microbes and organic carbon, so generic degradation pathways in different soil types can be determined. A more representative method is to monitor the effluent from soil columns for spiked explosives and their degradation products, but such methods need to be supported by additional degradation studies if the mechanism of degradation is not understood (Arthur et al., 2017; Mark et al., 2017).

2.3   Techniques for the extraction of explosives from soil

Explosive residues that are found in soils may be toxic and contribute to health issues, so it is necessary to extract these substances from environmental matrices when determining contamination levels (Ungrádová et al., 2013). Extraction is the process used to separate contaminants from specific soil matrices before chemical analysis (Dean, 2009). There are many different extraction techniques, such as Pressurised Solvent Extraction (PSE), Soxhlet, microwave and supercritical solvent extraction (Dean, 2009; Griest et al., 1992; Luque de Castro and Priego-Capote, 2012; Ungrádová et al., 2013). These methods all work in different ways and are not all equally suitable for particular soils and explosive materials because different explosives have different properties such as solubility and interactions with soil components (Evans et al., 2010). The extraction of contaminants from soil also varies in terms of extraction efficiency and the time and costs involved. One study focussed

on the extraction of conventional explosives (TNT, RDX and HMX) from 14 soil types, comparing five different extraction methods. In this case, the most efficient extraction techniques for most of the soils were PSE and Soxhlet, and the least efficient was microwave extraction (Ungrádová et al., 2013). This emphasises that not all techniques are appropriate for every type of soil.

2.3.1 Sonication and shaking (EPA 8330B)

One of the first reported extraction methods for explosives from soil used acetonitrile as a solvent and applied sonication for 18 h, followed by centrifugation and dilution of the supernatant with an equal volume of water (Jenkins and Walsh, 1987). This method was then applied to six different soil types that were contaminated with a selection of explosive residues, such as RDX, TNT and HMX. The authors reported analytical precision in the range 0.13–1.24 μg/g, and the efficiency was better than 95% in all cases. This method formed the basis for the commonly used SW-846 EPA 8330B standard endorsed by the EPA for the extraction of explosives from soil (US Environmental Protection Agency, 2006). The standard method involves placing 10 g of soil in a vial with 20 mL acetonitrile on a platform shaker or in a cooled (<30°C) ultrasonic bath, and the extraction process can often take more than 18 h (US Environmental Protection Agency, 2006). Although this method has been used to extract a wide range of traditional explosives from different soil types (Holmgren, Ek and Colmsjö, 2012; Lapointe et al., 2016; Mark et al., 2017; Pascoe et al., 2010; Russell et al., 2014; Thomas et al., 2018; Walsh et al., 2012), the method may not be suitable for IHE because NTO is hydrophilic and less likely to be extracted by the organic solvents most frequently used (Walsh et al., 2017). Because IHE are combinations of explosives, extracting with only water would not be suitable given that RDX and DNAN are only sparingly soluble in water. Therefore, an extraction method combining aqueous and organic solvents is required and preferably in a single step to minimise time and resource use.

Soil has been extracted using a 1:1 mixture of acetonitrile and water and was agitated for 24 hours to ensure complete extraction, which is 6 hours longer than the EPA 8330B method recommends (Mark et al., 2017). The authors reported full extraction but did not report the efficiency of this method even though NTO has not been extracted before using this method and full extraction may not be possible. Despite

the uncertain efficiency of EPA 8330B for the extraction of IHE, further studies have applied the same conditions to extract IMX-104 constituents, although again the efficiency was not reported and complete recovery was assumed (Arthur et al., 2018).

The EPA 8330B method was developed ~25 years ago and has been used successfully for the extraction of trace levels of traditional explosives. However, EPA 8330B may need to be modified to achieve efficient extraction of IHEs such as DNAN, NTO and NQ. A two-solvent procedure has therefore been developed, comprising an initial phase using a 3:7 ratio of acetonitrile and water with 0.1 M trifluoroacetic acid (TFA) and a second phase with acetonitrile alone, both steps involving sonication for 18 h (Felt et al., 2016). NTO was extracted in acid aqueous solution because it is less likely to be negatively charged, making it easier to extract from soil. However, as DNAN is more soluble in organic solvents it was extracted in pure acetonitrile. Complete extraction of both DNAN and NTO were observed in the first phase making the second step of the extraction unnecessary.

2.3.2 Soxhlet and Accelerated Solvent Extraction

Mechanical methods such as sonication, shaking and stirring can be improved by extraction at high temperatures and pressures using Soxhlet and Accelerated Solvent Extraction (ASE). At higher temperatures, contaminants become more soluble and therefore the extraction is faster and uses less solvent (Lou, Janssen and Cramers, 1997a). High pressure enables the extraction solvents to reach higher temperatures than their boiling points and remain liquid. In addition, these methods have enabled the extraction of explosives from complex and dense matrices, such as polymers (Vandenburg et al., 1998).

A Soxhlet extractor is designed to extract a liquid from a solid material by circulating the solvent through the matrix, and this method is often used to recover soluble materials from soil. Soxhlet extraction and sonication have been compared for the extraction of TNT from aggregates (Williford Jr and Mark Bricka, 1999). The Soxhlet extraction process involved two steps, namely an initial extraction for 5 h in 170 mL acetonitrile followed by two further extractions in the same volume of fresh acetonitrile for 4 h. The sonication process used 750 mL acetonitrile, and required a centrifugation step, sonication for 18 h, a second centrifugation step, then decanting into bottles. The results showed that Soxhlet was more efficient in terms of time and solvent use

(Williford Jr and Mark Bricka, 1999). A study to investigate the stability of tetryl (2,4,6-trinitrophenylmethylnitramine) in wet soils used Soxhlet extraction in methanol for 48 hours, and indicated that the recovery of tetryl was only 82%, confirming its lack of stability when extracted using this method (Jenkins and Walsh, 1994). Another study involving five different soil types from military sites contaminated with explosives used a range of extraction methods including Soxhlet (Bausinger, Dehner and Preuß, 2004). In the Soxhlet method 5.0–5.5 g of each soil type was extracted using 60 mL of acetonitrile for 6 hours achieving 100% extraction efficiency, although with a longer procedure time than the other methods.

ASE was introduced as a replacement for the Soxhlet extraction of explosives because it significantly reduces the extraction time and solvent volume without loss of efficiency and precision (Richter et al., 1996). ASE involves heating the solvent (up to 200°C) under high pressure (up to 1500 psi) in a closed system (Richter et al., 1996). Soxhlet extraction was used to isolate RDX, TNT and its degradation products from contaminated soils using a 1:1 ratio of methanol and acetonitrile in 30 min, although the temperature was kept at 100°C to avoid thermal degradation (Campbell et al., 2003). The ASE method achieved 90–120% extraction from spiked Ottawa sand, but as little as 70% with a standard deviation of 14% when using real soil samples due to the adsorption of the explosive. Using real samples of contaminated soil rather than spiked samples makes it difficult to report on the efficiency and precision of the method. When samples extracted using ASE with water were compared to extractions using EPA 8330B, the ASE samples contained higher concentrations of explosives (RDX and TNT).

Robust and reproducible extraction methods to determine the presence and residual concentration of explosives in PBX are needed to achieve reliable risk assessments for land management at affected sites (Giergielewicz-Mozajska, Dabrowski and Namiesnik, 2017). Soxhlet extraction is typically used to extract nitramines (RDX and HMX) from PBX, but this can take up to 48 hours and requires more than 150 mL of solvent per gram of soil (DuBois and Baytos, 1991). PBX samples usually consist of nitramines encased in a polymer matrix, and full extraction is required for mass balance calculations. The extraction of a chemical from a polymer initially requires the diffusion of the chemical from within the polymer to the surface, followed by transfer through the static solvent layer into the bulk solvent. The rate of mass transfer from

the polymer core to the bulk solvent is dependent on the structure and properties of the polymer and solutes, the extraction temperature and the type of solvent (Lou, Janssen and Cramers, 1997b). Selecting an appropriate solvent is essential for polymer extraction using high-temperature methods because the solvent must be able to dissolve the target analyte, while leaving the polymer intact (Primbs, Genualdi and Massey Simonich, 2008; Vandenburg et al., 1999). It is also important to ensure that the analyte does not degrade during the long (up to 48 hours) exposure to solvent at high temperatures (Bart, 2005). The most effective way of increasing extraction efficiency from polymers is to increase the temperature of the solvent and to grind the polymer particles to reduce the mass-transfer distance from the core of the polymer to the surface (Lou, Janssen and Cramers, 1997b). Due to the friction sensitivity of some of the explosives present in large amounts in polymer, PBX should not be ground to avoid accidental initiation (Walsh, Ramsey and Jenkins, 2002).

2.4 Conclusion

Many studies have addressed the fate and transport of conventional explosives. Both the explosives and their breakdown products are persistent hazards in the environment because they tend to be sparingly soluble in water, with low K_{OC} values, making them highly mobile in soils with high levels of organic matter. In contrast, the fate and transport of IHE have not been studied in detail. These materials have very different properties compared to conventional explosives. For example, they tend to be much more soluble (and thus more mobile in low organic content soils) but also show different degradation profiles depending on the soil type. The fate and transport of individual IHE constituents such as DNAN, NTO, NQ and RDX have been characterised, but these chemicals are typically utilised as mixtures and their behaviour in combination has not been investigated comprehensively. Furthermore, methods developed for the extraction of legacy explosives are not suitable for the extraction of IHE constituents because of their differing physicochemical properties. The knowledge gaps revealed by this literature review have therefore been used to develop a research program to investigate the fate and transport of IHE formulations focusing on the effects of climatic conditions on the dissolution of PBX and the mechanisms by which IMX and its degradation products are transported through soil. As part of this investigation, different extraction techniques have been compared and

selected to ensure that IHE components are fully extracted, increasing the efficiency and accuracy of the analysis. The work described in this thesis will therefore provide unique insight into the behaviour of IHE and their constituents in the environment.

3

Release of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) from polymerbonded explosives (PBXN-109) into water by artificial weathering

IHE are currently being brought into service as replacements for traditional RDX/TNT explosives. However, the environmental behaviour of these materials is not fully understood. Following the literature review it was evident that no research had been conducted on the dissolution of the encapsulated explosive from PBX under normal climatic conditions such as exposure to sunlight, varying temperatures and rainfall. Therefore, research was conducted to determine the effect of a variable climate on the rate at which RDX leaches from a PBX.

Chapter 3   Release of RDX from PBXN-109 into water by artificial weathering

3.1 Abstract

Polymer-bonded explosives (PBX) fulfil the need for insensitive munitions. However, the environmental impacts of PBX are unclear, even though it is likely that PBX residues from low-order detonations and unexploded ordnance are deposited on military training ranges. The release of high explosives from the polymer matrix into the environment has not been studied in detail, although polymers degrade slowly in the environment thus, we anticipate high explosives to be released into the environment. In this study, PBXN-109 (nominally 64% RDX) samples were exposed to variable UK climatic conditions reproduced in the laboratory to determine the effects of temperature, UV irradiation and rainfall on the release of RDX from the polymer binder. The most extreme conditions for spring, summer and winter in the UK were artificially reproduced. We found that up to 0.03% of RDX was consistently released from PBXN-109. The rate of RDX release was highest in samples exposed to the summer simulation, which had the lowest rainfall, but the highest temperatures and longest UV exposure. This was confirmed by additional experiments simulating an extreme summer month with consistently high temperatures and long periods of sunlight. These results probably reflect the combination of polymer swelling and degradation when samples are exposed to higher temperatures and prolonged UV irradiation.

3.1   Introduction

Polymer bonded explosives (PBX) are designed to meet the need for insensitive munitions, which minimise the risk of inadvertent initiation while reliably fulfilling their intended detonation functions (Ang and Pisharath, 2012). PBX compositions typically consist of a nitramine high explosive encapsulated by a polymer binder, which confers insensitivity by protecting the explosive with a flexible and rubber-like coating (Shee et al., 2015). One of the most common nitramines in PBX is 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), accounting for up to 95% of the composition.

RDX is a common soil contaminant at manufacturing sites and on military training ranges. Low order and blow-in-place detonations of legacy compositions such as Composition B can deposit thousands of milligrams of RDX on soil surfaces (Jenkins et al., 2006). Unexploded ordnance can also cause contamination when damaged because the high explosive filling is then exposed to the climate (DuBois and Baytos, 1991).

The fate and transport of RDX is highly dependent on location due to differences in climate and soil type (Larson et al., 2008). Solid RDX particles can remain in the top layer of soil for a long time (Sheremata et al., 2001) but are more likely to undergo slow biodegradation under anaerobic conditions, yielding other undesirable contaminants such as methanol and hydrazine. RDX does not significantly adsorb to soil (Singh et al., 1998) and dissolved RDX therefore tends to migrate (Selim, Xue and Iskandar, 1995). However, RDX has low solubility in water and is unlikely to exceed current threshold limits of 2 μg/l in groundwater (Gauthier et al., 2003; Pichtel, 2012). RDX becomes more soluble at higher temperatures, doubling in solubility with every 10°C increase, so water contamination is a more significant problem in warm, wet climates (Lynch, Brannon and Delfino, 2002). Because RDX leaches slowly in temperate regions, it accumulates on or just beneath the soil surface, presenting a risk to humans, animals and plants due to its extreme toxicity (Pennington and Brannon, 2002; Pichtel, 2012). This may be exacerbated by PBX materials because the polymer protects RDX from the climate and may prevent RDX crystal distribution, resulting in more surface contamination than non-bonded high explosive. However, many polymers swell at higher temperatures and degrade when exposed to UV light, which may release RDX into the environment (Adeniyi and Kolawole, 1984).

We investigated the environmental fate of PBXN-109, an aluminized, cast-and-cured secondary explosive containing 64% RDX and 8% polybutadiene binder. The aim was to determine the effect of a variable climate on the rate at which RDX leaches from the PBXN-109 polymer matrix under controlled laboratory conditions. Samples of PBXN-109 were exposed to predetermined doses of UV irradiation and water at controlled temperatures to simulate variable conditions,

i.e. cold and wet vs. hot and dry. The release of RDX from PBXN-109 was measured by analysing the RDX content of the collected water.

3.2   Materials and methods

3.3.1 Preparation of samples

Samples of PBX (RWM Italia SpA) were supplied as small spheres (~1.5 g each / diameter = 0.5mm) containing 64% RDX, 20% aluminium, 8% hydroxyl-terminated polybutadiene (HTPB) and 8% di-(2-ethylhexyl)-adipate (DOA). The RDX content was confirmed by acetone extraction from pristine PBXN-109 in a Soxhlet extractor. The samples were used as supplied and loaded into Buchner funnels (4 cm diameter) fitted with a glass frit before exposure to variable climate conditions (Taylor et al., 2009b, 2015a).

3.2.2 Simulating UK weather conditions

Climate conditions representing South-West England were simulated in the laboratory to mimic the exposure of PBXN-109 on military ranges. Climate data from 1990–2014 were obtained from the UK Meteorological Service website (Met Office website) (**Table 3-1**). The highest seasonal averages for rainfall, temperature and sunlight hours were identified and used in laboratory simulations to provide representative worst-case exposure scenarios. Autumn climate conditions were not reproduced in the laboratory due to the similarity between the autumn and winter rainfall and temperature, and number of daylight hour's falls between spring and winter values therefore can be estimated to be between the two.

The volume of simulated rainfall deposited on the PBXN-109 samples for winter, spring and summer was determined by calculating the equivalent rainfall on the area of the sample within the Buchner funnel housing. The rainfall was calculated by multiplying the maximum seasonal average rainfall (mm/m^2) by the area of the sinter funnel (0.00125 m^2). The average sunlight per day was determined by dividing the maximum seasonal average by 90 days (the average number of days in a season) (**Table 3-2**). Maximum and minimum average temperatures were also taken into consideration.

Table 3-1: Average climate conditions in South-West England during the period 1990–2014.

Season	Seasonal Rainfall		Seasonal Temperature		Seasonal Sunlight Hours	
	Season average (mm)	Equivalent artificial rainfall (mL)	Max. (˚C)	Min. (˚C)	Average (h)	Average/ day (h)
Winter	694	872	10±1	0±1	210	2.5
Spring	332	599	15±1	3±1	601	6.75
Summer	476	417	22±1	10±1	721	8
Autumn	624	784	9±1	5±1	360	4

Seasonal variations were simulated in the laboratory on an accelerated timescale of 11–15 days depending on the average number of rainy days in the 3 seasons under investigation. Duplicate samples, of individual spheres of PBXN-109 were housed in self-contained temperature controlled chambers to simulate the artificial seasons. The climate chambers were designed to eliminate any non-controlled sources of light, heat or water. Samples were exposed to the seasonal maximum and minimum temperatures over alternating 24-h periods to represent natural temperature fluctuations between night and day. Rainfall was simulated using peristaltic pumps to deliver a daily dose (8 mL/hour) of ultrapure water from a MilliQ Water Purification System equivalent to the average UK seasonal rainfall on a similar area (see Supporting Information for daily volumes of applied water). The maximum volume of water delivered each day was 90 mL, resulting in a minimum dry period of 11.5 hours per day. The run-off was collected in 500-ml wide-neck amber jars. Daylight hours of intense UV during the summer were simulated using a Philips high intensity UV lamp (HPW125WTPH), and daylight hours during the winter and spring were simulated using a BTL low-intensity UV tube lamp. Duplicate samples were simultaneously exposed to temperature, rainfall and sunlight representative of UK spring, summer or winter. The artificial conditions for each sample are summarized in **Table 3-2**.

Table 3-2: Summary of the conditions used for seasonal simulations.

Experiment reference	Sample Mass (g)	Temperature (°C)		Average UV (h/ day)	Total Rainfall (mL/ mm)	Duration of Artificial Season (days)
		Min (7 days)	Max (7 days)			
Winter 1	1.66	0	10	2.5	830/ 660	15
Winter 2	1.42				846/ 674	
Spring 1	1.60	5	15	6.75	572/ 455	11
Spring 2	1.60				451/ 360	
Summer 1	1.60	10	22	8.0	465/ 370	14
Summer 2	1.60				404/ 323	
Extreme 1	1.14	22		13	389/310	
Extreme 2	1.12				329/262	389/ 310

3.2.3 High performance liquid chromatography

Sample run-off was collected every 24 h and analysed by high performance liquid chromatography (HPLC) to determine the percentage loss of RDX from the PBXN-109 sample. The HPLC system consisted of a Waters Alliance 2695 equipped with a Waters 996 photodiode array detector. The chromatographic separations were performed on ACE UltraCore 2.5 SuperPhenylHexyl columns (100 x 4.6 mm internal diameter) maintained at 35°C. A mixture of acetonitrile/water (3:2) was used as the mobile phase at a flow rate of 1.5 ml/min. A linear calibration curve for RDX was obtained for the concentration range 0.1–20 µg/ml.

3.3   Results and discussion

The samples of PBXN-109 were formulated with 64% RDX, which gave ~1 g of RDX in each sample. The concentration of RDX found in each collected sample was determined by HPLC and expressed as a percentage based on the quantity of RDX in the sample. The total amount of pure RDX recovered from a single sphere of PBXN-109 during a laboratory season was small (3 mg), probably reflecting the inability of water to penetrate deeply into the insoluble polymer matrix. However, RDX contamination could still pose a problem when frequently using PBXN-109 filled munitions over long periods of time.

The results from the first series of experiments aiming to replicate UK spring, summer and winter seasons are shown in **Table 3-3**. They revealed that more RDX was lost from PBXN-109 samples exposed to summer conditions (up to 2.74 mg RDX lost by the season end). The summer samples were exposed to 50% less water than the winter samples, confirming that the polymer binder limits the migration of water to accessible RDX crystals regardless of the volume of water applied. The temperature of the applied water was identical for all samples, so the higher concentration of RDX is unlikely to reflect its greater solubility at higher water temperatures.

PBXN-109 samples under spring and winter conditions lost similar percentages of RDX even though the spring accelerated season ended four days sooner than the winter season and less water was used, again indicating that rainfall alone is not responsible for RDX release. The percentage of RDX migrating from each replicate summer sample was noticeably different, even though the two samples received similar volumes of water at identical temperatures with the same amount of UV exposure. These differences may reflect inconsistencies between the PBXN-109 samples in terms of composition, e.g. differences in the average RDX content, the accessibility of the RDX crystals, or the micro-structure of the polymer (such as cracking).

Table 3-3: Summary of mass and percentage release of RDX from PBXN-109 samples at the end of the artificial season.

Sample	RDX mass recovered (mg)	% Loss	Total UV Exposure	Total Rainfall (mL/ mm)	Days
Winter 1	1.56	0.11	37.5	830/ 660	15
Winter 2	1.40	0.12		846/ 674	
Spring 1	1.40	0.14	74.25	572/ 455	11
Spring 2	1.11	0.11		451/ 360	
Summer 1	1.75	0.19	112	465/ 370	14
Summer 2	2.74	0.33		404/ 323	

The rate of release indicated that RDX release was accelerated under the warmer and drier summer conditions compared to the cooler spring and winter conditions - 0.01%/ day for Winter 1 and Winter 2 samples compared to 0.013 %/day and 0.019 %/day for Summer 1 and summer 2 samples respectively (**Figure 3-1**).

Spring sample 1 was exposed to 121 mL more water than sample 2 and lost more RDX, but this difference is more likely to reflect random differences in the distribution of RDX and the polymer structure given that the opposite effect was observed for the summer samples.
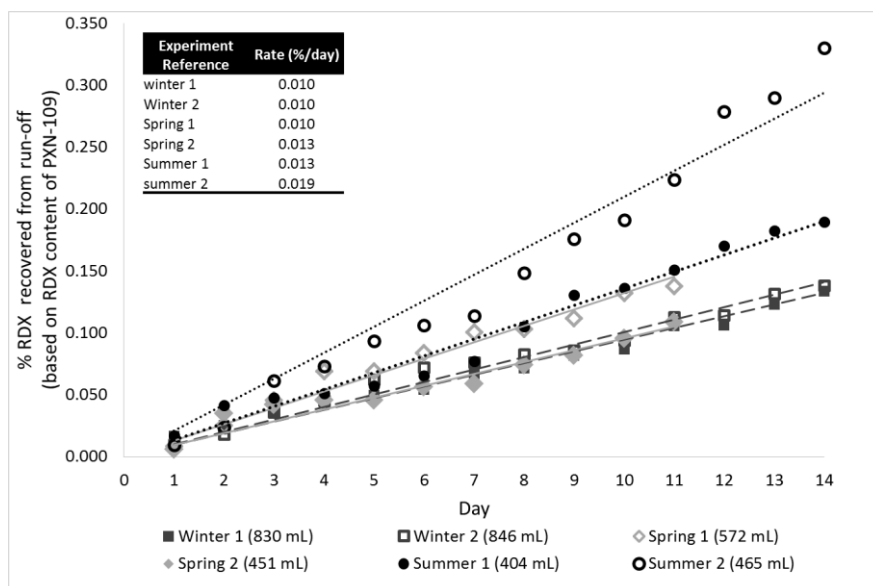
Figure 3-1: Rate of RDX release from PBXN-109 during artificial seasons: spring (11 days), summer (14 days), and winter (15 days).

These results suggest that the rate of RDX release from the PBXN-109 was accelerated by high temperatures and exposure to sunlight, and was not dependent on the volume of rainfall (Lynch, Brannon and Delfino, 2002). This differs from pure RDX, where the limiting factor is its solubility, which is mainly dependent on the water temperature and the volume of rainfall.

The effect of high temperatures and UV on the rate of release of RDX from PBXN-109 was investigated further by exposing two additional samples of PBXN-109 to a consistently warm climate (22°C) and 13 h UV irradiation per day, to simulate long periods of hot and bright weather (**Figure 3-2**). Water was applied at a volume that was representative of a dry summer (389 and 329 mL equivalent to 310 and 262 mm). The results confirmed that prolonged warm temperatures and intense UV exposure accelerate the release of RDX from PBXN-109 from 0.013%/day and 0.019%/day for summer 1 and summer 2 samples compared to

0.031%/day and 0.028%/day for Intense 1 and Intense 2 samples. The increase in rate of RDX release may reflect the swelling of the polymer matrix at higher temperatures, which would make it easier for water to penetrate. Furthermore, polybutadiene polymers are known to degrade under UV light, which might cause additional cracking in the matrix allowing water to penetrate deeper into the PBXN-109 and wash out the RDX.

Experiment Reference	Rate (%/day)
Summer 1	0.013
Summer 2	0.019
Intense 1	0.031
Intense 2	0.028

□ Summer 1 (465 mL)   ○ Intense 1 (389 mL)   ■ Summer 2 (465 mL)   ● Intense 2 (329 mL)
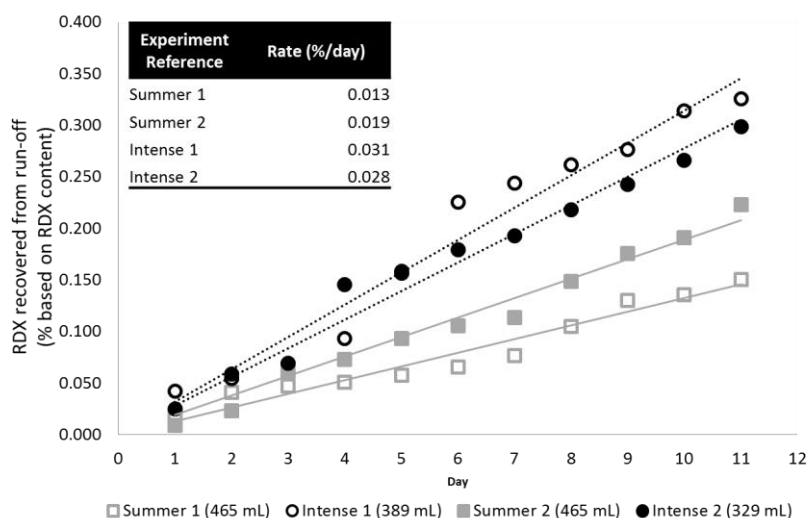
Figure 3-2: RDX release from PBXN-109 at constant 22°C temperature and maximum UV exposure (13 h/day).

3.4   Conclusion

RDX does migrate from the polymer matrix of PBXN-109 when exposed to simulated seasonal conditions. The rate of release is low but consistent, and PBXN-109 deposits on ranges are therefore likely to result in RDX contamination in the environment by dissolution and transport in water. We also found that the rate of RDX release is accelerated in warm temperatures with intense UV exposure, probably reflecting a combination of polymer swelling and degradation allowing more access to the encapsulated RDX crystals. The results presented in this manuscript are preliminary, and long term work is currently underway to fully investigate the rate of RDX release from PBXN-109 in artificial and real environments.

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Optimized accelerated solvent extraction of hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) from polymer bonded explosives'
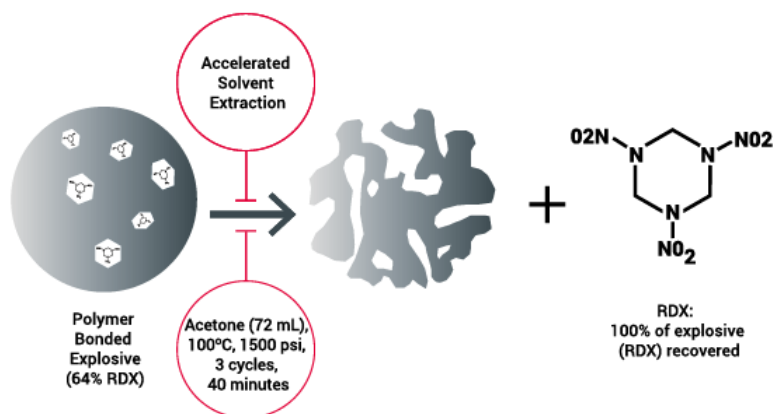
To fully confirm that only a small amount of RDX was released from the polymer matrix, a robust and efficient extraction method should be used. For the PBX dissolution work Soxhlet extraction was used, however, this method is time consuming and resource and consumable intensive. This chapter developed and optimised an extraction method for PBX using ASE that recovered a similar percentage of RDX to Soxhlet, although was significantly quicker and used much less solvent.

This work has been accepted with minor revisions in Propellants, Explosives, and Pyrotechnics (PEP)

Chapter 4   Optimised accelerated solvent extraction of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) from polymer bonded explosives

4.1 Abstract

An accelerated solvent extraction (ASE) method was developed and optimised to extract hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) from a polyurethane matrix. The ASE method development was benchmarked against Soxhlet extraction with a view to improving extraction efficiency in terms of time and solvent volume. Key parameters for the ASE method development involved selecting the most appropriate solvent, optimising static time, ensuring a safe oven temperature for explosives, determination of a sufficient number of rinse cycles and effective sample preparation. To achieve optimal extraction, cutting the PBX samples to maximise solvent exposure was essential. The use of acetone with a static time of 10 minutes at 100°C with three rinse cycles achieved 97% ± 10% extraction of RDX from PBX in 40 minutes using 72 mL solvent. Extraction time was reduced from 48 hours and solvent use by half compared to the standard Soxhlet extraction. To validate the developed ASE method, two other PBX samples containing different quantities of explosive were also fully extracted using the same parameters. Overall, ASE efficiency was comparable to Soxhlet, which places the ASE as a good alternative and shows potential for implementation as a standard method for other polymer based explosives.

4.2   Introduction

Robust and reproducible extraction methods to determine the presence and residual concentration of Polymer Bonded Explosives (PBX) are important to inform risk decision making and land management at impacted sites (Giergielewicz-Mozajska, Dabrowski and Namiesnik, 2017). PBX typically consist of a nitramine high explosive combined with a polymer. The most commonly used nitramine explosives include 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine   (HMX)   (Akhavan,   2011).

Currently, Soxhlet extraction is a commonly used method to extract nitramines from PBX, however this can take up to 48 hours and use over 150 mL of solvent per 1 g extraction (DuBois and Baytos, 1991; Kumar et al., 2017).

ASE has been successfully used to extract chemical components of polymers and was initially developed to replace extraction methods such as Soxhlet, and sonication (Fisher, Scarlett and Stott, 1997; Richter et al., 1996). ASE uses solvent at up to 200°C and 1500 psi pressure in a closed system to increase extraction efficiency, while minimising preparation time and solvent volume (Richter et al., 1996). Under these conditions the solvent may reach temperatures above its boiling point, which makes it less viscous and increases the solvent's capacity to dissolve the analyte. In addition, the increased pressure forces solvent into the pores of the sample material, making the analyte more readily available for extraction (Richter et al., 1996; Vandenburg et al., 1997).

The use of ASE to extract chemical components of polymers has not been widely reported in the literature, but the extraction of monomers and oligomers and low concentration chemical additives from polymers has been successful (Lou, Janssen and Cramers, 1997b; Möller, Strömberg and Karlsson, 2008; Vandenburg et al., 1999). Additives pose a particularly challenging analytical problem, as they are present at very low concentrations, often less than 1% of the mass of the polymer. ASE has been shown to successfully extract very low concentrations (0.02 to 0.1%) of additives with a relative standard deviation of 20%, which is acceptable for such low concentrations (Zhang et al., 2013).

To extract a chemical from a polymer it must diffuse from the polymer to the surface followed by transfer through the static solvent layer into the bulk solvent. The rate of mass transfer from the polymer core to the bulk solvent is dependent on the structure and properties of the polymer and solutes, the extraction temperature and the type of solvent (Lou, Janssen and Cramers, 1997b). Selecting an appropriate solvent is essential for ASE of polymers as it must be able to dissolve the chemical of interest, while leaving the polymer intact at high temperatures (Primbs, Genualdi and Massey Simonich, 2008; Vandenburg et al., 1999). It has been shown that the most effective way of increasing extraction

efficiency is to increase temperature. If it is not possible to increase temperature, mass transfer must be increased by other means such as reducing the size of polymer particles by grinding to reduce the distance from the core of the polymer to the surface (Lou, Janssen and Cramers, 1997b). Achieving high temperatures and grinding the sample present a challenge when extracting high explosive due to safety concerns as the temperature should be kept well below the explosive auto-ignition temperature, and samples should not be ground (Walsh, Ramsey and Jenkins, 2002).

To date, there have been no studies regarding the extraction of explosives from solid explosive matrices such as PBX using ASE. ASE of explosive residues (RDX and HMX) from soil samples has been developed and successfully used to completely extract RDX and 2,4,6-tri-nitrotoluene (TNT) and associated degradation products from contaminated soils (Campbell et al., 2003; Onuska et al., 2001). This method has also been used to extract RDX from animal liver tissue to assess toxicity, demonstrating the flexibility of ASE (Pan, Zhang and Cobb, 2005). Another study comparing four different extraction methods (ASE, Soxhlet, microwave assisted extraction and supercritical fluid extraction) for HMX, RDX and TNT from soil showed that ASE was the most efficient with 90% recovery. For all tested explosives, ASE extraction was comparable or better than Soxhlet extraction and was reproducible with a maximum of 10% standard deviation (Ungrádová et al., 2013).

The aim of this work was to develop and optimise a robust analytical method for the extraction of RDX from PBX. The optimised ASE method was successfully validated using two additional PBX compositions to demonstrate its broader applicability.

4.3   Materials and methods

4.3.1 PBX composition

PBX samples were obtained from an industrial supplier as 100 g slabs (10 × 5 × 2 cm) as described in **Table 4-1**. The PBX samples contain small amounts other

additives for stability and performance, although this research focussed specifically on the extraction of the energetic component.

Table 4-1: Composition of the PBX samples based on Safety Data Sheets including only the relevant percentages of the explosive extracted (RWM Italia, 2005, 2011).

PBX Sample	Explosive	Explosive (%)	Polymer (%)	Alumin- ium (%)	Auto- ignition temperature (°C)	Density (g cm^{-3})	Sensitiveness to Friction (N) (BAM Friction)
A	RDX	64	9	20%	206	1.65	> 360
B	HMX	87	6	-	230	1.65	>353
C	RDX Ammonium Perchlorate	20 43	6	25%	209	1.79	151

4.3.2 Optimisation of ASE method for PBX-A

A slab of PBX-A was scored using a ceramic knife and cut into 1 g cubes (1 cm^3). To decrease the volume and depth of solvent penetration required the 1g samples were cut into smaller cuboids of similar volume (approximately 0.5, 0.125, 0.065 and 0.008 cm^3, respectively). Samples of PBX-A were placed into stainless steel solvent extraction cells (33 mL) filled with Ottawa sand, or inside a cellulose thimble with and without sand to reduce solvent volume. Cells were placed in the ASE, and an initial 14 minute method was programmed according to the Application Note for extraction of traditionally used explosives, such as TNT from soil (Dionex, 2011). Briefly, using the standard mode with a system pressure of 1500 psi, oven temperature 100 °C, oven heating time 5 minutes, static time set at 5 minutes, the rinse volume was 60% of the cell volume and a rinse cycle with a 200 s purge (**Table 4-2**). These conditions were used as the baseline for further optimisation.

The PBX-A extraction method was systematically optimised by changing one perimeter at a time e.g. solvent, static time, rinse cycles, sample volume and cell preparation, as summarised in **Table 4-2**. The oven temperature, pressure, flush volume and oven heating time were not optimised.

Table 4-2: Summary of the initial method and the conditions optimised during method development.

Parameter	Application Notes method	Conditions tested for optimisation in this study
Cell size (mL)	33	Unchanged
Initial volume (mL)	38	Unchanged
Pressure (psi)	1500	Unchanged
Oven temperature (°C)	100	Unchanged
Oven heating time (min)	5	Unchanged
Solvents	Acetone or methanol	Acetonitrile or acetone or methanol
Static time (min)	5	5; 10; 20; 30
No. of rinse cycles	1	3
Rinse volume (%; mL)	60; 24	Unchanged
Purge time (s)	200	Unchanged
PBX-A sample volume (cm$^{3)}$)	1	1.0, 0.5, 0.13, 0.07 and 0.008
ASE cell preparation	Ottawa sand	Ottawa sand/ thimble and sand/ thimble only

Extracts (approximately 60 mL) were diluted by 100 using the extraction solvent, filtered (0.2 µm syringe filter) and analysed by HPLC immediately.

4.3.3 Accelerated solvent extraction of PBX-B and PBX-C

PBX-B (1 g) and PBX-C (1 g) were scored and cut into cuboids (0.008 cm^3) using a ceramic knife on filter paper. The PBX-B and PBX-C pieces were then transferred to a thimble, which was placed in a stainless steel extraction cell (33 mL). The cells were loaded into the ASE and the PBX were extracted with acetone at 100 °C, 1500 psi for 3 ten minute rinse cycles with a 5 minute oven heating time, 200 second purge time and a rinse volume of 60%. Extractions were completed in triplicate.

A sub-sample of the resulting extracts were diluted accordingly, filtered and analysed by HPLC.

4.3.4 Soxhlet extraction

PBX-A (1 g) was cut into 2 mm^3 pieces and placed in a glass thimble in a Soxhlet extractor (Kumar et al., 2017). The RDX was extracted from PBX-A with acetone

(150 mL) at 70°C for 48 hours. The resulting RDX extract was made up to 200 mL, diluted accordingly and analysed by HPLC.

4.3.5 Calibration solution preparation

The 50 ppm stock solutions of RDX and HMX respectively were prepared by dissolving accurately weighed standards in acetonitrile (ACN). Calibration standards, made daily by subsequent dilutions of the stock solution in acetonitrile, ranged from a concentration of 5 to 50 ppm.

4.3.6 Instrumental analysis

HPLC analyses were performed on a Waters Alliance 2695 separation module coupled to a Waters 996 photodiode array detector (PDA). Chromatographic separations were carried out isocratically with a NovaPak C8 (3.9 mm × 150 mm, 4 µm) column from Waters maintained at 35°C. The mobile phase consisted of 50% ACN and 50% H_2O with 0.1% formic acid with a flow-rate of 1.5 mL min-1 and the injection volume was 10 µl. RDX peak was identified by comparing its retention time and absorption spectrum in the samples with those of the standard solution. RDX was monitored at 235 nm.

The HPLC method was validated by assessing: (i) Specificity (analysis of solution of PBX); (ii) Linearity (measure of the correlation coefficient for each standard from the linear regression analysis in the concentration range of 0.05 to 50 µl/ml); (iii) Limit of Detection (LOD), Limit of Quality (LOQ) (measure of the residual standard deviation of the responses and slopes of the regression equation of the calibration curve (root mean square error approach)) and (iv) Precision (measure of the relative standard deviation of ten injections of each compounds at two concentrations). The results of the method validation are displayed in **Table 4-3**.

Table 4-3: Summary of method validation results.

Test	Results
Precision (%) @ 25 µl/ml	0.10
Precision (%) @2 µl/ml	0.38
Linearity (r^2)	1.00
LoD (µl/ml)	0.033
LoQ (µl/ml)	0.099

4.4 Results and discussion

4.4.1 ASE method development and optimisation

The ASE method was based on a Dionex Application Note designed to extract traditional explosives from soil, using methanol or acetone (**Table 4-2**) (Dionex, 2011). However, polymers are more difficult to extract compared to particulate matrices as the polymer must first swell to allow the solvent access to the RDX. Therefore, test solvents were chosen based on their use in the application note (i.e. methanol and acetone) and their ability to dissolve RDX and to swell the polymer. RDX is most soluble in acetone and acetonitrile especially at elevated temperatures (Sitzmann, 1973). In addition, acetone promotes swelling of the polymer (Jinlong et al., 2015). Methanol was also tested as it was used in the Application Note. RDX solubility in the chosen solvents is summarised in Table 4-4. PBX-A samples were extracted with the three solvents for five minutes (static time) at an oven temperature of 100°C, and 1500 psi.

The percentage recovery of RDX from 1 g of PBX-A was low for all tested solvents. Acetone was the most efficient with a recovery of 11%. Of the three solvents RDX is the most soluble in acetone and it is the preferred extraction solvent for Soxhlet which is often a good indication of solvents that may be successful for ASE (DuBois and Baytos, 1991; Kumar et al., 2017). Recovery of RDX using ACN was 6%. Methanol was the least efficient achieving only 2% recovery of RDX, probably due to a combination of poor RDX solubility and limited swelling effect (**Table 4-4**). Therefore, acetone was selected as the preferable solvent for the extraction of RDX from PBX-A and was used in all following extractions.

Table 4-4: RDX solubility in acetonitrile, acetone and methanol (Sitzmann, 1973) and the percentage recovery of RDX from PBX when varying solvent.

Solvent	RDX Solubility at 20°C	RDX Solubility at higher temperature	Solvent Boiling Point (°C)	Percentage Recovery
Acetonitrile	5.5	14 (60°C)	81.6	6%
Methanol	0.24	1.27 (64.5°C)	64.7	2%
Acetone	8.2	17 (60°C)	56.3	11%

Following solvent selection, the recommended next step in the optimisation process is to vary oven temperature (Thermo Sceintific, 2011). However, ASE has not previously been used to extract explosive formulations and the high temperatures may increase the likelihood of thermal decomposition (Campbell et al., 2003). Therefore, the temperature was held constant at 100°C to ensure that it remained below the auto-ignition temperature of RDX (197°C) and PBX-A (206°C) (Harris, 1976; RWM Italia, 2011). Unable to alter the temperature, the next stage was to optimise the static time. Increasing the static time exposes the sample to solvent for longer, allowing more time for the polymer to swell and the RDX to dissolve. The static time was increased progressively from five to thirty minutes. When the static time was increased from five to ten minutes RDX recovery improved from 11% to 32%. Increasing the static time from ten minutes to thirty minutes had no further effect on the percentage recovery of RDX, as it is likely that the system had reached equilibrium between extracted RDX in the solvent and RDX remaining in the polymer (**Figure 4-1**). Therefore, the optimal static time used in all following experiments was ten minutes.
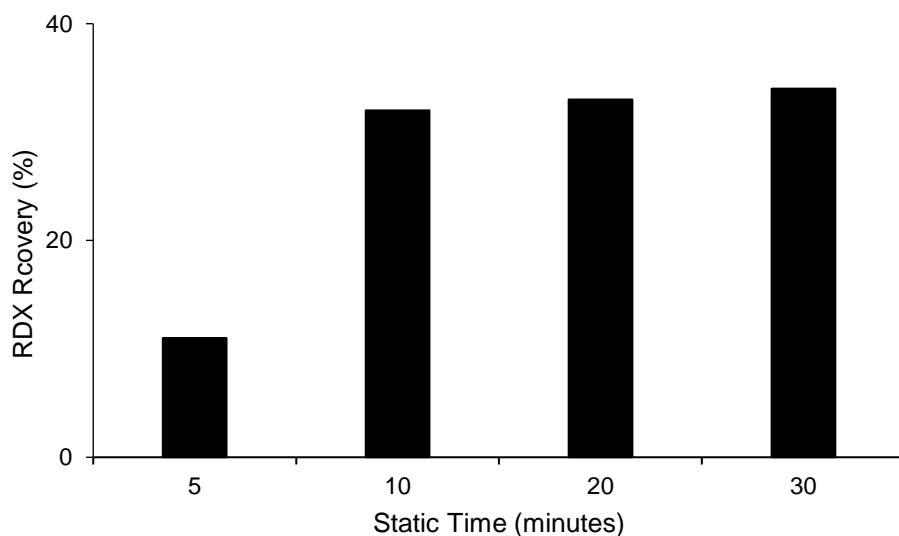
Figure 4-1: Percentage recovery of RDX from PBX-A when varying static time from 5 to 30 minutes.

In order to shift the equilibrium, the ASE method was further optimised to include rinse cycles during the extraction. This allows fresh solvent to be added, which helps to maintain a favourable extraction equilibrium and encourage further

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dissolution of the sample (Thermo Sceintific, 2011). Up to this point, each extraction only had the one rinse cycle as per the Application Note method (**Table 4-2**) which meant that at the end of the 10-minute static time the sample was rinsed with 60% of the cell's volume of solvent (e.g. 20 mL rinse for a 33 mL cell). The ASE enables the user to choose the number of rinse cycles for each extraction, which splits the volume of rinse solvent between the number of cycles. The PBX-A extraction was split into three ten minute rinse cycles, distributing an equal proportion of the solvent between each rinse cycle, which increased the percentage of RDX recovered by 16% to a total of 48% (**Figure 4-2**).
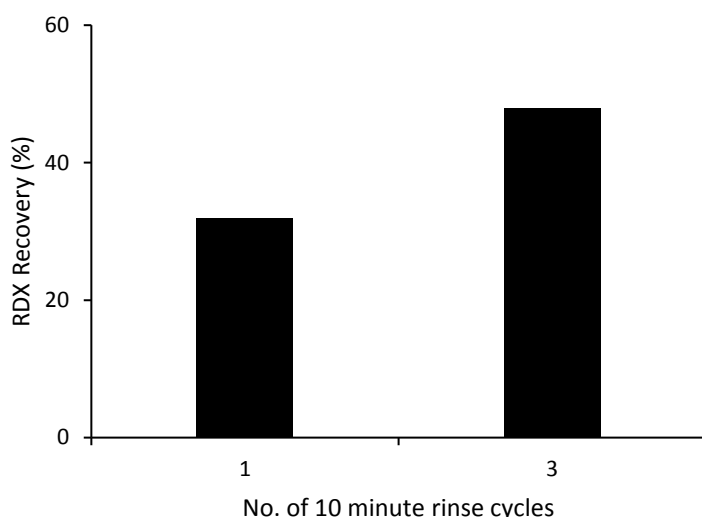
Figure 4-2: Percentage recovery of RDX from PBX-A when rinse cycles were added to the extraction.

It was clear that exposing the sample to fresh solvent increased the percentage recovery, although not achieving 100% suggesting that the solvent cannot ingress further into the polymer. However, due to the explosive nature of the sample cutting the sample further to increase surface area was avoided at this time. Therefore, the volume of solvent introduced to the cell was increased by reducing the amount of Ottawa sand in the cell surrounding the sample by half. The PBX-A sample was placed in a porous cellulose thimble, which leaves more space in the cell for solvent. The thimble was used with and without sand to achieve optimum dissolution.

As expected, increasing the volume of solvent in the cell by removing the sand increased the percentage recovery to 58%. Placing the sample in a thimble with sand resulted in a similar percentage recovery to the samples placed in a cell with sand only (48% and 50%) (**Figure 4-3**).
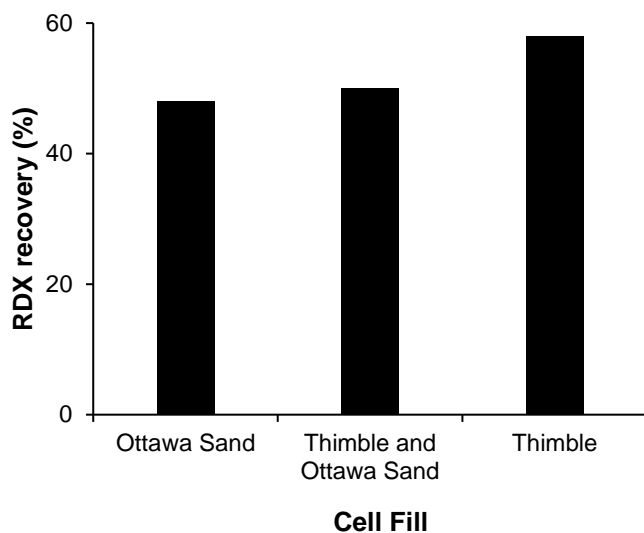
Figure 4-3: Effect of increasing the volume of solvent in the cell by removing Ottawa sand.

The improvement in the percentage recovery by removing Ottawa sand was minimal, and may be overcome by further optimisation to minimise solvent use. However, it may be necessary to compromise the volume of solvent for safety when extracting explosive formulations as the coarse sand may pose a friction hazard for some formulations. For all further extractions samples were placed in a cellulose thimble.

Having followed the recommended ASE method development for optimisation and improved extraction to 58% by optimising method parameters, the final step was to optimise the sample preparation. It is usually recommended grind samples to increase surface area and availability of the material to be extracted, however this would not be suitable for explosive formulations. Therefore, the PBX-A sample was cut into smaller uniform pieces to determine the optimal volume. The smallest size was limited by practicality, cutting the pieces smaller than 0.008 cm^3 was difficult, and resulted in RDX particles escaping the matrix. The cut PBX-A was transferred to a cellulose thimble.

Increasing the surface area resulted in a significant increase in RDX extraction. The smallest pieces (0.008 cm^3) resulted in complete extraction achieving 100% recovery of RDX. To confirm that 100% recovery was achieved, the extraction was repeated twice. Repeating the extraction enabled 100% recovery of RDX from the slightly larger 0.07 cm^3 pieces as well (**Figure 4-4**). Overall, increasing the surface area achieved the greatest percentage improvement in extraction of RDX although this was the least preferred optimisation route due to the necessity of cutting the explosive.
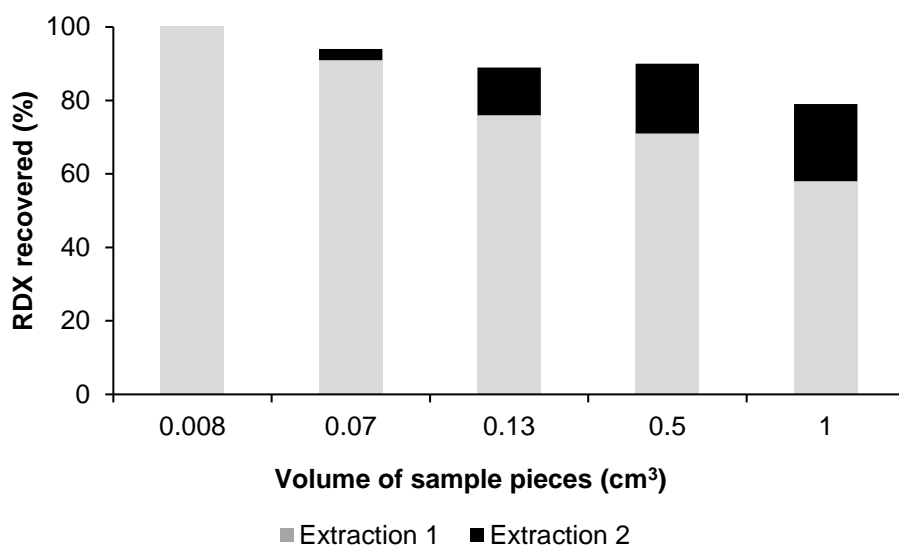
Figure 4-4: Percentage of RDX recovered from 1.0, 0.5, 0.13, 0.07 and 0.008 cm^3 pieces of PBX A.

Once the conditions to achieve 100% extraction has been determined, the optimised method was repeated on 6 samples of PBX-A to determine reproducibility. The percentage recovery averaged 97% with a standard deviation of 13%, which is similar to the standard deviation of other ASE methods found in the literature.(Campbell et al., 2003; Pan, Zhang and Cobb, 2005) Whilst this is often acceptable in the literature for other methods, it should be possible to improve the precision by continued optimisation. For example, RDX mass may have been lost during cutting of PBX-A although care was taken to ensure all material was account for. As a control measure, at least three replicates of each sample should be extracted to overcome any reproducibility issues.

The optimised ASE method for the extraction of explosive from PBX used acetone, a ten minute static time, with three rinse cycles, using 60% rinse volume at 100°C and 1500 psi with a 200 second purge summarised in **Table 4-5**. This method achieved 100% extraction of RDX from PBX in forty minutes, and used approximately 60 mL acetone.

Table 4-5: Summary of the optimisation for the extraction of RDX from PBX-A.

Step	Optimised parameter	Optimised condition	Percentage Recovery
1	Solvent	Acetone	11%
2	Static time	10 minutes	32%
3	Rinse cycles	3	48%
4	Cell preparation	Thimble only	58%
5	Sample size	0.008 cm^3	100%

4.4.2 Soxhlet extraction of RDX from PBX

To ensure the novel ASE extraction method was comparable to current best practice, PBX-A was extracted by Soxhlet, which is an established method in the literature (DuBois and Baytos, 1991; Kumar et al., 2017). The PBX-A sample was acquired from an industrial source, and the accompanying data sheet stated that it contained 64% RDX. Sub-samples for extraction were cut from the slab and were assumed to contain 0.64 g of RDX per 1 g of PBX-A. The calculated mass of RDX extracted was based on the actual mass of the cut sample. The Soxhlet extraction of PBX-A took forty eight hours and 150 mL of acetone, and achieved an average of 90% ± 0.5% recovery of the RDX (2 replicates). The two methods are compared in **Table 4-6.** During the extraction RDX precipitated around the edge of the round bottomed flask as solvent evaporated, which created an explosive hazard and therefore required close monitoring.

Table 4-6: Comparison of optimised ASE method and Soxhlet

Parameter/Method	ASE	Soxhlet
Solvent (volume)	Acetone (60 mL)	Acetone (150 mL)
Time	40 minutes	48 hours
Temperature	100°C	78°C
Solvent exposure	3 rinse cycles	Continuous
Percentage recovered	97% ± %	90% ± 0.5%

The ASE method was more efficient, achieving an average of 97% RDX extraction compared to 90% using Soxhlet. Even though the improvement in extraction of RDX appears small, the reduction in time was significant with the ASE only taking forty minutes in total, compared to forty-eight hours for Soxhlet. Also, the ASE used only 60 mL of solvent, compared to at least 150 mL Soxhlet.

The ASE also provides broader benefits in addition to resource efficiency. For example, the ASE is a closed system where solvent is automatically dispensed to the sample, whereas Soxhlet is more manual and requires frequent solvent refill. This causes a potential explosive hazard when solvent evaporates causing solid explosive to precipitate in the round-bottomed flask adjacent to the heating mantle. Overall, the ASE significantly reduces extraction time as it can automatically run up to twenty-four samples. It also requires less intensive monitoring compared to Soxhlet, which enables faster sample throughput.

4.4.3 Validation of optimised method

The optimised method was applied to two additional PBXs to determine the applicability of the method. PBX-B contained 87% HMX; PBX-C contained 20% RDX, 43% ammonium perchlorate, and 25% aluminium. The method enabled the successful extraction of HMX from PBX-B, with an average of 99% recovered in a single extraction (**Figure 4-5**).

Recovery of RDX from PBX-C was not as efficient with an average of 92% recovered after two extractions, however the consistency of PBX-C made it difficult to cut and the pieces used were slightly larger than the optimal 0.008 cm^3 possibly contributing to the slightly lower recovery (**Figure 4-5**). In addition, PBX-C is denser than the other two PBX's which may make it more difficult for solvent to ingress into the polymer to aid explosive extraction.
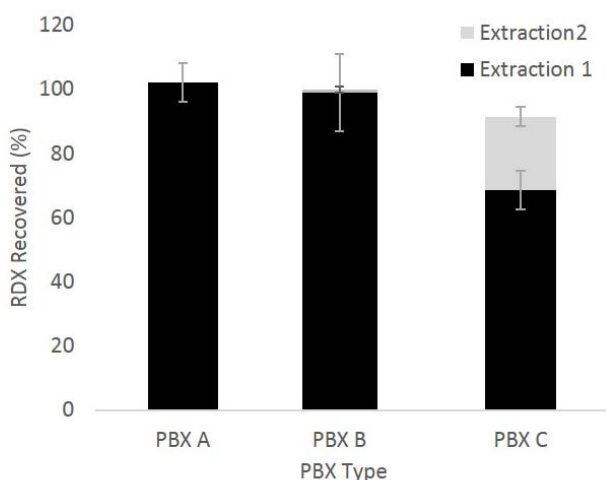
Figure 4-5: Comparison between percentage recovery of explosive using the optimised method for three different PBX (3 replicates).

4.5   Conclusion

The first reproducible method for the complete extraction of RDX/HMX from PBX using ASE was successfully optimised and validated. The method development aimed to follow the recommended optimisation procedures, however the extraction of explosives was more complex due to additional safety concerns e.g. auto-ignition and friction hazard. It was considered unsafe to optimise the temperature beyond 100°C, and placing the samples in a cellulose thimble reduced friction hazard whilst maintaining high recovery of the explosive. It was not considered ideal to cut the PBX smaller than necessary for the extraction therefore this optimisation step was consciously left as the last option. However, it was necessary to carefully cut the PBX to achieve full extraction. The optimised extraction method for the extraction of RDX/HMX from PBX using ASE was 100°C, 1500 psi, with a 10-minute static cycle, three rinse cycles in acetone and a 200 second purge achieving an average of 97% extraction. The samples were prepared by cutting to increase surface area, and placing in cellulose thimbles. The total extraction time was 40 minutes and used 60 mL solvent, which is a significant reduction when compared to Soxhlet extraction, as it requires 48 hours and over 150 mL solvent. It may be possible to reduce the extraction time further by reducing the static time between each rinse cycle. The success of this method

for three different PBX suggest that it would be applicable to other polymer based explosives. In addition, further work should include extraction of all components of the PBX, and it may be possible to develop a method with consecutive extractions to separate the different components.

Comparison of the efficiency of extraction methods for insensitive high explosive constituents from different soils
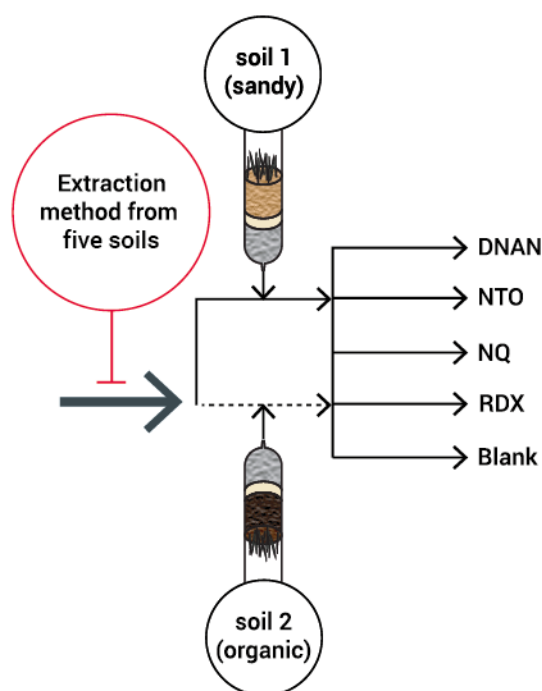
Having investigated the dissolution behaviour of PBX and developed an optimal extraction procedure, it was important to establish whether similar principles could be applied to other types of IHE formulations. Therefore, this paper investigated the feasibility of extracting four different IHE constituents from five soils using four different extraction methods. Results showed that it is possible to select any extraction method based on practicalities and available resources, although a percentage of water to organic solvent should be used and soils with high organic content are the most difficult to extract.

This paper is currently being prepared for submission.

Chapter 5   Comparison of the efficiency of extraction methods for Insensitive High Explosive constituents from different soils

5.1 Abstract

The standard extraction procedure EPA 8330B for the determination of nitro-aromatics, nitramines and nitrate esters in soil. This method is not appropriate for Insensitive High Explosives (IHE) containing mixtures of ,5-trinitroperhydro-1,3,5-triazine (RDX), 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazolin-5-one (NTO), 1-nitroguanidine (NQ), as their physicochemical properties significantly differ from traditional explosives constituents. In particular, the solubility of some IHE constituents (e.g. NTO) is lower in typical extraction solvents such as methanol (MeOH) and acetonitrile (ACN). Until now, the common approach has been to adapt the EPA 8330B method using a mixture of 1:1 ACN/water to ensure both the highly water soluble NTO and the organic soluble RDX are extracted in a single step. However, to date there is little information on extraction efficiency of IHE constituents in soil and there are to the best of the knowledge of the authors no systematic comparison studies of the extraction methods for IHE constituents from different soil types. In this study, five different soil types were spiked with a mixture of RDX, DNAN, NQ and NTO and extracted using four different one-step extraction methods including stirring, shaking, sonication, and accelerated solvent extraction (ASE). Results confirmed that the EPA 8330B method was not suitable for the extraction of IHE constituents from soil, therefore the adaption of this method by including a percentage of water (50-80%) in the solvent system as suggested by the literature was proven to be suitable. When the four extraction methods were compared, it was found that they were broadly successful for the extraction of all IHE constituents from all five soils. However, soils with high organic content (%Total Organic Content (TOC) $\geq$ 2%) were found to significantly affect extraction efficiency and reproducibility. Reproducibility was also affected by the extraction method as ASE extraction efficiency (110%-37%) was far more variable than shaking, sonicating (59%-98%) and stirring (77%-110%). Of the four tested methods shaking was found to be the most reproducible, though the

least efficient (64%-91%). Therefore, it is recommended that the efficiency of the selected extraction method should be validated by extracting known concentrations of the IHE from the soil of interest and that any required correction factors are reported.

Keywords: EPA 8330B, 3,5-trinitroperhydro-1,3,5-triazine (RDX), 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazolin-5-one (NTO), 1-nitroguanidine (NQ), Accelerated Solvent Extraction (ASE)

5.2 Introduction

Explosive contamination in the environment is commonly found at military and manufacturing sites (Clausen et al., 2004; Hewitt et al., 2005; Walsh et al., 2013). Under current environmental legislation the extent of the contamination must be identified by soil sampling and subsequent separation of the explosive contaminants from the soil matrix by extraction to enable chemical analysis and quantification (Dean, 2009). It is essential that the extraction method is efficient, which means 100% of all available explosive residue can be consistently recovered i.e. all materials that have not degraded or irreversibly bound to the matrix, so that any resultant risk is not underestimated.

Much of the early work on the extraction of conventional explosives such as 2,4,6-trinitrotoluene (TNT), 3,5-trinitroperhydro-1,3,5-triazine (RDX) and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from soil established standard procedures (Cragin et al., 1985; Jenkins and Leggett, 1985; Walsh et al., 1993). For example, it has become standard practice to air dry the soil prior to extraction to ensure that no water soluble contaminants are missed during extraction i.e. with a non-water miscible solvent (Cragin et al., 1985). Solvents have also been compared and acetone (Ac), methanol (MeOH) and acetonitrile (ACN) were identified as the most efficient, although Ac is often avoided when analysing HMX as the Ac obscures the HMX peak when detecting by High Performance Liquid Chromatography (HPLC) (Jenkins and Leggett, 1985). In a comparison of extraction techniques for explosives from soil the commonly used Soxhlet extraction technique has been disfavoured as extraction time can be up to 48

hours, and extraction efficiencies can be inconsistent due to irregular contact between the solvent and soil (Jenkins and Leggett, 1985). Instead, both sonicating (1- 4 hours) and shaking (24 hours) were recommended, with sonication providing slightly higher recovery of the explosives tested (TNT, RDX and HMX).

One of the first specifically developed methods for extraction of conventional explosives from soil was by sonicating samples in ACN for 18 hours, which formed the basis for the commonly used SW-846 US EPA 8330B standard (Jenkins and Walsh, 1987; US Environmental Protection Agency, 2006). The developed method reported extraction of RDX, TNT and HMX with an analytical precision in the range 0.13–1.24 μg/g, and accuracy > 95% in all cases. The method was then expanded and validated to include the extraction of all nitro-aromatic, nitramine and nitro-ester explosives from soil by both sonication and shaking (US Environmental Protection Agency, 2006; Walsh et al., 1993; Walsh, Jenkins and Thorne, 1995).

In recent years, other methods have been introduced to reduce extraction time and solvent use such as Accelerated Solvent Extraction (ASE), which uses high temperature and pressure to achieve full extraction of analytes in as little as fourteen minutes (Fisher, Scarlett and Stott, 1997; Lou, Janssen and Cramers, 1997a; Richter et al., 1996). An ASE method has been successfully developed to extract conventional explosives such as RDX and TNT from an inert matrix (quartz sand) with extraction efficiencies between 90 and 120% (Campbell et al., 2003; Dionex, 2011). However, recovery extraction was dramatically reduced (<70% ± 14% of TNT) in acidic soil samples (pH 5.26) with a high organic carbon content (3.89%), most likely due to strong interactions between the soil and the explosives (Campbell et al., 2003). However, the development of this method demonstrated the applicability of ASE for the extraction of explosives despite concerns over thermal decomposition of the explosives at high temperatures. This research found that maintaining the temperature at 100°C was sufficient to promote fast and efficient extraction (twenty minutes) while also preserving the explosives (Campbell et al., 2003).

Although the extraction of traditional explosives is well established (Holmgren, Ek and Colmsjö, 2012; Lapointe et al., 2016; Mark et al., 2017; Pascoe et al., 2010; Russell et al., 2014; Thomas et al., 2018; Walsh et al., 2012), the current methods may not be suitable to extract new generation Insensitive High Explosives (IHE) from soil (Felt et al., 2016; Taylor et al., 2013). The IHE currently being brought into service can consist of mixtures of up to three of the following energetic materials: RDX, 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazolin-5-one (NTO) and 1-nitroguanidine (NQ), which are likely to be deposited in combination on soil (Richard and Weidhaas, 2014a). Extraction of these combinations from soil may be problematic as they have significantly different solubility profiles in typical extraction solvents e.g. ACN, Ac and MeOH (Table 5-1). Therefore, extracting with only organic solvent as per the EPA 8330B standard may not be suitable. Despite concerns of the efficacy of EPA 8330B for the extraction of IHE, the method has continued to be used by agitating (stir, shake or vortex) with only ACN, which may explain the low reported recoveries of NTO (Arthur et al., 2018; William and Mark, 2016).

Table 5-1: Comparison of solubility and properties of IHE constituents.

IHE constituent	RDX	DNAN	NQ	NTO
Chemical composition	$C_3H_6N_6O_6$	$C_7H_6N_2O_5$	$CH_4N_4O_2$	$C_2H_2N_4O_3$
Physical form[1]	White crystalline solid	Tan to yellow crystalline solid	Pale yellow crystalline solid	White crystalline solid
Water solubility (g/L @ 25°C)[2]	0.06	0.28	3.0	16.6
ACN solubility (g/L @ 25°C)	55[3]	Soluble	Soluble	Low
MeOH solubility (g/L @ 25°C)	Soluble	Soluble	Low[4]	Soluble[5]
Ac solubility (g/L @ 25°C)	82[5]	Soluble[5]	Soluble	16.8[5]
ecomposition Temp (°C)[1]	213	295[3]	232	273
Ignition Temp (°C)[1]	210	347	N.A.	258-280

1. Akhavan J. 2011. The Royal Society of Chemistry; 2. Taylor, S. et al. 2015. Chemosphere, 134, p. 250; 3. Xing et al. 2012. Propellants, Explosives and Pyrotechnics, 37, p137; 4. Sitzmann, M.P. 1973. Silver Spring, Maryland. 5. Smith et al., 1999. Report: DSTO-TR-0796. N.A.: Data not available.

Therefore, new and adapted EPA 8330B methods have been developed such as a two-step procedure for the extraction of RDX, DNAN and NTO from soil that reported the use of sonication with a 3:7 mixture of ACN and acidified water (0.1 % trifluoroacetic acid), followed by 18 hours sonication in ACN (Felt et al., 2016). As NTO is predominantly negatively charged at environmentally relevant pH (pH 5-8), decreasing the pH of the water during the first step of the extraction was thought to reduce the affinity of NTO to soil making it easier to extract (Mark et al., 2016). The second step (18 hr ACN sonication) was then used to fully extract any remaining DNAN and RDX as they are less soluble than NTO in water (**Table 5-1**). However, the second step did not appear to provide any added benefit as all explosives were recovered in the first step (>100% recovery) suggesting that one-step methods may still be appropriate for IHE extraction.

Extraction of IHE has been reported using a single step procedure by modifying the EPA 8330B method to agitate the sample in a 1:1 mixture of ACN and water (Bergström, 1990). However, the study did not provide details of the extraction method or report the extraction efficiency rendering comparison and assessment of IHE constituent extraction difficult. The use of an ACN/water (1:3) solvent system has also been employed for the extraction of DNAN, NQ and NTO from soil using a modified ASE method for the extraction of conventional explosives (Campbell et al., 2003; Temple et al., 2018). DNAN and NQ were both efficiently extracted (~100%) from the two soil types (sandy and loamy), however only approximately 60% of NTO could be recovered therefore results were corrected for the missing mass with a recommendation for further development of the method (Temple et al., 2018).

As it can be seen, current practice for the extraction of combinations of IHE constituents from soil has been to adapt EPA 8330B to account for the differences in their physicochemical properties to ensure complete extraction of all available constituents (Richard and Weidhaas, 2014b). However, to date no systematic comparison studies of IHE extraction methods have been published. Therefore, the aim of this work was to compare the efficiency of four different one-step methods for the extraction of multiple constituents of IHE formulations from soil.

This was achieved by artificially contaminating five UK soil types with a mixture of RDX, DNAN, NQ and NTO. The explosives were then extracted from the soils by shaking, sonicating, stirring and ASE.

5.3 Methodology

5.3.1 Materials

Solvents (Ac, ACN, MeOH), deionised water and chemicals DNAN and quartz sand were used as supplied (Fischer Scientific). NTO and NQ were synthesised by standard literature methods (Lee and Coburn, 1988). Extractions were carried out using a Stuart™ Orbital shaker, Bibby Scientific™ magnetic stirrer, Clifton Ultrasonic bath and a Dionex Accelerated Solvent Extraction 350.

5.3.2 Soil collection and preparation

Soils (1 kg) were collected from five locations around the UK including West Freugh (WF), Eskmeals (ESK), Pendine (PEN), Shoeburyness (SBN) and Wiltshire (WLT) (**Figure 5-1**). Soils were air-dried for 3 weeks to constant weight and passed through a 2-mm sieve to remove non-soil material such as stones, debris etc. Particle size distribution was determined according to ASTM D 2487-11, and pH after twenty-four hours of shaking the soil in water. Soil texture was determined by the U.S Department of Agriculture (USDA) classification system based on grain size. Total Carbon Nitrogen Hydrogen (TCNH) content and Total Organic Carbon (TOC) were determined using Elementar Vario ELIII. The soil properties are summarised in **Table 5-2**.
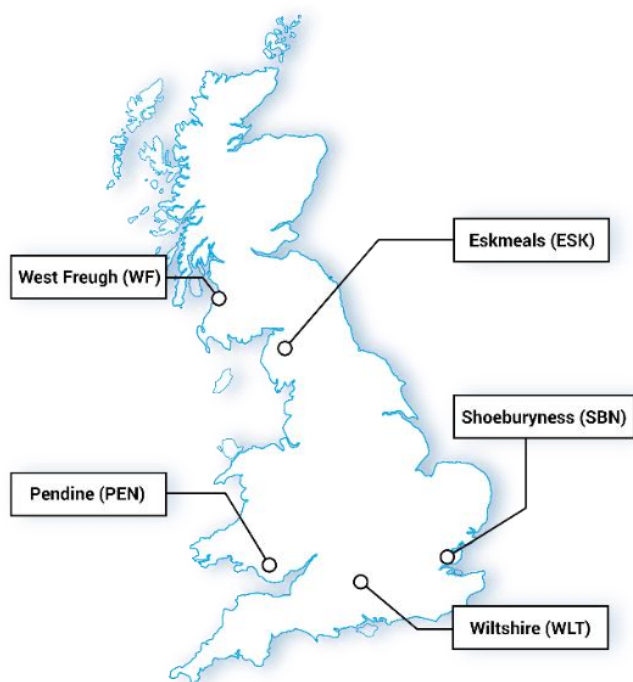
Figure 5-1: Collection locations for the five soil types.

Table 5-2: Characterisation of the five soil types.

	Texture (USDA)	pH	TOC (%)	Mode particle size (mm)
WF	Medium sand	6.8	0.9	0.21
ESK	Medium sand	6.5	2.9	0.21
PEN	Fine sand	7.8	2.1	0.15
SBN	Loam	7.9	6.5	0.06
WLT	Loamy sand	7.9	0.4	1.00

5.3.3 Artificial contamination of soil

RDX (268 mg), DNAN (253 mg), NQ (257 mg) and NTO (253 mg) were mixed and stirred in acetonitrile (500 mL) at ambient temperature for 24 h to make an approximately 500 ppm mixture stock solution referred to as '500 ppm stock solution'.

5.3.4 IHE extraction from soil

5.3.4.1 Standard extraction procedure (EPA 8330B)

To establish the efficacy of standard procedures for extraction of IHE from soil the method EPA 8330B for nitro-aromatics, nitramines and nitrate esters was followed (US Environmental Protection Agency, 2006). An inert matrix (10 g) (quartz sand) was prepared by contaminating with 1 mL of 500 ppm solution of mixed RDX, DNAN, NQ and NTO in ACN. The soil was evaporated to dryness (by weight) for four hours in a fume hood to enable complete evaporation, while minimising the potential for the IHE to sorb to soil or degrade (particularly DNAN and NTO).

5.3.4.2 Identification of appropriate ASE solvent

It was essential to identify a suitable ASE solvent system as an optimised extraction of IHE from soil using ASE has not previously been reported. The ASE method used the same operating parameters as previously published (Temple et al., 2018): 100°C oven temperature, 1500 psi pressure with a ten minute static time, 60% rinse volume and 200 second purge. The method took approximately twenty minutes to run. An appropriate solvent was identified by evaluating the efficiency of extractions of IHE from an artificially contaminated inert matrix (quartz sand). The inert matrix (30 g) was spiked with 1 mL of the 500 ppm stock solution and evaporated to dryness. Samples were evaporated for twenty-four hours as evaporation was slower from the sand in the ASE stainless steel cells. All solvent systems tested included a percentage of water in ACN, MeOH or Ac. The solvents were tested with 20%, 40%, 60%, 80% and 100% water.

For ACN/water and MeOH/water solvent systems the extract diluted to 150 mL in the extraction solvent and analysed by HPLC. For Ac/water extractions the solutions were evaporated (rotary evaporator) and re-dissolved in ACN (10 mL) for compatibility with the HPLC method.

5.3.4.3 Extraction methods: shaking, sonication, stirring, ASE

For shaking, sonicating and stirring 10 g soil was weighed into amber vials and artificially contaminated with 1 mL of the 500 ppm stock solution and evaporated

to dryness (4 hours). ACN/water 1:1 (20 mL) was added to the vials, as per methods reported in the literature (William and Mark, 2016). Samples were mixed by hand for 30 seconds before placing the vial on the shaker, stirrer or in the sonic bath. Samples were shaken or stirred for 18 hours, or sonicated for one hour. Upon completion samples could settle for thirty minutes before filtration through a 0.2 μm filter and analysis by High Performance Liquid Chromatography (HPLC).

For ASE soil (30 g) was spiked with 1 mL 500 ppm stock solution and evaporated overnight. Samples were extracted at 100°C, 1500 psi for twenty minutes, with a 5 minute static time and 60% rinse volume with 1:4 MeOH/water. The resulting extract (~60 mL) was made up to a 100 mL with extraction solvent and filtered prior to HPLC analysis. A summary of all four extraction methods is given in **Table 5-3**.

Table 5-3: Summary of extraction methods.

Method	Solvent	Solvent Volume (mL)	Soil mass (g)	Time (hours)
Shaking	ACN/Water (1:1)	20	10	18
Stirring	ACN/Water (1:1)	20	10	18
Sonicating	ACN/Water (1:1)	20	10	1
ASE	MeOH/ Water (1:4)	60	~30	0.5

5.3.4.4 High Performance Liquid Chromatography

An aliquot of the extracted samples (1.5 mL) was analysed by HPLC (Waters-Alliance 2696, USA) using a photodiode array detector (Waters, 996, USA). The components were separated on a ZORBAX Eclipse Plus C18 column (100 mm ✕ 4.6 mm, 3.5 μm particle size) from Agilent technologies (Wilmington, DE, USA) maintained at 35°C as previously reported (Temple et al., 2018). The mobile phase was methanol (solvent A) and water/0.1% formic acid (solvent B) with a flow rate of 0.75 mL min^{-1}.

Optimised separation conditions were achieved with a linear gradient. The injection volumes was 10 μL and the signal for each IHE constituent was targeted.

Calibration solutions were prepared from the initial stock solution at 50 ppm, 25 ppm, 12.5 ppm, 6.25 ppm and 2.5 ppm.

All extractions were repeated in triplicate and data averaged for analysis with one standard deviation used to calculate error. Results were normalised against quartz sand assuming 100% extraction from the inert matrix.

Principal component (PC) was computed with R Studio (Version 1.1.423 – © 2009-2018 RStudio, Inc.) to assess interrelationship among different variables, allowing detection and interpretation of sample similarities (groups). Data were pre-processed by scaling and centering with the function *prcomp* and plotted using "devtools" and "ggbiplot" libraries (Hadley et al., 2018; Wickham, 2016).

5.4 Results and Discussion

5.4.1 Suitability of EPA 8330B for IHE constituents

EPA 8330B was initially used as prescribed to confirm that is not suitable for extraction of the mixed IHE constituents, RDX, DNAN, NQ and NTO. These constituents were selected as they are commonly incorporated in IHE formulations. The soil was artificially spiked with a 500 ppm solution of RDX, DNAN, NQ and NTO in ACN to simulate a contaminated sample. The ACN was evaporated for four hours, the minimum time required for complete evaporation (determined by mass loss). Samples were extracted immediately to limit degradation or irreversible sorption of the explosive to the soil. Experiments were conducted using an inert matrix to minimise sorption and degradation due to soil interactions. This ensured that 100% of all available constituents were extracted enabling clear identification of any inadequacies of the method. Samples were extracted by sonicating and shaking for 18 hours in ACN as described in EPA 8330B.

As expected the EPA 8330B method was found not to be suitable for fully extracting all tested constituents of IHE from the inert matrix. Results showed that RDX and DNAN were successfully extracted by sonicating, 120% and 100% respectively. It was assumed that complete recovery of RDX was achieved and any errors were from handling and analysis accounting for the additional 20%.

However, NTO and NQ proved more difficult to fully extract by sonication with only 30% of NQ recovered, and 0% of NTO (**Figure 5-2**). This was most likely due to the low solubility of NTO and NQ in ACN (**Table 5-1**). In this experiment shaking did not appear to extract any of the IHE constituents in significant concentrations with only trace quantities of RDX and DNAN recovered.
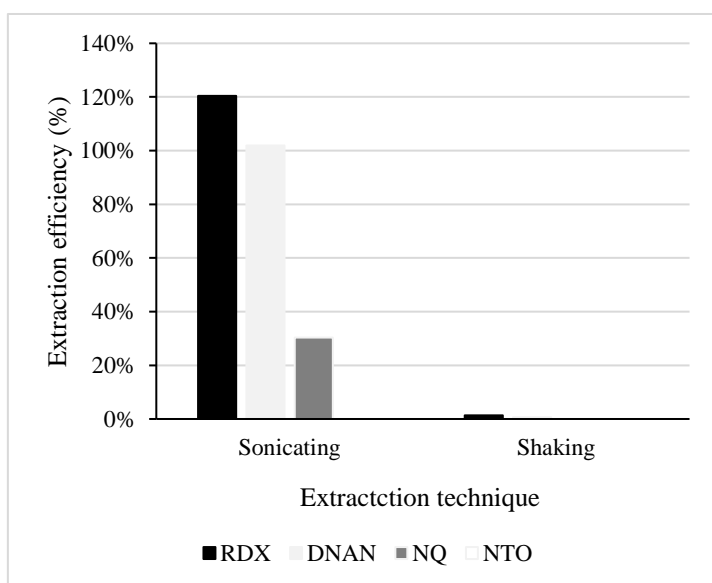
Figure 5-2: Extraction of RDX, DNAN, NQ and NTO by EPA 8330B.

5.4.2 Identification of appropriate ASE solvent

To use the ASE method to extract IHE from soil the identification of appropriate solvent was required. Therefore, guidance to do this was taken and adapted from the application note for the extraction of TNT and its degradation products from soil and a previous publication (Dionex, 2011; Temple et al., 2018). Extractions were carried out using a 14 minute method at 100°C, 1500 psi, with 5 minutes oven heating time and 5 minute static time in acetone or methanol (50 mL). As stated above a different solvent system including a percentage of water is required for the extraction of NTO and NQ. The ASE method was therefore screened with various mixtures of organic solvent to water ratios to identify the most effective solvent system. The application note recommended the use of Ac and MeOH, but as ACN is most commonly used for extraction of traditional explosives such as RDX, this was also included (Jenkins and Leggett, 1985).

Identification of an appropriate ASE solvent was carried out using an inert matrix (quartz sand) to eliminate sorption and reduce the likelihood of degradation. It was possible that the high temperatures employed in ASE could promote degradation, however the temperature was limited to 100°C for short periods (15-45 minutes) and significant degradation was considered to be unlikely.

Extractions of IHE from spiked quartz sand were carried out using various mixtures of 0-100% water and Ac, MeOH or ACN with other operating parameters kept constant. Results showed that Ac was the least efficient solvent, even with only 20% Ac in water it was not possible to extract any of the highly water soluble NTO (**Figure 5-3**). Extraction of RDX, DNAN and NQ was between 93% and 100% efficient across all solvent systems. Surprisingly, when extracting with 100% water it was possible to extract 82% RDX, 91% DNAN, 86% NQ and 92% NTO. This was unexpected given the very low solubility of RDX and DNAN in water, but emphasizes the effect of using combined high temperatures and pressures to improve extraction as it is possible to heat solvents above their boiling point and substantially increase the solubility of chemicals in the extraction solvent (Vandenburg et al., 1999).
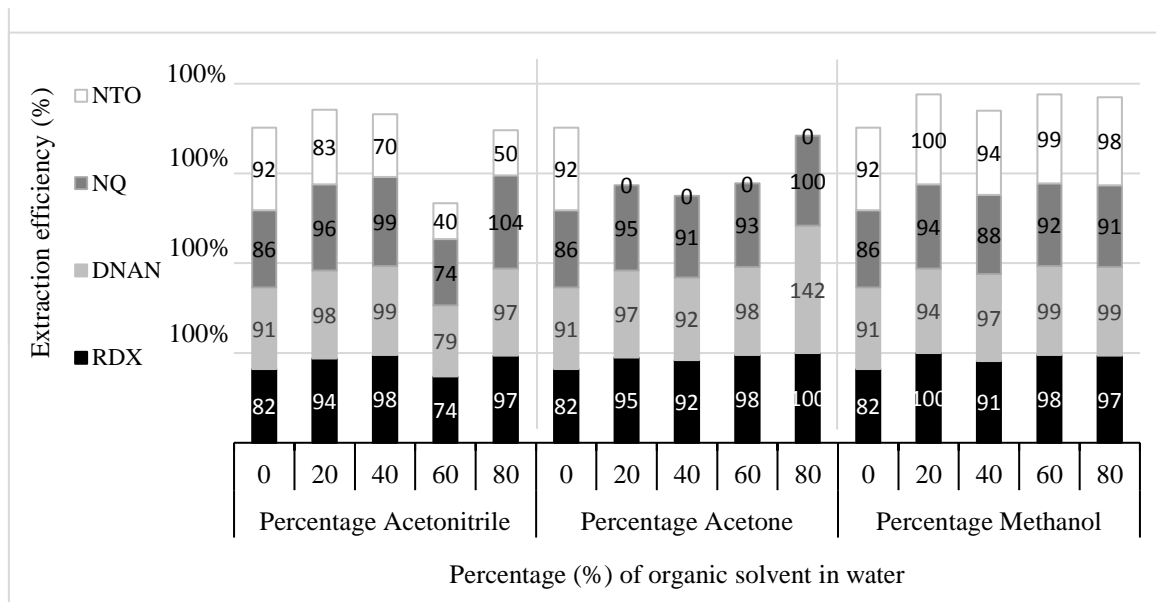
Figure 5-3: Comparison of ASE efficiency of IHE extraction from quartz sand using a range of solvent systems.

Extraction efficiency when using at least 40% ACN in water achieved high recovery (91% ± 10%) for all IHE constituents, but extraction of NTO reduced significantly with higher percentages of ACN (**Figure 5-3**). The most efficient and most reproducible extractions were achieved using a mixture of water and MeOH (94% ± 5%). Surprisingly, even at low percentages of water in methanol i.e 80% MeOH, it was still possible to extract over 90% of all IHE constituents. However, 20% methanol in water was the most efficient solvent system extracting 100% RDX, 94% DNAN, 94% NQ and 100% NTO. This may be due to the higher polarity of MeOH compared to ACN which has less effect on the polarity of the combined water/organic solvent mixture enabling complete extraction of both aqueous and organic soluble constituents. Therefore, 20% MeOH in water was used as the solvent for all ASE extractions.

5.4.3 Comparison of extraction methods

To compare extraction efficiencies of the four method, known concentrations of RDX, DNAN, NQ and NTO were extracted from five different UK soils with varying TOC (0%-7%, mode particle size (0.063-2.00 mm) and pH (6.5-7.9). Results were averaged over three replicates and normalised against quartz sand.

Almost all extraction methods were efficient to at least 70% for all IHE constituents from all soils, with an average of 84% ± 14% recovery across all 80 extractions. When results were analysed by PC variation ASE showed the greatest variance between extraction efficiencies for the four different IHE constituents from the five soils. Variance between results for the other three methods followed the order of sonicating>stirring>shaking (**Figure 5-4**). When comparing the results it was observed that extractions from the five soils could be grouped according to their organic content. The soil with significantly higher TOC (SBN) showed greatest variance from the norm, while the extraction efficiency from the other four soils could be grouped by their similarity in organic content e.g. WF (0.9%) and WLT (0.4%) and ESK (2.9%) and PEN (2.1%).
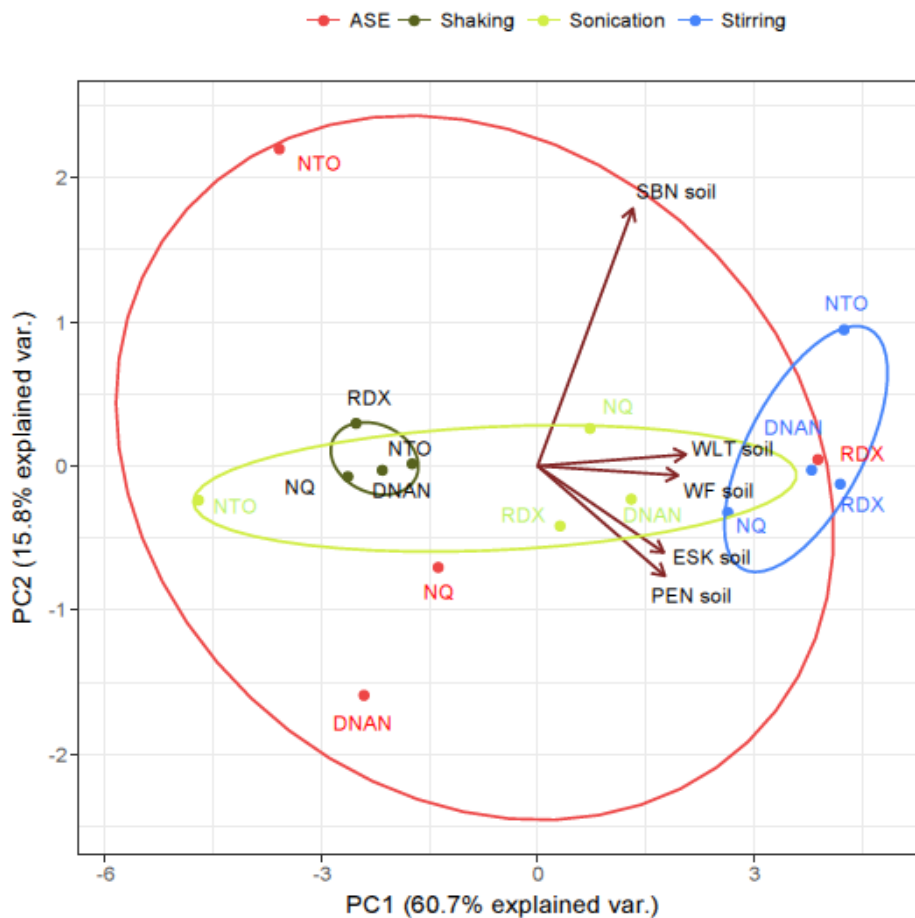
Figure 5-4: Analysis of extraction efficiencies for IHE from 5 soil types by PCA.

5.4.4 Extraction by ASE

ASE was the least consistent for extraction of IHE constituents, suggesting this technique was the most affected by differences in soil type (**Appendix 2 Fig. 1-4**). Of the explosives extracted NTO and DNAN had the least consistent extraction efficiency with poorest recovery of NTO as low as 37% ± 2% from ESK soil, and large discrepancies between identical replicates (Figure 5). Extraction efficiency of DNAN decreased with increasing TOC of the soil, with lowest recovery observed for SBN soil with 6.5% TOC (51% ±2.9%). This may be due to the tendency for DNAN to sorb to soils with high organic content, therefore it is possible that the short extraction time (10 min static time) used for ASE is not sufficient to desorb all DNAN even at high temperature and pressure. Conversely, for soils with lower organic content extraction achieved almost 100% (WLT and WF 93% ± 4.5% and 98% ± 2% respectively), suggesting that repeated

extractions or a longer extraction time may improve efficiency for soils with high TOC (**Figure 5-5**).
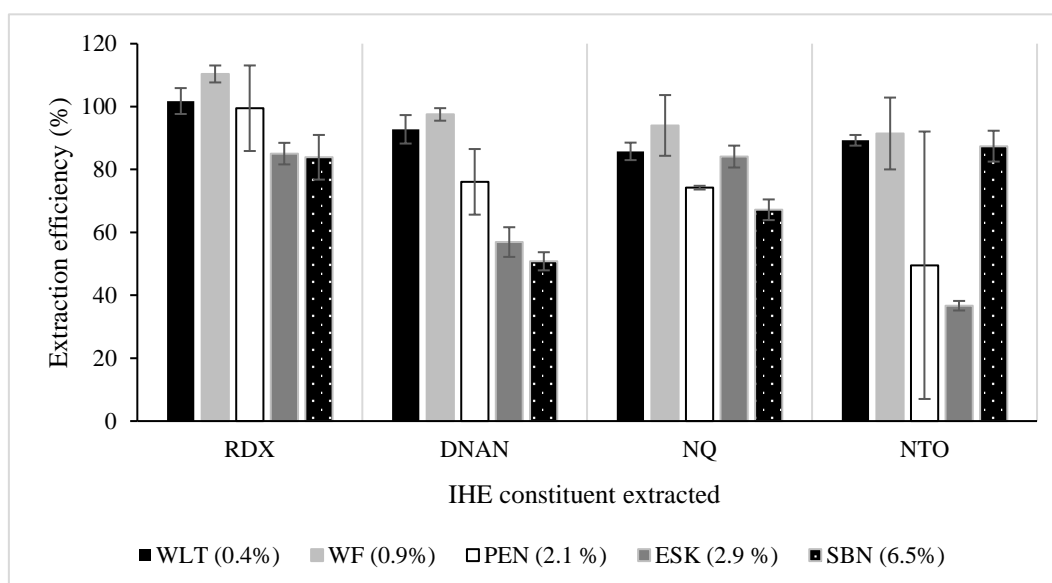
Figure 5-5: ASE extraction efficiency for IHE constituents from five soil types arranged by TOC.

Extraction efficiency of NTO was high from soils with low TOC 89% ± 1.7% and 91% ± 11.4% respectively from WLT (0.4%) and WF (0.9%) (**Table 5-4**). However, from soils with higher organic content the percentage of NTO extracted was lower: 50% ± 42.5% (PEN) and 37 ± 1.5% ESK) (**Figure 5-5**). Although NTO degrades in soils with high TOC, the IHE constituents were only exposed to soil for a maximum of 24 hours, which makes it unlikely to account for the 60% unrecovered material (Temple et al., 2018). In addition, SBN soil with the highest TOC (6.5%) did not fit the trend and it was possible to achieve good extraction efficiency (87% ± 4.9%). The high extraction efficiency for NTO in SBN soil may be due to a low mode particle size, which is significantly lower than for the other soils tested with a large percentage of silt (0.002- 0.0063). Reducing particle size or increasing surface area is often cited as one of the ways to improve extraction efficiency and reproducibility (Walsh, Ramsey and Jenkins, 2002). The naturally low mode particle size of this soil may have therefore contributed to an increased extraction efficiency despite the high organic content, highlighting the important of sample preparation (particularly grinding) for high organic content soils.

Table 5-4: Extraction efficiency of NTO by ASE compared to organic content and mode particle size

Soil Name	NTO Extraction Efficiency (%)	Total Organic Content (%)	Particle Size (mm)
WLT	89 ± 1.7	0.4	0.5-1
WF	91 ± 11.4	0.9	0.2
PEN	50 ± 42.5	2.1	0.2
ESK	37 ± 1.5	2.9	0.2
SBN	87 ± 4.9	6.5	0.063

Overall, ASE was more successful for the extraction of RDX and NQ from soil averaging 96% ± 11.4% and 81% ± 10.5% respectively compared to DNAN and NTO. Although, RDX extraction efficiency tended to be slightly lower for soils with higher organic content e.g. for SBN (67% ± 3.3%) and PEN (74% ± 0.6%) (**Figure 5-5**), although no clear trend between extraction efficiency and the soil properties i.e. organic content, pH and particle size could be drawn (**Appendix 2 Fig. 5**). Therefore, these observations may be due to other characteristics of the soil or inconsistencies in the ASE method. Further optimisation of the ASE method for different soils may help to improve consistency and efficiency. The method used for this comparison could be used as a starting point for optimisation of the number of extraction cycles and extraction with a sequence of solvents.

5.4.5 Extraction by sonication and stirring

Sonication and stirring behaved similarly in variance between extraction efficiency for different soil types (**Figure 5-4**). However, stirring was more efficient averaging 96% ± 9.2% compared to 83% ± 12% for sonication across all soils and explosives (15 extractions). Sonication achieved low extraction for NTO (72%), whilst DNAN, RDX and NQ averaged above 87% ± 11% (**Figure 5-6**), with generally poorer recovery in the higher TOC soils (ESK and SBN). The low extraction efficiency of NTO may be due to the shorter extraction time (1 hour)

when compared to shaking and stirring (18 hours), which may not give enough time for the NTO to fully migrate from the soil into the extraction solvent (1:1 ACN/water). Extraction may be improved if the extraction is continued for longer. This was supported by the observation that for ASE a mixture of 80% water and methanol was required to fully extract NTO, which is a more polar solvent mixture and therefore more likely to solubilise NTO. As extraction efficiency for RDX, DNAN and NQ was reasonably high the sonication method is a suitable technique for these materials. Some variability was observed between different soil types, particularly for soils with higher TOC (ESK, SBN) suggesting a need to fully understand the extraction efficiency so that results can be corrected accordingly.
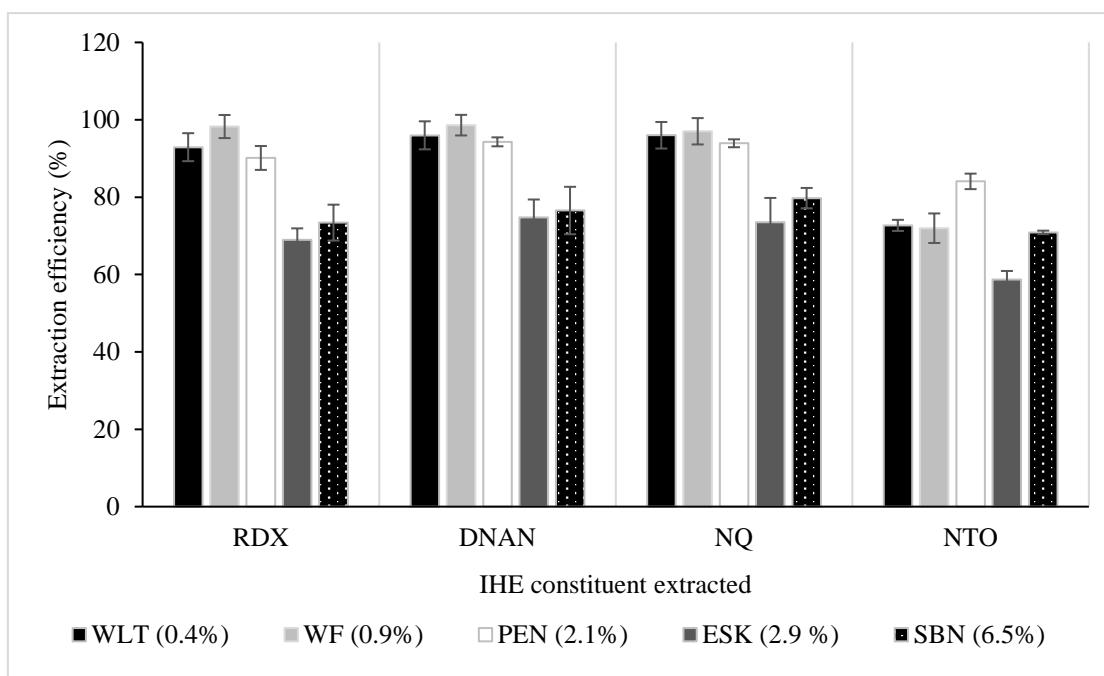
Figure 5-6: Efficiency of extraction of IHE constituents from five soil types arranged by TOC by sonication.

Stirring averaged almost complete recovery for all IHE constituents from all soils (RDX 102% ± 10.7%, DNAN 97%, ± 9.7%, NQ 92% ± 11.3% and NTO 97% ± 6.5%). Of interest the extraction of NTO by stirring was the most reproducible, which is in complete contrast to sonication and ASE in which NTO proved difficult to extract. Even though stirring was carried out using the same solvent system as sonication NTO recovery was more efficient. This may be due to the reduced time used for sonication extractions.

5.4.6 Extraction by shaking

Shaking was the most reproducible method with the least variability between results, suggesting this method was the least affected by soil properties (**Figure 5-7).** However, the extraction efficiency was lower than the other tested methods averaging 78% ± 9% across all soils and explosives (15 extractions) compared to 83% ± 12% for sonication, 96% ± 9.2%, for stirring and 81 ± 19% for ASE (**Appendix 2 Fig. 1-4**). These results were surprising as shaking is one of the most commonly used extraction methods and is often reported as being efficient and reproducible, whereas these results show that for IHE shaking is consistent but inefficient. Therefore, when extracting by shaking results should be corrected for the unaccounted mass.
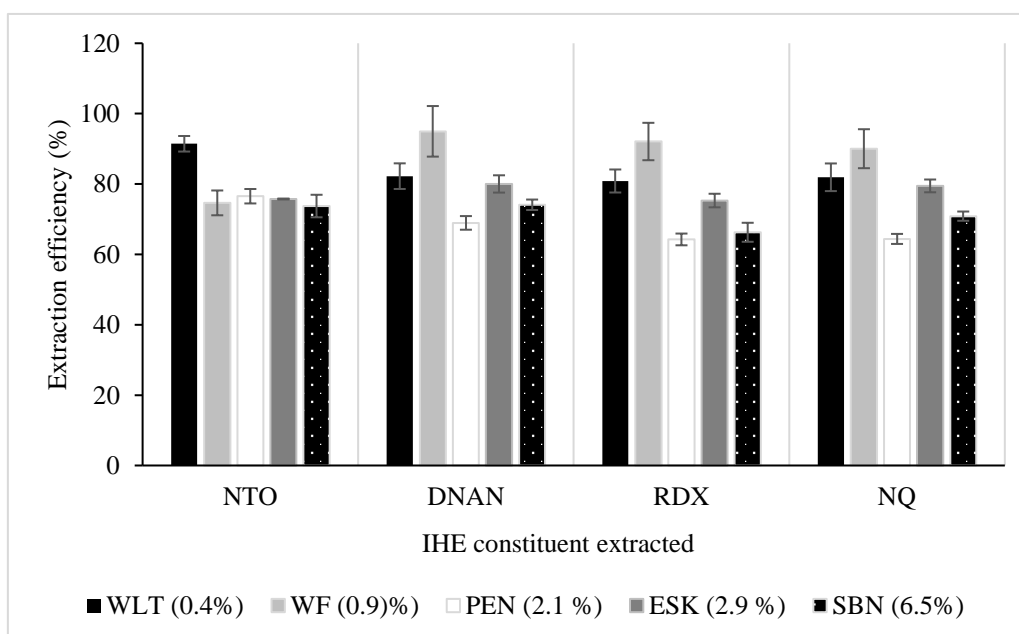
Figure 5-7: Comparison of extraction of RDX, DNAN, NQ and NTO from five soils by shaking.

5.5 Conclusion

This study confirmed that it is necessary to adapt the standard explosive extraction method EPA 8330B to achieve consistent and efficient extraction of IHE constituents from soil in a single step. To achieve this, a high percentage of water in an organic solvent ($\geq$ 50%) is essential for efficient extraction. The work also highlights the significant effect that soil type has on the extraction efficiency,

which has not previously been reported in the literature. This suggests that for any extraction of IHE from soil, data must be accompanied by a statement of efficiency and correction factor. It is therefore possible to select any extraction method based on practicalities and available resources. This includes new extraction methods, such as the ASE method developed for this work which fully extracted RDX, DNAN, NQ and NTO from several soil types, and could be further developed to achieve complete extraction from higher TOC soils. It is also recommended that prior to any extraction of IHE constituents from soils the method is validated by extracting known concentrations of the IHE from the soil of interest and that any required correction factors are reported.

Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil

2,4-dinitroanisole
DNAN

1-nitroguanidine
NQ

3-nitro-1,2,3-triazol-5-one
NTO

Unaccounted

2-ANAN Soil Extraction

Soil Extraction

Leachate

Percentage of parent explosive recovered

LOAM SOIL

SAND SOIL

DNAN NTO NQ DNAN NTO NQ
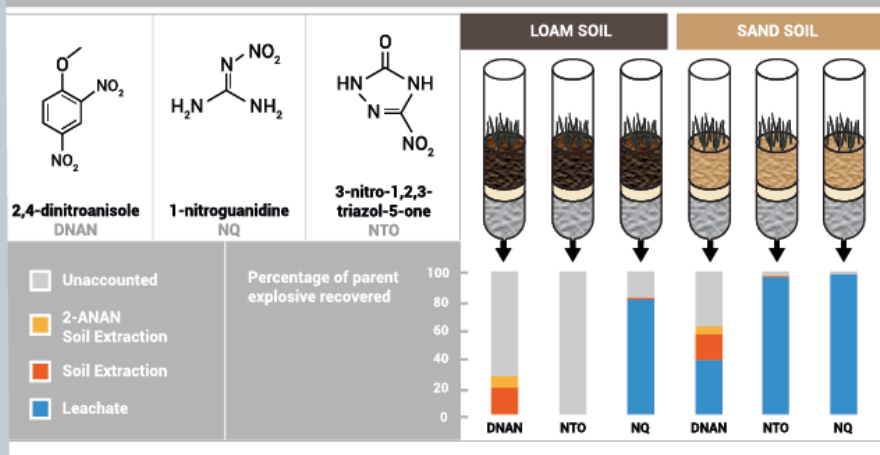
The development of an optimized method for the extraction of DNAN, NQ and NTO from IMX-101 was a prelude to the investigation of the fate and transport of the combined constituents in static soil experiments and vertical soil columns under controlled laboratory conditions. The static experiments were carried out so that full degradation profiles for the three explosives in different soil types could be determined prior to the soil column experiments. The novelty of this work was the investigation of the three explosives combined rather than individual testing. However, the results showed no evidence that the individual constituents (DNAN, NQ and NTO) interact with each other in soil. **This work was published in Science of the Total Environment (Temple et al. (2018), 625:1264-1271)....**

Chapter 6 Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil

6.1 Abstract

Contamination of military ranges by the use of explosives can lead to irreversible environmental damage, specifically to soil and groundwater. The fate and effects of traditional explosive residues are well understood, while less is known about the impact of Insensitive High Explosives (IHEs) that are currently being brought into military service. Current research has focussed on the investigation of individual constituents of IHE formulations, which may not be representative of real-world scenarios when explosive residues will be deposited together. Therefore, this study investigated the fate and transport of the combined IHE constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and 3-nitro-1,2,4-triazol-5-one (NTO) in two UK soil types.

Static experiments ran for 9 weeks to determine the fate of the combined explosive constituents in soil by monitoring the rate of degradation. Transport was examined by running soil column experiments for 5 weeks, with a watering regime equivalent to the average yearly UK rainfall. Both static and soil column experiments confirmed that DNAN and NTO started to degrade within twenty-four hours in soil with high organic content, and were both completely degraded within sixty days. NQ was more stable, with 80% of the original material recovered after sixty days. The major degradation product of DNAN in the test soils was 2-amino-4-nitroanisole (2-ANAN), with trace amounts of 4-amino-2-nitroanisole. NTO was rapidly degraded in soil with high organic content, although no degradation products were identified. Results supported work from literature on the individual constituents DNAN, NQ and NTO suggesting that the three explosives in combination did not interact with each other when in soil. This study should provide a useful insight into the behaviour of three combined insensitive high explosive constituents for the predication of soil and water contamination during military training.

6.2   Introduction

The chemical components of munitions are released into the environment during manufacture and by detonations through military activities, which has led to environmental contamination (Pichtel, 2012). Studies conducted on over 30 United States (US) military training ranges have shown that explosive contamination is common in surface soils, and can cause long-term irreversible environmental degradation (Jenkins et al. 2006; Walsh et al., 2005). In one particular case, high explosives were detected in groundwater at concentrations two orders of magnitude higher than the advisory drinking water limits (Morley et al., 2006). Transport of the explosives through soil to groundwater is dependent on the soil type in these areas e.g. loamy, sand, chalk or clay. In the United Kingdom (UK) for example, two of the main training areas are located on loamy soil and use imported sand for bullet catching and other training activities.

Traditional explosives such as 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and their known degradation products are toxic and potential human carcinogens (United States Environmental Protection Agency, 2014b, 2014a), which has led to more stringent environmental governance. The fate and effects of traditional explosive residues are well understood, while less is known about the impact of Insensitive High Explosives (IHEs) that are currently being brought into military service. For example, Insensitive Munitions Explosive (IMX) formulations that consist of mixtures of RDX, 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and 1-nitroguanidine (NQ) (Lee et al., 2010; Singh et al., 2010). Of particular interest for this paper is IMX-101 which consists of 2,4-dinitroanisole (43%) (DNAN), 1-nitroguanidine (37%) (NQ) and 3-nitro-1,2,4-triazol-5-one (20%) (NTO) (Lee et al., 2010). The impact of the three IHE constituents on the environment may be significant, as they are known to be toxic. DNAN is the most toxic with an LD_{50} of 199 mg kg^{-1} in rats (Dodd and McDougal, 2001; Williams, Eck and Johnson, 2014). This is comparable to the toxicity of RDX (100 mg/kg), which is known to contaminate soil and groundwater on training ranges and manufacturing sites (Bordeleau et al., 2008; Jenkins et al., 2006; Kalderis et al., 2011; Pichtel, 2012).

NTO and NQ are less toxic (Crouse, Lent and Leach, 2015; McCain, Williams and Grunda, 2013), but still may present a pollution issue under environmental legislation (The Environmental Permitting Regs 2010, 2010). NTO, DNAN and NQ are susceptible to degradation in the environment to potentially more toxic compounds.

Of the three constituents, DNAN is the most likely component to undergo photo-degradation as it has low solubility (276 mg/L) and may remain on the soil surface for longer periods of time (Taylor et al., 2017). The photo-degradation products include nitrate ions, ammonium ions, formaldehyde and formic acid, the latter via the intermediates hydroxy-nitroanisole (HO-NAN). Another degradation product has been identified as 2,4-dinitrophenol (DNP), although only in solution and therefore may not represent the degradation products from the breakdown of solid DNAN on the soil surface (Hawari et al., 2015; Rao et al., 2013) (Figure 2-5). DNP is of particular concern as it is more toxic than the parent compound with an LD_{50} of 30μg L^{-1}. DNAN has a greater affinity for soils with a higher organic content (Olivares et al., 2016), and degrades in soil into amino derivatives such as 2 and 4-amino-nitroanisole (2/4-ANAN) and di-aminoanisole (DAAN) which have a higher attenuation to soil (Arthur et al., 2017; Hawari et al., 2015) (Figure 2-5).

NTO is the most soluble of the three constituents (16,642 mg/L) and therefore has the potential to enter the soil at a rate dependent on rainfall (Braida et al., 2012). NTO is not likely to sorb significantly to soils as it is negatively charged at environmentally relevant pH (Mark et al., 2016; Smith and Cliff, 1999). However, NTO is susceptible to degradation in soils with high organic content which may be attributed to bio-degradation as NTO mass loss has been shown to be significantly lower in sterilized soils (Mark et al., 2017). Microcosm studies have shown that NTO is readily bio-degraded to give 3- amino-1,2,4-triazol-5-one (ATO) (Le Campion, Giannotti and Ouazzani, 1999; Krzmarzick et al., 2015; Richard and Weidhaas, 2014a) (Figure 2-4). Although mass loss of NTO has been readily observed in soil column and batch experiments, ATO has not yet been detected (Mark et al., 2017).

NQ is more soluble than DNAN (3800 mg/L) and does not sorb significantly to soil, so it is expected to be transported quickly to groundwater (Mirecki, Porter and Weiss, 2006). However, NQ is susceptible to photo-degradation and biodegradation in certain organic soils, forming mineralised products such as nitro-urea and ammonia (Kaplan and Kaplan, 1985; Richard and Weidhaas, 2014a). **Table 6-1** summarises the properties of the three IHE, and their degradation products.

Table 6-1: Toxicity, solubility and major degradation products of DNAN, NQ and NTO.

Explosive	Solubility (mg L^{-1})[1]	Oral toxicity (mg kg^{-1})	Major degradation products
DNAN	276	199[2]	2-ANAN, 4-ANAN, DAAN, DNP, 4-HONAN
NTO	16,642	>5000[3]	ATO
NQ	3800	>1000[4]	Nitro-urea, ammonia

1. (Taylor et al., 2015a); **2.** (Dodd and McDougal, 2001); **3.** (Williams, Eck and Johnson, 2014); **4.** (Crouse, Lent and Leach, 2015).

Therefore, the aim of this work was to investigate fate and transport of IHE constituents mixture consisting of DNAN, NQ and NTO in static soil experiments and vertical soil columns under controlled laboratory conditions. The static experiments were set-up to determine the degradation products of the IHE and the soil columns to determine the transport mechanisms and flow properties. Soil types with different percentages of organic content were chosen for these experiments so that the relationship between the soil characteristics and fate and transport of the IHE can be further understood from an environmental impact perspective. The highlight of this research was the investigation of the fate of DNAN, NQ and NTO as a mixture in soil. These compounds are used in combination in explosive formulations and are likely to be deposited in the environment as mixtures, and not as pure compounds.

6.3   Materials and methods

Samples of NTO and NQ were synthesised in-house at Cranfield University (Lee and Coburn, 1988). DNAN was purchased from Fischer Scientific UK. Analytical

samples of ATO and 4-ANAN were purchased from Fluorochem, DAAN was purchased from Sigma Aldrich, 2-ANAN was purchased from Alfa Aesar (Massachusetts, United States) and 2-HONAN and DNP (70% in water) were purchased from Thermo Fischer Scientific UK. All analytical samples were 98% or higher purity and were used without further purification. Methanol (MeOH) and Acetonitrile (ACN) High Performance Liquid Chromatography (HPLC) grade were purchased from Thermo Fischer Scientific UK. Deionised water (DI), 18.2 MΩ.cm at 25°C, from Millipore Synergy) was used for all experiments. Ottawa sand was also purchased from Thermo Fischer Scientific UK.

6.2.1 Soil physicochemical characteristics

Two soils were purchased from a building merchant in Oxfordshire (UK). The soils were air-dried for 2 weeks and passed through a 2-mm sieve. The soils were characterised by testing for humidity (BS 13772:1990), pH and total organic content (BS 13039:2001). Total carbon nitrogen hydrogen (TCNH) content and total organic carbon (TOC) were determined using Elementar Vario ELIII (Table 6-2).

Table 6-2: Characterisation of loamy and sandy soil, incinerated soil and Ottawa sand.

Soil	Description	Organic Content[1] (%)	TOC[2] (%)	TCNH[3] (%)				pH[4]
				N	C	H	C/N	
Loamy	UK top soil	8.0	4.1	0.30	5.11	0.74	17	8.0
Sandy	UK sand	4.9	0.43	0.012	7.22	0.30	600	7.9
Loamy Control	Incinerated loamy soil	0	1.32	LOD	1.14	0.14	N/A	8.1
Sandy Control	Incinerated sandy soil	0	0.06	LOD	6.73	0.14	N/A	7.9
Ottawa Sand	100% quartz	-	-	-	-	-	-	7.1

1. Determined by incineration at 400°C for three days; 2. Determined by Elementar Vario ELIII according to British Standard BS 7755 Section 3.8:1995; 3. Determined by Elementar Vario ELIII; 4. Determined by Griffin pH meter model 80; LOD: Limit of Detection.

The particle size distribution was determined according to ASTM D 2487-11, which classified the two soils as loamy and sandy. Two control soils were prepared by incinerating samples of the loamy and sandy soil at 400°C for 3 days

to vaporise all organic material. Ottawa sand was used as a blank. Soil characterisation is summarised in Figure 6-2.

6.2.2 Stock solutions of IHE constituents

Stock solutions for static experiments were prepared by stirring DNAN (0.423 g), NQ (0.367 g) and NTO (0.215 g) in DI water (1,500 mL) at ambient temperature for 72 hours (Stock Solution 1). The solution was filtered prior to use to remove any suspended particulate. The final concentration was 171 ppm DNAN, 97 ppm NTO and 233 ppm NQ as determined by HPLC. Six dispersions were prepared for the vertical soil column experiments containing DNAN (0.9 g, 42%), NQ (0.8 g, 37%) and NTO (0.45 g, 21%) in DI (100 mL). The solutions were sonicated for 2 hours, and left overnight to ensure minimum particle size and maximum dispersion. A third stock solution (DNAN, NTO, NQ 500 ppm) in ACN/water (1:1) was prepared for HPLC calibration (Stock Solution 2).

6.2.3 Static experiments

Soil (10 g) was placed in amber vials (60 mL) with stock solution 1 (15 mL). Twelve vials were prepared for each soil type: loamy, sandy, loamy control, sandy control and Ottawa blank and were placed in a container of sand (sand bath) to ensure constant temperature (19.5°C). One sample of each soil type was sacrificed after ten minutes (T0), further samples were sacrificed at hour 1, 3, 6, 24 and on day 7, 14, 20, 38, on day 62 samples were taken in triplicate. The IHE solution from the sacrificed samples was decanted, filtered and diluted by a factor of eight in a mixture of ACN/water for analysis by HPLC for the parent compounds, and expected degradation products. The remaining soil was extracted with ACN/water (1:1) by shaking for 18 hours at room temperature (Walsh, 2016). The solid phase extract was filtered, diluted by a factor of eight in a mixture of ACN/water (1:1) and analysed by HPLC. Blank samples of the stock solution 1, kept under the same conditions as the samples were tested periodically to ensure that the experimental conditions were not contributing to breakdown over time. Stock Solution 1, stored at 5°C throughout the experiment, was also evaluated for degradation at every time point.

6.2.4 Soil column experiments

Clear Perspex® columns (10 cm x 40 cm) with polyvinyl chloride (PVC) collection funnels fitted with stainless steel wire meshes were placed into collection containers (**Table 6-1**). Increments soil (100 g) were added to the column and compacted using a tamping rod (1.2 kg) until a height of 20 cm was achieved (Martel and Gélinas, 1996; Oliviera, Demond and Salehzadeh, 1996). Columns of loamy soil and sandy soil were prepared in triplicate and capped with a wire mesh and an 800 g weight with a hole through the top for access. The average packing density for the loamy soil was 1.27 ± 0.03 kg L^{-1} and 1.81 ± 0.02 kg L^{-1} for sandy soil. The columns were saturated with DI water and left to settle for 5 days without eluting water (**Figure 6-1**).

	a	Weight			Loamy soil	Sandy soil
	b	Thin mesh wire		Mass (g)	1270 ± 30	1810 ± 20
				Volume (cm³)	1571	1571
	c	Thick mesh wire		Packing density (kg L^{-1})	1.27 ± 0.03	1.81 ± 0.02
	d	40 mm h/10cm diameter perspex		Pore volume (cm³)	315	690
	e	Thin mesh wire				
	f	Thick mesh wire				
	g	PVC collection funnel				
	h	Collection bucket				
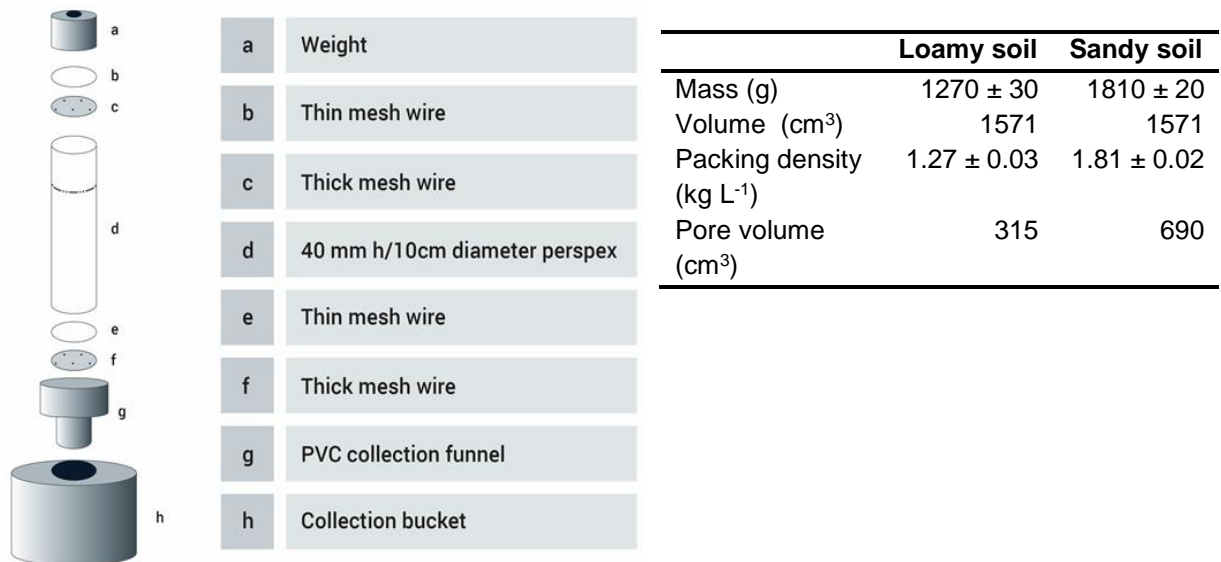
Figure 6-1: Schematic showing the construction of the soil columns and pore volumes

6.2.5 Vertical saturated soil columns

The soil columns were exposed to a volume of water equivalent to the average yearly rainfall in the UK (South West England and Wales) from 1995 to 2015 data calculated to be 1160 mm (Met Office). This is equivalent to the delivery of 9.11 L of water per column over the 5-week experiment, resulting in an artificial watering scheme representative of a full year's rainfall. The columns were treated with 260 mL water per day delivered in five increments (4 x 60 mL and 1 x 50 mL)

1 hour apart at a rate of 40 mL/min (Kramoer Dosing Pump, China). The leachate was collected weekly and analysed by HPLC within 5 days of collection. Sub-samples were stored at 4°C, pending analysis.

6.2.6 Accelerated solvent extraction

At the end of the 5 week experiment, the soil columns were disassembled and the loamy soil and sandy soil samples were divided into 4 sections (5 cm each). After air-drying in a cool dark place for 1 week, the soil was ground (Essa, LM2-P Pneumatic 380V, 50 Hz) and the explosives were extracted by ASE (Dionex ASE 350, Thermo Fisher Scientific, UK), using an adapted ASE explosive method to extract the highly water soluble NTO (Dionex, 2011). Samples were extracted using ACN/water (3:2) at 100°C, with a heating time of 5 minutes, a static time of 10 min and a 100 second purge. Using this method, DNAN and NQ were extracted with 100% efficiency and NTO with 60% efficiency. The results were corrected accordingly. The resultant extracts were analysed by HPLC.

6.2.7 High performance liquid chromatography analysis

Collected leachates were analysed by HPLC (Waters-Alliance 2696, USA) using a photodiode array detector (Waters, 996, USA). DNAN, NTO, NQ and degradation products 2-ANAN and 4-ANAN were separated on a ZORBAX Eclipse Plus C18 column (100 mm × 4.6 mm, 3.5 µm particle size) from Agilent (Wilmington, DE, USA) maintained at 35 °C. The mobile phase was methanol (solvent A), ACN (solvent B) and water/0.1% formic acid (solvent C) with a flow rate of 0.75 mL min^{-1}. Optimised separation conditions were achieved with a gradient program (Table 6-3: Mobile phase gradient program**Table 6-3**). The injection volume was 10 µL. Peak identification was performed by comparing the retention time and UV profile of the compounds to standard compounds. The output signals were monitored at a selective reference wavelength as displayed in **Table 6-4**. The HPLC method was validated by examining: (i) Specificity (analysis of aqueous solution of wetted soils); (ii) Linearity (measure of the correlation coefficient for each standard from the linear regression analysis in the concentration range of 0.6 to 20 µl/ml); (iii) Limit of Detection (LOD), Limit of Quality (LOQ) (measure of the residual standard deviation of the responses and

slopes of the regression equation of the calibration curve (root mean square error approach)) and (iv) Precision (measure of the relative standard deviation of six injections of each compounds at a concentration of 14 µl/ml). The results are displayed in **Table 6-3** and **Table 6-4**.

Table 6-3: Mobile phase gradient program

Time (Min)	Solvent A (%)	Solvent B (%)	Solvent C (%)
0	10	0	90
2.5	10	0	90
3	5	5	90
11	0	100	0
12	0	100	0
16	10	0	90

Table 6-4: Method validation parameters

Chemical	Wavelength (nm)	Linearity (R^2)	LOD/LOQ (µl/ml)	Precision (%)
NQ	264	0.9996	0.5/1.6	0.8
DNAN	296	0.9999	0.5/1.4	0.6
NTO	315	0.9995	0.5/1.4	0.8
2-ANAN	308	0.9999	0.2/0.7	0.8
4-ANAN	330	0.9999	0.2/0.6	1.1

6.3   Results and discussion

Loamy soil used in the static and soil column experiments was selected as it is similar to a specific military training range in the UK. Sandy soil was chosen as it is commonly used as an adsorbent for a variety of military activities. Both soil types were fully characterised to enable understanding of the relationship between soil properties and the fate and transport of the selected explosives. Particularly organic content, as this is known to affect the adsorption and degradation of DNAN and NTO (Arthur et al., 2017; Mark et al., 2017). Soil pH was also monitored throughout the experiment and remained consistent with the soil pH prior to addition of the explosive contaminants.

The mass of DNAN, NQ and NTO added to static experiments, and the soil columns was chosen to represent a specific IHE formulation. In order to accurately account for the fate of all constituents, they were added to the soil in

solution so that the dissolution rate of the solid did not affect the rate of transport or degradation in the soil.

6.3.1 Static experiments

Static experiments were designed to mimic the conditions found in a soil column to investigate the fate of the three IHE constituents, specifically to identify major degradation products in the two soil types. Both the liquid and solid phase were analysed for parent explosive and major degradation products at the specified time points. The liquid phase was isolated by decanting the solution, and taking a 1 ml aliquot which was then diluting in ACN/ water (1:1). The remaining soil was then treated with ACN/water (1:1), and shaken for 18 hours to extract any remaining explosive to account for explosive adsorbed to the soil. Major degradation products were identified from the literature prior to the experiments, and selected for commercial availability as 2-ANAN, 4-ANAN, DAAN, DNP and 4-HONAN for DNAN. ATO and triazolone (TO) were selected as major NTO degradation products. As NQ is not readily degraded in soil it was not possible to identify NQ degradation products by HPLC.

During the 62-day experiment, the concentrations of DNAN, NQ and NTO recovered from sandy soil remained high, with almost complete recovery of all explosives from the combined liquid and solid phases 93%, 99% and 99% respectively. DNAN and NTO concentration in loamy soil rapidly decreased, suggesting a relationship between DNAN and NTO loss and high concentrations of organic content in the soil, which supports previous literature (**Figure 6-2**) (Arthur et al., 2017; Mark, 2014; Olivares et al., 2016).

Results were normalised to the percentage of parent compound recovered from the Ottawa sand blank to minimise minor variations in percentage recovery due to changes to room temperature of the calibration standard. DNAN concentration in particular may have been affected by these temperatures changes as the concentration in the stock solution was at saturation. The average percentage recovery of all three explosives from Ottawa sand was 103% ± 3% compared to

Stock Solution 1, confirming that in the absence of soil, DNAN in solution with NTO and NQ, is stable up to nine weeks in the absence of UV.
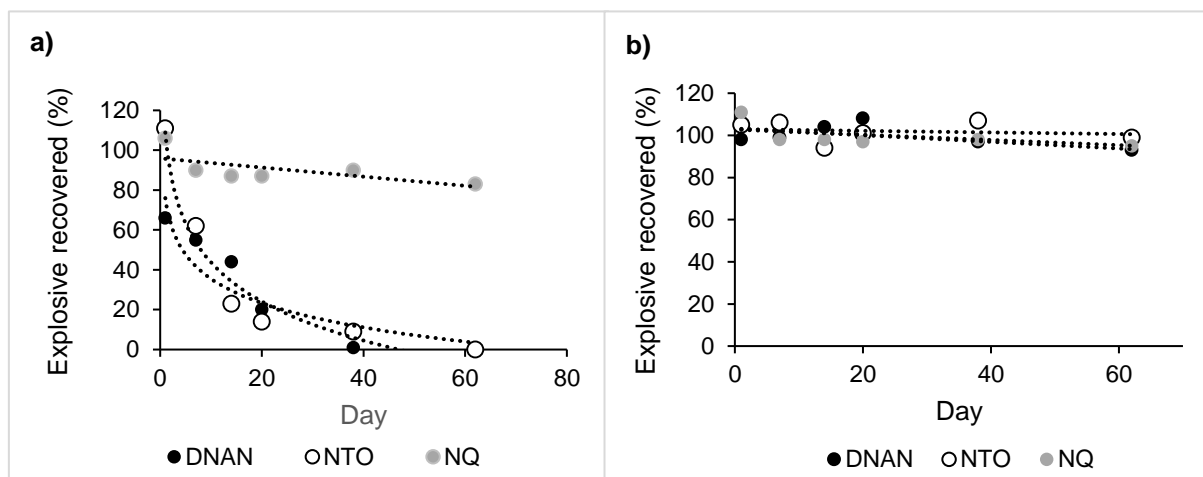

Figure 6-2: (a) Observed mass loss of DNAN, NQ and NTO in loamy soil static experiments over 62 days with linear or logarithmic trend lines applied; (b): Observed mass loss of DNAN, NQ and NTO in sand soil static experiments over 62 days with linear trend lines applied.

6.3.2 Effect of organic content on fate of DNAN, NQ and NTO

In order to assess the effect of organic content of the degradation of the three explosives, samples of the sandy soil and loamy soil were incinerated to vaporise bio-organisms and organic molecules. A comparison between the total percentage of DNAN and NTO recovered from both the liquid and solid phase of the loamy soil and sandy soil and the two incinerated soil controls is shown in **Figure 6-3**. The total percentage of DNAN recovered from loamy soil started to decrease within the first 24 hours, and after 38 days only trace amounts of the initial DNAN were recovered from the solid phase. However, the total percentage recovery of DNAN from incinerated loamy soil was still high after nine weeks, with only 14% mass loss (**Figure 6-3a**). This suggests a strong correlation between organic and bio-organic matter and the degradation of DNAN. Due to the high percentage of organic matter in the loamy soil, the incinerated samples still contained some organic matter which contributed to the 14% observed mass

loss. A slight decrease in the total percentage recovery of DNAN from sandy soil was observed over the course of experiment, which may be within experimental error. NTO was stable in sandy soil and the sandy control, with 100% total recovery after 62 days. In loamy soil, the concentration of NTO rapidly decreased in the liquid phase, and was not recoverable from the solid phase, suggesting that degradation had occurred (**Figure 6-3b**). Although rapid mass loss was observed in loamy soil, no NTO loss was observed in the incinerated loamy soil, suggesting a strong correlation between organic content and NTO mass loss.
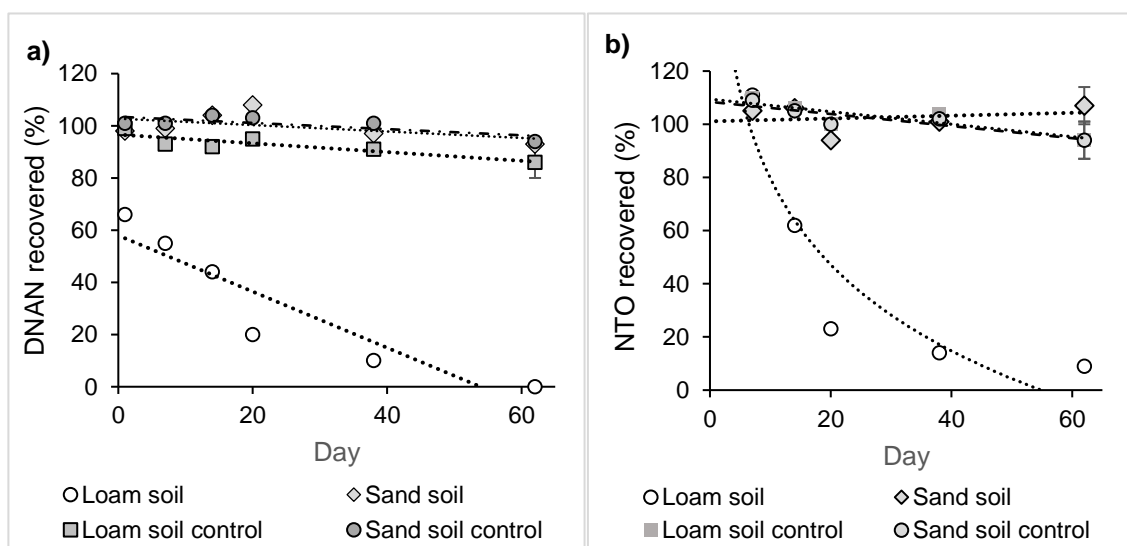
Figure 6-3 a) Total percentage recovery of DNAN (liquid and solid phase) from loamy soil, sand soil and both control soils with linear trend line applied; **b)** Total percentage recovery of NTO (liquid and solid phase) from loamy soil, sand soil and both control soils with linear or logarithmic trend line applied. All results were normalised to Ottawa sand blank. Day 62 results were averaged from triplicate**.**

A slight decrease in the concentration of NQ recovered from the combined liquid and solid phase in loamy soil, sandy soil and the incinerated sandy soil control was observed. It is likely that over prolonged periods of contact with soil, NQ slowly degrades. Mass loss observed in the incinerated sandy control samples was unexpected as NQ recovered from the sandy soil was consistent throughout the experiment averaging 99% ± 6%. Incineration of the sandy soil may change the composition of the soil allowing for an alternative mechanism of mass loss.

6.3.3 Adsorption of DNAN, NQ and NTO to soil

The two-stage recovery of explosives from the liquid followed by the solid phase highlighted the strong attenuation of DNAN to soil. In addition, DNAN attenuation to the loamy soil was more pronounced than attenuation to the sandy soil or incinerated sandy control suggesting that DNAN is more likely to adsorb to soils with high organic content, which supports the results of previous studies (Arthur et al., 2017). NTO and NQ did not adsorb significantly to any of the tested soils, and did not display any correlation between organic content of the soil and adsorption in line with current literature (Mark et al., 2016). The adsorption of DNAN to loamy soil was rapid. A liquid extraction after 10 minutes recovered only 53% of the DNAN. After 24 hours, only 30% of the DNAN was extractable from the liquid phase, with an additional 53% extracted from the solid phase (**Figure 6-5**). Interestingly, adsorption to incinerated loamy soil was equally as rapid as absorption onto the loamy soil, however after 24 hours a higher percentage of DNAN was recovered from the incinerated loamy soil solid phase (94% compared to 83% from loamy soil) suggesting faster degradation of DNAN in loamy soil. The DNAN adsorption to the four soils is in line with increasing organic content.
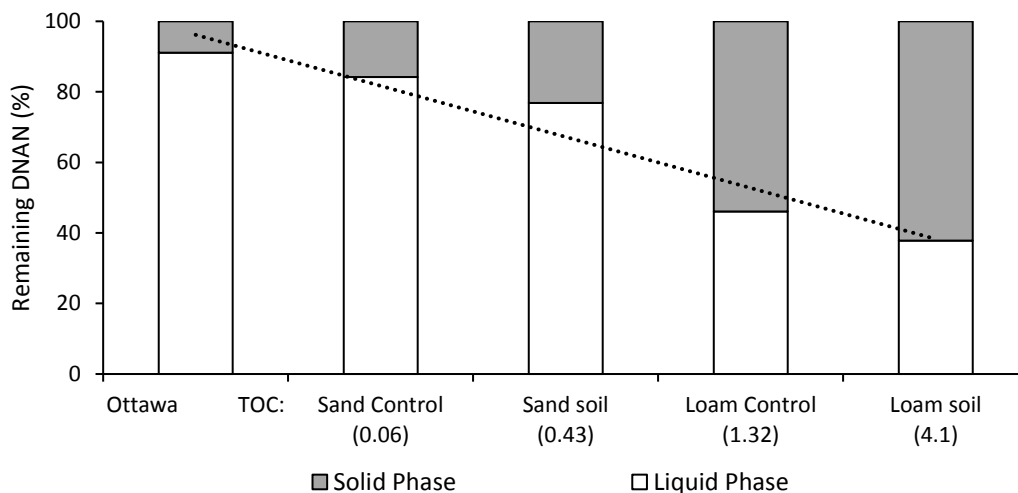

Figure 6-4: Figure 6-5: Percentage DNAN recovered from the liquid phase and solid phase at 24 hours normalised to the total percentage DNAN recovered. Linear trend line has been applied.

6.3.4 Identification of degradation products of DNAN, NQ and NTO in soil

Significant mass loss of DNAN and NTO was observed in loamy soil, as expected due to the high organic content which is thought to contribute to degradation of or sorption of these explosives. In static experiments, as the percentage recovery of DNAN reduced, the degradation products 2 and 4-ANAN were generated. As seen in previous literature, we observed that 2-ANAN was the dominant degradation product, with only trace amounts of 4-ANAN recovered (**Figure 6-6**) (Arthur et al., 2017; Hawari et al., 2015; Olivares et al., 2016). Although mass loss was far less pronounced in the loamy soil control, trace amounts of 2-ANAN were detected suggesting some degradation which may be attributable to the small amount of organic content remaining in the soil.
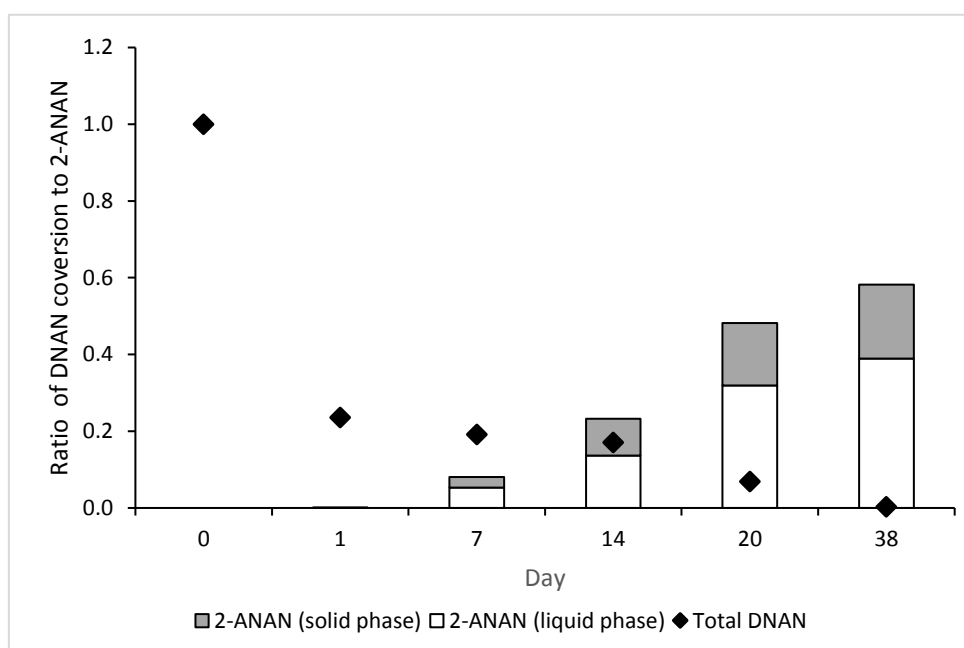
Figure 6-6: Molar ratio of DNAN converted to 2-ANAN recovered from the solid and liquid phase. The ratio was calculated from the concentration in moles, and assuming stoichiometric transformation.

Although DNAN mass loss was observed within the first 24 hours, significant concentrations of 2-ANAN were not recovered from the loamy soil liquid or solid phase until day 7. This may be due to the extraction method, which is known to extract DNAN from soil with 100% efficiency, but has not been proven for 2-

ANAN. In addition, 2-ANAN is more likely than DNAN to adsorb to soil both reversibly and irreversibly and so may be more difficult to recover (Hawari et al., 2015). **Figure 6-6** shows that 2-ANAN generation increased for five weeks, however an inconsistently low concentration of 2-ANAN was recovered from day 62 samples even though only trace amounts of DNAN were recovered. Samples on day 62 were taken in triplicate, and results from all three sacrificed samples were consistent. This may be explained by bio-transformation of 2-ANAN to DAAN under both aerobic and anaerobic conditions which has been reported in the literature (Hawari et al., 2015), however DAAN was not detected in either the solid or the liquid phase at any time point. DAAN is known to be unstable in air and can form di-azo compounds (Hawari et al., 2015). All experiments were conducted in enclosed vials with a natural atmosphere and exposed to air during analysis therefore dimerization of DAAN may have occurred, possibly explaining the gradual loss of 2-ANAN.

ATO, the expected degradation product of NTO, was not detected in any of the samples despite almost complete loss of NTO. New peaks were observed in the HPLC trace, but could not be resolved due to the close proximity between the NTO, and NQ peaks. Degradation of NTO was not observed in the loamy control sample, nor the sandy soil suggesting that high organic content is necessary for NTO degradation.

Exposure of the explosive constituents of a new IHE (DNAN, NQ and NTO) to soil under atmospheric conditions showed that in combination DNAN, NQ and NTO are unlikely to interact with one another. The results supported findings in the literature that DNAN and NTO are readily transformed in soils with high organic content most likely by bio-degradation, while NQ is much more stable (Arthur et al., 2017; Hawari et al., 2015; Olivares et al., 2016). In addition, DNAN and its major degradation product 2-ANAN, were more likely to be adsorbed to soil with high organic content.

6.3.4 Transport of DNAN, NQ and NTO in vertical saturated soil columns

Soil columns are a well-established method for determining the fate and mobility of contaminants through soil, (Lewis and Sjöstrom, 2010) and have been used to determine transport of explosives (Mark, 2014; Pennington and Brannon, 2002). Soil columns were designed to simulate the mobility of explosive contaminated water through soil matrices, whilst avoiding preferential pathways and sidewall flow. Therefore, we used closely packed saturated vertical columns with a 10 cm diameter as this has been proven to reduce sidewall effects, and ensure reproducibility between replicates (Lewis and Sjöstrom, 2010). The explosives were introduced to the soil columns in solution, the mass of NTO and NQ was well below the mass required for saturation, however the DNAN did not completely solubilise and was therefore added in suspension. The explosives were added in 150 mL water, which was then subtracted from the initial dose of water to ensure water delivery was consistent with average annual rainfall in the UK.

The soil columns were treated with water every day totalling the average yearly rainfall for the South West of England, so that the experiment was set in the context of UK rainfall patterns. The columns were dosed evenly throughout the five weeks in increments to avoid pooling of water on the column surface. The water leachate was collected and analysed every seven days, starting one week after the first dosing.

6.3.6 Transport of DNAN, NQ and NTO in sandy soil columns

Results from static experiments indicated that DNAN, NQ and NTO were not adsorbed nor degraded by sandy soil, therefore recovery of explosive constituents was expected from both liquid and solid phase. While this was true for NTO and NQ, which were fully eluted within the first seven days, complete recovery of DNAN was not achieved from the sandy soil column leachate (**Figure 6-7a**). The concentration of DNAN in the eluent gradually decreased, with a cumulative total of 38%. No expected degradation products were identified in the leachate.

After five weeks of water addition- equivalent to one year of rainfall- the columns were disassembled and the soil was extracted by accelerated solvent extraction (ACN/water, 3:2). An additional 18% of the DNAN was recovered from the top 5 cm of the sandy soil column, leaving 44% of DNAN unaccounted for. An equivalent of 5.5% of the unaccounted DNAN was detected as 2-ANAN in the top 5cm of soil, confirming that 2-ANAN is much less mobile in soil than DNAN, even in soils with low organic content. Almost 50% of the DNAN remained unaccounted for, but the presence of 2-ANAN suggests that it most likely degraded first into 2-ANAN, then further degraded possibly to DAAN so that quantitative recovery was not possible.

6.3.7 Transport of DNAN, NQ and NTO in loamy soil columns

Of the three explosives, only NQ was observed in the loamy soil columns during the five week experiment, with 81% of the initial material recovered. NTO and DNAN were not detected in the soil column leachate, which is consistent with their rapid degradation (**Figure 6-7**). However, given NTO's high solubility, and low attenuation to soil, we expected to see some NTO in the leachate during the first few weeks before much of the NTO had time to degrade, as in static experiments NTO took five weeks to fully degrade. The lack of NTO in the leachate suggests that the degradation mechanisms can be much quicker in dynamic environments than were seen in the static experiments, which may be due to the much larger mass of soil compared to explosive in the soil columns leading to greater chance of exposure to microorganisms.

The absence of DNAN in the loamy leachate was expected, as DNAN has a high affinity for the loamy soil, and in static experiments had started to degrade to 2-ANAN within the first seven days. Similarly, to the sandy columns, no DNAN degradation products were observed in the leachate, most likely due to their greater attenuation to soil, or rapid degradation into other compounds that were not in the analyte screen. Additionally, DNAN is the least soluble of the three constituents and was added to the columns in suspension. Time taken for DNAN to dissolve would also have slowed down the rate of DNAN transport.
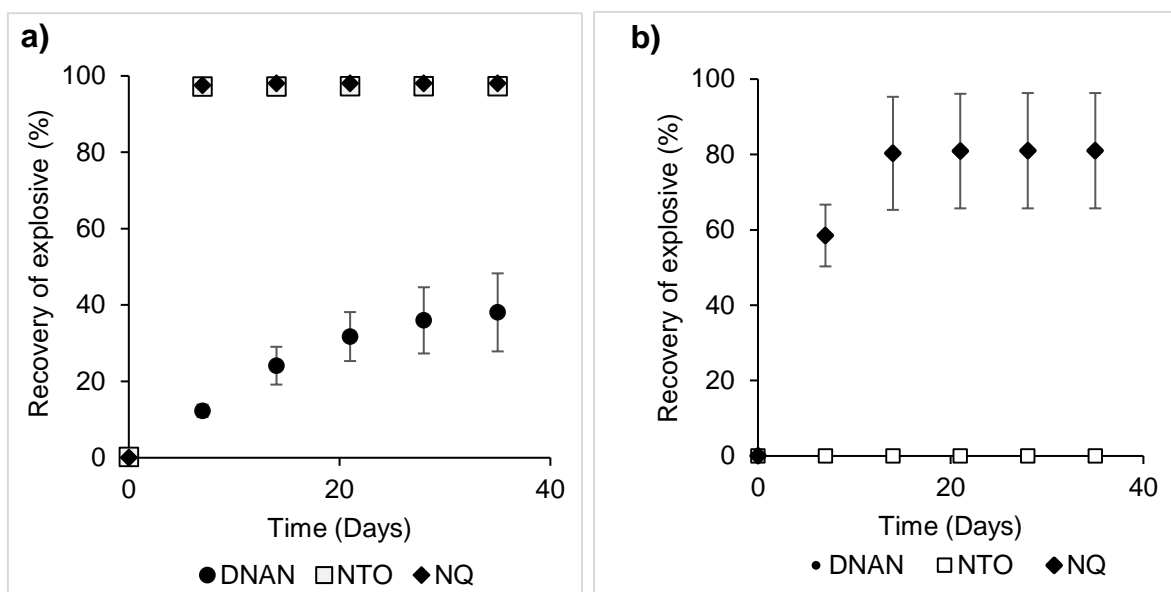
Figure 6-7: a) Recovery of explosive from sandy soil column leachate averaged over triplicates; b) recovery of explosive from loamy soil column leachate against time averaged over triplicates.

Interestingly, ASE extraction of the loamy soil columns led to the recovery of 19% DNAN, which is similar to the percentage recovered from sandy soil. This was unexpected, as in loamy soil static experiments all DNAN was degraded within five weeks. However, considering that identical solutions of explosives were added to each column, and a similar percentage of DNAN was recovered from both sandy and loamy soil columns, it is likely that the DNAN recovered from the top 5 cm of soil was undissolved particles from the initial addition.

An equivalent of 8% 2-ANAN was recovered from the top layer (5 cm) of the loamy soil columns, leaving 74% of the original DNAN unaccounted for by primary degradation products. In static experiments the recovery of 2-ANAN was high at five weeks, suggesting there was an increase in the rate of degradation in the soil columns.

Only trace amounts of NTO and NQ were recovered from the loamy soil solid phase, suggesting that all of the initial NTO and 20% of the NQ was degraded which is consistent with static experiments. Overall, there was good consistency between static experiments and soil column experiments confirming that the fate

of DNAN, NQ and NTO observed in static experiments can be used to explain soil column results (**Figure 6-8**).
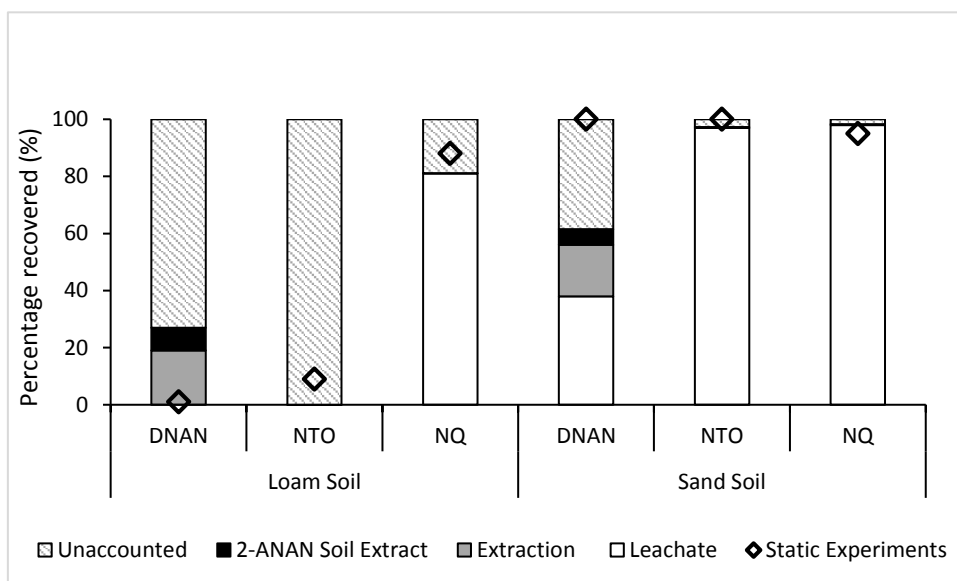
Figure 6-8: Summary of recovery and fate of DNAN, NQ and NTO in soil from static and batch experiments after 35 days.

Less time was required for complete degradation of DNAN, and NTO in soil columns compared to static experiments. The degradation of DNAN in sandy soil columns was particularly interesting due to the low organic content of the soil, and the stability of DNAN in static experiments. In future, it would be useful to ensure the ratio of explosive to soil is the same in both static and soil column experiments.

Despite slight differences in results between static and soil column experiments, DNAN, NQ and NTO behaviour supports current literature, and does not seem to be significantly altered by interactions between the three constituents under the evaluated conditions. Future work would benefit from focussing on the secondary degradation products of DNAN e.g. DAAN and its diazo compounds, and to establish NTO degradation products in real soil environments.

6.4   Conclusion

Military training with live fire munitions is essential for troops to maintain combat readiness, and it is inevitable that contamination of soil and groundwater will occur on and around these areas. As training ranges are located on wide variety of soil types it is difficult to predict how explosive contaminants will interact and how specific receptors will be affected. Traditional explosives such as TNT and RDX are well understood in terms of their fate and transport mechanisms although contamination still occurs. It is therefore essential that new IHE, that are being brought into military service, are understood and managed so that contamination can be avoided. This research investigated fate and transport of the combined constituents of an IHE consisting of DNAN, NQ and NTO in static soil experiments and vertical soil columns under controlled laboratory conditions. The static experiments were conducted so that full degradation profiles of the three explosives in varying soil types could be observed prior to conducting soil column experiments. The novelty of this work was the investigation of the three explosives combined rather than individual testing. Results supported work from literature on the individual constituents DNAN, NQ and NTO suggesting that the three explosives in combination did not interact with each other when in soil. This is significant when considering this type of IHE and its environmental impact e.g. adverse interactions due to soil conditions could generate more toxic and persistent contaminants.   Both static and soil column experiments confirm that soils with high organic content are more likely to degrade DNAN and NTO. Our results show that when this type of IHE is used on training ranges, the most significant environmental impacts may be from NTO. Even though NTO itself is not significantly toxic, it rapidly degrades in the environment into potentially toxic degradation products. DNAN is most likely to degrade in soils with high organic content, although into less toxic products.

Chapter 7   Overall conclusion, research implications and recommendation for future work

Training with live munitions is crucial to maintain the combat readiness of military forces, but traces of explosive materials are left on the training ranges after firing and after inefficient (lower-order) detonations (Taylor et al. 2015). The environmental behaviour of traditional explosives such as TNT is well understood because these materials have been used all over the world for more than 100 years (Akhavan, 2011). However, due to increasing concerns over safety, military organisations are moving towards the replacement of legacy explosives with insensitive munitions, which are designed to withstand inadvertent initiations (DOSR, 2015). The insensitive high explosive (IHE) fillings of this new generation of munitions include (1) energetic materials such as RDX and HMX bound in a polymer matrix (PBX); and (2) insensitive munitions explosives (IMX) which are directly melt-castable using a 2,4-dinitroanisole (DNAN) binder. The environmental behaviour of these materials is not yet well understood due to their shorter in-service history. In particular, it is unclear how easily the explosive materials are released from PBX in the UK climate and how the chemical components of IMX interact with each other under environmental conditions.

Therefore, the main aim of this thesis was to investigate the behaviour of PBX and IMX mixtures in the environment. The literature review (**Chapter 2**) identified that the environmental impacts of PBX have been minimally investigated to date and most of the environmental studies on the behaviour of IMX compounds have been carried out on single chemicals rather than as mixtures. The research in this thesis was therefore designed and developed around two main areas: (1) degradation, leaching and extraction of RDX from PBX and (2) the transport and degradation behaviours of IHE mixtures in two soil types including the development and optimisation of soil extraction methods.

7.1 Overview of the key findings and contribution to knowledge

To address the knowledge gap identified above, the first step of the work described in **Chapter 3** was to investigate the dissolution behaviour of RDX from a PBX formulation under simulated UK climatic conditions to emulate seasonal variations in temperature, rainfall and sunlight. Here it was hypothesized that explosives encased in polymers would dissolve more slowly (or not at all) because the polymer would act as a protective barrier, inhibiting the release of potential contaminants. The PBX of interest contained RDX (64%), aluminium (20%) and HTPB (8%). The results from **Chapter 3** showed that the polymer retained almost 97% of the explosive filling after one year's equivalent rainfall, which indicates that PBX formulations delay rather than prevent environmental contamination by IHE. Further, it showed that the rate of release of RDX was slow but consistent (0.01 to 0.02% per day from pristine samples of 1 g PBXN-109) and was correlated to seasonal conditions reflecting the combination of polymer swelling/cracking and therefore the release of the filling. For example, RDX release rate was increased under the warmer and drier summer conditions and prolonged UV exposure, compared to cooler spring and winter conditions

The transport of explosive contamination from PBX formulations is likely to be minimal due to the impermeable nature of the polymer, which does not readily degrade and may remain intact on the soil surface for long periods of time, making cumulative deposition more likely. This may be problematic for biological receptors, such as animals, as they pose a higher risk due to the increased concentration of RDX explosive with the potential to be ingested. However, range management and clean-up may be simpler as visible pieces of PBX are easier to remove from the soil surface.

To confirm that only a small amount of RDX was released from the polymer matrix, and that RDX was not degrading in the polymer or in the water leachate, the remaining RDX content was extracted using the well-established Soxhlet method (DuBois and Baytos, 1991). Soxhlet has proved to be efficient for extracting a wide range of contaminants from various matrices, although it can

take a long time (48 h) and requires a large amount of solvent (200 mL of acetone) per gram of PBX. It was therefore prudent to determine whether alternative extraction methods could be used to achieve the same results more quickly and more efficiently. The literature did not offer any other alternatives for extraction of explosives from polymers or provide information on the efficiency of the Soxhlet method. In most cases, the studies only reported that the extraction lasted between 18 and 48 hours and used large amounts of solvent, confirming our experience with the Soxhlet extraction described above.

The ASE method was considered as a promising candidate as it has been shown that TNT can be rapidly extracted from soil (14 min) using only a small amount of solvent (17-50 mL) (Thermo Scientific, 2011). ASE has been successfully used to extract chemical components of polymers and was initially developed to replace extraction methods such as Soxhlet and sonication (Fisher, Scarlett and Stott, 1997; Richter et al., 1996). This led to the development of the first reproducible method for the complete extraction of RDX/HMX from PBX using ASE (**Chapter 4**). The new ASE method was optimised and validated according to recommended optimisation procedures (Thermo Scientific and Thermo Sceintific, 2011), although the extraction of explosives required a more complex protocol due to additional safety concerns, such as the potential for auto-ignition and friction hazard. Accordingly, the extraction temperature was kept below 100°C and the samples were placed in cellulose thimbles to reduce friction. The ASE extraction of RDX from the polymer was successful and recovered an average of 97% ±13%. Reproducibility was tested by replicating the method six times with pristine samples, and subsequently using the method to extract weathered samples. The error was commensurate with other ASE methods that are seen in the literature (Campbell et al., 2003; Pan, Zhang and Cobb, 2005).

ASE proved to be a suitable extraction method for extracting explosives from a polymer matrix. Once an ASE method has been developed the process is straightforward and up to 20 samples can be run automatically within 15 hours, in comparison to 1 sample over 48 hours using Soxhlet. Though setting up and running Soxhlet is simple, it is time consuming and may be problematic if leaks

occur or glassware breaks. For a 48 hour method Soxhlet must run over night, which can be concerning when working with explosives as solid residue may accumulate in the flask close to the heat source. For both ASE and Soxhlet the PBX samples were cut into smaller pieces to expose more surface area to the solvent. The samples were placed into re-usable glass thimbles for Soxhlet and if the temperature was to increase and cause any type of initiation the glassware would shatter but no electrical elements are present making the resultant damage less significant compared to ASE. ASE minimised solvent use compared to Soxhlet, and required only 60 mL of acetone for each extraction, whereas Soxhlet required in excess of 200 mL of solvent for 1 g of PBX. However, operation of ASE requires other consumables e.g. seals for the vials, filters for the cells and cellulose thimbles, which can only be used once so any reduction in cost due to solvent reduction is negated by consumable turnover. Though ASE provided slightly higher extraction efficiency and reproducibility compared to Soxhlet, either method could be employed to successfully extract explosive from polymers. However, due to the significantly reduced running time and the associated improvement in safety, the developed ASE method was preferable and provides a reliable alternative to Soxhlet.

Having investigated the dissolution behaviour of PBX and developed an optimal extraction procedure, it was important to establish whether similar principles could be applied to other types of IHE after transportation through soil such as IMX formulations (**Chapter 6**). Therefore, this work firstly considered the use of the standard extraction method EPA 8330B to extract IHE from soil. This method has traditionally been used for the extraction of nitro-aromatics, nitramines and nitrate esters from soil by sonicating or shaking using ACN or MeOH. It was expected that this method would not be suitable for IHE due to their different solubility profiles. Results confirmed that this method was not appropriate for all IHE constituents in soil and in particular NTO and NQ as they are significantly less soluble in organic solvents, but very soluble in water. Literature has reported that the standard method has been adapted by using a 1:1 ACN/water to ensure the highly water soluble NTO is also extracted. To investigate the extraction efficiency of one-step methods, five soils from the UK were contaminated with a

solution of RDX, DNAN, NTO and NQ (500 ppm each) and extracted using four methods (stirring, shaking, sonicating, ASE). ASE was included in the extraction methods as it proved to be a powerful tool for the extraction of RDX from PBX (**Chapter 4**) and has also shown to be a quicker process that uses less solvent then other methods. For ASE an appropriate solvent system was identified and the most suitable was found to be a one to four ratio of MeOH and water.

The extractions methods mostly achieved above 70% recovery of all IHE constituents from all tested soils. Results were analysed using Principal Component Analysis (PCA), which displayed the variability of the results between the different methods showing that extraction efficiency is highly dependent on soil type. However, some methods performed better than others at consistently recovering RDX, DNAN, NQ and NTO from the various soil types. Shaking was the most consistent, although extraction efficiency averaged 78%. Whilst stirring was the most efficient with almost 100% recovery of all IHE from all tested soils, it was less consistent. Sonication recovered on average 83% IHE from all soils and showed similar variability to stirring. ASE was the least consistent and the most affected by soil properties especially for NTO and DNAN, which proved the most difficult to extract from with high organic content.

Conclusions drawn from this work support the use of an adapted EPA 8330b method and confirm that a high percentage of water in an organic solvent (e.g. 50%) is essential for complete and consistent extraction of all IHE constituents in a single step. The work also highlights the significant effect that soil type has on the extraction efficiency, which is not reported in the literature. This suggests that for any extraction of IHE from soil, data must be accompanied by a statement of efficiency and correction factor. It is therefore possible to select any extraction method based on practicalities and available resources with the caveat that further method development must be undertaken for specific soil types.

Shaking and stirring can take over 18 hours for full extraction and is limited by sample throughput e.g. size of equipment. Sonication, may cause noise nuisance when in use and may create thermodegradation as the temperature of the bath can be difficult to regulate. This type of extraction can also be limited by size as

sonic instruments can be small. ASE is the quickest and can reduce solvent use, however, the unit costs are very high and requires considerable maintenance and high consumable turnover. The results for ASE were the least consistent in comparison to the other methods and therefore extensive preparatory work is recommended prior to the use of this method.

This is the first time these extraction methods have been compared for their efficiency of IHE in soil and it therefore highlights the differences between extraction methods. It is recommended that prior to any extraction of IHE constituents from soils the method is validated by extracting known concentrations of the target analytes from the soil of interest in order to establish if any correction factors are required.

The development of an optimised method for the extraction of DNAN, NQ and NTO from soil was a prelude to the investigation of the behaviour of the combined constituents in static soil experiments and vertical soil columns under controlled laboratory conditions (**Chapter 6**). The static experiments were carried out so that degradation profiles for the three explosives in different soil types could be determined prior to the soil column experiments. The novelty of this work was the investigation of the three explosives as mixture rather than individually. The results showed no evidence that the individual constituents of IMX-101 (DNAN, NQ and NTO) interact with each other in soil. This is significant when considering this type of IHE and its environmental impact e.g. adverse interactions due to soil conditions could generate more toxic and persistent contaminants. Both the static and soil column experiments confirmed that soils containing high Total Organic Content (4%) degrade DNAN and NTO more rapidly. Even though NTO itself is not toxic, it is rapidly transformed in soils with high organic content into potentially toxic degradation products (Taylor et al., 2015a). DNAN also degrades more rapidly in soils with high levels of organic matter, although the degradation products are slightly less toxic than the parent compound. One significant finding was the generation of trace quantities of dinitrophenol (DNP), particularly in sand soil static experiments as it has previously only been identified as a photo-degradation product in the literature. NQ was the most stable of the three in both

soils, with 80% of the original material recovered after 60 days. As NQ is not significantly toxic toward humans or other environmental receptors (William and Mark, 2016), when this type of IHE is used on training ranges, the most significant environmental impacts may be from NTO due to the generation of unknown degradation products, and the strong yellow colour produced when NTO is in solution, even at low concentrations (100 ppm).

The use of soil columns for this work provided insights into the transport mechanisms of the IMX-101 constituents in soil. As stated in the literature, soil columns are not standardised and it is therefore difficult to draw precise conclusions from their performance in relation to real environmental behaviour. In this work, the literature was considered when designing the soil columns to try and create natural transport mechanisms for the contaminants. The columns used in **Chapter 6** were designed with a diameter wide enough to ensure minimal side-wall flow (> than 7.5 cm) and the explosives were positioned in the centre of the column with directed water flow. This was to try and direct the water through the centre of the column to avoid preferential flow. This method was slightly different to the reported method in the literature, which recommended a column length to diameter ratio of 1:4, however due to the large diameter of these columns side-wall flow was not observed even with a reduced ratio of 1:2 (Lewis and Sjöstrom, 2010).

Two soil types were used in the experiments allowing the effects of different levels of organic matter to be compared and thus confirming the degradation behaviour of DNAN in soils with high organic content (4%). The watering regime was based on actual UK rainfall, taken from the UK Met Office twenty-year average, which helped to determine how much water would be needed to transport these materials through the environment surrounding UK military training ranges. The transport of these materials can be understood by their chemical properties (e.g. a combination of their solubility, adsorption and degradation). As NTO is the most soluble, and has low adsorption to soil, it eluted from the sandy soil (0.4% TOC) within 7 days but complete recovery in loamy soil (4% TOC) was hampered by a rapid degradation, most likely due to the high organic content of this soil. DNAN

sorbed strongly to the loamy soil thus limiting its extractability and recovery, and although recovery was higher in the sandy soil, degradation was still observed, with 50% DNAN unaccounted for at the end of the experiment. NQ was the most stable and least likely to degrade or absorb on both sandy and loamy soils and therefore has a high potential to reach groundwater.

Overall, the results described in this thesis offer unique insights into the behaviour of IHE constituents in the environment. Many studies have addressed the fate and transport of individual IHE constituents but until now IHE formulations coming into service have received comparatively little attention. In this work, to establish the fate and transport of IHE several experimental methods have been employed to isolate the different environmental mechanisms that contribute to their behaviour. Dissolution experiments were used to determine rate of release of RDX from PBX; batch experiments were used to investigate degradation of IHE constituents in mixtures representative of IMX formulations; vertical soil columns were used to determine transport mechanisms and unique extraction methods were developed to support this research.

As very little work on the behaviour of PBX in the environment has been undertaken, this work concentrated on dissolution studies to determine if any of the explosive content could leach into the environment and cause irreversible contamination. RDX was found to migrate from the polymer very slowly as dissolution was inhibited by the impermeable polymer matrix (**Chapter 3**). However migration was consistent, and was exacerbated by extreme temperature and UV exposure which means environmental contamination may occur in the future. This information in itself is valuable for understanding how to manage potential risk from these materials.

To confirm results from PBX leaching experiments complete extraction of the polymer was required after exposure to environmental conditions to ensure all explosive was accounted for. However, current methods for extraction of polymers were unreliable and time consuming therefore the first ASE method for extraction of explosive from polymers was developed and optimised **Chapter 4**. The optimised method achieved complete (100%) recovery of explosive, and was

demonstrated to be applicable to other PBX formulations, making this available for other researchers.

Due to the successful development of an ASE method for polymers, the method was applied to the extraction of IHE constituents from soil, which has been shown to be challenging. The developed ASE method was then included for comparison with shaking, sonicating and stirring to identify suitable extraction methods for these materials. Until this point, methods reported in the literature were adaptations of the standard method of extraction for conventional explosives (EPA8330b), which did not report extraction efficiency making it difficult to reproduce and trust documented data. The output from this phase of the work has provided assurance that all extraction methods can be suitable, depending on the contaminants and soil type. Therefore, it is essential to report extraction efficiency when conducting environmental research to ensure good quality data with transparency.

Determination of extraction efficiency was a prelude to the final stage of work, which was to understand how explosives transport from the soil surface deeper into the soil matrix potentially reaching groundwater. As RDX is well understood in terms of fate and transport (**Chapter 2**), attention was turned to mixtures of IHE constituents and their degradation products. This was the first work published on a combined mixture of DNAN, NTO and NQ and demonstrated that there are no adverse interactions between these constituents in soil. This research is more representative of realistic scenarios where explosives are usually deposited in the soil as mixtures, rather than as individual components. This provides confidence to environmental risk assessors that the behaviour of mixtures of IHE is consistent with current literature.

Finally, the scientific results published in this body of work will assist those who have responsibility or interest in managing the impact of these materials in the environment.

7.2. Further Work

The advantage of using controlled conditions such as indoor soil columns and dissolution studies is that the experiments could be repeated with reproducible findings, lending greater confidence to the veracity of the data presented. However, the simulated environmental conditions could not fully represent the much more variable conditions to which IHE would be exposed in real military scenarios *e.g.* rainfall, UV exposure and soil types. Therefore, further work recommended may include:

- Elucidation of full mass balance for RDX migration from PBX to include polymer additives, oxidisers and any degradation products from these chemicals or the explosive.
- Outdoor soil column and dissolution experiments to expose materials to natural weathering and climate conditions.
- Include a wider range of soil types in outdoor and indoor experiments to fully understand interactions between IHE and soil.
- Further development of standardised extraction methods for IHE.
- Full understanding of the impact of IHE and their degradation products to environmental receptors.
- Identification of threshold limits for IHE contamination in soil and water in the UK and EU.
- Development of standardised experiments to enable prediction and risk assessment of environmental impact of IHE in any environment by military range managers and manufacturers.

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Appendix 1: Published paper: Release of RDX from PBXN-109 into water by artificial weathering

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Short Communication

Release of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) from polymer-bonded explosives (PBXN-109) into water by artificial weathering

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HIGHLIGHTS

- The effect of variable climates on the migration of RDX from PBXN-109 into water was investigated.
- Average seasonal rainfall, sunlight and temperature were simulated using climate control chambers.
- Small quantities of RDX were found to migrate from PBXN-109.
- Hot and bright conditions promoted the migration of RDX most efficiently.
- The migration of RDX was accelerated by exposure to UV and elevated temperatures.

ARTICLE INFO

ABSTRACT

Polymer-bonded explosives (PBX) fulfil the need for insensitive munitions. However, the environmental impacts of PBX are unclear, even though it is likely that PBX residues from low-order detonations and unexploded ordnance are deposited on military training ranges. The release of high explosives from the polymer matrix into the environment has not been studied in detail, although as polymers degrade slowly in the environment we anticipate high explosives to be released into the environment. In this study, PBXN-109 (nominally 64% RDX) samples were exposed to variable UK climatic conditions reproduced in the laboratory to determine the effects of temperature, UV irradiation and rainfall on the release of RDX from the polymer binder. The most extreme conditions for spring, summer and winter in the UK were artificially reproduced. We found that up to 0.03% of RDX was consistently released from PBXN-109. The rate of RDX release was highest in samples exposed to the summer simulation, which had the lowest rainfall, but the highest temperatures and longest UV exposure. This was confirmed by additional experiments simulating an extreme summer month with consistently high temperatures and long periods of sunlight. These results probably reflect the combination of polymer swelling and degradation when samples are exposed to higher temperatures and prolonged UV irradiation.

1. Introduction

Polymer bonded explosives (PBX) are designed to meet the need for insensitive munitions, which minimise the risk of inadvertent initiation while reliably fulfilling their intended detonation functions (Ang and Pisharath, 2012). PBX compositions typically consist of a nitramine high explosive encapsulated by a polymer binder, which confers insensitivity by protecting the explosive with a flexible and rubber-like coating (Shee et al., 2015). One of the most common nitramines in PBX is 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), accounting for up to 95% of the composition.

RDX is a common soil contaminant at manufacturing sites and on military training ranges. Low order and blow-in-place detonations of legacy compositions such as Composition B can deposit thousands of milligrams of RDX on soil surfaces (Jenkins et al., 2006). Unexploded ordnance can also cause contamination when damaged because the high explosive filling is then exposed to the climate (DuBois and Baytos, 1991).

The fate and transport of RDX is highly dependent on location

due to differences in climate and soil type (Larson et al., 2008). Solid RDX particles can remain in the top layer of soil for a long time (Sheremata et al., 2001) but are more likely to undergo slow biodegradation under anaerobic conditions, yielding other undesirable contaminants such as methanol and hydrazine. RDX does not significantly adsorb to soil (Singh et al., 1998) and dissolved RDX therefore tends to migrate (Selim et al., 1995). However, RDX has low solubility in water and is unlikely to exceed current threshold limits of 2 μg/l in groundwater (Gauthier et al., 2003; Pichtel, 2012). RDX becomes more soluble at higher temperatures, doubling with every 10 °C increase, so water contamination is a more significant problem in warm, wet climates (Lynch et al., 2002). Because RDX leaches slowly in temperate regions, it accumulates on or just beneath the soil surface, presenting a risk to humans, animals and plants due to its extreme toxicity (Pennington and Brannon, 2002; Pichtel, 2012). This may be exacerbated by PBX materials because the polymer protects RDX from the climate and may prevent RDX crystal distribution, resulting in more surface contamination than non-bonded high explosive. However, many polymers swell at higher temperatures and degrade when exposed to UV light, which may release RDX into the environment (Adeniyi and Kolawole, 1984).

We investigated the environmental fate of PBXN-109, an aluminized, cast-and-cured secondary explosive containing 64% RDX and 8% polybutadiene binder. The aim was to determine the effect of a variable climate on the rate at which RDX leaches from the PBXN-109 polymer matrix under controlled laboratory conditions. Samples of PBXN-109 were exposed to predetermined doses of UV irradiation and water at controlled temperatures to simulate variable conditions, i.e. cold and wet vs. hot and dry. The release of RDX from PBXN-109 was measured by analysing the RDX content of the water run-off.

2. Materials and methods

2.1. Preparation of samples

Samples of PBX (RWM Italia SpA) were supplied as small spheres (~1.5 g each/diameter = 0.5 mm) containing 64% RDX, 20% aluminium, 8% hydroxyl-terminated polybutadiene (HTPB) and 8% di-(2-ethylhexyl)-adipate (DOA). The RDX content was confirmed by acetone extraction from pristine PBXN-109 in a Soxhlet extractor. The samples were used as supplied and loaded into Buchner funnels (4 cm diameter) fitted with a glass frit before exposure to variable climate conditions (Taylor et al., 2015, 2009).

2.2. The UK climate

Climate conditions representing South-West England were simulated in the laboratory to mimic the exposure of PBXN-109 on military ranges. Climate data from 1990 to 2014 were obtained from the UK Meteorological Service website (Met Office website) (Table 1). The highest seasonal averages for rainfall, temperature and sunlight hours were identified and used in laboratory

simulations to provide representative worst-case exposure scenarios. Autumn climate conditions were not reproduced in the laboratory due to the similarity between the autumn and winter rainfall and temperature, and number of daylight hour's falls between spring and winter values therefore can be estimated to be between the two.

The volume of simulated rainfall deposited on the PBXN-109 samples for winter, spring and summer was determined by calculating the equivalent rainfall on the area of the sample within the Buchner funnel housing. The rainfall was calculated by multiplying the maximum seasonal average rainfall (mm/m^2) by the area of the sinter funnel. The average sunlight per day was determined by dividing the maximum seasonal average by 90 days (the average number of days in a season) (Table 1). Maximum and minimum average temperatures were also taken into consideration.

2.3. Simulating the UK climate under controlled conditions

Seasonal variations were simulated in the laboratory on an accelerated timescale of 11–15 days depending on the average number of rainy days in the 3 seasons under investigation. Duplicate samples, of individual spheres of PBXN-109 were housed in self-contained temperature controlled chambers to simulate the artificial seasons. The climate chambers were designed to eliminate any non-controlled sources of light, heat or water. Samples were exposed to the seasonal maximum and minimum temperatures over alternating 24-h periods to represent natural temperature fluctuations between night and day. Rainfall was simulated using peristaltic pumps to deliver a daily dose (8 mL/h) of ultrapure water from a MilliQ Water Purification System equivalent to the average UK seasonal rainfall on a similar area (see Supporting Information for daily volumes of applied water). The maximum volume of water delivered each day was 90 mL, resulting in a minimum dry period of 11.5 h per day. The run-off was collected in 500-ml wide-neck amber jars. Daylight hours of intense UV during the summer were simulated using a Philips high intensity UV lamp (HPW125WTPH), and daylight hours during the winter and spring were simulated using a BTL low-intensity UV tube lamp. Duplicate samples were simultaneously exposed to temperature, rainfall and sunlight representative of UK spring, summer or winter. The artificial conditions for each sample are summarized in Table 2.

2.4. High performance liquid chromatography

Sample run-off was collected every 24 h and analysed by high performance liquid chromatography (HPLC) to determine the percentage loss of RDX from the PBXN-109 sample. The HPLC system consisted of a Waters Alliance 2695 equipped with a Waters 996 photodiode array detector. The chromatographic separations were performed on ACE UltraCore 2.5 SuperPhenylHexyl columns (100 × 4.6 mm internal diameter) maintained at 35 °C. A mixture of acetonitrile/water (3:2) was used as the mobile phase at a flow rate of 1.5 ml/min. A linear calibration curve for RDX was obtained for the concentration range 0.1–20 μg/ml.

Table 1
Average climate conditions in South-West England during the period 1990–2014.

Season	Seasonal rainfall		Seasonal temperature		Seasonal sunlight hours	
	Season average (mm)	Equivalent artificial rainfall (mL)	Max. (°C)	Min. (°C)	Average (h)	Average/day (h)
Winter	694	872	10 ± 1	0 ± 1	210	2.5
Spring	332	599	15 ± 1	3 ± 1	601	6.75
Summer	476	417	22 ± 1	10 ± 1	721	8
Autumn	624	784	9 ± 1	5 ± 1	360	4

Table 2
Summary of the conditions used for seasonal simulations.

Experiment reference	Sample mass (g)	Temperature (°C)		Average UV (h/day)	Total rainfall (mL)	Duration of Artificial season (days)
		Min (7 days)	Max (7 days)			
Winter 1	1.66	0	10	2.5	830	15
Winter 2	1.42				846	
Spring 1	1.60	5	15	6.75	572	11
Spring 2	1.60				451	
Summer 1	1.60	10	22	8.0	465	14
Summer 2	1.60				404	
Extreme 1	1.14	22		13	389	11
Extreme 2	1.12				329	

Table 3
Summary of mass and percentage release of RDX from PBXN-109 samples at the end of the artificial seasonal.

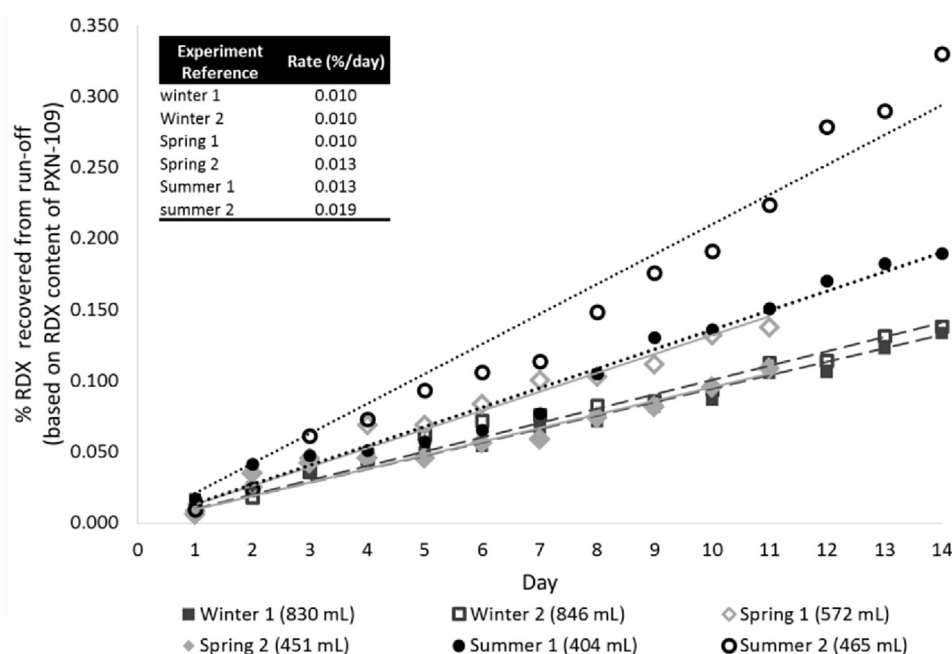| Sample	RDX mass recovered (mg)	% Loss	Total UV Exposure	Total Rainfall (ml)	Days
Winter 1	1.56	0.11	37.5	830	15
Winter 2	1.40	0.12		846	
Spring 1	1.40	0.14	74.25	572	11
Spring 2	1.11	0.11		451	
Summer 1	1.75	0.19	112	404	14
Summer 2	2.74	0.33		465	

3. Results and discussion

The samples of PBXN-109 were formulated with 64% RDX, which gave ~1 g of RDX in each sample. The concentration of RDX found in each run-off sample was determined by HPLC and expressed as a percentage based on the quantity of RDX in the sample. The total amount of pure RDX recovered from a single sphere of PBXN-109 during a laboratory season was small (3 mg), probably reflecting the inability of water to penetrate deeply into the insoluble polymer matrix. However, RDX contamination could still pose a problem when frequently using PBXN-109 filled munitions over long periods of time.
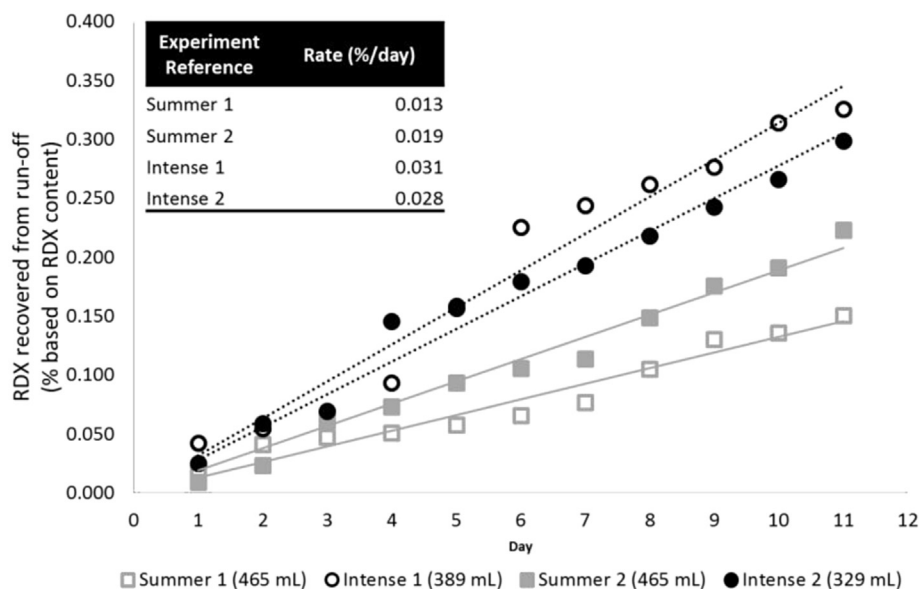
The results from the first series of experiments aiming to replicate UK spring, summer and winter seasons are shown in Table 3. They revealed that more RDX was lost from PBXN-109 samples exposed to summer conditions (up to 2.74 mg RDX lost by the season end). The summer samples were exposed to 50% less water than the winter samples, confirming that the polymer binder limits the migration of water to accessible RDX crystals regardless of the volume of water applied. The temperature of the applied water was identical for all samples, so the higher concentration of RDX is unlikely to reflect its greater solubility at higher water temperatures.

PBXN-109 samples under spring and winter conditions lost similar percentages of RDX even though the spring accelerated season ended four days sooner than the winter season and less

Graph 1. Rate of RDX release from PBXN-109 during artificial seasons: spring (11 days), summer (14 days), and winter (15 days).

Experiment Reference	Rate (%/day)
Summer 1	0.013
Summer 2	0.019
Intense 1	0.031
Intense 2	0.028

□ Summer 1 (465 mL) ○ Intense 1 (389 mL) ■ Summer 2 (465 mL) ● Intense 2 (329 mL)

Graph 2. RDX release from PBXN-109 at constant 22 °C temperature and maximum UV exposure (13 h/day).

water was used, again indicating that rainfall alone is not responsible for RDX release. The percentage of RDX migrating from each replicate summer sample was noticeably different, even though the two samples received similar volumes of water at identical temperatures with the same amount of UV exposure. These differences may reflect inconsistencies between the PBXN-109 samples in terms of composition, e.g. differences in the average RDX content, the accessibility of the RDX crystals, or the micro-structure of the polymer (such as cracking).

The rate of release indicated that RDX release was accelerated under the warmer and drier summer conditions compared to the cooler spring and winter conditions - 0.01%/day for Winter 1 and Winter 2 samples compared to 0.013%/day and 0.019%/day for Summer 1 and summer 2 samples respectively (Graph 1). Spring sample 1 was exposed to 121 mL more water than sample 2 and lost more RDX, but this difference is more likely to reflect random differences in the distribution of RDX and the polymer structure given that the opposite effect was observed for the summer samples.

These results suggest that the rate of RDX release from the PBXN-109 was accelerated by high temperatures and exposure to sunlight, and was not dependent on the volume of rainfall (Lynch et al., 2002). This differs from pure RDX, where the limiting factor is its solubility, which is mainly dependent on the water temperature and the volume of rainfall.

The effect of high temperatures and UV on the rate of release of RDX from PBXN-109 was investigated further by exposing two additional samples of PBXN-109 to a consistently warm climate (22 °C) and 13 h UV irradiation per day, to simulate long periods of hot and bright weather (Graph 2). Water was applied at a volume that was representative of a dry summer (389 and 329 ml). The results confirmed that prolonged warm temperatures and intense UV exposure accelerate the release of RDX from PBXN-109 from 0.013%/day and 0.019%/day for summer 1 and summer 2 samples compared to 0.031%/day and 0.028%/day for Intense 1 and Intense 2 samples. . The increase in rate of RDX release may reflect the swelling of the polymer matrix at higher temperatures, which would make it easier for water to penetrate. Furthermore, polybutadiene polymers are known to degrade under UV light, which might cause additional cracking in the matrix allowing water to penetrate deeper into the PBXN-109 and wash out the RDX.

4. Conclusion

RDX does migrate from the polymer matrix of PBXN-109 when exposed to simulated seasonal conditions. The rate of release is low but consistent, and PBXN-109 deposits on ranges are therefore likely to result in RDX contamination in the environment by dissolution and transport in water. We also found that the rate of RDX release is accelerated in warm temperatures with intense UV exposure, probably reflecting a combination of polymer swelling and degradation allowing more access to the encapsulated RDX crystals. The results presented in this manuscript are preliminary, and long term work is currently underway to fully investigate the rate of RDX release from PBXN-109 in artificial and real environments.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.11.107.

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Appendix 2: Comparing extraction efficiency of Insensitive High Explosives constituents from soil additional figures
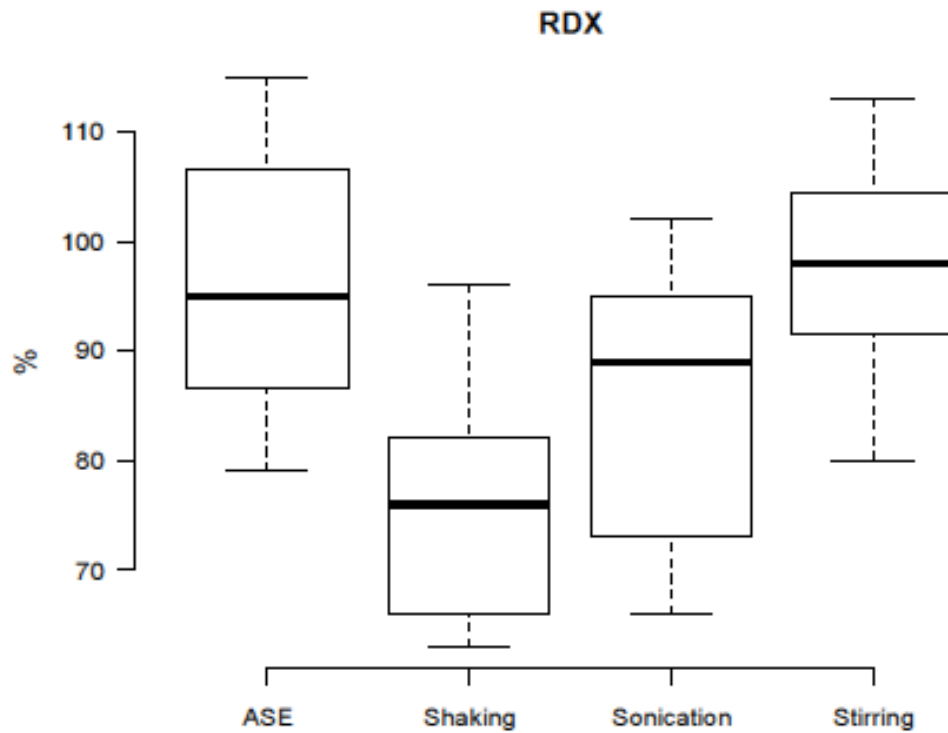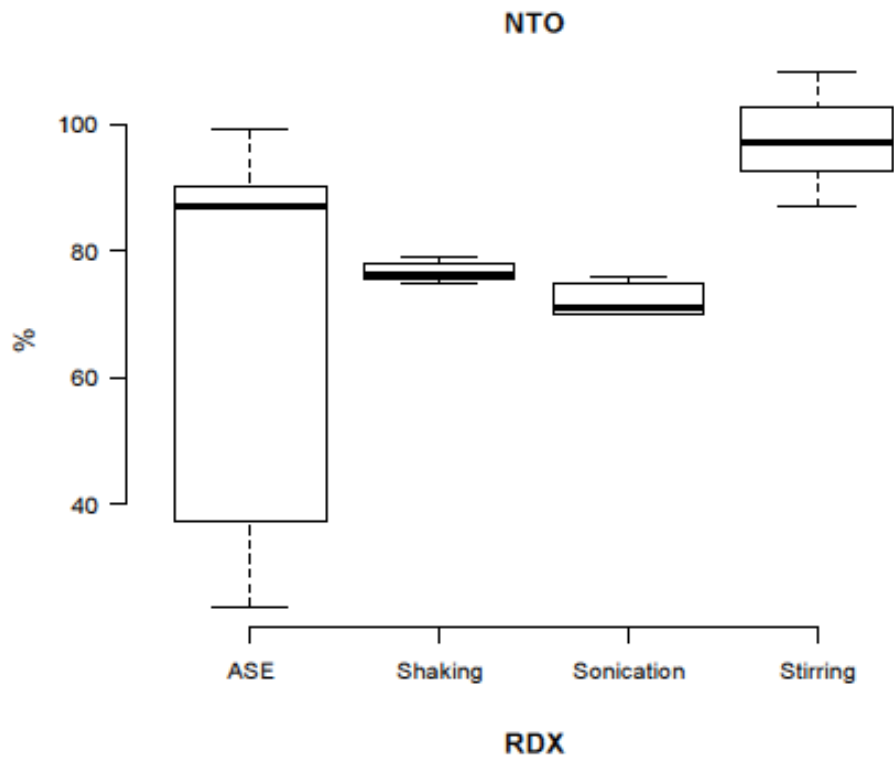

Appendix 2 Fig. 1: Box plot with whiskers from maximum to minimum showing the variation in percentage extraction efficiency for RDX across all soils by ASE, shaking, sonication and stirring.
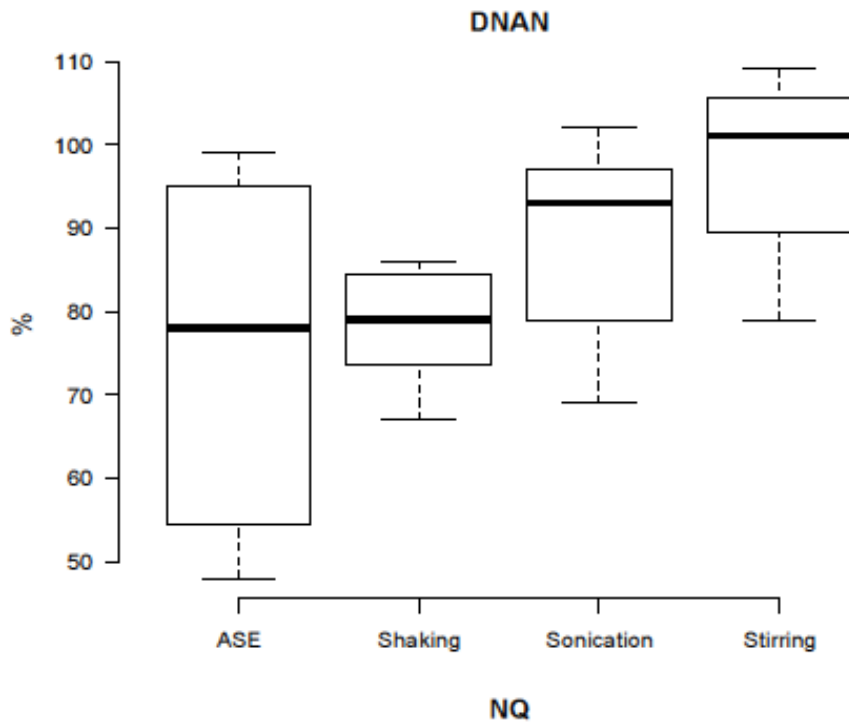
DNAN

Appendix 2 Fig. 2: Box plot with whiskers from maximum to minimum showing the variation in percentage extraction efficiency for DNAN across all soil types by ASE, shaking, sonication and stirring.

NQ
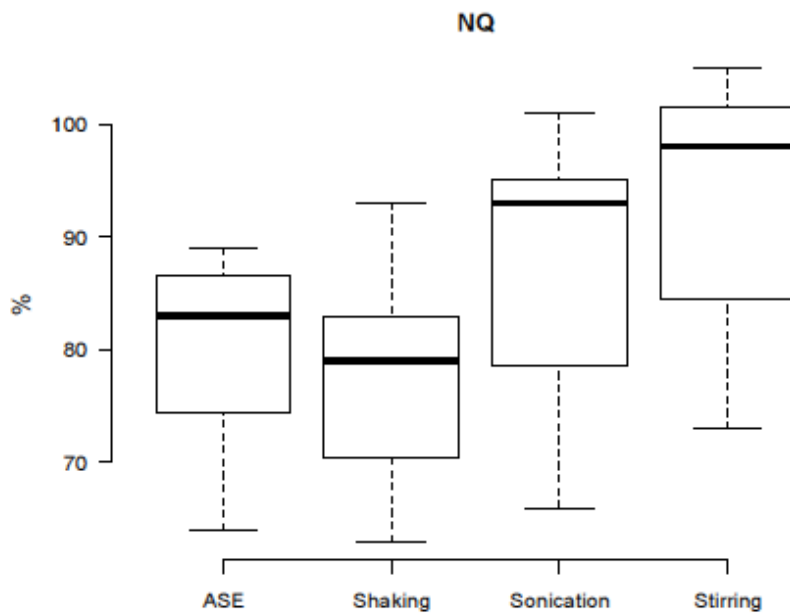
Appendix 2 Fig. 3: Box plot with whiskers from maximum to minimum showing the variation in percentage extraction efficiency for NQ across all soil types by ASE, shaking, sonication and stirring.

NTO

RDX

Appendix 2 Fig. 4: Box plot with whiskers from maximum to minimum showing the variation in percentage extraction efficiency for NTO across all soil types by ASE, shaking, sonication and stirring.
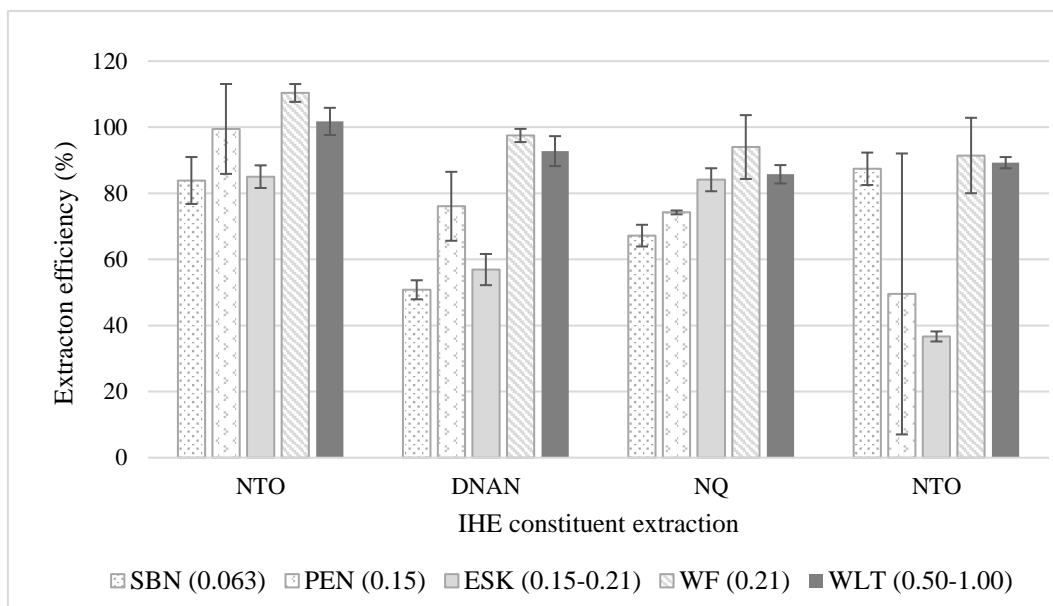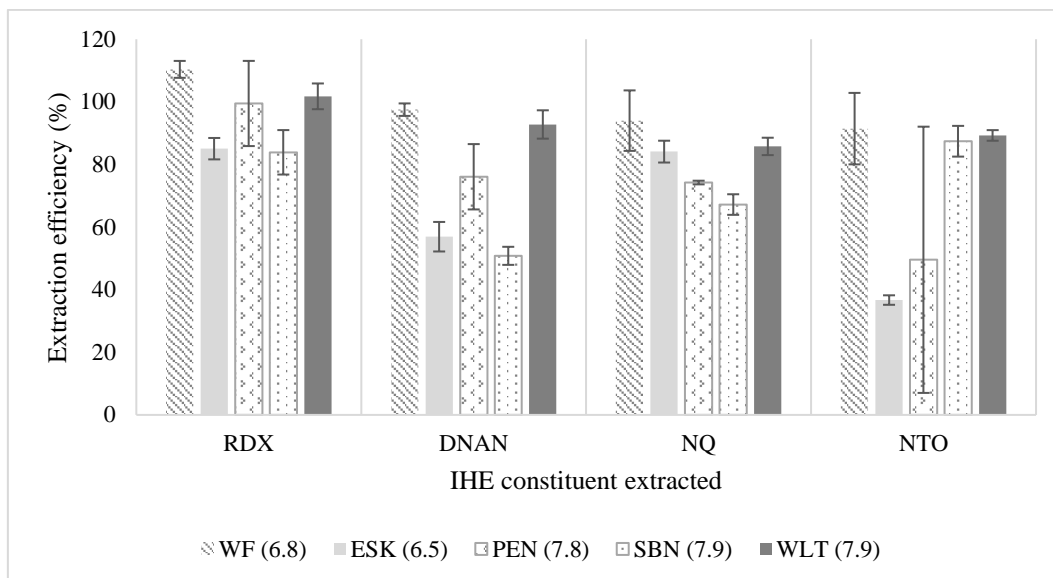

Appendix 2 Fig. 5: Efficiency of extraction of IHE constituents from five soil types arranged by particle size by ASE

Appendix 2 Fig. 6: Efficiency of extraction of IHE constituents from five soil types arranged by soil pH by ASE.

Appendix 3: Published paper: Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil

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Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil

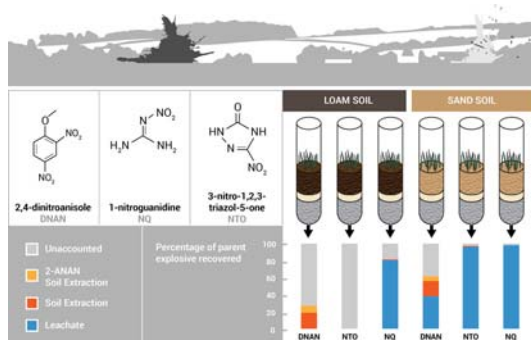Temple T. [a,*], Ladyman M. [a], Mai N. [a], Galante E. [a], Ricamora M. [a], Shirazi R. [a], Coulon F. [b]

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HIGHLIGHTS

- No adverse interactions between the combined Insensitive High Explosive constituents DNAN, NTO and NQ in soil were observed.
- DNAN and NTO were more rapidly degraded in soils with higher organic content.
- Degradation rates were increased in soil columns, compared to static soil experiments.
- Insight into the fate and transport of three Insensitive High Explosive constituents in combination in soil.

GRAPHICAL ABSTRACT

ABSTRACT

Contamination of military ranges by the use of explosives can lead to irreversible environmental damage, specifically to soil and groundwater. The fate and effects of traditional explosive residues are well understood, while less is known about the impact of Insensitive High Explosives (IHEs) that are currently being brought into military service. Current research has focussed on the investigation of individual constituents of IHE formulations, which may not be representative of real-world scenarios when explosive residues will be deposited together. Therefore, this study investigated the fate and transport of the combined IHE constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and 3-nitro-1,2,4-triazol-5-one (NTO) in two UK soil types.

Static experiments ran for 9 weeks to determine the fate of the combined explosive constituents in soil by monitoring the rate of degradation. Transport was examined by running soil column experiments for 5 weeks, with a watering regime equivalent to the average yearly UK rainfall. Both static and soil column experiments confirmed that DNAN and NTO started to degrade within twenty-four hours in soil with high organic content, and were both completely degraded within sixty days. NQ was more stable, with 80% of the original material recovered after sixty days. The major degradation product of DNAN in the test soils was 2-amino-4-nitroanisole (2-ANAN), with trace amounts of 4-amino-2-nitroanisole. NTO was rapidly degraded in soil with high organic content, although no degradation products were identified. Results supported work from literature on the individual constituents DNAN, NQ and NTO suggesting that the three explosives in combination did not interact with each other when in soil. This study should provide a useful insight into the behaviour of three combined Insensitive High Explosive constituents for the predication of soil and water contamination during military training.

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1. Introduction

The chemical components of munitions are released into the environment during manufacture and by detonations through military activities, which has led to environmental contamination (Pichtel and Pichtel, 2012). Studies conducted on over 30 United States (US) military training ranges have shown that explosive contamination is common in surface soils, and can cause long-term irreversible environmental degradation (Jenkins et al., 2006; Walsh et al., 2005). In one particular case, high explosives were detected in groundwater at concentrations two orders of magnitude higher than the advisory drinking water limits (Morley et al., 2006). Transport of the explosives through soil to groundwater is dependent on the soil type in these areas e.g. loamy, sand, chalk or clay. In the United Kingdom (UK) for example, two of the main training areas are located on loamy soil and use imported sand for bullet catching and other training activities.

Traditional explosives such as 2,4,6-trinitrotoluene (TNT), and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and their known degradation products are toxic and potential human carcinogens (United States Environmental Protection Agency, 2014a, 2014b), which has led to more stringent environmental governance. The fate and effects of traditional explosive residues are well understood, while less is known about the impact of Insensitive High Explosives (IHEs) that are currently being brought into military service. For example, Insensitive Munitions Explosive (IMX) formulations that consist of mixtures of RDX, 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and 1-nitroguanidine (NQ) (Lee et al., 2010; Singh et al., 2010). Of particular interest for this paper is IMX-101 which consists of 2,4-dinitroanisole (43%) (DNAN), 1-nitroguanidine (37%) (NQ) and 3-nitro-1,2,4-triazol-5-one (20%) (NTO) (Lee et al., 2010). The impact of the three IHE constituents on the environment may be significant, as they are known to be toxic. DNAN is the most toxic with an LD_{50} of 199 mg kg^{-1} in rats (Dodd and McDougal, 2001; Williams et al., 2014). This is comparable to the toxicity of RDX (100 mg kg^{-1}), which is known to contaminate soil and groundwater on training ranges and manufacturing sites (Bordeleau et al., 2008; Jenkins et al., 2006; Kalderis et al., 2011; Pichtel and Pichtel, 2012). NTO and NQ are less toxic (Crouse et al., 2015; McCain et al., 2013), but still may present a pollution issue under environmental legislation (The Environmental Permitting (England and Wales) Regulations, 2010 SI 675., 2010). NTO, DNAN and NQ are susceptible to degradation in the environment to potentially more toxic compounds.

Of the three constituents, DNAN is the most likely component to undergo photo-degradation as it has low solubility (276 mg L^{-1}) and may remain on the soil surface for longer periods of time (Taylor et al., 2017). The photo-degradation products include nitrate ions, ammonium ions, formaldehyde and formic acid, the latter via the intermediates hydroxy-nitroanisole (HO-NAN). Another degradation product has been identified as 2,4-dinitrophenol (DNP), although only in solution and therefore may not represent the degradation products from the breakdown of solid DNAN on the soil surface (Hawari et al., 2015; Rao et al., 2013). DNP is of particular concern as it is more toxic than the parent compound with an LD_{50} of 30 μg L^{-1}. DNAN has a greater affinity for soils with a higher organic content (Olivares et al., 2016), and degrades in soil into amino derivatives such as 2 and 4-amino-nitroanisole (2/4-ANAN) and diamino-anisole (DAAN) which have a higher attenuation to soil (Arthur et al., 2017; Hawari et al., 2015).

NTO is the most soluble of the three constituents (16,642 mg L^{-1}) and therefore has the potential to enter the soil at a rate dependent on rainfall (Braida et al., 2012). NTO is not likely to sorb significantly to soils as it is negatively charged at environmentally relevant pH (Mark et al., 2016; Smith and Cliff, 1999). However, NTO is susceptible to degradation in soils with high organic content which may be attributed to bio-degradation as NTO mass loss has been shown to be significantly lower in sterilized soils (Mark et al., 2017a). Microcosm studies have shown that NTO is readily bio-degraded to give 3- amino-1,2,4-triazol-

5-one (ATO) (Krzmarzick et al., 2015; Le Campion et al., 1999; Richard and Weidhaas, 2014a). Although mass loss of NTO has been readily observed in soil column and batch experiments, ATO has not yet been detected (Mark et al., 2017a).

NQ is more soluble than DNAN (3800 mg L^{-1}) and does not sorb significantly to soil, so it is expected to be transported quickly to groundwater (Mirecki et al., 2006). However, NQ is susceptible to photo-degradation and biodegradation in certain organic soils, forming mineralised products such as nitro-urea and ammonia (Kaplan and Kaplan, 1985; Richard and Weidhaas, 2014b).

Table 1 summarises the properties of the three IHE, and their degradation products.

Therefore, the aim of this work was to investigate fate and transport of IHE constituents mixture consisting of DNAN, NQ and NTO in static soil experiments and vertical soil columns under controlled laboratory conditions. The static experiments were set-up to determine the degradation products of the IHE and the soil columns to determine the transport mechanisms and flow properties. Soil types with different percentages of organic content were chosen for these experiments so that the relationship between the soil characteristics and fate and transport of the IHE can be further understood from an environmental impact perspective. The highlight of this research was the investigation of the fate of DNAN, NQ and NTO as a mixture in soil. These compounds are used in combination in explosive formulations and are likely to be deposited in the environment as mixtures, and not as pure compounds.

2. Materials and methods

Samples of NTO and NQ were synthesised in-house at Cranfield University (Lee and Coburn, 1988). DNAN was purchased from Fischer Scientific UK. Analytical samples of ATO and 4-ANAN were purchased from Fluorochem, DAAN was purchased from Sigma Aldrich, 2-ANAN was purchased from Alfa Aesar (Massachusetts, United States) and 2-HONAN and DNP (70% in water) were purchased from Thermofischer Scientific UK. All analytical samples were 98% or higher purity and were used without further purification. Methanol (MeOH) and Acetonitrile (ACN) High Performance Liquid Chromatography (HPLC) grade were purchased from Thermofischer Scientific UK. Deionised water (DI), 18.2 MΩ·cm at 25 °C, from Millipore Synergy was used for all experiments. Ottawa sand was also purchased from Thermofischer Scientific UK.

2.1. Soil

Two soils were purchased from a building merchant in Oxfordshire (UK). The soils were air-dried for 2 weeks and passed through a 2-mm sieve. The soils were characterised by testing for humidity (BS 13772:1990), pH and total organic content (BS 13039:2001). Total carbon nitrogen hydrogen (TCNH) content and total organic carbon (TOC) were determined using Elementar Vario ELIII. The particle size distribution was determined according to ASTM D 2487-11, which classified the two soils as loamy and sandy. Two control soils were prepared by incinerating samples of the loamy and sandy soil at 400 °C for 3 days to vaporise all organic material. Ottawa sand was used as a blank. Soil characterisation is summarised in Table 2.

Table 1
Toxicity, solubility and major degradation products of DNAN, NQ and NTO.

Explosive	Solubility (mg L^{-1})[1]	Oral toxicity (mg kg^{-1})	Major degradation products
DNAN	276	199[2]	2-ANAN, 4-ANAN, DAAN, DNP, 4-HONAN
NTO	16,642	>5000[3]	ATO
NQ	3800	>1000[4]	Nitro-urea, ammonia

1. (Taylor et al., 2015); 2. (Dodd and McDougal, 2001); 3. (Williams et al., 2014); 4. (Crouse et al., 2015).

2.2. Stock solutions

Stock solutions for static experiments were prepared by stirring DNAN (0.423 g), NQ (0.367 g) and NTO (0.215 g) in DI water (1500 mL) at ambient temperature for 72 h (Stock Solution 1). The solution was filtered prior to use to remove any suspended particulate. The final concentration was 171 ppm DNAN, 97 ppm NTO and 233 ppm NQ as determined by HPLC. Six dispersions were prepared for the vertical soil column experiments containing DNAN (0.9 g, 42%), NQ (0.8 g, 37%) and NTO (0.45 g, 21%) in DI (100 mL). The solutions were sonicated for 2 h, and left overnight to ensure minimum particle size and maximum dispersion. A third stock solution (DNAN, NTO, NQ 500 ppm) in ACN/water (1:1) was prepared for HPLC calibration (Stock Solution 2).

2.3. Static experiments

Soil (10 g) was placed in amber vials (60 mL) with Stock Solution 1 (15 mL). Twelve vials were prepared for each soil type: loamy, sandy, loamy control, sandy control and Ottawa blank and were placed in a sand bath to ensure constant temperature (19.5 °C). One sample of each soil type was sacrificed after ten minutes (T0), further samples were sacrificed at hour 1, 3, 6, 24 and on day 7, 14, 20, 38, on day 62 samples were taken in triplicate. The IHE solution from the sacrificed samples was decanted, filtered and diluted by a factor of eight in a mixture of ACN/water for analysis by HPLC for the parent compounds, and expected degradation products. The remaining soil was extracted with ACN/water (1:1) by shaking for 18 h at room temperature (Walsh, 2016). The solid phase extract was filtered, diluted by a factor of eight in a mixture of ACN/water (1:1) and analysed by HPLC. Blank samples of the stock solution 1, kept under the same conditions as the samples, were tested periodically to ensure that the experimental conditions were not contributing to breakdown over time. Stock Solution 1, stored at 5 °C throughout the experiment, was also evaluated for degradation at every time point.

2.4. Soil column experiments

Clear Perspex® columns (10 cm × 40 cm) with polyvinyl chloride (PVC) collection funnels fitted with stainless steel wire meshes were placed into collection containers (Fig. 1). Increments soil (100 g) were added to the column and compacted using a tamping rod (1.2 kg) until a height of 20 cm was achieved.(Oliviera et al., 1996) Columns of loamy soil and sandy soil were prepared in triplicate and capped with a wire mesh and an 800 g weight with a hole through the top for access. The average packing density for the loamy soil was 1.27 ± 0.03 kg L^{-1} and 1.81 ± 0.02 kg L^{-1} for sandy soil. The columns were saturated with DI water and left to settle for 5 days without eluting water (Fig. 1).

Table 2
Characterisation of loamy and sandy soil, incinerated soil and Ottawa sand.

Soil	Description	Organic content[1] (%)	TOC[2] (%)	TCNH[3] (%)				pH[4]
				N	C	H	C/N	
Loamy	UK top soil	8.0	4.1	0.30	5.11	0.74	17	8.0
Sandy	UK sand	4.9	0.43	0.012	7.22	0.30	600	7.9
Loamy control	Incinerated loamy soil	0	1.32	LOD	1.14	0.14	N/A	8.1
Sandy control	Incinerated sandy soil	0	0.06	LOD	6.73	0.14	N/A	7.9
Ottawa sand	100% quartz	–	–	–	–	–	–	7.1

1. Determined by incineration at 400 °C for three days; 2. Determined by Elementar Vario ELIII according to British Standard BS 7755 Section 3.8:1995; 3. Determined by Elementar Vario ELIII; 4. Determined by Griffin pH meter model 80; LOD: Limit of Detection.

2.5. Vertical saturated soil columns

The soil columns were exposed to a volume of water equivalent to the average yearly rainfall in the UK (South West England and Wales) from 1995 to 2015 data calculated to be 1160 mm.(Met Office, n.d.) This is equivalent to the delivery of 9.11 L of water per column over the 5-week experiment, resulting in an artificial watering scheme representative of a full year's rainfall. The columns were treated with 260 mL water per day delivered in five increments (4 × 60 mL and 1 × 50 mL) 1 h apart at a rate of 40 mL min^{-1} (Kramoer Dosing Pump, China). The leachate was collected weekly and analysed by HPLC within 5 days of collection. Sub-samples were stored at 4 °C, pending analysis.

2.6. Accelerated solvent extraction

At the end of the 5 week experiment, the soil columns were disassembled and the loamy soil and sandy soil samples were divided into 4 sections (5 cm each). After air-drying for 1 week, the soil was ground (Essa, LM2-P Pneumatic 380 V, 50 Hz) and the explosives were extracted by Accelerated Solvent Extraction (ASE) (Dionex ASE 350, Thermo Fisher Scientific, UK), using an adapted ASE explosive method to extract the highly water soluble NTO (Dionex, 2011). Samples were extracted using ACN/water (3:2) at 100 °C, with a heating time of 5 min, a static time of 10 min and a 100 s purge. Using this method, DNAN and NQ were extracted with 100% efficiency and NTO with 60% efficiency. The results were corrected accordingly. The resultant extracts were analysed by HPLC.

2.7. HPLC analysis

Collected leachates were analysed by HPLC (Waters-Alliance 2696, USA) using a photodiode array detector (Waters, 996, USA). DNAN, NTO, NQ and degradation products 2-ANAN and 4-ANAN were separated on a ZORBAX Eclipse Plus C18 column (100 mm × 4.6 mm, 3.5 μm particle size) from Agilent (Wilmington, DE, USA) maintained at 35 °C. The mobile phase was methanol (solvent A), ACN (solvent B) and water/0.1% formic acid (solvent C) with a flow rate of 0.75 mL min^{-1}. Optimised separation conditions were achieved with a gradient program (Table 2). The injection volume was 10 μL. Peak identification was performed by comparing the retention time and UV profile of the compounds to standard compounds. The output signals were monitored at a selective reference wavelength as displayed in Table 3. The HPLC method was validated by examining: (i) Specificity (analysis of aqueous solution of wetted soils); (ii) Linearity (measure of the correlation coefficient for each standard from the linear regression analysis in the concentration range of 0.6 to 20 μL/mL); (iii) Limit of Detection (LOD), Limit of Quality (LOQ) (measure of the residual standard deviation of the responses and slopes of the regression equation of the calibration curve (root mean square error approach)) and (iv) Precision (measure of the relative standard deviation of six injections of each compounds at a concentration of 14 μL/mL). The results are displayed in Table 3.

3. Results and discussion

Loamy soil used in the static and soil column experiments was selected as it is similar to a specific military training range in the UK. Sandy soil was chosen as it is commonly used as an adsorbent for a variety of military activities. Both soil types were fully characterised to enable understanding of the relationship between soil properties and the fate and transport of the selected explosives. Particularly organic content, as this is known to affect the adsorption and degradation of DNAN and NTO (Arthur et al., 2017; Mark et al., 2017b). Soil PH was also monitored throughout the experiment and remained consistent with the soil pH prior to addition of the explosive contaminants.
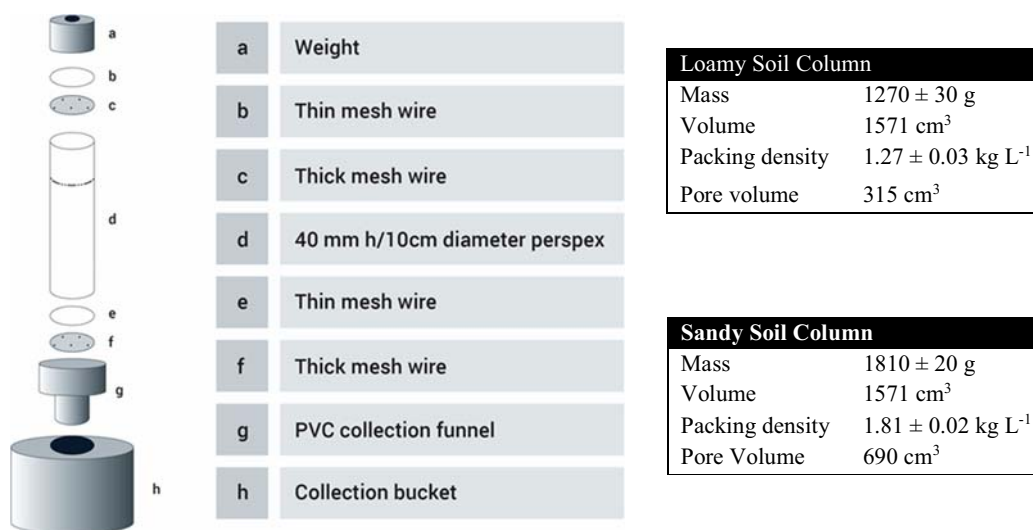
Loamy Soil Column	
Mass	1270 ± 30 g
Volume	1571 cm^3
Packing density	1.27 ± 0.03 kg L^{-1}
Pore volume	315 cm^3

Sandy Soil Column	
Mass	1810 ± 20 g
Volume	1571 cm^3
Packing density	1.81 ± 0.02 kg L^{-1}
Pore Volume	690 cm^3

Fig. 1. Schematic showing the construction of the soil columns.

The mass of DNAN, NQ and NTO added to static experiments, and the soil columns was chosen to represent a specific IHE formulation. In order to accurately account for the fate of all constituents, they were added to the soil in solution so that the dissolution rate of the solid did not affect the rate of transport or degradation in the soil.

3.1. Static experiments

Static experiments were designed to mimic the conditions found in a soil column to investigate the fate of the three IHE constituents, specifically to identify major degradation products in the two soil types. Both the liquid and solid phase were analysed for parent explosive and major degradation products at the specified time points. The liquid phase was isolated by decanting the solution, and taking a 1 mL aliquot which was then diluting in ACN/water (1:1). The remaining soil was then treated with ACN/water (1:1), and shaken for 18 h to extract any remaining explosive to account for explosive adsorbed to the soil. Major degradation products were identified from the literature prior to the experiments, and selected for commercial availability as 2-ANAN, 4-ANAN, DAAN, DNP and 4-HONAN for DNAN. ATO and triazolone (TO) were selected as major NTO degradation products. As NQ is not readily degraded in soil it was not possible to identify NQ degradation products by HPLC.

During the 62-day experiment, the concentrations of DNAN, NQ and NTO recovered from sandy soil remained high, with almost complete recovery of all explosives from the combined liquid and solid phases 93%, 99% and 99% respectively. DNAN and NTO concentration in loamy soil rapidly decreased, suggesting a relationship between DNAN and NTO loss and high concentrations of organic content in the soil, which supports previous literature (Fig. 2) (Arthur et al., 2017; Mark, 2014; Olivares et al., 2016).

Results were normalised to the percentage of parent compound recovered from the Ottawa sand blank to minimise minor variations in percentage recovery due to changes to room temperature of the calibration standard. DNAN concentration in particular may have been affected

Table 3
Method validation parameters.

Chemical	Wavelength (nm)	Linearity (R^2)	LOD/LOQ (μL/mL)	Precision (%)
NQ	264	0.9996	0.5/1.6	0.8
DNAN	296	0.9999	0.5/1.4	0.6
NTO	315	0.9995	0.5/1.4	0.8
2-ANAN	308	0.9999	0.2/0.7	0.8
4-ANAN	330	0.9999	0.2/0.6	1.1

by these temperatures changes as the concentration in the stock solution was at saturation. The average percentage recovery of all three explosives from Ottawa sand was 103% ± 3% compared to Stock Solution 1, confirming that in the absense of soil, DNAN in solution with NTO and NQ, is stable up to nine weeks in the absence of UV.

3.1.1. Effect of organic content on fate of DNAN, NQ and NTO

In order to assess the effect of organic content of the degradation of the three explosives, samples of the sandy soil and loamy soil were incinerated to vaporise bio-organisms and organic molecules. A comparison between the total percentage of DNAN and NTO recovered from both the liquid and solid phase of the loamy soil and sandy soil and the two incinerated soil controls is shown in Fig. 3. The total percentage of DNAN recovered from loamy soil started to decrease within the first 24 h, and after 38 days only trace amounts of the initial DNAN were recovered from the solid phase. However, the total percentage recovery of DNAN from incinerated loamy soil was still high after nine weeks, with only 14% mass loss. This suggests a strong correlation between organic and bio-organic matter and the degradation of DNAN. Due to the high percentage of organic matter in the loamy soil, the incinerated samples still contained some organic matter which contributed to the 14% observed mass loss. A slight decrease in the total percentage recovery of DNAN from sandy soil was observed over the course of experiment, which may be within experimental error. NTO was stable in sandy soil and the sandy control, with 100% total recovery after 62 days. In loamy soil, the concentration of NTO rapidly decreased in the liquid phase, and was not recoverable from the solid phase, suggesting that degradation had occurred. Although rapid mass loss was observed in loamy soil, no NTO loss was observed in the incinerated loamy soil, suggesting a strong correlation between organic content and NTO mass loss.

A slight decrease in the concentration of NQ recovered from the combined liquid and solid phase in loamy soil, sandy soil and the incinerated sandy soil control was observed. It is likely that over prolonged periods of contact with soil, NQ slowly degrades. Mass loss observed in the incinerated sandy control samples was unexpected as NQ recovered from the sandy soil was consistent throughout the experiment averaging 99% ± 6%. Incineration of the sandy soil may change the composition of the soil allowing for an alternative mechanism of mass loss.

3.1.2. Adsorption of DNAN, NQ and NTO to soil

The two-stage recovery of explosives from the liquid followed by the solid phase highlighted the strong attenuation of DNAN to soil. In
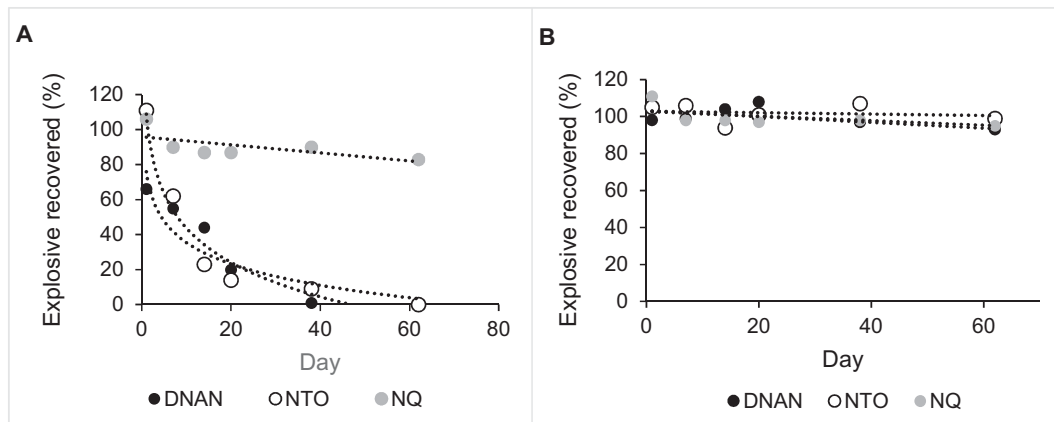
Fig. 2. (A): Observed mass loss of DNAN, NQ and NTO in loamy soil static experiments over 62 days with linear or logarithmic trend lines applied; (B): Observed mass loss of DNAN, NQ and NTO in sand soil static experiments over 62 days with linear trend lines applied.

addition, DNAN attenuation to the loamy soil was more pronounced than attenuation to the sandy soil or incinerated sandy control suggesting that DNAN is more likely to adsorb to soils with high organic content, which supports the results of previous studies (Arthur et al., 2017). NTO and NQ did not adsorb significantly to any of the tested soils, and did not display any correlation between organic content of the soil and adsorption in line with current literature (Mark et al., 2016). The adsorption of DNAN to loamy soil was rapid. A liquid extraction after 10 min recovered only 53% of the DNAN. After 24 h, only 30% of the DNAN was extractable from the liquid phase, with an additional 53% extracted from the solid phase (Fig. 4). Interestingly, absorption to incinerated loamy soil was equally as rapid as absorption onto the loamy soil, however after 24 h a higher percentage of DNAN was recovered from the incinerated loamy soil solid phase (94% compared to 83% from loamy soil) suggesting faster degradation of DNAN in loamy soil. The DNAN adsorption to the four soils is in line with increasing organic content.

3.1.3. Identification of degradation products of DNAN, NQ and NTO in soil

Significant mass loss of DNAN and NTO was observed in loamy soil, as expected due to the high organic content which is thought to contribute to degradation of or sorption of these explosives. In static experiments, as the percentage recovery of DNAN reduced, the degradation products 2 and 4-ANAN were generated. As seen in previous literature,

we observed that 2-ANAN was the dominant degradation product, with only trace amounts of 4-ANAN recovered (Fig. 5) (Arthur et al., 2017; Hawari et al., 2015; Olivares et al., 2016). Although mass loss was far less pronounced in the loamy soil control, trace amounts of 2-ANAN were detected suggesting some degradation which may be attributable to the small amount of organic content remaining in the soil.

Although DNAN mass loss was observed within the first 24 h, significant concentrations of 2-ANAN were not recovered from the loamy soil liquid or solid phase until Day 7. This may be due to the extraction method, which is known to extract DNAN from soil with 100% efficiency, but has not been proven for 2-ANAN. In addition, 2-ANAN is more likely than DNAN to adsorb to soil both reversibly and irreversibly and so may be more difficult to recover (Hawari et al., 2015). Fig. 5 shows that 2-ANAN generation increased for five weeks, however an inconsistently low concentration of 2-ANAN was recovered from day 62 samples even though only trace amounts of DNAN were recovered. Samples on day 62 were taken in triplicate, and results from all three sacrificed samples were consistent. This may be explained by biotransformation of 2-ANAN to DAAN under both aerobic and anaerobic conditions which has been reported in the literature, (Hawari et al., 2015) however DAAN was not detected in either the solid or the liquid phase at any time point. DAAN is known to be unstable in air, and can form di-azo compounds (Hawari et al., 2015). All experiments were conducted in enclosed vials with a natural atmosphere and exposed to
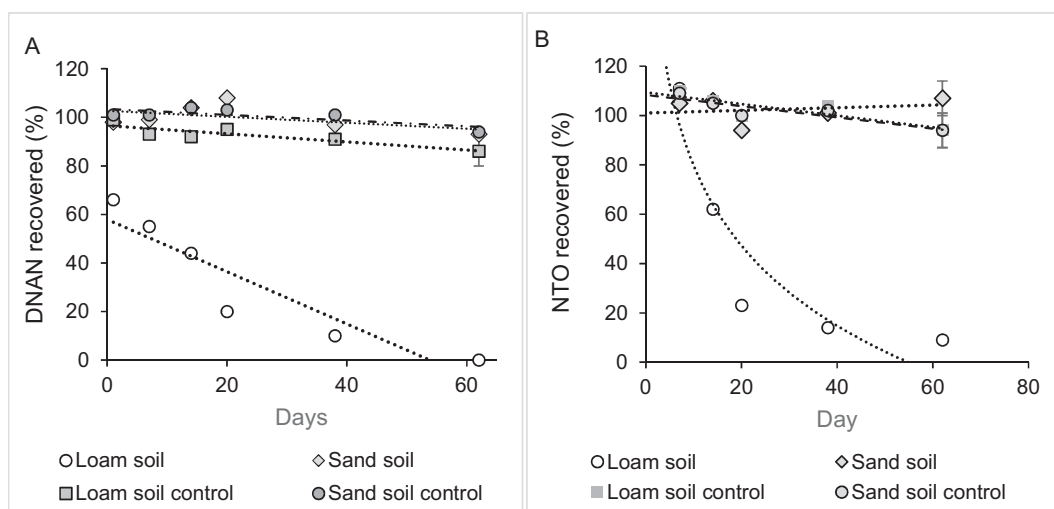

Fig. 3. A: Total percentage recovery of DNAN (liquid and solid phase) from loamy soil, sand soil and both control soils with linear trend line applied; B Total percentage recovery of NTO (liquid and solid phase) from loamy soil, sand soil and both control soils with linear or logarithmic trend line applied. All results were normalised to Ottawa sand blank. Day 62 results were averaged from triplicate.
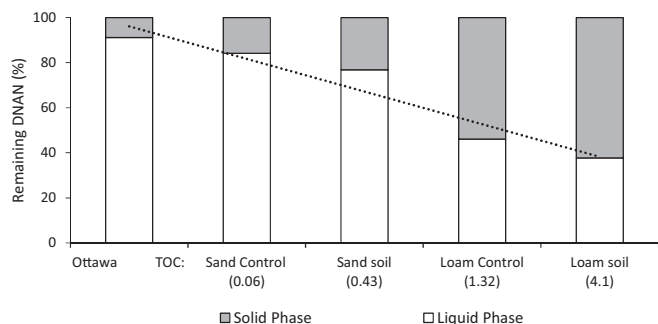
Fig. 4. Percentage DNAN recovered from the liquid phase and solid phase at 24 h normalised to the total percentage DNAN recovered. A linear trend line has been applied.

air during analysis therefore dimerization of DAAN may have occurred, possibly explaining the gradual loss of 2-ANAN.

ATO, the expected degradation product of NTO, was not detected in any of the samples despite almost complete loss of NTO. New peaks were observed in the HPLC trace, but could not be resolved due to the close proximity between the NTO, and NQ peaks. Degradation of NTO was not observed in the loamy control sample, nor the sandy soil suggesting that high organic content is necessary for NTO degradation.

Exposure of the explosive constituents of a new IHE (DNAN, NQ and NTO) to soil under atmospheric conditions showed that in combination DNAN, NQ and NTO are unlikely to interact with one another. The results supported findings in the literature that DNAN and NTO are readily transformed in soils with high organic content most likely by biodegradation, while NQ is much more stable (Arthur et al., 2017; Hawari et al., 2015; Olivares et al., 2016). In addition, DNAN and its major degradation product 2-ANAN, were more likely to be adsorbed to soil with high organic content.

3.2. Transport of DNAN, NQ and NTO in vertical saturated soil columns

Soil columns are a well-established method for determining the fate and mobility of contaminants through soil, (Lewis and Sjöstrom, 2010) and have been used to determine transport of explosives (Mark, 2014; Pennington and Brannon, 2002). Soil columns were designed to simulate the mobility of explosive contaminated water through soil matrices, while avoiding preferential pathways and sidewall flow. Therefore, we used closely packed saturated vertical columns with a 10 cm diameter as this has been proven to reduce sidewall effects, and ensure reproducibility between replicates (Lewis and Sjöstrom, 2010). The explosives were introduced to the soil columns in solution, the mass of NTO and NQ was well below the mass required for saturation, however the
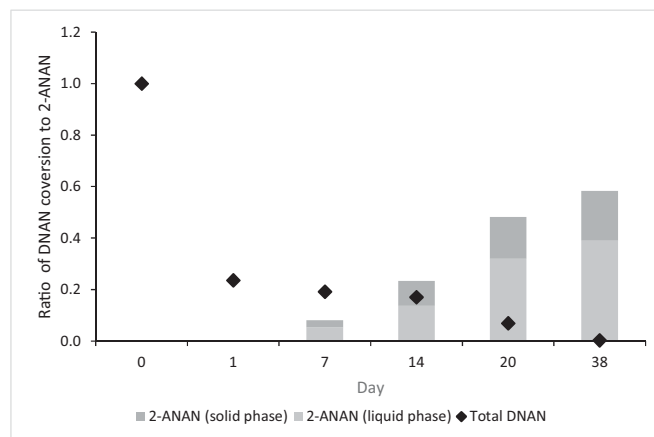

Fig. 5. Molar ratio of DNAN converted to 2-ANAN recovered from the solid and liquid phase. The ratio was calculated from the concentration in moles, and assuming stoichiometric transformation.

DNAN did not completely solubilise and was therefore added in suspension. The explosives were added in 150 mL water, which was then subtracted from the initial dose of water to ensure water delivery was consistent with average annual rainfall in the UK.

The soil columns were treated with water every day totalling the average yearly rainfall for the South West of England, so that the experiment was set in the context of UK rainfall patterns. The columns were dosed evenly throughout the five weeks in increments to avoid pooling of water on the column surface. The water leachate was collected and analysed every seven days, starting one week after the first dosing.

3.2.1. Transport of DNAN, NQ and NTO in sandy soil columns

Results from static experiments indicated that DNAN, NQ and NTO were not adsorbed nor degraded by sandy soil, therefore recovery of explosive constituents was expected from both liquid and solid phase. While this was true for NTO and NQ, which were fully eluted within the first seven days, complete recovery of DNAN was not achieved from the sandy soil column leachate (Fig. 6A). The concentration of DNAN in the eluent gradually decreased, with a cumulative total of 38%. No expected degradation products were identified in the leachate.

After five weeks of water addition- equivalent to one year of rainfall- the columns were disassembled and the soil was extracted by accelerated solvent extraction (ACN/water, 3:2). An additional 18% of the DNAN was recovered from the top 5 cm of the sandy soil column, leaving 44% of DNAN unaccounted for. An equivalent of 5.5% of the unaccounted DNAN was detected as 2-ANAN in the top 5 cm of soil, confirming that 2-ANAN is much less mobile in soil than DNAN, even in soils with low organic content. Almost 50% of the DNAN remained unaccounted for, but the presence of 2-ANAN suggests that it most likely degraded first into 2-ANAN, then further degraded possibly to DAAN so that quantitative recovery was not possible.

3.2.2. Transport of DNAN, NQ and NTO in loamy soil columns

Of the three explosives, only NQ was observed in the loamy soil columns during the five week experiment, with 81% of the initial material recovered. NTO and DNAN were not detected in the soil column leachate, which is consistent with their rapid degradation (Fig. 6B). However, given NTO's high solubility, and low attenuation to soil, we expected to see some NTO in the leachate during the first few weeks before much of the NTO had time to degrade, as in static experiments NTO took five weeks to fully degrade. The lack of NTO in the leachate suggests that the degradation mechanisms can be much quicker in dynamic environments than were seen in the static experiments, which may be due to the much larger mass of soil compared to explosive in the soil columns leading to greater chance of exposure to bio-organisms.

The absence of DNAN in the loamy leachate was expected, as DNAN has a high affinity for the loamy soil, and in static experiments had started to degrade to 2-ANAN within the first seven days. Similarly to the sandy columns, no DNAN degradation products were observed in the leachate, most likely due to their greater attenuation to soil, or rapid degradation into other compounds that were not in the analyte screen. Additionally, DNAN is the least soluble of the three constituents and was added to the columns in suspension. Time taken for DNAN to dissolve would also have slowed down the rate of DNAN transport.

Interestingly, ASE extraction of the loamy soil columns led to the recovery of 19% DNAN, which is similar to the percentage recovered from sandy soil. This was unexpected, as in loamy soil static experiments all DNAN was degraded within five weeks. However, considering that identical solutions of explosives were added to each column, and a similar percentage of DNAN was recovered from both sandy and loamy soil columns, it is likely that the DNAN recovered from the top 5 cm of soil was undissolved particles from the initial addition.

An equivalent of 8% 2-ANAN was recovered from the top layer (5 cm) of the loamy soil columns, leaving 74% of the original DNAN unaccounted for by primary degradation products. In static experiments
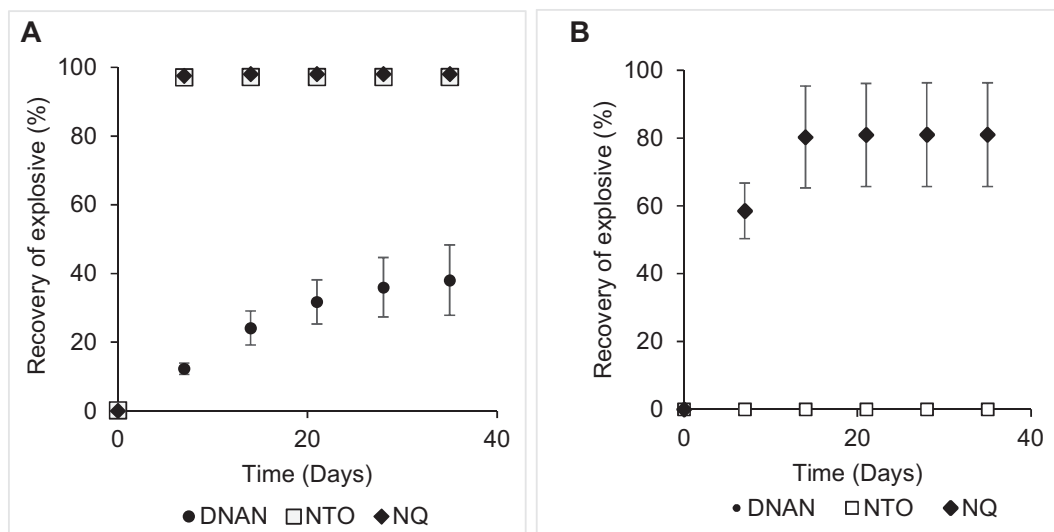
Fig. 6. A: Recovery of explosive from sandy soil column leachate averaged over triplicates; B: recovery of explosive from loamy soil column leachate against time averaged over triplicates.

the recovery of 2-ANAN was high at five weeks, suggesting there was an increase in the rate of degradation in the soil columns.

Only trace amounts of NTO and NQ were recovered from the loamy soil solid phase, suggesting that all of the initial NTO and 20% of the NQ was degraded which is consistent with static experiments. Overall, there was good consistency between static experiments and soil column experiments confirming that the fate of DNAN, NQ and NTO observed in static experiments can be used to explain soil column results (Fig. 7).

Less time was required for complete degradation of DNAN, and NTO in soil columns compared to static experiments. The degradation of DNAN in sandy soil columns was particularly interesting due to the low organic content of the soil, and the stability of DNAN in static experiments. In future, it would be useful to ensure the ratio of explosive to soil is the same in both static and soil column experiments.

Despite slight differences in results between static and soil column experiments, DNAN, NQ and NTO behaviour supports current literature, and does not seem to be significantly altered by interactions between the three constituents under the evaluated conditions. Future work would benefit from focussing on the secondary degradation products of DNAN e.g. DAAN and its diazo compounds, and to establish NTO degradation products in real soil environments.

4. Conclusion

Military training with live fire munitions is essential for troops to maintain combat readiness, and it is inevitable that contamination of

soil and groundwater will occur on and around these areas. As training ranges are located on wide variety of soil types it is difficult to predict how explosive contaminants will interact and how specific receptors will be affected. Traditional explosives such as TNT and RDX are well understood in terms of their fate and transport mechanisms although contamination still occurs. It is therefore essential that new IHE, that are being brought into military service, are understood and managed so that contamination can be avoided. This research investigated fate and transport of the combined constituents of an IHE consisting of DNAN, NQ and NTO in static soil experiments and vertical soil columns under controlled laboratory conditions. The static experiments were conducted so that full degradation profiles of the three explosives in varying soil types could be observed prior to conducting soil column experiments. The novelty of this work was the investigation of the three explosives combined rather than individual testing. Results supported work from literature on the individual constituents DNAN, NQ and NTO suggesting that the three explosives in combination did not interact with each other when in soil. This is significant when considering this type of IHE and its environmental impact e.g. adverse interactions due to soil conditions could generate more toxic and persistent contaminants. Both static and soil column experiments confirm that soils with high organic content are more likely to degrade DNAN and NTO. Our results show that when this type of IHE is used on training ranges, the most significant environmental impacts may be from NTO. Even though NTO itself is not significantly toxic, it rapidly degrades in the environment into potentially toxic degradation products. DNAN is most likely to degrade in soils with high organic content, although into less toxic products.

Fig. 7. Summary of fate of DNAN, NQ and NTO in soil from static and batch experiments.

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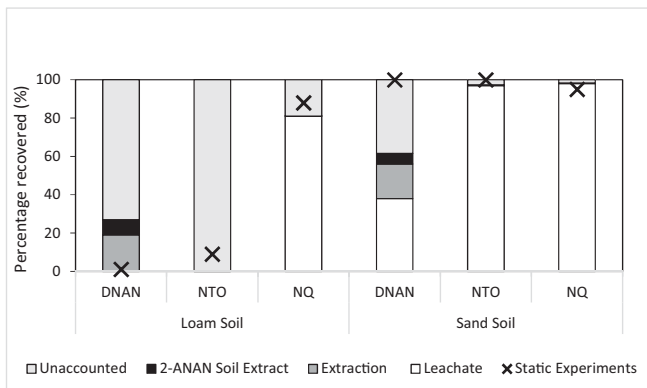
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