CRANFIELD UNIVERSITY

ERICK BRAGA FERRÃO GALANTE

INVESTIGATION OF ENVIRONMENTAL IMPACTS OF EXPLOSIVES BY OPEN BURNING

CRANFIELD DEFENCE AND SECURITY
PhD in Defence and Security

PhD
Academic Year: 2015 - 2018

Supervisor: Ms Tracey J. Temple and Dr Phillip P. Gill
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This thesis is submitted in partial fulfilment of the requirements for the degree of Enter degree

ABSTRACT

New safety requirements are pressuring military organizations to replace TNT with insensitive high explosives (IHEs) containing DNAN, NTO and RDX but little is known about the behaviour IHE components and formulations in the environment. The environmental impact of ordnance during the in-service phase has been studied, but most reports concern TNT-based legacy explosives and their impact on soil rather than other environmental compartments.

To address this knowledge gap, IHE samples ranging from milligrams in a closed system to grams and kilograms in an open system were tested in the laboratory and field, yielding environmental impact data that helps to determine the behaviour of the materials during open burning. The prediction software HYDRUS 1D was then fed with the empirical data and the actual and predicted outcomes for the behaviour of DNAN, NTO, RDX and the IHE formulation were compared to determine whether this software can be used to predict said impacts. The thermodynamic properties of DNAN make it more likely to melt, boil and sublimate during open burning, leaving ~70 % behind as unreacted residues. DNAN also inhibits the burning of RDX and NTO, such the near zero residual mass when these are burned as pure compounds increases to ~20 % of the initial mass when the formulation is burned.

Overall, the experiments showed that DNAN-based IHEs behave in a similar manner to TNT-based legacy explosives regarding emission of greenhouse gases, but worse in terms of solid residues. Ultimately, the body of work reported through this thesis has shown that traditional open burning of DNAN-based IHE could leave as much as 12 % (w/w) of unburnt explosive on the soil. We have therefore concluded that the open burning methodology adopted for TNT-legacy munitions should be avoided for disposing of IHE explosives.

Keywords: Open burning, laboratory-scale experiments, close-system experiments, open-system experiments, environmental impacts, DNAN

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PUBLICATIONS, CONFERENCES AND OUTPUTS

Publications and presentations:

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Temple, T.J., Ladyman, M., Cipullo, S., Galante, E., Coulon, F. and Mai, N. (2018) 'Comparison of the efficiency of extraction methods for Insensitive High Explosives constituents from different soils', *Journal of hazardous material*. Submission date: 08th August 2018

Galante, E., Mai, N., Ladyman, M., Gill, P.P. and Temple, T. (2018) Observations of the combustion behaviour of insensitive high explosives under low confinement, *Explosives Engineering - Oficial Journal of the Institute of Explosives Engineers*, September 2018, pp. 18–20. Available at: https://iexpe.org/information-library/publications/about-the-journal/

Temple, T., Ladyman, M., Mai, N., Galante, E., Ricamora, M., Shirazi, R. and Coulon, F. (2018) 'Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil', *Science of the Total Environment*, 625 Elsevier B.V., pp. 1264–1271. Available at: https://doi.org/10.1016/j.scitotenv.2017.12.264

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SERPD/2018 - Strategic Environmental Research and Development Program (SERDP), 28–30 November 2017, Washington-DC, USA

DSDS/2017 - Defence and Security Doctoral Symposium, 14–15 November 2017, Cranfield Defence and Security, Cranfield University, UK

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OME/2016 - Ordnance munitions and explosives symposium, 1 – 2 November 2016, Cranfield Defence and Security, Cranfield University, UK

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LIST OF ABBREVIATIONS

ADNT	Aminodinitrotoluene
ASE	Accelerated solvent extraction
BKW	Becker-Kistiakowsky-Wilson equation of state for gaseous detonation products
BSI	British Standards Institution
CAD	Central ammunition depot
CADMID	Concept, assessment, development, manufactory, in-service and disposal
CL-20	Hexanitrohexaazaisowurtzitane
CRREL	Cold Regions Research and Engineering Laboratory
DANT	Diaminonitrotoluene
DNAN	2,4-dinitroanisole
DSC	Differential scanning calorimetry
EFM	Environmental feature matrix
EIA	Environmental impact assessment
EIS	Environmental impact statement
EMAS	Eco-Management and audit scheme
EMP	Environmental management procedure
EMS	Environmental management system
EPA	Environmental Protection Agency (USA)
ERLCD	European reference life cycle database

ESS	Environmental screening and scoping
EU	European Union
FTIR	Fourier transform infrared spectroscopy
GC/FID	Chromatography/flame ionization detection
GCMS	Gas chromatography / mass spectrometry
HMS	Her Majesty Ship
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High performance liquid chromatography
HTPB	Hydroxyl-terminated polybutadiene
ICT	Fraunhofer Institute for Chemical Technology
IHE	Insensitive high explosive
IMX	Insensitive munition explosive
ISO	International Organization for Standardization
JSP	Joint service publication
LCA	Life cycle assessment
LCEA	life cycle environmental assessment
Mil Std	Military standard (USA)
MOD	Ministry of Defence
MSIAC-NATO	Munitions safety information analysis center of the north Atlantic treaty organization
NATO	North Atlantic treaty organization
NOx	Nitrogen oxides

NTO	3-nitro-1,2,4-triazol-5-one
PAH	Polycyclic aromatic hydrocarbon
PBX	Polymer-bonded explosives
PCDD/F	Polychlorinated dibenzofuran
PIB	polyisobutylene
POEMS	Process orientated environmental management system
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
REACH	Registration, evaluation, authorisation and restriction of chemicals
SERDP	Strategic environmental research and development program
SMART	Specific, measurable, achievable, relevant and time-bound
SOP	Standard operating procedures
SPR	Source - pathways - receptor
SSSI	Sites of special scientific interest
SVOC	Semi-volatile organic compound
TGA	Thermogravimetric analysis
TNT	2,4,6-trinitrotoluene
UK	United Kingdom
USA	United States of America
USS	United States Ship
VOC	Volatile organic compound

1 INTRODUCTION

Explosives are energetic materials that are designed to undergo chemical transformation, thus generating heat and pressure to do work. As such, they can be used for both military applications and in civil engineering, e.g. mining and excavation. Explosives can survive for decades under appropriate storage conditions, but ultimately they degrade and disposal is therefore necessary.

As for most solid wastes, the most common disposal method used for explosives at the end of their operational lifespan is the conversion to smaller and more stable molecules by burning, ideally CO_2 and H_2O. However, the efficiency of such reactions never reaches 100 %. Therefore, intermediate products are formed, and residues of the original explosives remain behind.

To minimize the environmental impact of such residues, explosives and other solid wastes should be incinerated at approved installations, usually in safe and isolated locations on an industrial site. The burning area is constructed in such a way that the soil is protected from direct contamination, e.g. by burning on a concrete substrate or removable metal trays (Figure 1-1).

Figure 1-1 Removable metal trays on concrete pads at an installation used for the burning of explosives [1]

In contrast to the controlled burning of explosives at approved disposal facilities, explosives that are used on military training ranges or in theatre are subject to less stringent controls, leading to environmental concerns. The most common method for the disposal of military explosives [2,3] (and other ordnance) involves the construction of a borehole and the incineration of unwanted materials encouraged by the addition of an accelerant, typically diesel fuel. The use of a bore hole avoids fragmentation and blast damage, and reduces the size of the safety zones required to protect personnel and equipment. The size of the borehole can also be selected to accommodate different quantities of material.

Despite the practical advantages of in-borehole burning, this approach raises serious environmental issues because burning on unprotected soil increases the severity of contamination caused by metal fragments and chemical residues. Furthermore, the design of the borehole limits oxygenation and heat flow, reducing the efficiency of burning. The poor reaction conditions also favour incomplete combustion (CO over CO_2, for example), which can cause accidents and deaths, like the death of three UK soldiers by CO poisoning at Central

Ammunition Depot (CAD) Kineton, UK, on 17th July 1989 [4,5] following routine shell disposal by open burning.

The frequent use of burning by the military since World War I has resulted in cumulative environmental contamination in military training areas, mainly reflecting the disposal of explosives containing trinitrotoluene (TNT). The degradation of TNT in the environment is well understood. TNT is stable, having a melting point of ~81 ºC (purity dependant) [6], which allows melt-casting under hot water. TNT is inexpensive compared to explosives such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX). TNT is therefore a staple in military ordnance globally, regardless of the environmental impact of manufacturing.

However, the accidental detonation of TNT-based ordnance carried by shipping in the 1960s (particularly incidents involving USS *Forrestal* and USS *Enterprise*) promoted interest in the development of safer ordnance based on explosives that were more difficult to ignite inadvertently. The discussion intensified following the sinking of the Royal Navy destroyer HMS *Sheffield* by the Argentine Navy during the Falklands war, when a single Exocet missile hit the ship causing uncontained fires [7], and the Doha Dash incident on 11th July 1991 [8], in which a malfunctioning vehicle heater accidentally initiated heavy carrier ammunition leading to a series of massive secondary explosions that ultimately caused losses far greater than combined the combat losses during the Second Gulf War.

New safety requirements were developed [9] to ensure that ordnance could withstand fires and other unintentional stimuli with minimal consequences, but would remain sensitive enough to ignite when triggered deliberately. The military began searching for new binders, and hence moved away from TNT. The use of polymers was considered, accounting for the success of polyisobutylene (PIB) as a binder for RDX [10], yielding the military staple demolition explosive known as

C-4. Many formulations known as polymer-bonded explosives (PBX) were produced, in which the explosive compound was embedded in a matrix generated by crosslinking polyurethane, in particular hydroxyl-terminated polybutadiene (HTPB), mixed with a curing agent. Although suitable for use in bombs, PBX formulations are not melt-castable and are not compatible with the existing infrastructure used to fill artillery rounds, most of which hence still use TNT as a melt-castable binder.

The scientific community has therefore started looking for melt-castable materials more suitable than cured polyurethane polymers [8], and 2,4-dinitroanisole (DNAN) [11] is a promising candidate. DNAN is a melt-castable and stable organic compound with an oxygen balance lower than that of TNT, yet it is highly energetic (its enthalpy of formation is –186.65 kJ.mol^{-1} [11]). Several formulations using DNAN instead of TNT have been tested recently, including insensitive munition explosives (IMX) such as IMX101 and IMX104 [12]. The latter is a mix of DNAN (~20%), RDX (~30%) [10] and 3-nitro-1,2,4-triazol-5-one (NTO, ~50%) [13], and is currently under consideration by the US military [14] and NATO as a new staple formulation to replace a 60/40 RDX/TNT mixture [15–18]. IMX104 has been tested and assessed for performance and stability, but only a few studies have addressed the environmental impact of ordnance and rounds containing IMX104. These studies found that some residual explosive is left in the soil, leading to further studies focusing on the fate and transport of this formulation (and its ingredients and degradation products) through the soil.

Very little is known about the environmental impact of the disposal of DNAN melt-castable formulations by open burning, how these chemicals interact with each other during burning, what gases and vapours are generated by burning, and whether simulations can be used to pre-empt the environmental impacts. One of the key problems is that the most effective strategies to monitor the gases and vapours released by burning explosives have yet to be established and validated. Because the empirical data have not been produced it has also been impossible to determine whether simulations of the burning process are informative and accurate. The broad aims of the work in this thesis are to address these key questions.

1.1 Aims and Objectives

The aim of this project is to investigate the environmental impact of open burning for the disposal of DNAN melt-castable formulations, and to determine whether it is possible to use calculations and simulations to predict these impacts more or less precisely. The experiments focused on newer insensitive high explosive (IHE) formulations (containing RDX, DNAN and NTO) using the flow of work presented in Figure 1-2.

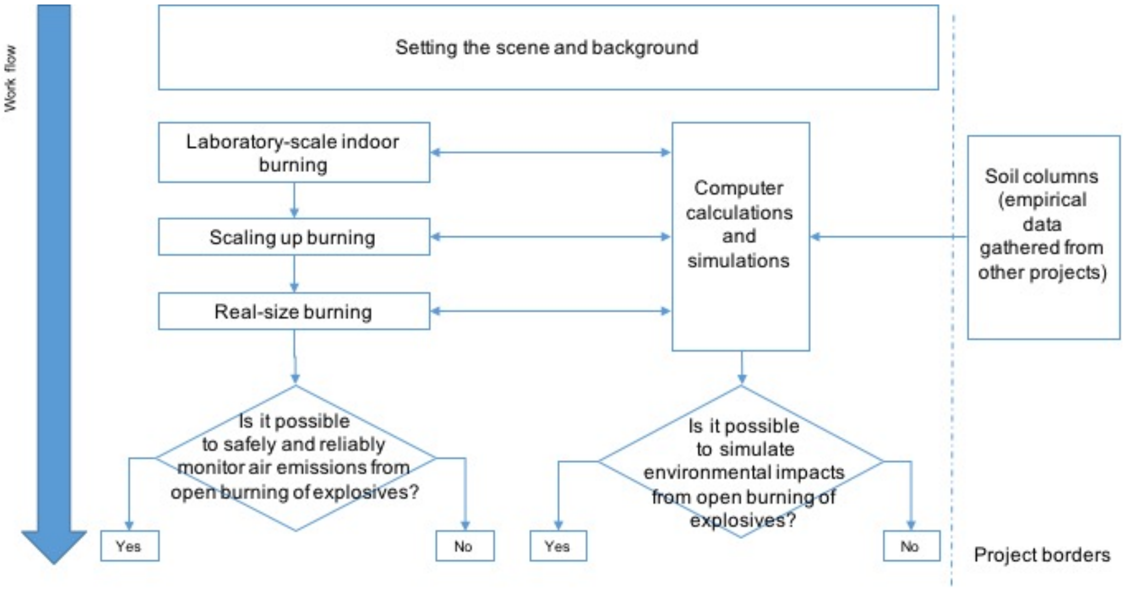

Figure 1-2 The flow of work described in this thesis.

The project addresses five key objectives:

1. Set the scene and contextualize the project by assessing the status of environmental management systems in the military.
2. Develop, test and implement a laboratory-scale method to generate, capture and analyse emissions from the burning of IHEs.
3. Carry out indoor experiments to generate a library of potential emissions from the combustion of tested IHEs.
4. Develop, implement and test an open experimental setup to analyse the solids and gaseous products produced when burning IHEs.
5. Investigate soil contamination caused by the disposal of IHEs by testing commercially-available software.

1.2 Thesis structure

This thesis is presented for assessment as a ‘thesis by publication’ based on the objectives listed above. The structure of the thesis is summarized in Table 1-1.

Table 1-1 Thesis structure and summary of the relationships among the published papers. Appendices and annexes are not listed.

Chapter	Paper	Objective	Title	Journal	Status
1	-	-	Introduction	-	-
2	1	-	Literature review	Journal of Aerospace, Management and Technology	Prepared to be submitted
3	2	1	The UK Ministry of Defence Project Orientated Environmental Management System (POEMS)	Propellants, Explosives and Pyrotechnics	Propellants, Explosives and Pyrotechnics, January 2017, Vol. 42 Issue 1 p36-43, 8p (1)
4	3	2	Small-scale combustion evaluation of DNAN-based insensitive high explosive by GCMS	Journal of the Total Environment	Prepared to be submitted
5	4	3, 4	Evaluation of open burning of DNAN-based insensitive high explosives	Journal of Hazardous Materials	Prepared to be submitted
6	5	5	Simulation of the transportation of DNAN and NTO through soil using HYDRUS 1D	SERPD/ Propellants, Explosives and Pyrotechnics	Presented/ Prepared to be submitted
7	-	-	Overall discussion	-	-
8	-	-	Conclusions and Further Work	-	-

(1) http://onlinelibrary.wiley.com/doi/10.1002/prep.201600193/full

1.2.1 Chapter 2: Literature Review

Chapter 2 provides a critical review of the relevant literature covering all the work described in this thesis. The chapter comprises six sections, the first five offering a literature analysis and the last highlighting the knowledge gap revealed by the review and linking it to the work described in subsequent chapters.

The first section of the literature review describes environmental management systems and life cycle analysis, switching focus in the second section to the final phase of an explosive's life cycle, i.e. disposal. In the third section, the review considers earlier work covering the environmental aspects and impacts of explosives and propellants, in particular impacts related to open burning. These first three sections reveal that most of the published work thus far concerns TNT, which is likely to be replaced by DNAN (mixed with NTO and RDX) in the future. The fourth section therefore provides relevant background information concerning these chemicals. The fifth section introduces the computer codes that have been considered to help predict the environmental impact of explosives, in particular the impacts caused by the open burning of energetic materials. The final section summarizes the literature review, and shows how each chapter of the thesis links together to form a coherent investigation addressing the knowledge gaps identified during the literature survey.

This chapter has been tailored and prepared for publication as a paper by Erick Galante, Melissa Ladyman, Nathalie Mai, Philip P. Gill and Tracey Temple and is currently ready for submission to the *Journal of Aerospace, Management and Technology* (www.jatm.com).

1.2.2 Chapter 3: The UK Ministry of Defence Project Orientated Environmental Management System (POEMS)

The Project Orientated Environmental Management System (POEMS) is the UK Ministry of Defence (MOD) bespoke environmental management system based on international standards ISO14001 and ISO14040. This chapter sets out the POEMS procedure for both experts and non-experts, and demonstrates the implementation of POEMS using a 105-mm howitzer artillery round as a case study. The chapter also discusses the CADMID model (conception, assessment, development, manufacture, in-service and disposal), pointing out that the disposal of explosives is still not fully understood and that there are several outstanding environmental issues, providing the motivation for this entire thesis.

This chapter was published as a paper by Erick Galante, Tracey Temple, Melissa Ladyman and Philip P. Gill in *Propellants, Explosives and Pyrotechnics* (http://onlinelibrary.wiley.com/doi/10.1002/prep.201600193/epdf).

1.2.3 Chapter 4: Small-scale combustion evaluation of DNAN-based insensitive high explosive by GCMS

The direct monitoring of air emissions, particularly gaseous products from the open burning of explosives, is highly challenging because the effectiveness of monitoring systems requires knowledge of the products, but the chemical species present in the gaseous products released from burning explosives are not always known. The literature provides many examples of decomposition products of explosives, but most of the data were obtained by differential scanning calorimetry (DSC), which helps to determine the chemical decomposition kinetics of energetic materials, not environmental impacts. But the gaseous products released from burning explosives are largely uncharacterized.

To address this knowledge gap, the work discussed in Chapter 4 consists of a simple and reproducible laboratory experiment (10–20 mg of explosives) that generates gaseous products from burning explosives followed by gas chromatography/mass spectrometry (GCMS) analysis. One IHE formulation containing RDX, NTO and DNAN was chosen, and its components were used as a case study, mainly because it is a novel formulation still in the initial phase of its life cycle, i.e. munitions containing this IHE have entered service during this decade.

This chapter has been prepared for publication as a paper by Erick Galante, Nathalie Mai, Tracey Temple, Melissa Ladyman and Philip P. Gill. It has been prepared for submission to the journal *Science of the Total Environment (STOTEN)*.

1.2.4 Chapter 5: Evaluation of the open burning of DNAN-based insensitive high explosives

Chapter 5 takes the information generated in the 10–20 mg scale closed laboratory experiments described in Chapter 4 and advances knowledge by designing and implementing different sizes of open-system experiment to generate, collect and analyse emissions from burning explosives. The aim is to determine how the open burning of newer IHE material can impact the environment, as well as to demonstrate the safe monitoring of air emissions during the open burning of explosives.

This chapter has been prepared for publication as a paper by Erick Galante, Nathalie Mai, Tracey Temple, Melissa Ladyman and Philip P. Gill. It has been prepared for submission to the *Journal of Hazardous Materials*.

1.2.5 Chapter 6: Simulation of the transportation of DNAN and NTO through soil using HYDRUS 1D

One final issue raised during the disposal of explosives by open burning is soil contamination. The soil can be contaminated directly by ash and solid waste, but also indirectly by the precipitation of fumes and smoke. Given that soil contamination can lead to groundwater contamination and subsequent transfer to other locations, it is necessary to act pre-emptively and minimize underground contamination.

Chapter 6 describes the use of HYDRUS 1D, a software platform that performs calculations based on Fick's law and Navier–Stokes equations, to characterize the dispersion of DNAN and NTO through the soil, compared to empirical experimental data. HYDRUS 1D was selected because it was designed to model the dispersion of pesticides through soil in an agricultural context, but a small number of published articles already describe its application to explosives. However, to the best of our knowledge, the simultaneous modelling of the transportation of multiple contaminants has not been attempted before.

This chapter was published as a Strategic Environmental Research and Development Program (SERDP)/2017 conference paper and has since been updated and expanded. The expanded version is presented in this thesis and has been prepared as a paper by Erick Galante, Nathalie Mai, Tracey Temple, Melissa Ladyman and Philip P. Gill for publication in the journal *Propellants, Explosives and Pyrotechnics*.

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2 LITERATURE REVIEW

Military services must deliver stability and security, as well as projecting force where necessary. This involves the deployment of ordnance and explosives, which is not possible without adequate training. To comply with civil regulations, and to satisfy the demands of taxpayers, the ordnance and explosives must also be handled in an environmentally sustainable manner.

In a civilian context, environmental awareness and responsibility are achieved by implementing an environmental management system (EMS), typically in compliance with ISO 14001:1996 [1] (and later versions), which covers "environmental awareness and environmental aspects and impacts control" [1], and ISO 14040:2006 [2], which covers life cycle assessment (LCA) [2]. These guidelines are not suitable for the dynamic military environment, a limitation addressed by the UK Ministry of Defence (MOD) through the introduction of a bespoke platform known as the Project Oriented Environmental Management System (POEMS), which is based on ISO 14001:1996 [1], ISO 14040:2006 and the US Department of Defense Military Standard 882 (MIL-STD-882-E) covering risk assessment [3]. POEMS was designed to cover the risks and environmental impacts of acquisition projects and services, although it can also be used to consider the environmental aspects and impacts of ordnance throughout the product life cycle. This is achieved by aligning it to the MOD's LCA strategy, which is the concept, assessment, development, manufacturing, in-service and disposal (CADMID) cycle, as elaborated in Section 2.1 of this literature review.

The environmental impact of ordnance can only be determined by the full implementation of POEMS [4–6]. The first three phases (concept, assessment and development) have a minimal impact, so environmental efforts have focused on the fourth phase (manufacturing) for several decades [7–10]. However, the last two phases (in-service and disposal) have been largely overlooked.

Military services have been training with 2,4,6-trinitrotoluene (TNT)-based explosives since before World War II, and this is covered by the in-service phase of CADMID. The soil and groundwater of training ranges have been contaminated with TNT-based explosives [11–18], but the environmental impact of disposal has not been fully investigated. Several disposal methods are available (Section 2.2), including the common approaches of open burning and open detonation. The impact of open burning in terms of air quality is considered in detail in Section 2.3. But most previous studies covering this topic have only considered TNT and its impact on soil.

Furthermore, TNT-based formulations are being replaced with insensitive high explosives (IHEs), such as formulations in which 2,4-dinitroanisole (DNAN) is used instead of TNT as the melt-castable binder. Because such formulations have only recently been considered for service, the body of literature concerning these substances is not as extensive as that available for legacy explosives. The available literature describing the topic of IHEs is considered in Section 2.5.

Finally, as this literature review shows, most of the available data were gathered either from contaminated ranges or through expensive empirical experiments. This means that the damage has already been done before the impact can be assessed. It would be preferable to predict the environmental impact of IHEs in specific scenarios and locations. This requires prediction software that considers not only the behaviour of the explosives but also the influence of different environmental conditions. There are some software platforms that could, in the near future, be valuable as tools to predict environmental impacts caused by the open burning of the latest generation of IHE materials (Section 2.6).

The literature review is brought to a close by setting out some partial conclusions and describing how the knowledge gap in the current literature led to the experimental strategy and work plan described in the rest of this thesis.

2.1 Environmental Management Systems/Life Cycle Analysis

For many years, environmental management has been limited to post-damage evaluation, leaving mitigation and remediation as the only options for returning the environment to its original state. Given recent technological advances and increasingly strict regulation, relying solely on mitigation is no longer acceptable. Therefore, to be pre-emptive, companies and enterprises can be required by legislation to implement an EMS – a comprehensive, planned and documented system that integrates procedures and processes for monitoring and reporting environmental performance. The primary aim of an EMS is to identify any environmental aspects (causes) and impacts (effects) by scrutinizing activities that may impact the environment.

An EMS can be implemented around two international standards: ISO 14001:1996 [1], which presents guidelines for the assessment of environmental impacts, and ISO 14040:2006 [2], which covers LCA. The latter is a technique used to assess the environmental impact of a product throughout its life cycle, from the extraction of raw materials to disposal, often described as "cradle to grave". More recently, LCA concepts are increasingly moving towards the "cradle to cradle" approach, which integrates the end-of-life product back into the manufacturing process [2,19,20].

Both ISO 14001:1996 [1] and ISO 14040:2006 [2] were created around fixed locations and industrial sites, which does not match the dynamic aspects of military applications. To address this gap, the UK MOD created POEMS [4–6], a military-orientated EMS that incorporates aspects of both ISO 14001:1996 and ISO 14040:2006 as well as safety aspects from MIL-STD-882-E [3]. Chapter 3 of this thesis has been published and presents a case study to address the use of POEMS in detail.

2.2 Life Cycle: Disposal Procedures

The environmental fate of explosives has been associated with disposal practices since before World War II [21]. Any product or process has a life cycle covering all stages from cradle to grave, as espoused in general by ISO 14040:2006 [22,23] and specifically for UK MOD by POEMS as discussed above [4–6]. POEMS uses the CADMID cycle: concept, assessment, demonstration, manufacture, in service, and disposal [5]. This typically runs from cradle to grave (Figure 1-1), but if practicable it can also be modified to run from cradle to cradle.

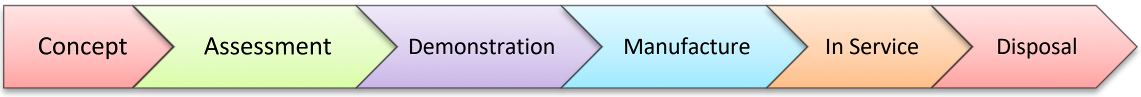


Figure 2-1 The CADMID cycle

POEMS addresses CADMID through eight core procedures. The first four allow the assessment of potential causes of environmental damage (aspects) and their effects (impacts) at each relevant step in the CADMID cycle. The next three describe how to develop an environmental management plan (EMP) spanning the life cycle of the equipment or activity. The final procedure is a continuous review process to ensure any changes are captured during the life cycle of the equipment. Regardless of the CADMID phase, POEMS should be carried out for all future phases. Any in-service equipment should have an EMP that details all in-service activities, including maintenance, mid-life upgrades and ‘business as usual’ processes, as well as a disposal plan.

2.2.1 Disposal Methods

The disposal of ordnance and explosives has been defined as the process of rendering inert or removing the energetic ingredients contained in munitions that are defective, obsolete, unsafe, or otherwise no longer required in the military inventory [24,25]. Disposal can also include the removal of aging ingredients when the casing is refilled with new explosives or propellants.

One of the first patents addressing the need for non-polluting methods to dispose of explosives and propellants considered a chemical disposal strategy [26]. This 1973 document claimed that explosives and propellants could be destroyed in a safe and non-polluting manner by mixing them with a hot molten salt, preferably eutectic mixtures of NaOH-KOH and Li_2CO_3-Na_2CO_3-K_2CO_3. To the best of our knowledge, there are no recent publications describing the use of this method in practice, and the equipment requirements would render the method too expensive and impractical for use in military scenarios.

A patent issued in 1995 described an improved non-pyrolytic disposal process for nitrocellulose-based explosives and rocket propellants, in which the explosive and propellant particles would be digested by contact with an aqueous solution containing 5–20 % NaOH maintained at 50–100 ºC under constant agitation [27]. The inventors claimed this process would minimize environmental concerns brought about by the open burning of high-energy materials, but did not consider the environmental impact of transporting materials to the facility nor the disposal of the digested waste. Two further patents describing chemical disposal methods were granted in the same decade. The first, granted in 1996 [28], claimed a one-step process to denitrify explosives and propellants, reclaim the evolved nitrogen and modify the carbon-rich residue into chemicals suitable for use as plant fertilizers. To the best of our knowledge, there is no evidence that this method was ever developed, perhaps due to financial constraints. The second, granted in 1998, claimed a method for the decomposition of explosive materials into water-soluble products, which can be disposed of using thermal or biochemical processes [29]. This approach appears to require an ultimate burning step, therefore providing no advantage over open burning in terms of post-burning residues and the number of steps. More recently, a hydrolysis-based method was proposed for the disposal of industrial propellants, but this produces ammonia, hydrogen, nitrogen oxide gases, soluble inorganic and organic salts, and insoluble polymeric and metallic materials, indicating that the emissions to air could have a similar impact to open burning [29].

Other patents have considered heat-based means of disposal rather than the induction of chemical transformation by adding other compounds to the mix. In 1974 a patent was granted claiming that incineration would be a suitable alternative to open burning [30]. It described a process in which the waste propellant or explosives were mixed with water to form an aqueous suspension (thus improving safety), which would then be burned in a rotary incinerator under conditions that allowed the evaporation of water to dry the particulate matter, followed by ignition. The combustion gases would be scrubbed with water before emission to the atmosphere, which would make this method more environmentally friendly than open burning, regardless of the higher costs and installation requirements.

In 1978, the US Environmental Protection Agency (EPA) [31] compared known disposal methods and issued a report (EPA-600/2-78-012 [25]) proposing six categories of disposal: washout, deactivation furnace, open detonation, open burning, new developments, and advanced technology in chemical disposal. The deactivation furnace concept relates to the 1974 patent described above [30].

In 1995, a patent was granted claiming a new process for the combustion of explosive substances within a closed reactor, in which combustion would be initiated by an open flame [32]. In this system, the combustion gases would be removed from the combustion zone to cool and mix with air before returning to the combustion chamber. A further patent granted in the same year claimed an incineration tray for burning explosives, characterized by a vat constructed from heat-resistant material mounted on a base plate [33]. The method described in the first patent involves burning explosives within a controlled chamber, and is therefore more environmentally friendly than the second method, but it also requires more complex machinery, so the method described in the second patent is closer to the current approach favoured by industry [33].

In 2002, Duijm [34] addressed what he called “traditional ways” to dispose of ammunition, which included open burning and open detonation. These are performed in the open air, and the waste products (solid residues, dust, and combustion gases) are directly emitted to the environment without any control or treatment (although sometimes the solid residues are collected). Alternatives discussed in the same article included closed detonation, closed incineration primarily using existing stationary facilities like a rotary kiln, and fluidized bed combustion. Other alternatives include dumping at sea (which is now banned) and detonation in abandoned mines (which is location-dependent) [35], so only open burning and open detonation are still considered acceptable.

Open detonation is not carried out as often as open burning, and is used only to dispose of explosives that cannot be burnt for safety and security reasons (open detonation generates blast and fragments). It may require a detonator and primer, according to the sensitivity of the explosive [36]. In contrast, open burning is a classic approach which is carried out in places where there is no danger of fire spreading. The method involves digging a trench or channel whose dimensions are governed by the quantity of material for disposal. The trench is then loaded with unwanted explosives and/or ordnance and burned, often using an accelerant such as diesel fuel [36,37]. The clearance area is at least 20 x 20 m [36,37] and contains an excavated channel at least 50 cm wide and 25 cm deep [36,37]. The quantity of burnt munitions is governed by the recommendations of the manufacturing plant (where known) and otherwise by instructions drawn up by the military service. The use of a bore hole avoids fragmentation and blast damage, and reduces the size of the safety zone required for the protection of personnel and equipment. Open burning was confirmed as the preferred disposal approach following a 2009 LCA study carried out by the Swedish Army [38] and this has been echoed more recently by the US Army [39] due to the inherent simplicity and safety of this method.

Open burning and, to a lesser extent, open detonation have therefore become the standard approaches for the disposal of explosive materials and propellants due to the combination of convenience, scalability and applicability in a range of different operational settings. Therefore these two methods are described in more detail below.

2.2.2 Guidelines for Open Detonation and Open Burning

According to guidelines developed by Tetra Tech [40], many waste explosives and ordnances are too dangerous for conventional methods of hazardous waste management, and open burning or open detonation must be used instead. Specifically, US Army Pamphlet 385–64 (Ammunition and Explosive Safety Standards) [39] states that the open burning of hazardous waste is prohibited except for the open burning and detonation of waste explosives. Waste explosives include waste that has the potential to detonate, and bulk military propellants that cannot be safely disposed of through other modes of treatment [39].

US Army Pamphlet 385–64 [39]mandates that open burning is to be conducted only at sites selected particularly for this purpose. Open burning and open detonation areas for ammunition and explosives must be separated from other facilities. They must also make use of burning pans or trays appropriately constructed and grounded. Burning pads must be constructed from concrete and covered with a minimum of four inches of bed sand to protect the concrete. When the user intends to dispose of the sand, tests for hazardous waste characteristics are required.

US Army Pamphlet 385–64 [39]also states that burning sites must have a means to collect remnants, ultimately to dispose of any hazardous waste produced during the operation. Moreover, the burning sites must ensure that the items to be burned are spread evenly over the burning pan or pad, so that the depth of the material does not exceed 3 inches. Items larger than 3 inches in diameter may be burned, provided they are stacked only one item high. Although not clear in the document, the limitation to 3 inches is a safety restriction applied to avoid pressure building up, thus minimizing the risk of an unintended transition from burning to detonation.

2.3 Environmental Aspects and Impacts

The concept of “environmental aspects and impacts” is derived from health and safety studies, particularly risk assessment tools such as MIL-STD-882-E [3]. The original version of this standard dates back to 1972, when it was published by the US Department of Defense [41], and it proposes that risk can be understood as a combination of frequency and severity. More recently, OHSAS 18001:2007 [42] provided guidelines for a health and safety management system, and ISO 31000:2009 [43] and the more recent ISO 31000:2018 [44] proposed risk assessment methods also using the same definition of risk.

As environmental awareness has increased, so has the importance of implementing an EMS such as ISO 14001:2004 [1] and, more recently, ISO 14040:2006 [2,19]. The focal point of the ISO 14040 series is to carry out LCA for products and services, assessing their impact by mapping inputs and outcomes, both qualitative and quantitative. Several software platforms are available for the quantitative calculations, including OpenLCA [45], SimaPro [46] and Gabi [47].

The LCA can be used as a methodology to determine environmental problems in multiple scenarios [48]. It can be considered a specific elaboration of a generic environmental evaluation framework [20] whereas an environmental impact assessment (EIA) is a procedure rather than a tool, within which LCA may certainly be a useful component. In strategic and project-related EIAs, environmental comparisons of process and abatement alternatives may be relevant. Although these alternatives may lead to different emissions and effects at the location of the process itself (which is usually the focus in project EIAs), they can also influence the demand for activities upstream and downstream in the production chain. Including such secondary effects in an EIA, which may be necessary for a proper comparison of alternatives, requires a systematic approach that takes into account all relevant effects, and this is the essential basis of LCA. A review of five different case studies (crude oil refinery, installations for the storage and disposal of radioactive waste, construction of long-distance railways and airports, installations for the treatment of hazardous waste, and transport pipes for gas, water and other liquids) confirmed the feasibility of including elements of LCA in the context of an EIA [20].

Few LCA studies concerning military environments have been described in the literature, mostly because the available LCA databases were created around industrial applications and chemical standards, making them unsuitable for military applications. The Swedish army reported an LCA for the destruction of obsolete ammunition [38]. They used established LCA databases to compare open burning, open detonation, static kiln incineration with air pollution control combined with metal recycling, and a combination of incineration with air pollution control. They concluded that open detonation with or without metal recycling was the worst alternative from a life cycle perspective, because it compromises any material recycling. In a further study concerning the LCA of a military explosive production unit [49], the OpenLCA platform [45] was combined with the European Reference Life Cycle Database (ERLCD) to help build a library that could determine the environmental impact of manufacturing hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). This revealed that ecotoxicity and global warming (related to CO_2 generation) are the worst impacts. Another study considered the environmental LCA of a pre-fragmented high-explosive grenade [50], identifying aspects of the life cycle with the largest environmental impact, suggesting improvements, comparing different approaches for the waste management of munitions, and demonstrating the application of LCA to munitions. It appears that no LCA work on unburnt munitions has been published to date.

Historically, most efforts to understand and control the environmental impact of explosives have focused on manufacturing, which is an industrial process [51,52]. These efforts were used to ensure the compliance of manufacturing plants rather than to develop a scientific understanding of the environmental impact of explosives. However, the environmental and toxicological impact of munitions during their life cycle has become more important to nations and the international community [53], in particular since changes to the European chemicals legislation. Specifically the REACH legislation (Registration, Evaluation, Authorisation and restriction of CHemicals) [54] requires a better understanding of the chemical toxicity of energetic materials and compositions. Researchers at the Munitions Safety Information Analysis Center of the North Atlantic Treaty Organization (MSIAC-NATO) therefore issued a report [53] in which a case study was developed using two energetic material compositions (Comp B and PBXN-109). They claimed to have reviewed the life cycles of both materials from manufacture through to disposal. In their assessment, they followed the UK CADMID approach [5] from the POEMS methodology [4,5], combined with the USEtox platform to provide LCA toxicology parameters for comparisons [55–60]. Ultimately, this report did not fully address all the CADMID phases. It focused on bioaccumulation and toxicity, as well as applying USEtox as a source toxicity assessment of chemicals left unattended in the environment.

Research conducted at the Cold Lake Air Weapons Range in Canada evaluated the direct environmental impacts of bombs, rockets, strafing, and open burning/open detonation on the quality of soil, groundwater, surface water, and lake sediments [61]. There was evidence that metal contamination in soil may be related to the use of bombs (Cd, Cu and Pb), strafing (Cu), and rockets (As, Ba, Cd, Cr, Cu, Fe, Ni, Pb, U, V and Zn). TNT was abundant in the soil, whereas RDX accumulated to higher levels in groundwater, along with aluminium, nitrate, and ammonium perchlorate from live bombing or rockets. This research helped to build a library of potential soil and groundwater environmental impacts from the disposal of ordnance, but the data are only valid for the parameters and materials tested.

Another study addressed the effects of undetonated artillery shells and mortar rounds filled with RDX and TNT, leaving explosive residues unattended on the soil [62]. The authors found that particles in the >12.5 mm size fraction were predominant among the residues and that the RDX:TNT ratio in the original Comp B was conserved. Although the information about residual solids remaining after detonation is a strong indication that the same pattern would be displayed during open burning, the preservation of the RDX:TNT ratio in Comp B is particularly interesting because it suggests that each explosive behaves independently in the mixture.

Other studies have focused on energetic residues from the disposal of gun propellants in the field [63]. The Cold Regions Research and Engineering Laboratory (CRREL) burned propellants containing energetic compounds such as nitroglycerine and 2,4-dinitrotoluene (2,4-DNT) on a snow pack and in a pan surrounded by snow, aiming to demonstrate that climate, especially in winter, can play a significant role in the effectiveness of disposal methods. They reported the recovery rates from double-base mortar propellant disposed of in a burn pan (0.21 %), on frozen soil surrounded by snow (5 %) and on snow (18 %), showing how the disposal setup changes its efficiency. The experimental setup was designed to assess potential soil contaminants by collecting and testing the snow after burning. Although the experiment was interesting, by using snow as a matrix the authors omitted any interaction between the contaminants and the soil, addressing only potential leftover contaminants. Moreover, their setup was not designed to analyse gaseous emissions, even though some gases could have been trapped in the snow [63]. The same CRREL group later investigated the contamination caused by live-fire training on snow, as a way to control for soil interference when measuring explosive residues [64]. Both studies focused on the potential impact on the soil, and as such gases and vapours were not considered, therefore ignoring any impact on air quality. The CRREL group also assessed energetic residues from the detonation of 60-mm and 81-mm mortar rounds loaded with IMX104 [65]. Their experiments showed that ~0.5–1.5 % of the payload was left unreacted, which suggests that open burning would leave at least the same mass of residues.

More recently Hristov [12] has published a work addressing training and test ranges contamination levels of explosives and heavy metals in soil and groundwater, which was classified as a serious international concern. This work conduced a survey in several ranges (Table 1-1), concluding that contaminations are caused from both high and low order detonations, which showed that environmental impacts might occur even when the ordnance functions as indented.

Table 2-1 Mass of explosive deposited from High-Order Detonations and Low-Order Detonations [12]

	High-Order Detonations			Low-Order Detonations		
Weapon system	**Explosive**	**Percent of original explosive deposited**	**Mass deposited [mg]**	**Explosive**	**Percent of original explosive deposited**	**Mass deposited [mg]**
Mortar 60 mm	RDX	3x10^{-5}	94	Composition B	35	67
Mortar 81 mm	RDX	2x10^{-3}	8500	Composition B	42	300
Mortar 81 mm	TNT	3x10^{-4}	1100			
M67 Hand Grenade	RDX	2x10^{-5}	25	-	-	-
Howitzer 105 mm	RDX	7x10^{-6}	95	Composition B	27	620
Howitzer 105 mm	TNT	2x10^{-5}	170			
Howitzer 155 mm	RDX	5x10^{-6}	310	TNT	29	2000

From all these studies, there is now a better understanding that explosives and propellants are not always fully consumed when detonated or burned in ranges, potentially leaving residues on the soil. Therefore, the fate and transport of the residues must be understood to allow for a full LCA [66]. Review articles published in 2009 [67] and 2012 [16] describe contemporaneous studies concerning the fate and transport of legacy explosives and propellants, i.e. the combination of decomposition, chemical and biochemical transformation, and the transport of chemical species through soil, air and water. The first article considered transformation routes for TNT, DNTs, aminodinitrotoluenes (ADNTs), diaminonitrotoluenes (DANTs) and cyclic nitramines such as RDX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and hexanitrohexaazaisowurtzitane (CL-20). The second article discussed the distribution and fate of military explosives and propellants in soils worldwide, covering manufacturing, military training and military operations, and the open burning/open detonation of obsolete munitions. The article included data on TNT, RDX and HMX, as well as the propellant ingredients nitroglycerine, nitroguanidine, nitrocellulose, 2,4-DNT and perchlorate. More recently, the life cycle environmental assessment (LCEA) of military munitions [68] revealed that deposits on ranges from detonations and disposal during training are only peripherally examined by the assessment of combustion products derived from closed-chamber testing or models [68].

The legacy explosives TNT, RDX and HMX have been in service since before World War II, which has resulted in the significant contamination of soil and groundwater [69]. The fate and transport of these materials has therefore been studied in detail. For example, a series of experiments was conducted to assess the adsorption and degradation behaviour of RDX, HMX, TNT and DNT and the impact of pH, ionic strength and dissolved organic matter on sorption in two volcanic soils on a former military training range in Hawaii, USA [70]. This study used the agriculture-focused software HYDRUS 1D [71,72] to try to predict the fate and transport of these explosives, indicating that HYDRUS 1D is a promising tool for the prediction of contamination caused by TNT and HMX.

Taken together, these studies [11–18,61–64,67] showed that unattended and uncontrolled explosives will be transformed and/or transported through soil, leading to groundwater contamination and further environmental damage. However, although these studies addressed the fate of ground residues comprehensively [16,61–64,67], they did not consider gases and vapours, thus ignoring the direct impact of burning or detonating explosives on air quality, as well as indirect soil contamination caused by the dispersion and precipitation/condensation of these gases and vapours.

For completeness, it is necessary to address the fact that explosives have dual-applications and can used both in military and civil activities. In the later, emulsions, slurries and ammonium-nitrate fuel-oil (ANFO) explosives play crucial roles in mining, quarrying, tunnelling and many other infrastructure activities [73]. These explosives raise environmental concerns, in particular regarding atmospheric pollution, which includes emission of harmful gases, dust, explosive residues and particulate matters (PM) [74–81]. In mining operations the major gaseous load from corresponds to NOx, sulfur oxides, carbon oxides, photochemical oxidants, volatile organic compounds (VOCs) and methane [78,82–84].

Mining explosives cans also impact water, land and soil. The first refers to drop and alteration in groundwater table [78], whilst the Land and soil contamination refers to physical subsidence and topographical disturbances [78,85–87], as well as soil contamination via chemical channel [88], where the common contaminants include heavy metals and inorganic ions that can persist long after mine remediation [88–91]. Other environmental issues explosives usage in mining include thermally-related losses, waste treatment and disposal, ecological imbalance, noise and vibration pollution, resettlements, habitat loss and fragmentation, and economic waves [78][92]. Overall, however, the main environmental and health issue related to mining operations with explosives is the high NOx concentration (500 ppm) observed in the plumes from blasting, which exceeding up to 3000 times the international standards for this chemical [73–81].

2.4 Environmental Impact of Open Burning / Detonation

Emissions from open burning sites are more extensive (larger areas and volumes of gases) than those produced by the well-controlled combustion of materials such as paper, animal carcasses and automobile shredder fluff fires. Volatile organic compound (VOC) and polycyclic aromatic hydrocarbon (PAH) data are available for many of these sources, and non-PAH semi-volatile organic compound (SVOC), carbonyl and polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/F) data are available for others [93–97]. These studies revealed that, for common types of solid waste, biomass open burning typically produces higher levels of carbonyls than anthropogenic solid wastes, probably due to the oxygenated structures derived from the thermal decomposition of cellulose. This highlights the importance of having acceptable test data for PCDD/F and PBT emissions from open burning so that the contributions of sources to the overall PCDD/F and PBT emissions inventory can be better quantified. The studies listed above did not attempt to determine impacts from the open burning of explosives or propellants.

In terms of environmental effects and human health, the classic methods for the disposal of explosives have disastrous impacts: heavy metal emissions (lead, antimony and barium), toxic gas emissions (HCl, SO_2 and HCN) [98], the emission of stable toxic substances such as asbestos, and the contamination of soil and groundwater [98]. For personnel dealing with munitions disposal, and also the inhabitants of nearby towns and cities, this means an increased risk of cancer and heavy metal poisoning in addition to the direct risks posed by the explosive materials [24,99,100]. However, the explosives themselves can be toxic and harmful [13], as well as its plumes and smokes [14].

The quality of data concerning the fate and transport of explosives and propellants depends on which analytical tools are used. In the context of soil experiments, the extraction method is also important, because this determines which IHE components can be detected. Accordingly, a two-stage extraction procedure was developed and tested on several soil types to improve the minimum detection limits for all IHE compounds and to reduce the influence of soil composition on recovery [101]. The first extraction involved mixing the soil with 30:70 acetonitrile (ACN) in 0.1% TFA : nanopure water, cooling to 4 °C, sonicating for 18 h before centrifuging at 2900 rpm for 10 min. The second extraction involved the addition of 10 ml ACN to the previously extracted samples, which were sonicated and centrifuged as a above and analysed following the Method EPA 8330B [102].

The analysis of soil samples, particularly in soil column experiments, has provided useful data about both legacy explosives and newer IHE formulations [17,103–107]. For example, the fate and transport of nitroaromatic and nitramine explosives in soil following open burning and open detonation have been studied in the US, confirming that open detonation on ranges is likely to contaminate the upper layer of soil with RDX, HMX and TNT (as well as forms of DNT) based on the leachate collected from soil column experiments [17,103]. Similarly, the dissolution, sorption and phytoremediation of the IMX101 components DNAN, 3-nitro-1,2,4-triazol-5-one (NTO) [104,105], and nitroguanidine has been investigated, indicating that their dissolution, if unattended, may lead to the contamination of underground water sources (directly from the explosive or from its biodegradation products).

A larger-scale study looked at heavy metal (specifically lead) emissions from the open burning of artillery propellants because lead foils are used in propellant charges and are sewn directly to the charge cloth bags [108]. The uncontrolled burning of such propellants was shown to promote the accumulation of 2,4-DNT, nitroglycerine and lead on the soil surface. This study indicated that most of the residual lead was found in the burn trays (77 %) and nearby soils (21 %), which suggests that lead-containing emissions can cause the precipitation of lead compounds near the burning area, but the nature of the gaseous emissions was not addressed directly.

Touching on the topic of air emissions, a hybrid-optical remote sensing method (hybrid-ORS) was developed to assess the particulate matter (aerodynamic diameter ≤10 μm, PM10) from the open burning/open detonation of nitrocellulose and nitroglycerine or TNT [109]. It was possible to measure the particulates, but with uncertainty levels that could only be quantified for specific measurements, which limits the application of this method. The authors used optical sensors to detect the intensity of a light beam passing through the smoke, and from these data calculated the particle density. This technique was not suitable for the analysis of vapours or gases because it did not determine the individual chemical species. The overall aim of this work was to assess the method, which for TNT involved the detonation of 50 lb and 100 lb samples.

For non-explosive fires, laboratory-scale methods are designed around a closed chamber in which the fuel is exposed to a constant source of heat, including methods such as the smoke density chamber (ISO 5659-2) [110], the controlled atmosphere cone calorimeter [111], the fire propagation apparatus [112], the non-dynamic tube furnace [113], and the steady-state tube furnace [114]. The smoke density chamber [110] is the most widely used fire-testing apparatus, and is stipulated in the smoke-detection regulations of most countries, whereas the controlled atmosphere cone calorimeter [111] is probably the most widely used apparatus for the measurement of properties such as ignitability and heat release rate. The fire propagation apparatus [112] is similar in principle to the cone calorimeter but the fire zone is contained within a vertical silica tube, allowing better mixing of the fuel oxidant and avoiding contact with the heaters. The non-dynamic tube furnace [113] thermally decomposes a small sample in a furnace with a metered air flow, whereas the steady-state tube furnace [114] feeds the sample into its hot zone at a fixed rate, under a controlled air supply. Moreover, these techniques commonly couple the gaseous exhaust to gas chromatography/mass spectrometry (GCMS) apparatus to assess its composition. However, these methods cannot easily be used to measure emissions from burning explosives because the quantities required by these techniques could make the experiments unsafe.

In 1977, Woolley and Fardell [115] described the composition of smoke caused by the burning of non-energetic materials. They carried out controlled burning experiments using a special burner system and full-scale fires to induce material decomposition, followed by GCMS for product analysis. In contrast, most of the data concerning the behaviour of explosives has been gathered for small samples (in the milligrams range) by differential scanning calorimetry (DSC), which is safer because it involves thermal decomposition rather than violent exothermic reactions [116–119]. For example, DSC was used to study the thermal decomposition of potential replacements for the primary explosive tetrazene [120]. Nitrogen gas was continuously purged throughout the DSC scans, which were carried out at heating rates of 2.5–40 K.min^{-1} over a temperature range of 340–600 K. However, instead of analysing gaseous decomposition products, the authors assessed decomposition kinetics [81].

Similarly, the thermal decomposition behaviours of HMX, RDX, and NTO have been determined [119] based on DSC and thermogravimetric analysis (TGA). However, the focus of this study was solely to determine Arrhenius kinetic parameters (such as activation energy and reaction order), missing the opportunity to observe and analyse gaseous emissions. Nevertheless, the accurate use of TGA techniques revealed that solid-phase NTO thermally decomposes at temperatures above 200 °C without melting. This behaviour has been studied in more detail [121–124], including analysis by fast thermolysis/Fourier transform infrared (FTIR) spectroscopy [122] and T-jump/FTIR [123] to determine the kinetic constants for decomposition of flash-heated NTO. The T-jump/FTIR technique involves a temperature jump induced by laser followed by FTIR spectroscopy to find hidden intermediates [124]. This approach has been used to assess the rapid the thermal decomposition of nitramines such as HMX [125], the surface chemistry of a propellant and other energetic materials burning at high temperatures, including NH_4ClO_4, NH_4NO_3, $NH_4[N(NO_2)_2]$, HMX and RDX [126], and Arrhenius parameters for the pyrolysis of organic polymers [124]. Ultimately, the work published by William and Brill [121] determined the global decomposition and sublimation kinetics of NTO and the corresponding energies of activation, but did not address the gaseous emissions.

In summary, a large body of literature has accumulated concerning the thermolysis, thermal decomposition and decomposition studies of nitroaromatic explosives and other energetic materials, such as HMX, RDX and NTO [119,121,127–139]. In particular, the decomposition of NTO [119,121,129,131] has been studied by various techniques, such as spectroscopy, chromatography, thermochemical and photothermal analysis. All these studies concluded that heated NTO sublimes and condenses once thermolysis is completed, but there appears to be no consensus regarding the initial decomposition product and hence the decomposition pathway of NTO. Furthermore, none of the studies considered the gaseous emissions from NTO during pyrolysis, heating or burning.

Thermal decomposition and combustion-like pyrolysis [124] have also been assessed by controlled flash pyrolysis and real-time detection of the vaporized products (FTIR spectroscopy). This approach has been used to analyse RDX [140] following transient pyrolysis using a pulsed CO_2 laser. This caused the scission of an N–N bond, leading to the formation of N_2O_4, which was then detected by transmission FTIR spectroscopy. This experiment revealed the origin of the nitrogen isotopes in the N_2O_4 product and showed that RDX mainly produces N_2O, H_2O, HCN, NO and CH_2O during thermal decomposition. When a similar technique was used to study NTO during pyrolysis under a low-oxygen atmosphere [129], the majority of the residual solid mass was an insoluble condensed-phase brown product, whereas the gaseous decomposition products detected by GCMS were a mix of N_2 (43 %), N_2O (6 %), NO (8 %), CO_2 (37 %) and CO (6 %).

As well as shifting the focus from stability and storage-like information towards environmentally friendly disposal, another important difference between assessing thermostability and environmental impact during open burning is the presence of oxygen from the air and how it influences the burning process and composition of the gaseous emissions. Some literature regarding the role of oxygen balance on the thermal decomposition behaviour of composite propellants has been published [141], but the aim of the study was to determine the best ratio of fuel and oxidizer in an ammonium perchlorate HTPB-based polyurethane propellant.

The most comprehensive information published thus far concerning emissions from explosives during open burning was based on the use of BangBoxes [95]. These are concrete pads divided into two sections, one featuring an inflatable hemispherical test chamber (930 m^3 volume, 16.5 m high) made from a flexible polyvinyl-coated polyester fabric, and the other a 5.5 x 2.1 x 2.5 m building (airlock) with a plywood front and a wood frame covered in the same material. The test chamber is kept inflated by two high-capacity blowers, and six fans spaced 60 m apart circulate the air in the test chamber to produce a homogeneous pollutant mix that is sampled with instruments in the chamber and the attached air lock. The energetic materials are burned or detonated in stainless-steel burn pans placed on a concrete pad located in the centre of the test chamber.

In the original BangBox study [95], the chamber was equipped, among other analytical capabilities, with sensors for the detection of CO, CO_2, NO, NO_2, O_2 and HCl, as well as canisters for measuring VOCs. The authors measured the quantities of particles, SVOCs, polychlorinated dibenzo-p-dioxins and furans, toxic metals, VOCs, and inorganic gases released when 0.22 kg of energetic material was detonated or 2.2 kg of the same material was burned in the hemispherical test chamber. They concluded that the main emissions are greenhouse gases and particulates. Furthermore, they suggested that the data generated using the BangBox can be used to predict the emission of products that would be released from detonations and burns at much larger scales, and that both open burning and open detonation are environmentally sustainable ways to dispose of many energetic materials. However, their experimental setup relied on closed burning followed by detonation and was specific for the test samples they used, which did not include explosive formulations such as IHEs developed after the publication (1998). The gases trapped using the canister were analysed for total non-methane hydrocarbons using two techniques: gas chromatography/flame ionization detection (GC/FID) and GCMS. The composited filters were extracted using the Soxhlet method prior to GCMS analysis.

For larger quantities of explosives, the EPA has tested the use of balloons to monitor emissions from the open detonation, open burning and static firing of obsolete military munitions [142]. They used a helium-filled aerostat (4.3 m diameter) carrying the analytical package, attached to two ground vehicles, each mounted with a remote-controlled electric winch with 305-m tethers. This setup was used to anchor the aerostat and manoeuvre it into the emission plume. The setup was based on the use of balloons to monitor CO and CO_2 emissions from forest fires [143]. The EPA tested RDX and TNT mixtures, nitrocellulose and nitroglycerine propellants, and (on a smaller scale) also Sparrow rocket motors containing ammonium perchlorate.

The analytical package consisted of an on-board computer with a data acquisition and control program, and wireless communications to allow real-time data viewing and sampling control from the ground. The analytical instrumentation varied depending on the waste composition, but CO_2 was measured continuously in all the trials. The energetic compounds HMX, RDX, and TNT (and any by-products) were analysed from the particulate matter (PM) collected on a large (20.3 × 25.4 cm) quartz filter, whereas gases and vapour emissions were ignored because of the low quantities involved. Furthermore, an enclosed 37-mm preweighed filter cassette provided a simultaneous total PM gravimetric sample, which was used to calculate a photometric calibration factor. Accounting for weight limitations, the samplers were modified to include a total PM filter measurement on the cartridge impactor plate. Ultimately, the EPA authors used the carbon mass balance method to calculate emission factors [144], i.e. the ratio of the sampled target pollutant concentration was compared to the total carbon sampled from the detonation or burn, the latter represented by the increase in CO_2 levels from ambient conditions. They concluded that significantly more particulate matter was produced by soil-covered versus surface detonations. Their work also showed that energetic materials in the detonation plumes represented less than 0.0005 % of the original munitions and individual emissions typically represented less than 0.05 % by mass of the munition. The conclusions from the study mainly concerned the particulates because this was the focus of the analysis. Although the results were promising, the logistical requirements of balloon deployment over areas containing large piles of explosives limit the practicability of such tests as a daily monitoring technique. Moreover, the authors tested the method using an open setup which prevented the achievement of mass balances, thus making it impossible to determine the efficiency of disposal.

In contrast to the EPA method, the BangBox setup described above [95] allows a broad survey of the gases generated during the burning of energetic materials by deploying canisters that could trap gases samples for GCMS analysis. Although this is a comprehensive approach, it requires the ability to burn explosives within a large container, which is very difficult to implement in practice, especially during military training and in theatre. Moreover, the median recovery of carbon as carbon oxides (CO_2 and CO) from the burned materials was 98.5 %, compared to 0.9 % for nitrogen oxides (NOx). The authors proposed that remaining nitrogen was probably converted to N_2 in agreement with detonation and decomposition theories [122,134,137].

Given the lack of air monitoring data in open military scenarios, one practical solution could involve the application of health and safety protocols that are currently used to monitor air quality in the workplace [145]. These are designed around live sensors (with or without loggers) or sorbent tubes [146]. Although sensors can determine the concentration of chemicals over time, sorbent tubes provide instant measurements. The live sensor approach was adopted by the EPA for the balloon experiments discussed above [142].

Live sensors interface with a logger and provide immediate readings, whereas sorbent tubes/traps require more effort because they are usually combined with GC instruments to monitor the vapour phase fraction of organic compounds in air. Applications range from atmospheric research and ambient air monitoring (indoors and outdoors) to occupational hygiene (personal exposure assessment) and measuring chemical emission levels [147]. Moreover, the type of chemical used in a sorbent tube and the analytical method applied after sampling determine which gases can be detected. Sorbents are classified according to the mechanism used to recover the trapped compounds, i.e. solvent extraction or thermal desorption [148]. The use of sorbents is distinct from alternative sampling procedures such as collecting whole air samples using canisters [147], as deployed in the abovementioned BangBox study [95].

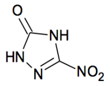
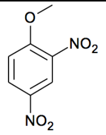
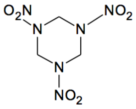
If canisters are not suitable for sample collection, a solid matrix can be used to adsorb contaminants for screening. In such cases, the choice of sorbent will determine the success of the screening experiment. Many different sorbents are available, but most applications involve the use of activated carbon [147,149] , which is efficient, inexpensive and relatively easy to analyse. Activated carbon is not suitable for the analysis of CO and CO_2 (because they are not absorbed) or for NO and NO_2 (because they cannot be desorbed) but it is ideal for most other compounds. Moreover, desorption can be induced by heating the carbon [150], followed by GCMS analysis or by solvent extraction then GCMS or high performance liquid chromatography (HPLC). For the analysis of IHEs, the choice of sorbents for air emissions depends on the thermodynamic properties of the explosives, and such data can be retrieved from the literature [117].

2.5 Insensitive High Explosives: DNAN as a Binder

TNT is a stable hydrocarbon compound with a melting point of ~81 ºC (purity dependant) [151], which allows melt-casting under hot water (Table 1-1), making TNT the main explosive in military ordnance worldwide for many decades. However, due to concerns about accidental ignition [152–162], TNT is likely to be replaced by DNAN for US military applications in the near future [163,164].

DNAN is a hydrocarbon compound that melts at 94.5 °C and can mimic TNT as a melt-cast binding agent in explosive formulations. One IHE of particular interest contains 51–55 % (w/w) NTO, 30–34 % (w/w) DNAN and 13–17 % (w/w) RDX [69] (Table 1-1).

Table 2-2 Chemical properties of NTO, DNAN and RDX.

Explosive	**Empirical formula**	**Chemical structure**	**Oxygen balance (%)** [151,165]	**Enthalpy of formation (kJ mol^{-1})**	**Solubility at 25 °C in water (mg L^{-1})** [166]
NTO [167]	$C_2H_2N_4O_3$		-24.6	-100.8	16,642
DNAN [168]	$C_7H_6N_2O_5$		-96.9	-186.7	276
RDX [169]	$C_3H_6N_6O_6$		-21.6	66.9	60
IMX 104 [170]	$C_{3.7}H_4N_{3.8}O_{4.2}$	NTO / DNAN / RDX	-47.4	-107.8	N/A

NA – Not available

2.5.1.1 Environmental Impact

The environmental impact of RDX has been studied extensively, but the impact of NTO and DNAN is less well understood. The environmental impact of RDX/NTO/DNAN mixtures has not yet been fully characterized [171], but is currently being studied because one such mix (IMX104) is under development for military applications in the USA [171]. Among the three components, NTO is the most soluble whereas RDX and DNAN are only sparingly soluble in water (Table 1-1) [166]. The overall dissolution kinetics of IHEs depend on DNAN, which acts as a matrix for NTO and RDX [172]. At the same time, the loss of NTO increases the surface area of DNAN, making it more susceptible to dissolution although at a slower rate. NTO is a particular concern, not only due to its high solubility in water, but also due its high acidity, with a pK_a of 3.76 [173,174].

2.5.1.2 Degradation of RDX, NTO and DNAN

Once exposed to the environment, chemicals are degraded via three main mechanisms: photo-degradation, physical degradation and biodegradation. Photo-degradation is most likely to occur when chemicals are dissolved in water on the soil surface. Degradation can occur in the presence of oxygen (aerobic degradation) or in its absence (anaerobic degradation). In particular for the explosives of interest herein, RDX degrades slowly in the soil environment and forms a number of degradation products via several different anaerobic transformation pathways [21,175]. Laboratory studies have shown that NTO can undergo biodegradation [105], but the extent of this process in the real environment is largely untested. DNAN can undergo biodegradation in the soil via both anaerobic and aerobic biotic and abiotic processes [176].

2.5.1.3 Toxicity of RDX, NTO and DNAN

Among the three components of IHEs, RDX is the most toxic to mammals, followed by DNAN, and NTO is the least toxic (50 times less toxic than RDX). Table 1-2 presents key toxicity parameters for the three chemicals.

Table 2-3 Summary of the toxicity parameters of NTO, DNAN and RDX

Explosive	Solubility (mg L^{-1} at 25 °C) [166]	Lethal dose (LD_{50}) (mg kg^{-1} in rats)	Skin exposure	Human skin penetration rate (µg cm^{-2} h^{-1})
NTO [167]	16,642	>5000 [177]	mild, short-term irritation [177]	332 [178]
DNAN [168]	276	300 [179,180]	mild dermal irritant (recovery expected within 2) [181]	1.10 [178]
RDX [169]	60	100 [182]	NA	NA

NA – Not available

DNAN and its degradation products show significant toxicity in aquatic environments [183–186] indicating that DNAN presents a risk to all freshwater aquatic species including microbes, invertebrates, fish and amphibians. RDX appears unlikely to bioaccumulate in the environment [187–189] but the behaviour of NTO is unclear. It should become mobile once dissolved in water and bioaccumulation is unlikely, but the bioaccumulation of NTO in the open environment does not appear to have been investigated in detail.

2.5.1.4 Fate and Transport of NTO/RDX/DNAN in the Environment

Predicting the behaviour of contaminants in the environment is typically very challenging due to the many variables that affect fate and transport, e.g. chemical properties of the contaminants, soil properties and climatic conditions. Among the three materials considered, NTO is the most soluble and, as such, is more likely to be quickly dissolved and transported through both soil and water [174,190]. Recent studies using vertical saturated columns packed with loamy soil (high organic content) and sandy soil (low organic content) revealed a correlation between organic content and the loss [107] and degradation [107] of NTO. An additional concern with NTO is the acidity of its aqueous solutions, which increases the soil pH and promotes the leaching and migration of heavy metals [174], which may accelerate the spread of metals originating from discarded ordnance in soil and groundwater.

DNAN is much less soluble than NTO (0.21 g/L) and is likely to adsorb to the organic components of soil [190]. Theoretical predictions have been confirmed in the laboratory, with complete mineralization of DNAN to nitrites within 100 h [191]. DNAN is more mobile in soils with a lower organic content [192], although recent work suggests that even in sandy soil, with a very low content of organic carbon, some DNAN is adsorbed and degraded [107]. The degradation products are also more likely to adsorb irreversibly to soil and therefore are less likely to enter groundwater [192].

RDX does not attenuate significantly in soil, making it highly mobile in soil environments and likely to contaminate groundwater as seen at several training ranges [16,61,193,194] Where RDX does remain in soil, it can be taken up by plants and can have a damaging effect at concentrations >1.5 $mg.L^{-1}$ [195]. In addition, RDX bioaccumulates in edible plant species such as lettuce, corn and tomato even at approved post-remediation concentrations (5.8 $mg.kg^{-1}$) [196], which suggest that the threshold value of 5.8 $mg.kg^{-1}$ for RDX contamination should be reduced.

2.6 Prediction Models

As environmental research has matured [197], so has the understating of the source-pathway-receptor (SPR) pollutant linkage model, which has encouraged the development of pre-emptive analysis to protect the environment and prevent further impacts from the use of IHEs (Figure 1-2).

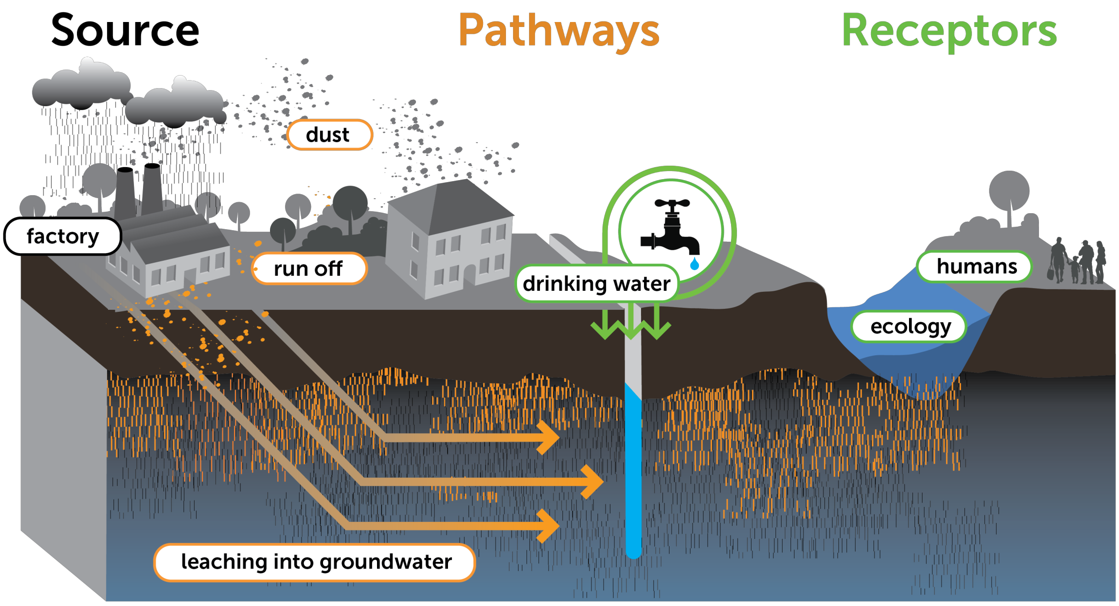


Figure 2-2 The source-pathway-receptor (SPR) model.

The SPR model conceptualizes the potential risks caused by a source of contamination, such as a leaking tank or contaminated soil or water. The pathway is the route the contaminant takes from the source to reach a given receptor. Potential pathways include air, water, soil, animals and vegetation. A receptor may be a human, animal, plant, ecosystem, property or controlled waters. A pollutant linkage occurs when there is a viable route from a source to a receptor. If the SPR linkage can be broken between the source and pathway, or between the pathway and receptor, then environmental damage can be minimized or avoided.

The SPR pollutant linkages in a specific environment can be described mathematically using a series of equations [198,199]. The Navier-Stokes equation (Equation 1) describes the motion of viscous fluids by balancing equations arising from Newton's second law of fluid motion. The viscous flow can be determined for different conditions when the Navier-Stokes equation is solved in conjunction with energy (Equation 2) and mass (Equation 3) conservation. Specifically, the Navier-Stokes equation can model the velocity fields, e.g. the velocity and direction of a contaminant travelling through a medium, the energy conservation (Equation 2), and the temperature fields, as well as source terms from the chemical reaction. Adding Fick's law (Equation 4) allows the modelling of different chemicals, thus providing a modelling approach for spillages and the dispersion of specific chemicals. This is possible because Fick's first law is based on the concept of diffusion, i.e. a solute will move from an area of high concentration to an area of low concentration along a concentration gradient. Ultimately, these equations can be used in conjunction with other mathematical approaches to predict the dispersion of pollutants in fluids such as air or water [200].

$$\frac{dU}{dt} = \nu \nabla U - \frac{1}{\rho} \Delta P \tag{1}$$

$$\frac{dT}{dt} = -\alpha \nabla^2 T + Q \tag{2}$$

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i \tag{3}$$

$$\nabla(\rho v) = 0 \tag{4}$$

where t is time, U is the velocity field (in x, y and z dimensions), P is pressure, T is the temperature field and C is the concentration of the chemical species.

In the context of explosives, these equations have been applied in computer fluid dynamics (CFD) simulations, in particular using ANSYS FLUENT as the model and solver of choice [201]. For example, one CFD simulation used FLUENT to model the disposal of RDX in a rotary kiln by thermal decomposition, focusing on the phase changes and degradation reactions [202], whereas another [203] made use of the same code to simulate the cook-off and thermal decomposition of confined highly-energetic materials such as RDX, HMX and TNT [203]. These studies revealed that bringing computer-aided calculations into the realm of explosives can reduce the number of experiments required to determine how a particular explosive would behave in a given scenario.

2.6.1 Vulnerability Models / Environmental Impact Predictions

Vulnerability calculations are models that predict how a given scenario would be affected by changes in pressure, chemical concentration and temperature without solving the system of equations derived from thermodynamics and conservation balances (mass, motion and energy). This is particularly important when addressing the environmental impact of industrial activity, burning, or chemical plume dispersion. These approaches have been used to predict environmental damage [204,205] and are at the core of software such as ETH Risk [206] and MARPLOT [207,208], which is recommended by the EPA [31] to address environmental contamination.

The most accurate approach is to fully solve (numerically) the system of Equations 1–4 for a particular scenario, in which case the solution provides the temperature, pressure, vorticity, and concentration fields. However, this requires a complex series of mathematical procedures and is very demanding in terms of computational resources and time. Most environmental dispersion models therefore make use of a simplified hypothesis, with less complex equations and probability models to predict the potential environmental damage. Typically, the models predict how a given environment would be affected by any given hazard (in terms of pressure, velocities, concentration and temperature fields), which is generally achieved using probabilistic models such as probit functions [205,209,210].

In the environmental context, probit models are used to predict the extent of damage to vulnerable areas (regions affected by accidental releases) [211,212] following the mathematical approach shown in Equation 5:

$$Y = K_1 + K_2 \ ln(V) \qquad 5$$

Where Y is the value of probit related to the death percentage affected by the accident, V provides a measure of the intensity of the physical effect (e.g. pressure, impulse, thermal radiation) or dispersion agent concentration, and K_1 and K_2 are dimensionless coefficients specific for each substance or kind of damage.

The coefficients K_1 (location parameter) and K_2 (slope parameter) are determined from empirical data and vary according to the desired scenario. Based on the vulnerability model, the probit equations refer to the following effects: thermal radiation (death by burning), explosion (death by impact) and toxic gas (death by intoxication).

Ultimately, the probit equations vary slightly depending on the environmental hazard. The human impact caused by a cloud of toxic gas (Equation 6) depends on the type of gas, the concentration of the gas and the exposure duration, whereas the probability of death *vs* distance to the epicentre of the toxic clouds, fire puddles, fireballs and fire-jets is calculated using Equation 7. This approach can also predict the effects of a boiling liquid expanding vapour explosion (BLEVE) as shown in Equation 8, accounting for the effective duration of the fireball effect and the thermal radiation generated in each accidental scenario. For explosions (cloud explosions, rather than explosive materials), the probit calculations separate the effects of pressure and impulse effects through lung haemorrhage risk for peak pressure (Equation 9) and death by fragmentation (Equation 10).

$$Y = K_1 + K_2 \ln (C^n t) \tag{6}$$

$$Y = -14.9 + 2.56 \ln \left(t\, I^{4/3}\, 10^{-4} \right) \tag{7}$$

$$T_{BLEVE} = 0.826\, M^{0.26} \tag{8}$$

$$Y = -77.1 + 6.91 \ln(\Delta P) \tag{9}$$

$$Y = -46.1 + 4.82 \ln(J) \tag{10}$$

where K_1 and K_2 are dimensionless parameters that are specific for each substance or kind of damage, C is the toxic cloud concentration (ppm), t is the exposure time, I is the thermal radiation intensity ($W.m^{-2}$), ΔP is the increase in pressure ($N.m^{-2}$), J is the impulse ($N.s.m^{-2}$), T_{BLEVE} is the duration of the fireball and M is the initial flammable liquid mass.

Overall, probit models do not calculate pressure, temperature, physical or chemical properties and can only be applied to validate a hypothesis, i.e. the condition (parameter) established in the environmental standards available for environmental risk studies.

2.6.2 HYDRUS 1D as a soil impact assessor aid

HYDRUS 1D [71,72,213] is a model designed for agricultural, industrial and environmental applications, which predicts the dispersion of solutes through a soil matrix. At its core, HYDRUS 1D is a finite element model that simulates the one-dimensional movement of water, heat and multiple solutes in variably saturated media, and then calculates Richard’s equation (Equation 11) for both saturated and unsaturated water flows, as well as Fickian-based dispersion equations for heat and solute transport. The software estimates parameters using the interactive technique of Marquardt-Levenberg.

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\left(\frac{\partial h}{\partial z} + 1\right)\right] \qquad 11$$

where K is the hydraulic conductivity, h is the matric head induced by capillary action, z is the elevation above a vertical datum, θ is the volumetric water content, and t is time.

For HYDRUS 1D, the main processes are water flow, solute transport, heat transport, and inverse parameter optimization. Although it was originally designed to model the behaviour of pesticides and fertilizers, HYDRUS 1D has also been used to model the transport of explosives through soil [70,214–217], including TNT and HMX [70], TNT, RDX and Comp B [215], 2,4-DNT and 2,6 DNT from M1 propellant [216], and most recently NTO [217]. The experimentally determined adsorption coefficients (K_d) for pure explosive compounds such as TNT and RDX [215] closely resemble the values predicted by HYDRUS 1D. However, although HYDRUS 1D was also able to predict the K_d for Solid Comp

B, it underestimated the values for dissolved Comp B. HYDRUS 1D has also been used to calculate the K_d for NTO [190,217], IMX101 and IMX104 [218].

These previous studies indicate that HYDRUS 1D can be used to determine the fate and transport parameters of energetic materials through soil, but not without limitations. For example, differences between the simulated results and empirical data were mainly due to the chemical decomposition and degradation of the explosive chemicals, which is not addressed by Richard's equation.

2.6.3 Thermodynamic codes

The models and calculations presented in the previous sections have one common aspect: they do not help users to determine which chemicals are dispersed, which are unaffected and which undergo reactions. This information must be gathered by the user, and manually inputted to the model. The information can be determined empirically, which can be very precise, but this approach is also time-consuming and expensive. An alternative approach is to use thermodynamic codes that are designed to predict chemical reactions, thermodynamic equilibria and transformations based on the laws of thermodynamics [219].

In the field of energetic materials, suitable thermodynamic codes include (but are not limited to) CERV [219,220], CHEETAH [219,221–223], REAL [219], TANAKA [219,224], EKVI [225–227], Explo5 [228] and ICT [229–231]. Each code has particular strengths and weakness. CERV was developed to determine the complex equilibrium compositions of non-ideal mixtures comprising numerous imperfect gases, compressible liquid and solid species with phase transitions, for closed-vessel applications [219,220]. In contrast, CHEETAH [222,223] is a thermochemical-kinetics code which is used to solve chemical equilibrium and kinetic equations, and has been applied during the development, characterization and assessment of explosives, pyrotechnics, gun and rocket propellants and other materials [219,221].

The REAL code is a computer code that can model chemical equilibria in complex reactive systems under high pressures (< 800 MPa) and temperatures (< 6000 K) [219], It was initially designed to evaluate the performance characteristics of gun powders and rocket propellants. TANAKA is a thermochemical database for numerical studies of shock waves, detonation and explosion phenomena, comprising information on shock compression, and detonation properties in gases and condensed matter, using thermodynamic data such as initial density, enthalpy and heat of formation [219].

The Explo5 code [228] calculates the equilibrium composition and thermodynamic properties of chemicals at a given volume, pressure and temperature by applying free energy minimization techniques. Explo5 is based on the chemical equilibrium, steady-state model of detonation that uses Chapman-Jouguet detonation theory, the Becker-Kistiakowsky-Wilson (BKW) equation of state for gaseous detonation products, and Cowan-Fickett's equation of state for solid carbon to calculate values of detonation velocity, pressure, temperature, heat, energy, and the composition of detonation products [232,233]. Some work has been published [234] addressing BKW equation usage for DNAN-Based Melt-Cast Explosives.

Finally, the older codes are EKVI [225–227] and ICT. The first was designed in the late 1970s [219,235] around a thermochemical database used for thermodynamic equilibrium calculations in systems composed of pure condensed phases and a gas phase. The ICT code dates back to 1969, when the Fraunhofer Institute for Chemical Technology developed a FORTRAN program for the calculation of chemical equilibria, which they have been improving ever since

[219,229–231]. The ICT Thermodynamic Code uses mass action and mass balance expressions to calculate chemical equilibria. Thermodynamic equilibria can be calculated under constant pressure conditions or constant volume conditions, especially for the high-pressure conditions of closed vessels and gun weapons. Calculating the heat of explosion is particularly useful because it avoids the need for experimental measurements using a calorimetric bomb, which is challenging and dangerous in the context of explosives due to the high temperatures and erosive reaction products.

A common feature is that most of these codes can be used to determine thermodynamic properties in the complex realm of detonations and explosions, where pressures and temperatures are very intense. Ultimately, some of these codes have been used during the pre-experimental phase for the design and assessment of explosives and their chemical properties [118].

In summary, there are several mathematical simulations that can be used to predict behaviour of explosives and other materials. However, a simulation result is only as accurate as the input data, which raises questions about the suitability of these calculations to predict IHE behaviour during open burning due to the novelty of IHEs and the paucity of experimental data compared to legacy explosives. Several studies have addressed the kinetics of thermal decomposition of RDX, HMX and NTO among others but not in the context of open burning [119,121,127–134], and hardly any information is available in the literature concerning the behaviour of DNAN. Moreover, it appears that none of the studies using codes have applied them to explosive residues.

2.7 Partial Conclusions and Summary

Analysis of the literature concerning EMS, the environmental fate and impact of legacy explosives and more recent IHE formulations, and the use of predictive algorithms to determine the impact of such formulations in different scenarios, led to the following major conclusions which provided the basis for the research described in the subsequent chapters of this thesis.

First, an EMS requires reliable data for its implementation, and the data must cover the entire spectrum of CAMID, particularly the disposal aspects, which currently receive comparatively little scrutiny.

Second, the disposal of explosive waste is a controversial topic. Environmental authorities typically recommend that open burning and open detonation should cease, but the technical challenges of disposal and the lack of alternatives compel military organizations to continue the practice.

Third, some work has been carried out on the environmental impact of ordnance during the in-service phase, but this has almost exclusively focused on (a) TNT-based legacy explosives and (b) the impact on soil rather than other environmental compartments. Very few previous studies consider air emissions, and the two most prominent examples focused on TNT/RDX and nitroglycerine/nitroguanidine propellants, restricting the conclusions to these materials.

Fourth, safety legislation is pressuring military organizations to replace TNT with DNAN. The latter is a melt-castable binder and fuel, but not an explosive, which affects its behaviour during disposal. There is very little information in the literature about the behaviour of DNAN in the environment, and as above all the studies focus on soil rather than air emissions. It appears that no previous studies have addressed the behaviour of DNAN-based formulations during open burning and open detonation.

Finally, the empirical analysis of the fate and impact of explosives is expensive and any results obtained are restricted to the specific experimental scenario tested. Computer algorithms could help to predict the behaviour of these explosives during open burning and open detonation, covering a wider range of environmental scenarios. However, the algorithms used to predict the environmental behaviour of chemicals are seldom applied to open burning and open detonation.

The gaps in the literature identified above are addressed in this thesis by applying POEMS to an idealized case study, which reveals the quantity of data and empirical analysis required (Chapter 3). To gather the missing data for IHEs, experiments were designed and implemented to test DNAN-based IHE samples ranging from milligrams in a closed system (Chapter 4) to grams and kilograms in an open system, both in the laboratory and the field (Chapter 5). This allowed the collection of specific behavioural data for a specific IHE formulation comprising DNAN, NTO and RDX during open burning. To account for the possibility that some explosive residues may be left on the soil after burning, HYDRUS 1D (Chapter 6) was fed with empirical data concerning the behaviour of the IHE formulation [107], and was then used to compare the actual and predicted outcomes in order to determine whether HYDRUS 1D is currently suitable to predict the fate and impact of IHEs in the environment.

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3 THE UK MINISTRY OF DEFENCE PROJECT ORIENTATED ENVIRONMENTAL MANAGEMENT SYSTEM (POEMS)

Abstract:

The Project Orientated Environmental Management System (POEMS) is the UK Ministry of Defence (MOD) bespoke environmental management system (EMS) for the acquisition and use of equipment. The full implementation of a site-specific EMS is challenging for the MOD because there are many permanent MOD sites with transient populations, frequently changing site activities and diverse types of equipment. Nevertheless, MOD policy requires that all sites are covered by an EMS. POEMS is based on international standards ISO14001 and ISO14040, which focus on EMS and life cycle assessment, respectively. The primary aim of POEMS is to identify and manage any environmental aspects (causes) and impacts (effects) by scrutinizing MOD equipment and activities during acquisition, operation and disposal ('from cradle to grave'). This is achieved by drawing up a priority list of activities associated with the equipment based on anticipated environmental impact scores, resulting in an environmental management plan that spans the life cycle of the equipment and any corresponding activities. This article describes the POEMS procedure for both experts and non-experts, and demonstrates the implementation of POEMS using a 105-mm howitzer artillery round as a theoretical case study. The results anticipated at each stage of the POEMS procedure are discussed in detail, and the documentation necessary to verify the correct application of POEMS is demonstrated.

Keywords: POEMS, environmental management system, life cycle assessment, International Organization for Standardization, UK Ministry of Defence

3.1 Introduction

An environmental management system (EMS) is a comprehensive, planned and documented system that integrates procedures and processes for monitoring and reporting environmental performance. The primary aim of an EMS is to identify any environmental aspects (causes) and impacts (effects) by scrutinizing activities that may be detrimental to the environment. An EMS also helps an organization to comply with environmental laws and policies, and organizations may choose to become accredited by an external standard-setting body such as the International Organization for Standardization (ISO), the Eco-Management and Audit Scheme (EMAS), or the British Standards Institution (BSI) Group. Registration with these organizations is voluntary, but is often valuable from a reputational and business perspective [1,2]. An EMS can be implemented throughout a site or company, or can be restricted to individual areas or business sectors.

The full implementation of a site-specific EMS standard is challenging for the UK Ministry of Defence (MOD) because there are many permanent MOD sites with transient populations and frequently changing site activities and equipment [3,4]. Nevertheless, MOD policy requires that all sites are covered by an EMS based on ISO 14001 [5], the EMS standard. Therefore, a different environmental management approach is applied during the acquisition of new MOD equipment, which can range from fitting out a new office to the commission of a new fleet of ships. The MOD has developed a bespoke platform known as the Project Orientated Environmental Management System (POEMS) [6], which was designed to facilitate the application of EMS to specific MOD activities and equipment throughout the life cycle.

POEMS is based on the international standards ISO 14001 [5] and ISO 14040 [7], the former representing the cornerstone of EMS and the latter covering life cycle assessment (LCA). LCA is a technique used to assess the environmental impact of product throughout the entire life cycle from the extraction of raw materials to disposal, often described as cradle-to-grave. In recent years there has been increasing interest in cradle-to-cradle thinking, which integrates the end-of-life product back into manufacture [7–9]. POEMS also incorporates elements from the US Department of Defence's Military Standard 882, entitled Standard Practice for System Safety [10–12]. POEMS involves eight major procedures, known as Environmental Management Procedures (EMPs), that can be implemented in numerical order or in whichever order is most convenient in terms of the information available, making it a flexible approach. POEMS can be mapped onto the guidelines in ISO 14001 [5] and ISO 14040 [7] as shown in Table 3-1.

Table 3-1 Alignment of POEMS EMPs to ISO 14001 and ISO14040 guidelines

POEMS EMPs	Equivalent guidelines from ISO standards	
	ISO 14001	**ISO 14040**
EMP01: Stakeholders and standards identification	Identification of compliance requirements	No equivalent
	Define resources, roles, responsibilities and authorities	
	Communication plan	
EMP02: Screening and scoping	Identification of aspects and impacts	Define scope and system boundaries
EMP03: Impact priority evaluation	Identification of significant impacts organization may cause	No equivalent
EMP04: Environmental impact assessment (EIA) plan	No equivalent	Data quality requirements
EMP05: EIAs and reporting	No equivalent	Life cycle impact assessment
EMP06: Environmental management plan (objectives and targets)	Identification of objectives and targets with their environmental management plan	Life cycle interpretation
EMP07: Operational controls	Development of document and operational control procedures, development of emergency procedure plans	No equivalent

POEMS EMPs	**Equivalent guidelines from ISO standards**	
	ISO 14001	**ISO 14040**
EMP08: Continuous review	Monitor and measure environmental impact	Critical review
	Evaluate compliance	
Audit	Management of non-conformance, preventative actions; records management; internal audit, management review	No equivalent

As part of the POEMS implementation process, the environmental impact is assessed throughout the life cycle of the equipment or activity using a qualitative ranking system, which is similar to ISO 14040. In POEMS, LCA is represented by the CADMID cycle (concept, assessment, demonstration, manufacture, in service, disposal), which describes the lifetime of a system from cradle to grave (Figure 3-1), or if practicable from cradle to cradle.

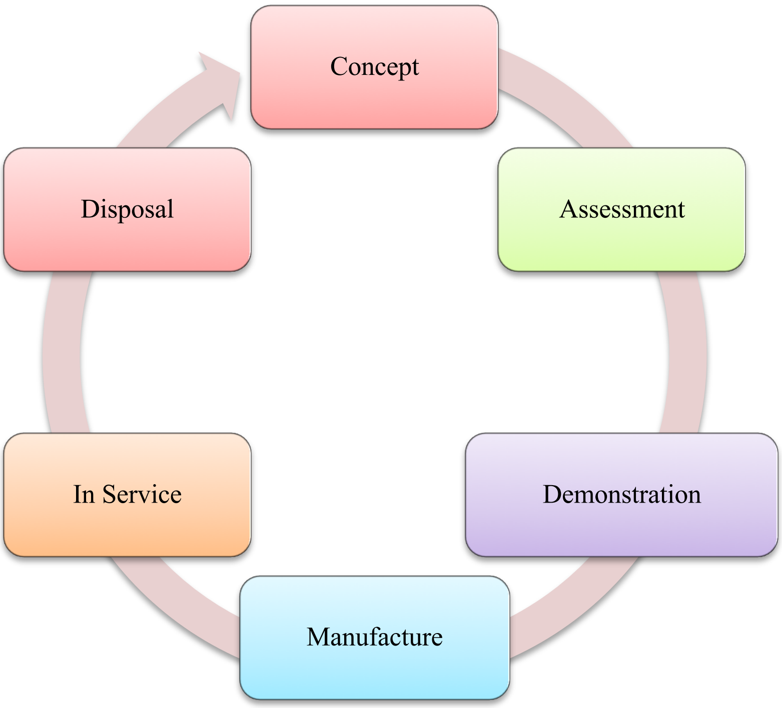


Figure 3-1 The CADMID cycle

The first four POEMS EMPs allow the assessment of potential causes of environmental damage (aspects) and their effects (impacts) at each relevant step in the CADMID cycle. EMPs 01–04 include data gathering steps such as compiling stakeholder and standards registers, gaining an understanding of the equipment and setting the boundaries for POEMS implementation. It also includes the development of a priority list for the associated activities and their environmental impacts. The next three procedures (EMPs 05–07) describe how to develop an environmental management plan spanning the life cycle of the equipment or activity. The final procedure (EMP08) is a continuous review process to ensure any changes are captured during the life cycle of the equipment. As stated earlier, POEMS is intentionally designed to be flexible, and this can be demonstrated by applying it to legacy equipment that may already be in service, as well as commercial off-the-shelf products and conceptual projects. Regardless of the CADMID phase, POEMS should be carried out for all future phases. Any in-service equipment should have an Environmental Management Plan that details all in-service activities, including maintenance, mid-life upgrades and 'business as usual' processes, as well as a disposal plan.

The environmental management plan is not the end of the process. Once POEMS has been completed and the environmental targets have been set, a plan must be put in place for reviews. These may take the form of internal and external audits, or may be triggered by certain events during the life cycle such as a mid-life upgrade, which may introduce new materials and therefore require an updated disposal plan.

Here we describe the implementation of the eight core POEMS procedures to a 105-mm howitzer high-explosive artillery round stored and used at a theoretical UK training base. We have focussed on the in-service phase because the earlier stages, including manufacture, are complete and can no longer be influenced by LCA. However, the EMS element may be able to influence certain aspects of the supply chain for future manufacturing, as well as the disposal of waste products.

The main purpose of this article is to provide guidance that both experts and non-experts can use to implement POEMS, using a theoretical case study to illustrate key aspects of the procedure and documentation.

3.2 Case Study: 105-mm round

The 105-mm howitzer artillery round is routinely used for training at a range in the southwest of England, and for the purposes of this article we are assuming that training with the round will increase in the future. The following sections outline a hypothetical yet realistic POEMS procedure applied to an active training range including details of the artillery round, the training regime and the location.

3.2.1 The Training Area

Training takes place in an area of 640 km^2 (40 x 16 km) within a larger estate in the southwest of England. The estate also contains approximately 2300 archaeological sites including features dating back to 4000 BC, along with evidence of Roman settlements. The southwest of England is a large area of chalk grassland, one of the largest in northwest Europe, and accounts for 40 % of the total area of this habitat remaining in the UK. The estate and training area geology primarily comprise of chalk deposited during the Upper Cretaceous (100 million years ago). The chalk strata in this area can be divided into three broad categories:

- Upper chalk – a white, uniform, massively-bedded deposit, up to 400 m in thickness, of almost pure calcium carbonate;
- Middle chalk – a white homogenous deposit with occasional marl deposits;
- Lower chalk – relatively soft and greyish in colour, with a clay content that increases with depth.

The training area is located over a major aquifer, with a soil covering that permits high to intermediate levels of leaching. This means that liquid contaminants can readily pass through the soil to the underlying strata and possibly to groundwater. However, because the hydraulic conductivity of the chalk mass is low, water and contaminants are transmitted through fissures in the rock, which are more likely to form in the harder and more brittle chalk bands. Groundwater in the area is potable and is therefore used for the public water supply. Although all of the abstraction points are just outside the central impact area (in which most rounds are fired), the aquifer beneath the central impact area is a catchment for many of the public supply wells, and is therefore closely monitored for pollution. The training area also includes seven different Sites of Special Scientific Interest (SSSI) and is home to 13 species of nationally rare plants, and 70 species of rare invertebrates including several rare butterflies such as the marsh fritillary, Adonis blue and brown hairstreak (Table 3-2).

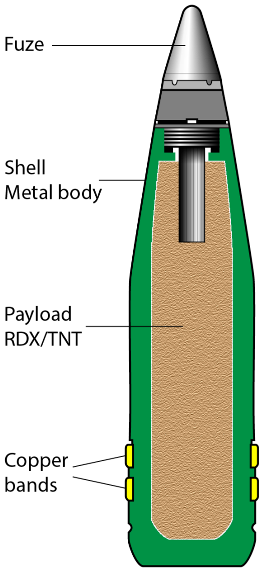
It is important to note that approximately 10 km^2 of the estate is permanently closed to the public for safety reasons (artillery impact and live firing areas). The training area routinely offers live firing and other facilities for armoured vehicles, artillery, engineers, infantry and aircraft. There is also active management of the airspace over both the estate and its adjacent areas, which is used day and night by military aircraft from all three UK Services, sometimes complemented by NATO aircraft.

Table 3-2 **Summary of training area characteristics**

Area	640 km^2 in intermittent use
Features	Embedded in larger estate
Geology	Mostly upper chalk
Hydrogeology	Overlying a major aquifer, with moderate likelihood of pollutant leaching
Groundwater	Potable water abstraction and supply
Land use	Flanked by public roads to the east and west, bordered by numerous villages Land north and south is predominantly used for farming Some recreational use

3.2.2 The 105-mm howitzer artillery round

The tactical applications and worldwide stockpiles of the 105-mm high-explosive artillery round make it ideal for this case study. Several manufactures produce this type of round and they can be approached for key information [13–17]. Technical specifications vary between manufacturers reflecting the use of different facilities, assembly lines and materials. For this study, we selected the 105-mm HE lightgun [18]. This device weighs 15.1 kg and the payload is 2.5 kg TNT/RDX (L31 type) with a lead azide-based L116 multi-role fuze (Figure 3-2).



Description	Specifications
Shell	105 mm FDHE L31A1
Explosive	TNT/RDX
Cartridge case	105 mm
Cartridge	195 mm FD normal L35A1
Fuze	Point detonation
Primer	Electrical
Muzzle velocity	621 m/2
Projectile weight	16 kg
Maximum range	15.3 km
Temperature range (firing)	-40°C to 50°C
Packaging	Wooden box (two rounds per box)

Figure 3-2 Description of the 105-mm howitzer round

3.2.3 The training regime

The range serves four artillery battalions, each carrying out two training sessions per year. The military, including the USA and UK, class the 105-mm round as light artillery, mainly used for field or airborne artillery battalions and batteries. In modern warfare, and for the purposes of this article, a typical field artillery battalion consists of three artillery batteries each led by a captain. A battery in turn includes 6–8 howitzers, each operated by a six-man crew, so a battalion would have 18–24 howitzers at its disposal.

Each howitzer fires up to 100 rounds per training session, i.e. 1800–2400 rounds per battalion, making a total of 3600–4800 rounds per battalion per year. Therefore, the total number of rounds fired on a training range used by four battalions will be 14,400–19,200 per year. We selected the lowest figure (14,400 rounds) as the basis for the POEMS case study.

The following section will outline in more detail what POEMS is and how it is implemented in the theoretical scenario described above. It will include the anticipated results at each stage of the POEMS process and the content and description of the corresponding documentation.

3.3 Results and discussion

POEMS consists of eight core EMPs based on ISO14001 [5] and ISO14040 [7], which are designed to be flexible in their application. Before starting the formal POEMS process, it is helpful to contextualize the project to gain a high-level understanding of the equipment. This can be visualized by creating a context diagram outlining the CADMID cycle and the activities associated with each life-cycle phase. Each activity in the context diagram usually requires materials and/or energy as an input (e.g. fuel) and is associated with outputs that have a potential environmental impact (e.g. emissions). As part of the POEMS procedure, inputs and outputs are described as the ‘embodied’ and ‘emitted’ aspects, respectively (Figure 3-3). The POEMS process can then be implemented, usually in a linear manner, from EMP01 through to EMP07, as shown for the 105-mm round below and summarized in Table 3-3. EMP08 is a continuous review, which runs throughout the POEMS process and beyond.

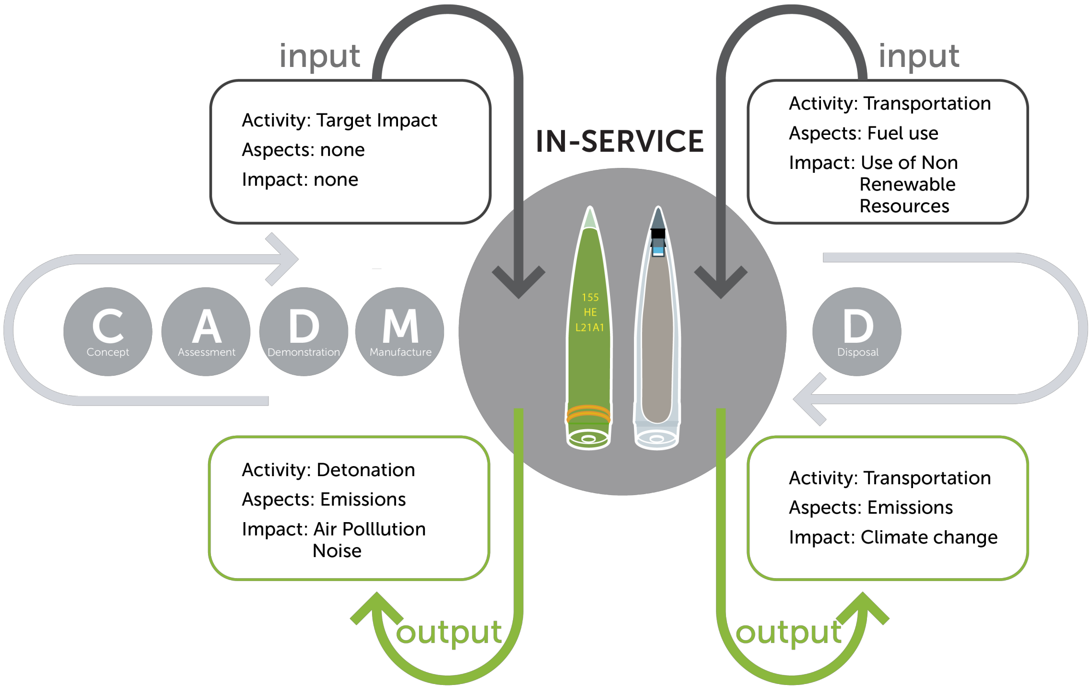


Figure 3-3 A simplified context diagram for the 105-mm round during the in-service phase, detailing two activities: target impact and transportation, and the associated aspects and impacts

Where possible, POEMS should be applied to the whole CADMID cycle. However, this paper only considers the target impact activity during the in-service phase because the 105-mm round has already been manufactured and is in use. In reality, the POEMS implementation would also consider the disposal phase as early as possible.

The first phase of POEMS is used to gather and record information about the equipment, such as key stakeholders and standards. It is important to engage with stakeholders, to understand their concerns and requirements, and to collect information pertinent to the project such as training schedules, manufacturer and purchasing information, and user requirements. This also helps to establish multiple communication pathways, which should be recorded in a communications plan. The core stakeholders for the 105-mm round include the military using the munition for training, and estates concerned about soil and water contamination or noise. The latter is a particular concern because the training area is located near several local villages and a noise nuisance could be negatively perceived by the public. Other stakeholders (inner and outer, see Table 3) include the Environment Agency, archaeologists, and local farmers who protect and use the land.

The second requirement is a list of all standards relevant to the activities conducted with the 105-mm round, including relevant UK and international legislation, MOD policy and site orders for anywhere the 105-mm round is stored, transported or used. The MOD translates legislation into policy through Joint Service Publication (JSP) documents, such as the environmental protection policy (JSP418). For example, the Environmental Protection Act 1990 (EPA 1990) [19] regulates emissions to air, land and water, and also covers statutory noise nuisance regulations. However, EPA 1991 [19] does not stipulate daytime noise limits and so the standards register was supplemented with the Control of Noise at Work Regulations 2005 [20], which stipulates that noise should be kept below health and safety limits (87 decibels). Compliance with the EU Water Framework Directive [21], through the Water Act 2003 [22] in the UK, was particularly relevant in this case because the training area is located over an aquifer. This aquifer feeds potable water sources and must not breach regulatory limits for certain substances such as aluminium (200 $\mu g.L^{-1}$), copper (2 $g.L^{-1}$), lead (10 $\mu g.L^{-1}$) and mercury (1 $\mu g.L^{-1}$) [23]. Single firings of the 105-mm round are unlikely to breach any legislation, but the training schedule shows that up to 14,400 rounds are fired each year and the cumulative effects may be significant.

EMP02 states that the boundaries of POEMS implementation are established through a ‘screening and scoping’ process. However, the context diagram (Figure 3-3) captured the important information and was useful during the information-gathering phase (EMP01). At this stage, the boundaries were officially defined to cover only the in-service phase and to disregard the firing platform because this was already covered by a separate POEMS process. This stage also requires the identification of all activities associated with the 105-mm round, their embodied and emitted aspects, and anticipated environmental impacts. No aspects or impacts associated with embodied materials were identified for the 105-mm round because these were deemed to be associated with the firing platform (e.g. burning the propellant to fire the round). However, aspects were identified for the detonation of the 105-mm round, such as the gaseous detonation products, blast wave and noise. The products from a full-order detonation of a 105-mm round are listed in Table 3-4.

Table 3-3 Outline of the POEMS procedures (EMPs 1–8) and the outputs associated with the 105-mm round

EMP	Procedures (relating to activity: target impact)	Expected output	Outcome for case study
1	Stakeholders and standards identification	A stakeholders register: detailing core, inner and outer[a] stakeholders including information and relevant requirements.	Core: Users (safety, handling, requirements), POEMS project delivery team. Inner: MOD estates organization (where and when to fire), environmental test and assurance, programme managers. Outer: Environment Agency (monitoring), neighbours (famers), archaeologists (define usable areas, control water quality, noise (when/how often) and vibration).
	Identification of relevant legislation	A legislation register to ensure compliance with UK or strictest relevant legislation in area of use including guidance, policy and associated documents.	A non-exhaustive list includes: Environmental Protection Act 1991, including water, land and air emissions; Control of Noise at Work Regulations (2005); EU Water Framework Directive (2012); Water Act (2003) and JSP418.
2	Screening and scoping	List of embodied and emitted[b] aspects (causes) and impacts (effects) of the activities. Setting	Embodied aspects/impacts: There are no embodied aspects (although there are embodied materials) in this case because we did not consider the firing platform (howitzer) as part of this POEMS project.

<table>
<thead>
<tr><th>EMP</th><th>Procedures (relating to activity: target impact)</th><th>Expected output</th><th>Outcome for case study</th></tr>
</thead>
<tbody>
<tr><td></td><td></td><td>the boundaries of the project.</td><td>Emitted aspects: emissions, blast.
Emitted impacts: cumulative effects; air pollution (noxious gases), nuisance, cumulative land contamination from metal scraps/fumes/ other constituents.</td></tr>
<tr><td>3</td><td>Impact priority evaluation</td><td>A prioritization table (environmental feature matrix, EFM) that ranks aspects and impacts from both embodied and emitted materials. Priorities are determined by multiplying a severity score (1-6) and a frequency score (1-6) resulting in EFM values of 1–36.</td><td>
<table>
<tr><th rowspan="2">Aspect (Detonation)</th><th colspan="2">Receptor</th><th rowspan="2">Severity</th><th rowspan="2">Freq.</th><th rowspan="2">Priority</th></tr>
<tr><th>Water</th><th>Human</th></tr>
<tr><td>Lead fumes (from fuze)</td><td>X</td><td></td><td>4</td><td>3</td><td>12</td></tr>
<tr><td>Noise</td><td></td><td>X</td><td>1</td><td>3</td><td>3</td></tr>
</table>
A representative EFM used for this case study is provided as Supplementary Data.</td></tr>
<tr><td>4</td><td>Environmental impact assessment (EIA) plan</td><td>Outline strategy for conducting an environmental impact assessment, if the priority established in the EFM is greater than 12.</td><td>In this case the impact priority evaluation showed that there were two scores of 12, associated with soil/water contamination caused by lead azide combustion products. Noise impacts did not score more than 12, although perception issues could require some mitigation.</td></tr>
<tr><td>5</td><td>EIAs and reporting</td><td>Environmental impact assessment, using experts if required, and preparation of an EIA report.</td><td>A specialist would assess the level of noise from the activity and compare this to threshold levels.</td></tr>
<tr><td>6</td><td>Environmental management plan (objectives and targets)</td><td>Setting specific, measurable, achievable, realistic and time-bound (SMART) objectives to meet targets set within the environmental management system.</td><td>Noise: Monitoring; rotating and/or re-locating firing areas; continuous communication through newsletters and periodic meetings with stakeholders.
Lead: Monitor lead concentrations in local water supplies to ensure there is no breach of threshold levels at any time (the UK drinking water limit for lead is10 µg.L^{-1}).</td></tr>
<tr><td>7</td><td>Operational controls</td><td>Controls to achieve the targets set in EMP06.</td><td>Writing standard operating procedures such as the rotation of firing areas, and stating procedures if threshold levels are breached.</td></tr>
<tr><td>8</td><td>Continuous review</td><td>Continuous improvements of EMS outputs at</td><td>Undertake scheduled internal reviews of POEMS to ensure the consistency of the plan-do-check-act cycle. A review would be</td></tr>
</tbody>
</table>

EMP	Procedures (relating to activity: target impact)	Expected output	Outcome for case study
		specific set of intervals or trigger points. Record all reviews and outcomes/changes triggered.	undertaken due to changes in the firing schedule, manufacturer of the round, person responsible for POEMS.

a Core stakeholders = directly involved with project (daily basis); inner stakeholders = some involvement with project on a regular basis; outer stakeholders = interest in project, but minimal contact. b Embodied = input materials/energy (e.g. fuel); emitted = output materials/energy (e.g. emissions).

The emitted chemicals listed in Table 3-4 were calculated using data available in the literature [24–27]. The calculations were based on the reaction conditions (confinement, high pressures, the rate of reaction and the lack of oxygen available) and the deviation from typical products expected from a combustion reaction (such as CO_2 and H_2O).

Table 3-4 Embodied and emitted aspects (materials) for a single 105-mm high-explosive round

Material	Embodied		Emitted	
	Component	Quantity (kg)	Description	Quantity (kg)
Metals	Brass	13.5	Metal fragments and fumes	13.5
	Copper			
	Steel			
Explosives	TNT	0.975	CO_2	0.236
			CO	0.353
			CH_4	0.004
			H_2O	0.005
			C_2H_2	0.014
			HCN	0.014
			H_2	0.008
			N_2	0.162
			NH_4HCO	0.035
			C	0.093
	RDX	1.5	HCN	0.367
			N_2O	0.299
			H_2O	0.122
			NO	0.204
			CH_2O	0.204
	Wax	0.025	Negligible	
Primers and fuse	Lead azide	(1)	Lead contamination	
	Booster charge		Negligible	

The impact priority evaluation (EMP03) is the crucial element of the POEMS procedure because it ranks all of the environmental impacts associated with the equipment to determine the priorities for mitigation or management. The impact priority evaluation can be undertaken using an environmental features matrix (EFM) on a spreadsheet that automatically calculates the priority list by multiplying the severity and frequency scores (Table 3-3). If the EFM score is below 12 for each activity, the environmental impact can be considered minimal and no further action is required other than the continuous review process. If any activities score between 12 and 24, the environmental impact is significant and may require mitigation, and if the score is above 24 the impact is severe and should be re-assessed (and if possible stopped).

In this case study, the priority evaluation was undertaken for one full year of training with the 105-mm round, therefore accounting for cumulative effects (approximately 14,400 rounds fired). Most aspects scored lower than 12 on the EFM, e.g. dispersion of metal shrapnel, blast effects and gaseous emissions, indicating they would have a low-to-negligible environmental impact. However, two of the aspects scored 12, which is the threshold between minimal and significant impact, and may therefore require further investigation. One of the concerns was the contamination of soil and water by the lead azide primary explosive within the fuze, which may cause the deposition of lead particles around the impact site. Another concern was noise nuisance, where the score was higher to pre-empt the aforementioned potential for negative public perception, even though the actual noise from the detonations would be well below health and safety recommendations for nearby populations (87 decibels). By flagging the potential for noise nuisance at this stage, it would be possible to incorporate into the POEMS procedure the management of public perception towards noise.

The collated documentation from the first three EMPs forms the basis of an environmental case and thus the foundation of the POEMS documentation. At this point, an Environmental Screening and Scoping (ESS) report is usually produced along with an Environmental Impact Statement (EIS), detailing the most significant environmental impacts. An EIS is a non-technical summary of the POEMS implementation such that any interested stakeholder would be able to understand the outcomes.

If the priority evaluation (EMP03) indicates the equipment has a limited environmental impact, then it may be unnecessary to carry out the remaining stages of POEMS. In such cases, the POEMS procedure would be summarized in a report and regular reviews would be carried out to capture any changes. However, most POEMS implementations do identify some aspects that cross the minimal threshold score (12) and require further investigation in the form of an Environmental Impact Assessment (EIA). EMP04 describes how to outline a strategy for the further assessment of identified environmental impacts. For the 105-mm round, the EFM established the potential for lead contamination in the local water and soil, and therefore during the EIA planning stage we would consider contracting specialists to investigate how much lead is deposited on the training range per year. However, we also looked at other POEMS implementations for similar equipment using the same training area and found that it was unnecessary to conduct full-scale research because sufficient work had been carried out previously, and on-site monitoring for lead concentrations in potable water sources was already in place.

As mentioned above, the potential for noise nuisance was considered based on anticipated negative perception, and a noise level monitoring programme was suggested during training with the 105-mm round. Currently there is no breach of statutory noise levels, so no EIA would be required. However, a report should be produced listing all decisions taken during the POEMS process, a summary of previous research and links to full reports, and a record of current monitoring programmes.

At this point, objectives and targets are usually set in order to ensure continual compliance with legislation and to address stakeholder concerns wherever possible. For POEMS, objectives are established to achieve a positive environmental effect, and targets provide verifiable evidence that each objective has been met. Best practice is to ensure that targets are specific, measurable, achievable, relevant and time-bound (SMART). For the 105-mm round, there was no record of any lead contamination on the site, and noise nuisance was well below statutory limits. In addition, training with the 105-mm round is conducted alongside other training activities for which lead and noise monitoring is already in place so the data can be assimilated for this particular round.

Standard operating procedures (SOPs) written during EMP07 describe how the objectives will be met within the required time. For the 105-mm round, the objectives were to ensure continued compliance with the threshold for lead contamination in soil and groundwater (10 $\mu g.L^{-1}$) [23] as well as statutory noise limits. To achieve these objectives, the SOPs included timetables for rotation of the firing area, plans for monitoring and recording lead concentrations and noise levels, and emergency controls should lead levels in the local drinking water exceed the threshold.

The entire body of documentation generated during the POEMS process forms the EMS for the 105-mm round. Once the environmental management plan was in place, annual reviews were planned, with documentation prepared to record any changes to the POEMS after the review. Trigger points were also identified, such as planned changes in the training schedule, or changes introduced during the manufacture of the round. Unplanned events, such as incidents of lead contamination, a change in legislation, or a change in the personnel responsible for POEMS would also trigger a review.

3.4 Conclusions

The UK MOD POEMS process is an effective EMS that has the ability to identify monitor and manage any environmental aspects and impacts related to the use of defence equipment. The process itself is based on ISO 14001 and ISO 14040, but has been designed to be applicable to individual projects rather than whole sites, the latter being difficult for MOD sites due to the diverse and fluctuating activities and the transient populations. Because POEMS is based on two well-known international standards, stakeholders and personnel are immediately familiar with many aspects of the process, and regulatory bodies can be assured that MOD environmental management aims to achieve the highest standards.

POEMS consists of eight core EMPs that are designed to be flexible and straightforward to implement by non-specialists. The case study described herein was based on a 105-mm artillery round and provides insight into the practical aspects of POEMS by detailing how each EMP is implemented based on theoretical outcomes. The overall conclusion from this particular case study is that firing the 105-mm round would cause a negligible environmental impact, although issues may arise due to the large number of rounds fired each year specifically concerning lead residues in soil and groundwater.

Another benefit to POEMS is the ability to address non-conventional issues such as public perception, which is particularly of interest to the MOD. For the 105-mm round, noise issues have the potential to generate a negative perception even if they do not breach statutory limits. Even so, as part of the POEMS procedure, anticipated perception issues were mitigated by implementing noise-monitoring regimes, which might not be identified when applying ISO 14001.

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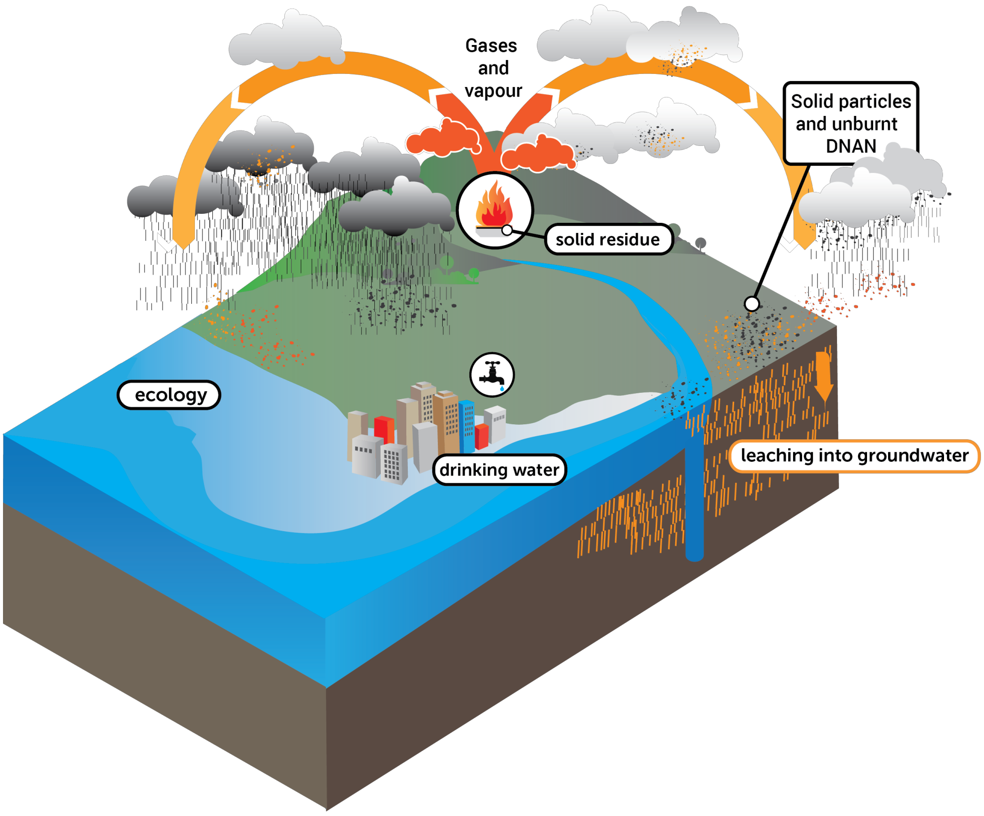
4 SMALL-SCALE COMBUSTION EVALUATION OF DNAN-BASED INSENSITIVE HIGH EXPLOSIVE BY GCMS

Graphical Abstract



Abstract

The increasing use of insensitive high explosives (IHEs) means that the open burning of such materials on military ranges is likely to become more common. However, this waste-management practice has the potential to contaminate the environment. To minimize environmental damage, it is necessary to verify the effectiveness of open burning for the disposal of IHE formulations, to identify the chemical signatures of the gases and vapours formed during combustion, and to characterize the residues left behind. This type of analysis can be challenging because many variables affect the open burning process and diverse chemical species are generated. To assess the efficiency of open burning, we designed a controlled laboratory experiment to burn the IHE components 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanisole (DNAN) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX). The samples were heated to combustion. Gas chromatography/mass spectrometry (GCMS) was used to measure the oxygen consumption and to identify the gases that were generated. The solid residues were analysed by high-performance liquid chromatography (HPLC). The energetic materials were analysed individually and in combination to assess how their behaviour changes when in a mixture. We found that DNAN was the most resilient to burning, thus leaving significant quantities of unreacted starting material. In mixed formulations, DNAN inhibited the combustion of NTO and RDX. The gases emitted during the open burning of IHE components and mixtures in laboratory-scale controlled experiments included CO, CO_2 and N_2O as expected, but the proportions differed when the components and mixture were compared, reflecting the influence of DNAN on the burning behaviour. Overall, our data suggest that open burning in an oxygen-restricted environment is an environmentally unfavourable waste-management practice for the disposal of IHEs mainly due to generation of solid residues by inefficient combustion.

Keywords: insensitive high explosives, laboratory-scale testing, open burning

4.1 Introduction

The environmental impact of emissions from burning insensitive high explosives (IHEs) is not fully understood, reflecting the novelty of such formulations and technical challenges associated with the real-time analysis of gases released by the burning of energetic materials such as 3-nitro-1,2,4-triazol-5-one (NTO) [1–4], 2,4-dinitroanisole (DNAN) [5] and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) [6]. These materials are combined to make the fillings of insensitive munitions, which are deemed safer than conventional explosives [7–12]. As well as enforcing safety measures, military ranges and burning areas must minimize their environmental impact [13,14]. However, insufficient data are available for the implementation of an environmentally-friendly waste management plan for such materials, and for the development of procedures that ensure the effective disposal of IHE formulations, which are known to leave unreacted explosives in the soil even after the detonation of ordnance and munitions [15–18].

In most melt-castable IHE formulations, TNT is replaced with DNAN as a melt-castable binding agent for energetic materials such as NTO and RDX. All these components can be toxic towards humans and are environmentally hazardous (Table 1-1). Their chemical behaviour and potential environmental impact must therefore be evaluated and understood.

Table 4-1 Toxicity and chemical properties of NTO, DNAN and RDX

Explosive	**Solubility** (**mg L^{-1} at 25 °C**) [3]	**lethal dose (LD$_{50}$)** (**mg kg^{-1} in rats**)	**human skin penetration rate (μg cm^{-2} h^{-1})**
NTO [2]	16,642	>5000 [19]	332 [20]
DNAN [5]	276	300 [21,22]	1.10 [20]
RDX [6]	60	100 [23]	NA

Legend: NA – Not applicable

The impact of RDX on the environment has been studied, but the effects of NTO and DNAN are unclear, as is the effect of the RDX/NTO/DNAN mixtures currently being tested for military applications mainly in the US [24]. NTO is the most soluble of the three components, whereas RDX and DNAN are only sparingly soluble in water [3]. The overall dissolution kinetic behaviour is therefore dependent on DNAN, which acts as a matrix for NTO and RDX [25].

If left unattended in the environment, NTO quickly dissolves during periods of rainfall, leaving some DNAN and most of the RDX behind. RDX is relatively stable and does not undergo significant attenuation in soil, so it is mobile in soil environments and is likely to contaminate groundwater, as seen at several training ranges [26–28]. Explosives must therefore be disposed of responsibly, which is usually achieved by washout or steam out, confined detonation or burning in a rotary kiln, open detonation [29] or open burning [30]. The last two options are the most widely adopted methods in the military [31–33]. Open burning and open detonation are conducted in a safe and secure environment and are the simplest and least expensive techniques for the disposal of ammunition, missiles and explosives [34]. But despite the widespread use of these methods, the open detonation and open burning of high explosives carries an environmental risk due to the possibility of heavy metal contamination from the shell, as well as gaseous emissions and unburnt residues from the explosive fillings. Understanding the behaviour of the new IHE formulations is very important for environmental conservation and protection.

Little is yet known about the emissions produced during the open burning of IHE formulations, but several studies have looked at TNT-based explosives in this context [35,36]. Accordingly, the environmental impact caused by the open burning of TNT is well understood [37,38] at least in terms of the effect on soils and groundwater contaminations. IHEs are also known to leave residual unreacted explosives in the soil after detonation, and they also produce gases and vapours [15–18].

Much of the behavioural data available for energetic materials has been generated by conducting thermodegradation and thermostability tests, in many cases by differential scanning calorimetry (DSC) [39–42]. Complementary thermal decomposition and combustion-like pyrolysis data have been provided using techniques such as controlled flash pyrolysis and the real-time detection of vaporized products by Fourier-transform infrared (FTIR) spectroscopy [43]. FITR has been used to analyse RDX following transient pyrolysis with a pulsed CO_2 laser, revealing the scission of an N-N bond leading to the formation of N_2O_4 [44]. This experiment identified the origin of the nitrogen atoms in the N_2O_4 product and showed that RDX mainly produces N_2O, H_2O, HCN, NO and CH_2O during thermal decomposition. A similar technique was used to study NTO [45]. Following pyrolysis under low-oxygen conditions, the majority of the residual solids formed an insoluble condensed-phase brown product, whereas the gaseous decomposition products detected by gas chromatography/mass spectrometry (GCMS) comprised a mixture of N_2 (43 %), N_2O (6 %), NO (8 %), CO_2 (37 %) and CO (6 %). Moreover, NTO can sublimate and condensate during thermolysis [46].

It may be expensive and time consuming to apply the techniques described above to some explosives, so computer simulations can be considered as an alternative. The ICT thermodynamic codes [47–49] and ANSYS FLUENT [41,42] have both been used to model the behaviour of TNT, RDX and HMX. The ICT codes use mass action and mass balance expressions to calculate chemical equilibria. Thermodynamic equilibria can be calculated under constant pressure conditions or constant volume conditions, especially for the high-pressure conditions of closed vessels and gun weapons. To achieve this output, when modelling mixed formulations, the ICT codes treat the mixture as a single component based on its empirical formula, thus disregarding further interactions between the individual ingredients.

To the best of our knowledge, none of the studies described above (experimental or computational) focused primarily on the gaseous emissions generated during the decomposition of explosives. Moreover, we understand that the proper assessment of residues and emissions derived from IHEs requires apparatus that can achieve mass balance, so a closed-chamber, laboratory-scale method is ideal. For non-explosive fires there are some laboratory-scale methods available [50–54] to generate emission gases for analysis (particularly by GCMS), to determine their chemical composition.

In the context of explosives, Mitchell and Suggs [55] assessed the open burning and open detonation of mainly TNT (~2.2 kg) using a 930 m^3 container (described as a BangBox) comprising stainless-steel burn pans placed on a concrete pad located at the centre of the test chamber. They deployed sensors for the detection of CO, CO_2, NO, NO_2, O_2 and HCl, as well as canisters for measuring volatile organic compounds (VOCs). The gases trapped using the canister were analysed for total non-methane hydrocarbons using two techniques: gas chromatography/flame ionization detection (GC/FID) and GCMS. The composited filters were extracted using the Soxhlet method prior to GCMS analysis.

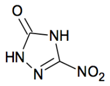
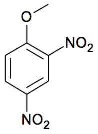
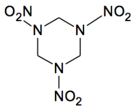
Here we describe a laboratory-scale setup for the burning and testing of IHE materials, based upon a new scaled-down version of the Mitchell and Suggs BangBox [55]. The large parabolic tent described in the original study is here replaced with small headspace vials, corresponding to a scale-down factor of 10^7 in terms of air volume. Our samples were heated to combustion, and the remaining oxygen and decomposition gases were measured by GCMS. The solid residues were characterized by high-performance liquid chromatography (HPLC). This allowed us to investigate the combustion efficiency of an IHE formulation containing NTO, RDX and DNAN to gain insight into the impact of open burning methods when applied to these materials. The materials were also tested by DSC to determine their thermostability.

4.2 Materials and methods

4.2.1 Chemicals

NTO [2] was manufactured in-house following a patented synthesis method [56]. DNAN [5] was purchased from Alfa Aesar [57], whereas both RDX [6] and the IHE formulation (described hereafter as Formulation 1) were already available at Cranfield University. Table 1-2 presents the oxygen balance [11,12], enthalpy of formation and other relevant characteristics of our test samples. Acetonitrile was purchased from Sigma-Aldrich and ultra-pure water was obtained from Merck-Millipore.

Table 4-2 Chemical properties of the explosive materials

Explosive	**Empirical formula**	**Chemical structure**	**Oxygen balance (%)** [11,12]	**Melting point (ºC)**	**Decomposition temperature (ºC)**	**Enthalpy of formation $\Delta H_f°$solid (kJ mol^{-1})**
NTO [2]	$C_2H_2N_4O_3$		-24.60	270	270–273	-100.75
DNAN [5]	$C_7H_6N_2O_5$		-96.90	94-96	NA	-186.65
RDX [6]	$C_3H_6N_6O_6$		-21.60	190	190-200	66.94
Formulation 1	$C_{3.7}H_4N_{3.8}O_{4.2}$	NTO / DNAN / RDX	-47.44 (1)	90	NA	-107.8 (2)

Legend:	*NA*	*Not applicable*
	(1)	*Calculated from the empirical formula*
	(2)	*Calculated from the enthalpy of formation of NTO, RDX and NTO*

4.2.2 Experimental setup

The experimental setup (Figure 4-1) consisted of a sealed 10 cm^3 Chromacol 10-CV-P715 GC headspace vial containing small samples (10–20 mg) of the selected energetic material. The vial was placed on a custom-made aluminium block (50 x 50 x 10 mm) with a 2-mm thermocouple slot drilled from the edge to the centre and a 5 mm central groove for the headspace vial. A calibrated thermocouple was attached, and the apparatus was placed on a tripod. The heat source was a hand-held PT-200 butane blowtorch. The temperature data were collected using a Pico data logger USB TC-08 attached to an IEC-KX-2 thermocouple and the data were recorded using PicoLog Recorder software v5.25.3 [58] at a rate of one measurement per second. The reported results are the average of 25 replicates.

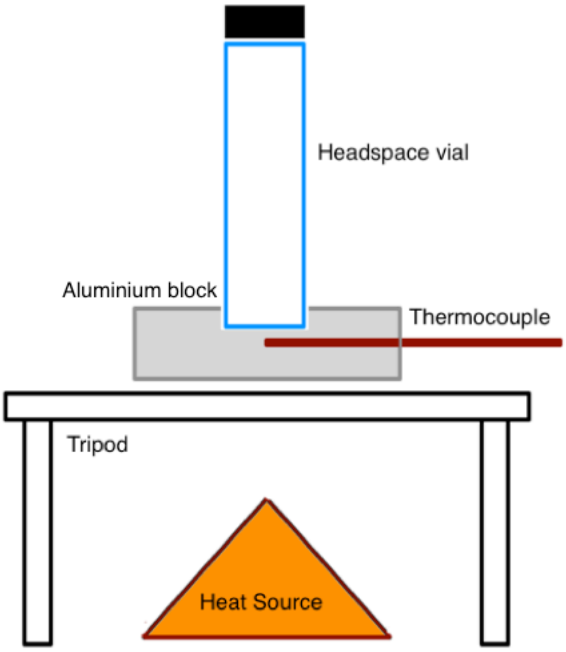


Figure 4-1 Schematic illustration of the experimental setup for the closed-vial combustion tests

To determine whether the septum contaminated the samples during heating, experimental trials were conducted using four types of Chromacol septum (20-CB3-510, 20-AC-CBT3-719, 20-ST3HT-610 and 20-CBT30). None of the septa contaminated or interfered with the gaseous analysis, probably due to the short duration of each experiment (the heating phase was less than 6 min). Septum 20-CB3 510 showed evidence of mechanical deformation due to the increase in pressure within the headspace vial, whereas the other three septa were unaffected. Septum 20-ST3HT-610 was selected for the subsequent tests based on the manufacturer's recommendations regarding high-temperature experiments. An aluminium KIMBLE chromatography 73822A-20 20-mm seal was used to crimp each headspace vial. For each experiment, the temperature gradient was recorded and values for the first 100 samples gave an average rate of 43 ± 1 °C min^{-1}.

4.2.3 Chemical analysis

The initial materials were tested by DSC, and after burning the gaseous products were analysed by GCMS. Finally the solid residues were analysed and the explosive residues were quantified by HPLC.

4.2.3.1 Differential scanning calorimetry

The materials were thermally characterized using a Mettler Toledo LF1100 TGA/DSC 3+, equipped with a DSC sensor controlled by Stare System software v15.00 (build 8992). The samples were placed in a 40 µL aluminium pierced crucible. The tests were conducted under an inert atmosphere (N_2 flowing at 50 cm^3 min^{-1}) and at two heating rates: 10 and 40 °C min^{-1}.

4.2.3.2 Gas chromatography/mass spectrometry

Following the burning phase, the sample was left to cool down (for no more than 12 h) and the gaseous content of the vial was characterized by GCMS using an Agilent Technologies 7890B GC system coupled to an Agilent Technology 5977A MSD. The GCMS method followed Bellerby et al. [59], in which the system was controlled using Agilent Chemstation software. For chromatography, the initial temperature was set to –80 °C for 1 min, followed by a heating rate of 60 °C min^{-1} until the temperature reached 150 °C, and then a 5 min heating period after the sample was injected into the Agilent ParaPlot Capillary Column (25 m length, 0.25 mm internal diameter and 8 μm film thickness) with a flow of helium at 1.2 cm^3 min^{-1}. The split ratio was 50:1 and the injection volume was 100 μL. The mass spectrometer (EI mode) set at 70 eV ran in full-scan mode from 10 to 100 *m/z*. The GCMS data are reported in terms of relative percentage composition.

4.2.3.3 High-performance liquid chromatography

The solid residues were dissolved in 10 cm^3 acetonitrile, passed through a 0.24-μm Nylon Fishedbrand syringe filter and analysed using a Waters-Alliance 2695 HPLC system connected to a Waters-Alliance 996 photodiode array detector. The samples were fractionated on an analytical Waters NovaPak C8 column (150 mm × 3.9 mm, 4 μm particle size) maintained at 30 °C. The mobile phase was 40:60:0.1 (v/v/v) acetonitrile/water/formic acid with a flow rate of 1.5 mL min^{-1}. The injection volume was 10 μL and the output signals were analysed at 296 nm for DNAN, 264 nm for RDX and 315 nm for NTO. To quantify each substance, a calibration curve was generated by plotting peak area versus the mass of the explosives injected. The HPLC was calibrated for each explosive from 10–50 ppm through six calibration points.

4.2.4 Thermodynamic calculations

The gases detected by GCMS were compared to simulated results obtained using the ICT Thermodynamic Code [47,48,60] (Windows Fronted, v1.00) and the Database of Thermochemical Values. The simulations were carried out using the explosive formulation alone (to represent a detonation) and also with 20 % (w/w) oxygen added to the formulation (to represent open burning). This figure was calculated by converting the volume of oxygen within the vial into mass, which was added to the explosive sample.

4.3 Results and discussion

Although open burning is the most widely used method to dispose of explosives, it is not suitable for the assessment of burning efficiencies because it does not preserve the reaction products or the mass balance. We therefore developed a laboratory-scale closed-chamber system to impose a heat flow that simulates the open burning of explosive samples. Under these conditions, we found that RDX underwent a violent reaction once vaporization was complete [61], breaching the vial seal and making it challenging to capture the gaseous emissions. Because RDX showed no reaction until 280 ºC was reached, its heating cycle was interrupted at 270 ºC (to preserve the sample by avoiding violent reactions), allowing the residual heat to safely warm the sample until it reached 280 ºC. Even in this short test, we observed RDX evaporating and decomposing, but we assumed the decomposition mechanism could be closer to pyrolysis than full burning. Table 1-3 lists the maximum temperature recorded for each compound before ignition wax observed. The values are higher than the decomposition temperature available in the literature, which reflects a thermal lag introduced by our setup: we recorded the temperature in the aluminium base, which is hotter than the explosive itself.

Table 4-3 Temperatures of combustion observed during the closed heating of IHE components

Compound	Highest recorded temperature before ignition was observed	Decomposition Temperature
Formulation 1	300 °C	NA
NTO	315 °C	270–273 °C
RDX	280 °C	190–200 °C
DNAN	350 °C	NA

The main purpose of open burning is to convert energetic and meta-stable chemicals (explosives) into more stable and less energetic forms such as CO_2 and H_2O, ideally leaving no explosive materials among the solid residues. Our experimental setup achieved a full mass balance for both solid residues and gaseous emissions. When we tested the pure components, we found that ~75 % (w/w) of the DNAN remained unreacted after burning, whereas only 1 – 2 % (w/w) of the NTO and RDX were unburnt. When the same test was conducted on Formulation 1 (Figure 1-2) the solid residues were in the order of ~23 %. For Formulation 1, DNAN not only showed resistance to burning, but was also able to draw heat from the system, increasing the amount of unburnt NTO and RDX residues.

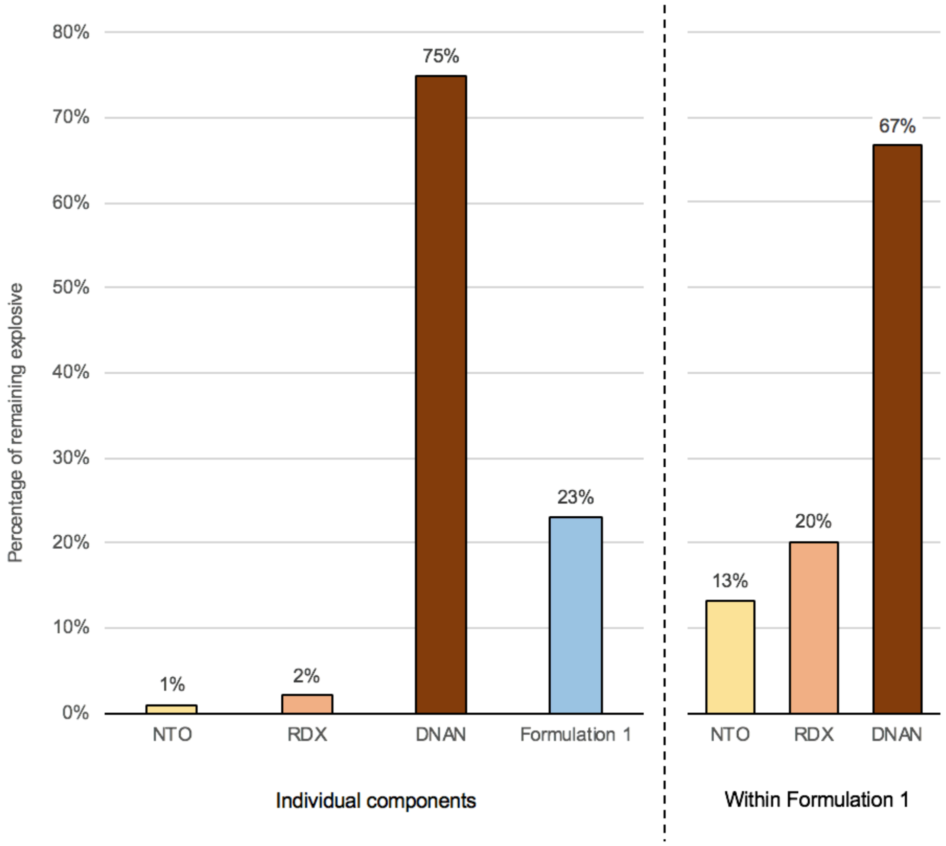


Figure 4-2 **Percentage of unburnt explosives remaining after combustion determined by HPLC – RDX/NTO/DNAN (individually and combined as Formulation 1)(average results of 100 samples)**

DNAN was the most volatile of the three substances we tested [40]. Recent decomposition tests revealed evidence of decomposition at 200–300 ºC after 5 days of continuous heating [39]. Our data support the hypothesis that DNAN sublimes, drawing energy from the system and reducing the energy available for ignition of NTO and RDX thus increasing the quantity of residual solids. This behaviour was supported by thermo-characterization experiments, which showed no significant differences ay heating rates of 10 – 40 °C min^{-1} (Figure 4-3). Under an inert atmosphere, NTO melted at ~280 °C (278 °C at 10 °C min-1 heating rate and 282 °C at 40 °C min-1 heating rate), whereas Formulation 1 melted at 220 – 260 °C when heated at the slower rate and at 220 – 280 °C when heated at the faster rate. DNAN was able to undergo both sublimation, melting and evaporation. It melted at ~100 °C at both heating rates (98 °C at the slowest heating rate and 101 °C at the fastest heating rate), but it evaporated at 280 °C when heated at 10 °C min-1 and at 320 °C when heated at 40 °C min-1. NTO melted at 280 °C (278 °C at 10 °C min^{-1} heating rate and 282 °C at 40 °C min^{-1} heating rate), whereas Formulation 1 melted at 220–260 °C when heated at the slower rate and at 220–280 °C when heated at the faster rate. DNAN was able to undergo both melting and evaporation. It melted at ~100 °C at both heating rates (~98 °C at the slowest heating rate and 101 °C at the fastest heating rate) but it evaporated at 280 °C when heated at 10 °C min^{-1} and at 320 °C when heated at 40 °C min^{-1}. These experiments were used to specify the maximum temperature for burning in the headspace vials. Moreover, DNAN sublimed without melting, whereas the DSC data indicated melting, which is due to the temperature gradient present in the experimental setup.

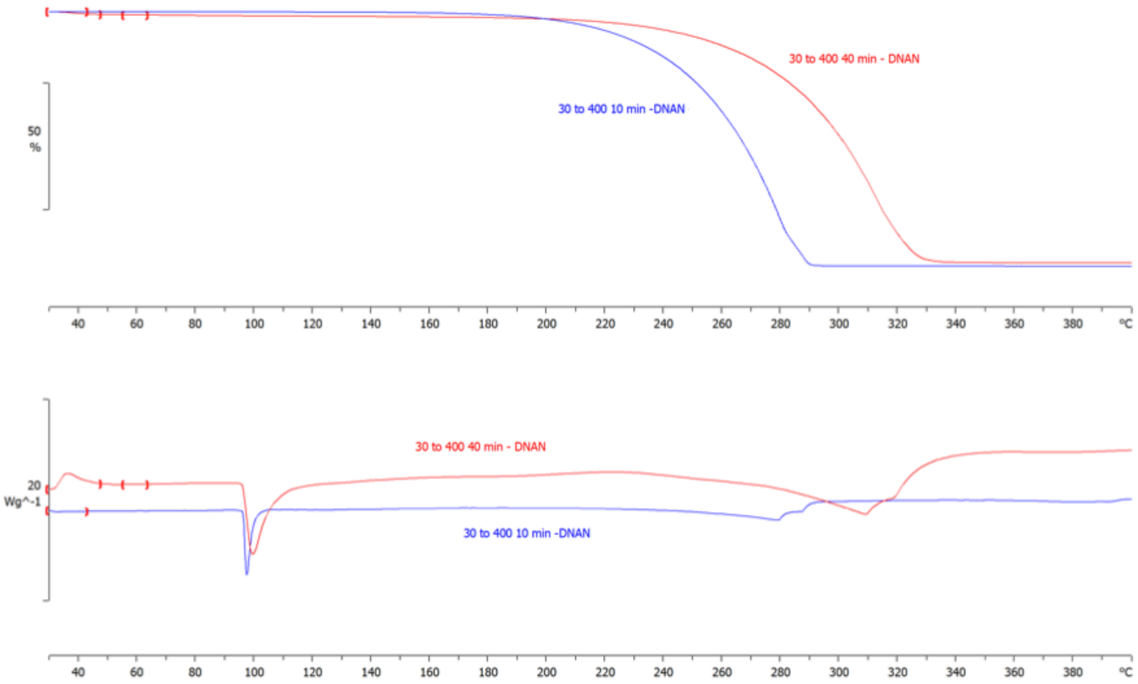


Figure 4-3 Thermogravimetric analysis and differential scanning calorimetry results showing that DNAN sublimes before reaching a sufficient temperature for combustion (average results of three replicates)

The experiments described above indicate that, during open burning, DNAN does not burn completely but becomes a vapour and is transported in an unreacted state away from the burning area. Ultimately, this would spread contamination caused by unreacted explosives across a wider area, defeating the purpose of open burning.

As well as investigating the solid residues, we also assessed the gaseous emissions in the headspace vial. Initially we sought to determine whether the vial contains sufficiently oxygen-rich air atmosphere for our samples. Both RDX and NTO consumed far less oxygen than was available in the 10 cm^3 vial, which suggests that 10 cm^3 of air is in stoichiometric excess when burning 10 mg of these compounds (Figure 4-4). Furthermore, there was a direct correlation between the oxygen balances of RDX and NTO [11,12] and the oxygen remaining in the vial (Table 1-2). In contrast, DNAN underwent a phase transition, partially sublimating, partially melting and evaporating, and moved to the top of the vial instead of burning, but it still consumed most of the oxygen available within the vial. The temperature gradient present in the experimental setup favoured the sublimation of DNAN followed by its solidification on the upper parts of the vial, remaining in an unreacted state.

In the context of Formulation 1, we observed that the DNAN sublimed (endothermic process) removing energy from the system, which reduces the combustion (exothermic reaction) efficiency of the other explosives causing a difference in the oxygen consumption trend compared to pure RDX and NTO (Figure 4-4). Overall, the data indicated that burning a mixture containing DNAN is less efficient than burning pure RDX and/or NTO, which leaves more solid residues, increasing the potential environmental impact. Interestingly, NTO is known to undergo sublimation [45,46], but the heat flow provided by the experiment was sufficient to achieve its ignition temperature. The remaining oxygen as shown in Figure 4-4 is a proportion of the starting amount (20.95% oxygen in air). In summary, the oxygen consumption of RDX, NTO and

Formulation 1 followed the same pattern as observed for the oxygen balance: the more oxygen-deficient the explosive, the more oxygen is used in the headspace vial. Although DNAN was the most oxygen deficient of the materials we tested, it nevertheless used approximately the same amount of oxygen as Formulation 1 due to its sublimation instead of burning. Moreover, we propose that Formulation 1 consumes all the oxygen available within the headspace vial and the values recorded by the GCMS can be considered within the range of experimental error.

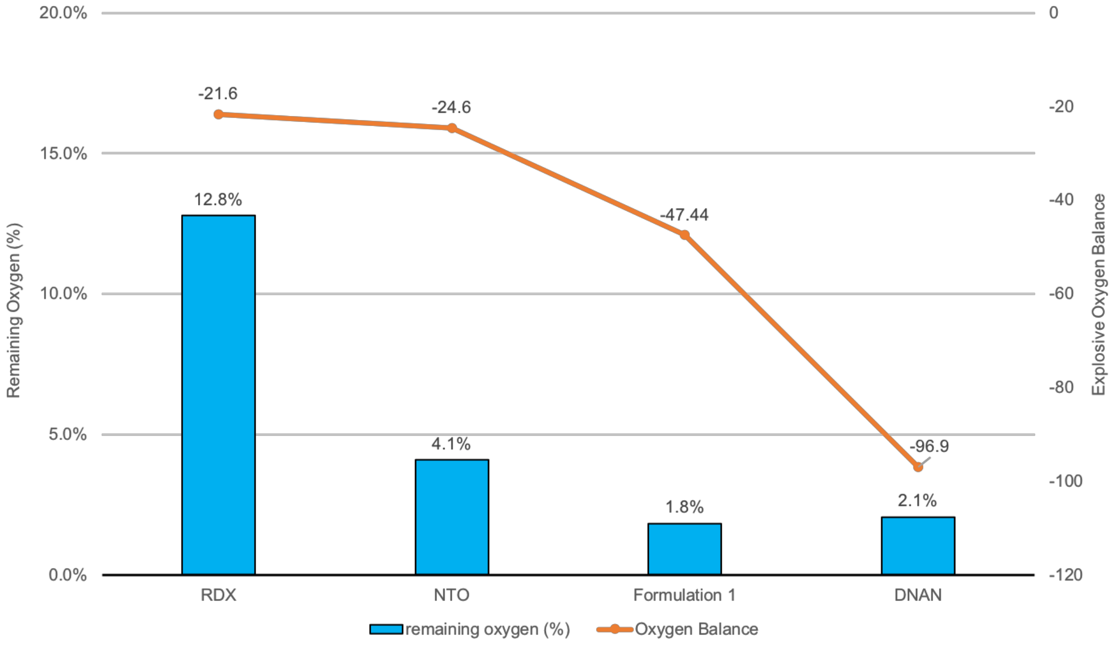


Figure 4-4 The oxygen balance of different explosives and mixtures compared to the oxygen remaining in the vial after combustion, the latter expressed as percentage of the initial concentration (average results of 100 samples)

The analysis of other gaseous products in the headspace vial (Figure 4-5) revealed that N_2 levels increased above background for all samples, and water was also detected. The burning of RDX and NTO (together they represent 80 % of Formulation 1) is responsible for producing the CO_2 observed during the burning of Formulation 1. NTO makes up ~50 % of Formulation 1, and although it is more insensitive than RDX, it nevertheless plays an important role in producing this gas. Our solid residue analysis indicated that not all the raw materials burnt evenly, but across all the samples less CO than CO_2 was produced. This confirms that O_2 from the air plays a significant role in the burning reaction, thus indicating that our samples underwent combustion instead of pyrolysis or thermal decomposition.

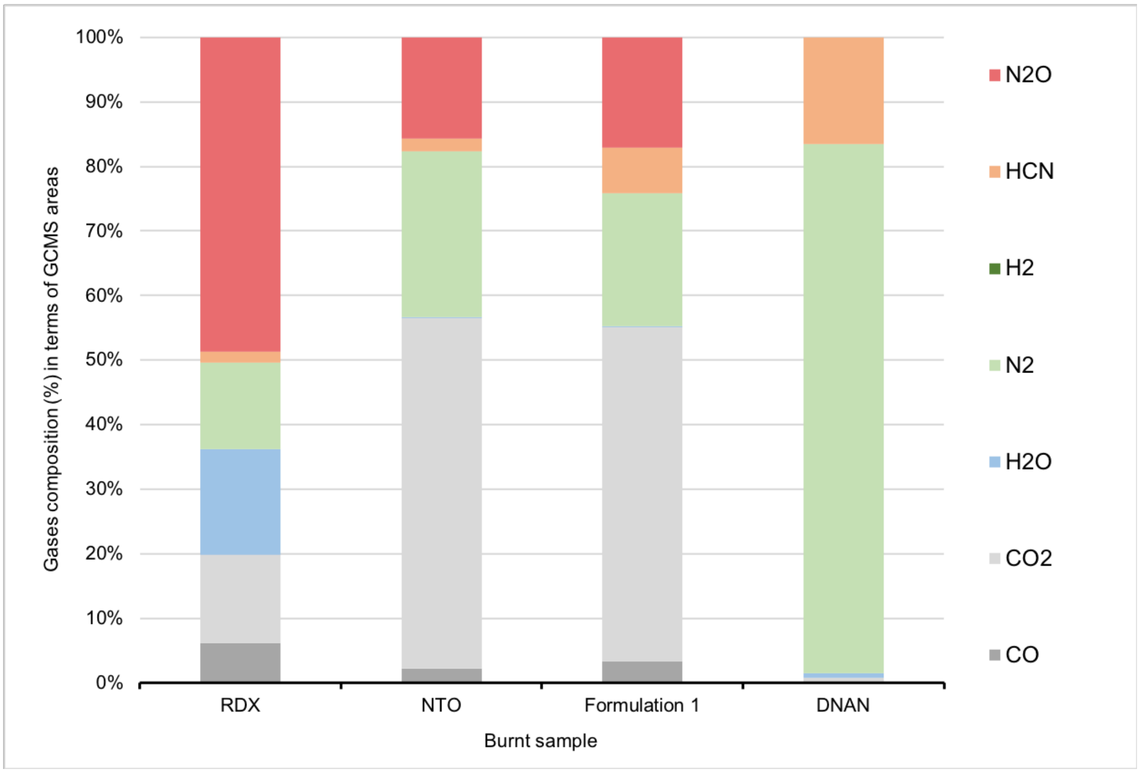


Figure 4-5 Combustion products observed when burning RDX/NTO/DNAN (individually and combined) in a 10 cm^3 headspace vial. (average results of 100 samples)

As expected from previous studies [44], RDX produced the highest levels of N_2O as an intermediary product [44], before forming other species such as H_2O, HCN and NO, all of which were detected in our experiment. NTO produced the same qualitative gaseous emission mix as detected in an earlier pyrolysis experiment

[45], but the amount of CO_2 was much higher (54 %) in our study compared to the previous study (37 %). Similarly, the amount of N_2O increased from 6 % in the pyrolysis study to 16 % in our tests, which reinforces our conclusion that oxygen from the air plays a significant role in the gaseous emissions generated by NTO. Moreover, the gaseous products released by NTO, combined with the HPLC analysis of the solid residues, indicated a chemical reaction instead of phase transitions (sublimation and condensation) as observed in previous thermolysis tests [46].

DNAN produced the lowest levels of CO, CO_2 and other chemical species, which is consistent with the poor efficiency of burning observed during the analysis of solid residues. NO_2 was not analysed by GCMS due to the limitations of the column. Moreover, HCN has been detected in thermal decomposition studies of RDX and NTO, which suggests that DNAN produces HCN by thermal decomposition in our experiments. Unfortunately, it was not possible to investigate this phenomenon further using our experimental setup. The large amount of N_2 reported for DNAN is due to the very low amount of gas generated – hence the N_2 comes from the air.

A previous work on open burning of explosives [37] showed that the major reaction products from an unconfined detonation are primarily the fully oxidized, thermodynamically stable compounds: N_2, CO_2, and H_2O. The detonation also produces small quantities of incompletely oxidized, combustible products, such as, elemental carbon (soot), CO, H_2, CH_4, NO, NO_2, HCl, C_2H_2, C_2H_2, C_2H_6, and CH_2O. Most of these chemicals were observed in our close-system experiments, which is another evidence that our small-scaled close system can be used as a preliminary experiment for observing potential pollutants from open burning of explosives.

We also compared our results with those published within the 402.05762.00001 report [38], we can observe a large concern on particulate material (PM_{10}) [62], which was not the focus of this work. Moreover, their report showed that the disposal of explosives by open burning will lead to the release to atmosphere of a range of compounds, typically combustion products such as carbon dioxide and water but also trace amounts of combustion pollutants (such as oxides of nitrogen and sulphur dioxide) and products of incomplete combustion such as carbon monoxide, ammonia and volatile organic compounds, which is aligned with the results we report in this work. Table 1-4 provides a comparison of the calculated mass of pollutants likely to be released in the environment based upon our experiments compared against TNT values from the 402.05762.00001 report [38], showing that Formulation 1 produces less CO and more HCN than TNT.

Table 4-4 Emission Factors (kg/tonne) for Explosives tests: Close system experiments compared against published values from TNT

	NTO(1)	RDX(1)	DNAN(1)	Formulation 1(1)		TNT [38]
CO	25	75	-	38		398
CO_2	1061	275	20	1021		
H_2	-	-	-	-		
H_2O	-	129	8	-		
N_2	325	175	1025	263		
HCN	24	24	193	84		13
N_2O	314	963	-	334		
C_2H_4	-	-	-	-		
Acetone	-	-	-	-		

1 – Values calculates (stoichiometrically) from Figure 4-5

Moreover, the EU Directive 2000/76/EC [37,63] regulates maximum concentration of 50 $mg.m^{-3}$ for CO when incinerating hazardous waste, being particulate material (PM) and metals the main pollutants addressed by this bill, which were not measured as part of the experiments reported within this paper.

The thermodynamic calculations (Figure 4-6) indicated that most of the nitrogen available in the sample would be converted into N_2 (with trace amounts of HCN). This is consistent with the oxygen-rich environment in the experiments compared to the low-oxygen environment assumed by the calculations. A key difference between the theoretical calculations and experiments was the CO/CO_2 ratio. The calculations predicted more CO than we observed, and again this is consistent with the assumed low-oxygen burning environment.

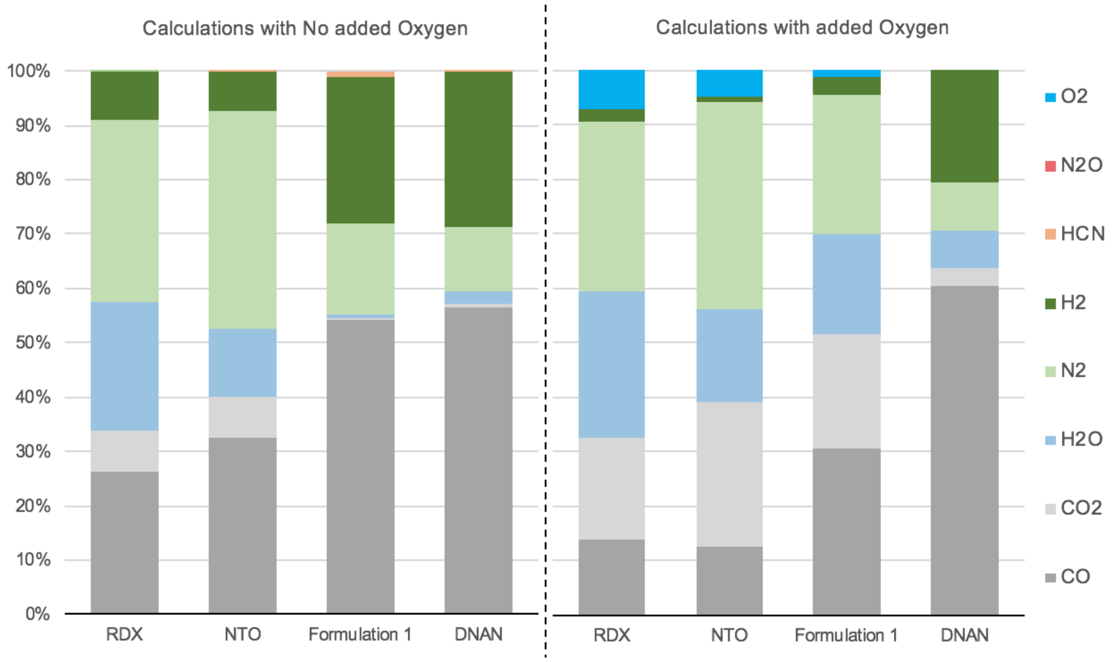


Figure 4-6 Combustion products predicted when burning RDX/NTO/DNAN (individually and combined) as calculated using ICT codes, with and without added oxygen. (average results of 100 samples)

The data presented in Figure 4-6 compares the results from the ICT code (output measured in moles) against the empirical GCMS data, which refers to GC comparative peak areas. Although this could introduce a deviation factor for the concentrations and percentages, it does not compromise the results in terms of the chemical species observed and calculated.

When the ICT codes [47–49] were used to predict the chemical species produced during burning, we observed compositional variation between the predicted and experimental results, which is likely to reflect the code design assumptions. The temperature gradient we applied was ~43 ºC min^{-1} up to 300 ºC, whereas the ICT code applies thermodynamic calculations for decomposition under constant pressure and a detonation temperature of 1500 ºC. Differences between the simulation and empirical results were also caused by the additional oxygen available in the experiments which was not automatically added by the ICT code, thus the user must introduce the required adjustments to match the amount of oxygen available under the experimental conditions. To compensate for the low-oxygen atmosphere in the calculations, we repeated the calculations adding 20 % (w/w) of oxygen into the mix, representing the amount of oxygen in air in the headspace vial and the average mass of explosive. When this adjustment was made, the simulation results for NTO and RDX moved closer to the experimental observations in the burning experiments. In the case of DNAN, the predicted gaseous products were completely different from those observed during the experiment, which supports our findings that DNAN is highly resilient to burning, undergoes melting and sublimation, and is transported away from the burning area. Our data adds to the body of evidence available for decomposition and stability studies focusing on RDX [44] and NTO [45], although the samples in these earlier studies were heated for longer and were maintained under vacuum to determine their stability behaviour. In contrast, our study focused on the behaviour and potential environmental impact of IHE disposal by open burning.

As expected, the gases generated during the burning of Formulation 1 were not directly comparable to those produced by burning each pure component separately. This is likely to reflect the different oxygen balance in the mixture compared to each individual constituent [64], and the combination of different thermal decomposition behaviours as indicated by DSC analysis.

Given the volatility of DNAN and its positive heat of vaporization, it rapidly removes the heat generated when NTO and RDX are burning, reducing the available energy to sustain their combustion and rapidly moving away from the burning area while remaining unreacted. Therefore, although DNAN is less toxic than NTO and RDX, our work has shown that it is more resilient to burning and can leave more explosive residues after open burning, which may become an environmental hazard. Similarly, our results showed that the ~23 % residues of Formulation 1 left unreacted on the soil after open burning comprise ~67 % of the initial mass of DNAN and 13–20 % of the initial masses of NTO and RDX, which might become an environmental concern in the future. Robust and safe strategies for the disposal of DNAN (which is a fuel, not an explosive) must therefore be developed to avoid soil residues after detonation and open burning, and such methods should be made available before IHE rounds need to be decommissioned and disposed of in bulk.

4.4 Conclusion

By measuring the consumption of oxygen, we confirmed that our laboratory-scale experimental system was able to simulate the open burning of IHEs. The thermodynamic calculations showed promising results when predicting the qualitative composition of gaseous emissions from RDX and NTO, as long as the available oxygen was taken into account. However, the simulation was less accurate when predicting the behaviour of DNAN. This material has a greater degree of insensitivity than RDX and NTO. DNAN was resistant to burning and less reactive than the other materials, and its sublimation and melting reduced the energy available for the other compounds and therefore increased the quantity of residues left behind. The replication of such behaviour in the field would defeat the purpose of open burning, because much of the explosive material would be left behind in an unreacted state. The experimental system described herein is constructed from inexpensive equipment but is versatile. In the future, it could be used to test the behaviour of IHEs and other novel formulations during burning, pyrolysis and heating cycles, providing much-needed insight into the behaviour of such materials in the environment. Finally, this work can be used to determine how to test and monitor the combustion behaviour of DNAN-based IHEs in small and medium scale open burning setups, which will provide insight into the environmental impact of emissions from the burning of IHEs in realistic military scenarios.

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5 EVALUATION OF THE OPEN BURNING OF DNAN-BASED INSENSITIVE HIGH EXPLOSIVES

Abstract

The disposal of explosive materials is achieved using methods classed either as closed (performed inside a special facility) or open (conducted in the open air). The open methods are the simplest and least expensive to implement both on training ranges and in theatre, although the only such methods still considered acceptable are open burning and open detonation. One drawback of these methods is that waste products (solid residues, dust, and combustion gases) are directly emitted to the environment without any control or treatment, although sometimes the solid residues are collected. Moving on from previous work describing the emissions from insensitive high explosives burning in a small-scale closed system, we designed a larger-scale analytical approach using gas capture combined with sensors for CO, CO_2, NO and NO_2 and activated carbon as a sorbent material, which was extracted using both the Soxhlet method and accelerated solvent extraction to recover the chemicals for analysis. A series of experimental trials was carried out, scaling from grams to kilograms in an open system to provide good-quality data concerning the open burning of an insensitive formulation comprising DNAN, NTO and RDX. These tests revealed that DNAN takes energy from the burning of RDX and NTO when it melts and sublimates, becomes mobile and spreads to the surrounding areas. Moreover, by reducing energy availability in the bulk of the burning material, the solid residues of NTO and RDX increase to ~20 % of their initial masses. The experiments also showed that the emitted gaseous products tend towards greenhouse gases, whereas the solid residues and particulate material are more likely to constitute environmental hazards.

Keywords: Insensitive high explosives, open burning, laboratory-scale testing, scale-up trials, real-size trials, gaseous emissions

5.1 Introduction

The disposal of explosive materials is necessary when ordnance and munitions reach the end of their service life or when a military campaign is complete and surplus materials remain in theatre. Many different disposal methods have been proposed and implemented over the last few decades and these can generally be described either as closed, meaning they are conducted inside a special facility, or open, meaning they are conducted in the open air. In 1978, the US Environmental Protection Agency (EPA) [1] compared known disposal methods and issued a report (EPA-600/2-78-012 [2]) proposing six categories of demilitarization: washout, a deactivation furnace, open detonation, open burning, new developments, and advanced technology in chemical demilitarization. In 2002, Duijm addressed what he called “traditional ways” to dispose of ammunition [3], including closed detonation, closed incineration primarily using existing stationary facilities like a rotary kiln, fluidized bed combustion, open burning and open detonation. The open methods are the simplest and least expensive to implement both on training ranges and in theatre, and given that other open methods (such as dumping at sea) have become illegal or impractical [4], open burning and open detonation are now the only methods still considered acceptable. However, one drawback is that the waste products (solid residues, dust and combustion gases) are generally emitted directly into the environment without any control or treatment.

In terms of environmental effects and human health, open methods for the disposal of explosives have disastrous impacts: toxic gas emissions (HCl, SO_2 and HCN) and the contamination of groundwater and soil with residues [5]. For personnel dealing with disposal, and the inhabitants of nearby towns and cities, this means an increased risk of cancer and heavy metal poisoning as well as direct risks from the explosive materials [6–8]. The disposal of legacy explosives such as trinitrotoluene (TNT) has been studied in detail [3,4,9–22] but the same cannot be said for newer insensitive high explosives (IHEs) that use 2,4-

dinitroanisole (DNAN) [23] as a melt-castable binder, particularly IHE formulations in which DNAN is combined with 3-nitro-1,2,4-triazol-5-one (NTO) [24–26] and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) [27]. The lack of data compromises the implementation of measures to monitor and control the environmental impact of IHEs on military ranges [28,29].

Previous studies concerning legacy explosives have been based on the analysis of real soil environments [9,10,13,14,17–22] or laboratory simulation experiments such as soil columns [11,12]. Overall, the studies showed that unattended and uncontrolled explosives are transformed into derivative substances and/or transported through the soil, leading to groundwater contamination and further environmental damage. When DNAN, RDX and NTO are left unattended (either intentionally or due to an inefficient disposal method) they can also become environmental hazards that are toxic towards humans (Table 1-1).

Table 5-1 Toxicity and chemical properties of NTO, DNAN and RDX

Explosive	**Solubility (mg L^{-1} at 25 °C)** [25]	**lethal dose (LD$_{50}$) (mg kg^{-1} in rats)**	**human skin penetration rate (µg cm^{-2} h^{-1})**
NTO [24]	16,642	>5000 [30]	332 [31]
DNAN [23]	276	300 [32,33]	1.10 [31]
RDX [27]	60	100 [34]	NA

Legend: NA – Not applicable

Predicting the behaviour of environmental contaminants is typically challenging because there are many variables that affect fate and transport, including the chemical characteristics of the contaminants, soil properties and climatic conditions. The impact of RDX on the environment is well understood, but the impact of NTO and DNAN is unclear, as is the effect of IHE formulations containing various proportions of these substances, even though such mixtures are already being tested for military applications in the USA [17,18,25,35–37].

Several reports have addressed the decomposition kinetics and thermal stability of explosives, including RDX and NTO [38–52]. These studies made use of analytical techniques such as differential scanning calorimetry (DSC) combined with thermogravimetric analysis (TGA) [52–56], fast thermolysis/Fourier transform infrared (FTIR) spectroscopy and T-jump/FTIR [40,57–59]. This approach has been used to analyse RDX [60] following transient pyrolysis with a pulsed CO_2 laser, revealing the origin of the nitrogen isotopes in the N_2O_4 product and showing that RDX mainly produces N_2O, H_2O, HCN, NO and CH_2O during thermal decomposition as implemented in this particular experiment. NTO, when tested for pyrolysis under a low-oxygen atmosphere [42], generated a mix of N_2 (43 %), N_2O (6 %), NO (8 %), CO_2 (37 %) and CO (6 %) as gaseous emissions detected by gas chromatography/mass spectrometry (GCMS).

One of the major limitations of almost all previous studies is that they either assessed thermal stability alone or, when environmentally focused, considered the solid residues left on the ground but not the gases and vapours, thus ignoring the direct impact on air quality caused by burning or detonating explosives as well as indirect soil contamination caused by the dispersion and precipitation of burnt residues and smoke particles. The impact of open burning has been investigated for various non-explosive materials (such as paper, animal carcasses and automobile shredder fluff fires) focusing in many cases on the emission of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs), but in other studies also including non-PAH semi-volatile organic compounds (SVOCs), carbonyl and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) [61–65]. Reports have been published regarding the PM10 contaminants (particulate matter ≤10 μm in diameter) released during the open burning/open detonation of legacy explosives [66], and BangBoxes have been used to detect the emission of gases (CO, CO_2, NO, NO_2, O_2 and HCl) and VOCs, the latter analysed by GCMS after collection [63], These studies concluded that the gases generated when burning TNT are mainly greenhouse gases. More recently, the EPA [67] used a helium-filled aerostat (4.3 m in diameter) to carry an analytical package into the smoke plume of burning explosives. The energetic compounds HMX, RDX and TNT (and any by-products) were analysed from the particulate matter collected on a quartz filter, whereas gases and vapour emissions were ignored because of the low quantities involved [68]. Although innovative, this method is expensive and time consuming for monitoring large piles of burning explosives and does not allow for mass balances, thus making it impossible to determine the burning efficiency and the quantity of unreacted residues.

Given the lack of air monitoring data in military open-burning scenarios, one practical solution could involve the application of health and safety protocols that are currently used to monitor air quality in the workplace [69]. They are designed around live sensors (both infrared and electrochemical, with or without loggers) or sorbent tubes [70]. The live sensor approach was adopted by the EPA for the balloon experiments discussed above [67].

Live sensors interface with a logger and provide immediate readings. Some commercially available sorbent tubes/traps can also provide instant data [71] but they are often designed for screening, in which case they are usually combined with GC instruments to monitor the vapour phase fraction of organic compounds in air and thus require more effort. Applications range from atmospheric research and ambient air monitoring (indoors and outdoors) to occupational hygiene (personal exposure assessment) and measuring chemical emission levels [72]. Moreover, the type of chemical used in a sorbent tube and the analytical method applied after sampling determine which gases can be detected. Sorbents are classified according to the mechanism used to recover the trapped compounds, i.e. solvent extraction or thermal desorption [73]. The use of sorbents is distinct from sampling procedures such as collecting whole air samples using canisters [72], as deployed in the abovementioned BangBox study [63].

If canisters are not suitable for sample collection, a solid matrix can be used to adsorb contaminants for screening. In such cases, the choice of sorbent will determine the success of the screening experiment. Many different sorbents are available, but most applications involve the use of activated carbon [72], which is efficient, inexpensive and relatively easy to analyse [72,74]. Activated carbon is not suitable for the analysis of CO and CO_2 (because they are not absorbed) or for NO and NO_2 (because they cannot be desorbed) but it is ideal for most other compounds. Moreover, desorption can be induced by heating the carbon [75] followed by GCMS analysis, or by solvent extraction then GCMS or high-performance liquid chromatography (HPLC).

Having established the emissions from IHEs burning in a small-scale closed system, here we developed an open burning scenario similar to the typical methods used by military organizations. Our analytical approach was similar to the BangBox concept [63] in which canisters were used for the direct assessment of gases. However, we scaled down the previously-reported metal burning trays [16,76] for TNT (~2.2 kg) in a 930 m^3 container [63], and used modified 10 cm^3 headspace vials as canisters. We also combined the headspace vials with live sensors for CO, CO_2, NO and NO_2 as well as activated carbon as a sorbent material, which was extracted using both the Soxhlet and accelerated solvent extraction (ASE) methods to recover the chemicals for analysis. Activated carbon was selected because it is inexpensive and easy to source, making it the most commonly used sorbent material for organic substances [72]. This would make it economically the best choice for monitoring the open burning of explosives. This experimental setup was used in a series of trials, scaling up from grams to kilograms in an open system (in the laboratory and field) to test and validate our small-scale method and, at the same time, provide good-quality behavioural data concerning the open burning of an IHE comprising DNAN, NTO and RDX.

5.2 Materials and methods

The overall approach behind the methodology described herein was to scale-up the burning of selected IHE formulations from grams to kilograms, following the approach laid out in Figure 1-1. The first step (small-scale closed burning) has been reported previously [77], whereas the other steps are described here for the first time.

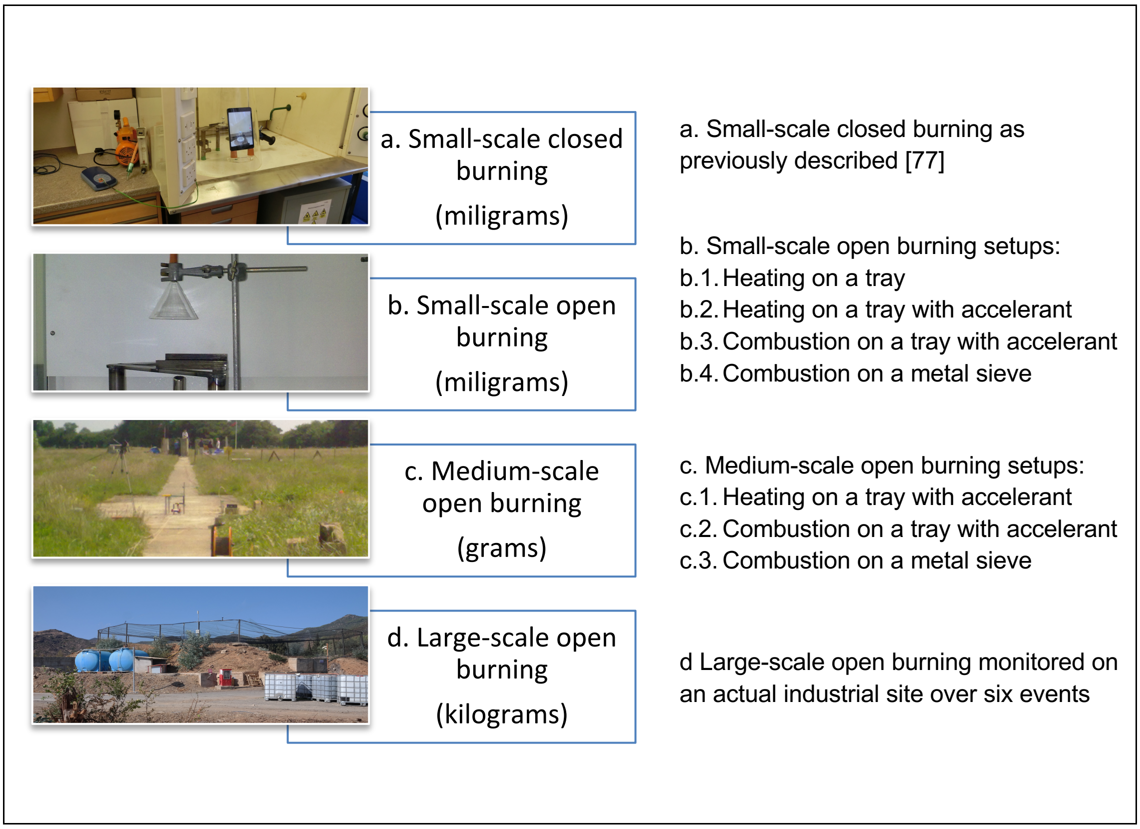


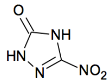
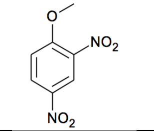
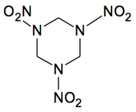
Figure 5-1 The scale-up approach

Small-scale open burning was conducted within a fume cupboard, whereas the medium-scale and large-sale burning were conducted outdoors using a metal tray and accelerant. The experimental setup for each sample size is described in detail bellow. The materials and analytical techniques were common across all the experiments. The sample sizes and further details are summarized in Table 5-3 (Section 1.2.3.1) and Table 5-4 (Section 1.2.3.2).

5.2.1 Chemicals

NTO [24] was prepared in-house using a patented synthesis method [78]. DNAN [23] was commercially sourced from Alfa Aesar [79], whereas both RDX [27] and the IHE formulation (described hereafter as Formulation 1) were kindly provided by BAE Systems. For larger-scale burning we assessed an RDX-based plastic explosive (described hereafter as PBX1) due to production schedules and material availability at the site of our industrial partner. Table 4-2 also presents the oxygen balance [80,81], enthalpy of formation and other characteristics of our test samples. Acetonitrile and acetone were both purchased from Sigma-Aldrich and ultra-pure water from Merck-Millipore. The activated carbon (standard EN14387) was purchased in the form of type-A2 packed canisters from Allpipe Hazmat Control Company.

Table 5-2 Chemical properties of the explosive materials

Explosive	Empirical formula	Chemical structure	Oxygen balance (%) [80,81]	Melting point (ºC)	Decomposition temperature (ºC)	Enthalpy of formation ΔH_f°solid (kJ mol^{-1})
NTO [24]	$C_2H_2N_4O_3$		-24.60	270	270–273	-100.75
DNAN [23]	$C_7H_6N_2O_5$		-96.90	94-96	NA	-186.65
RDX [27]	$C_3H_6N_6O_6$		-21.60	190	190-200	66.94
Formulation 1	$C_{3.7}H_4N_{3.8}O_{4.2}$	NTO / DNAN / RDX	-47.44 (1)	90	NA	-107.8 (2)
PBX1 (3)	$C_3H_6N_6O_6$	RDX based	-89.68 [82]	NA	NA	8.43 [82]

Legend: *NA – Not applicable*

(1) Calculated from the empirical formula
(2) Calculated from the enthalpy of formation of NTO, RDX and NTO
(3) This material was monitored during the large-scale burning due to production schedules

5.2.2 Chemical Analysis

The initial materials were tested by DSC, and after burning the gaseous products were analysed by GCMS. Finally, the solid residues were analysed and quantified by HPLC.

5.2.2.1 Differential scanning calorimetry

The materials were thermally characterized using a Mettler Toledo LF1100 TGA/DSC 3+, equipped with a DSC sensor controlled by Stare System software v15.00 (build 8992). The samples were placed in a 40-µL aluminium pierced crucible. The tests were conducted under an inert atmosphere (N_2 flowing at 50 cm^3 min^{-1}) and at two heating rates: 10 and 40 °C min^{-1}.

5.2.2.2 Gas chromatography-mass spectrometry

Following the burning phase, the sample was left to cool down (for no more than 12 h) and the gaseous content of the vial was characterized by GCMS using an Agilent Technologies 7890B GC system coupled to an Agilent Technologies 5977A MSD. The GCMS system was controlled using Agilent Chemstation software. For chromatography, the initial temperature was set to –80 °C for 1 min, followed by a heating rate of 60 °C min^{-1} until the temperature reached 150 °C, and then a 5 min hold period. The sample was injected into the Agilent ParaPlot Capillary Column (25 m length, 0.25 mm internal diameter and 8 µm film thickness) with a flow of helium at 1.2 cm^3 min^{-1}. The mass spectrometer (EI mode) was set at 70 eV and was run in full-scan mode over the range 10 – 100 *m*/*z*. The GCMS data are reported in terms of relative percentage composition. No external calibration of concentrations was possible.

5.2.2.3 High performance liquid chromatography

The solid residues were dissolved in 10 mL acetonitrile, passed through a 0.24-µm Nylon Fishedbrand syringe filter and injected into a Waters-Alliance 2695 HPLC system connected to a Waters-Alliance 996 photodiode array detector. The samples were separated on an analytical Waters NovaPak C8 column (150 mm × 3.9 mm, 4 μm particle size) maintained at 30 °C. The mobile phase was 40:60:0.1 (v/v/v) acetonitrile/water/formic acid with a flow rate of 1.5 mL min^{-1}. The injection volume was 10 μL and the output signals were quantified at 296 nm for DNAN, 264 nm for RDX and 315 nm for NTO. To quantify each substance, a calibration curve was generated by plotting peak area versus the mass of the explosives injected. The HPLC was calibrated for each explosive from 10–50 ppm through six calibration points.

5.2.2.4 Solvent Extraction

The chemicals adsorbed by the activated carbon were extracted via Soxhlet [83–87] and Accelerated Solvent extraction (ASE) [88] methods. The first method is reliable, yet time consuming technique to extract contaminants form solid matrix, whilst the ASE is a newer technique and could be proved useful, reliable and faster. This paper tested both approaches to determine whether ASE can be used as a replacement for Soxhlet.

5.2.2.4.1 Solvent extraction by Soxhlet

The chemicals adsorbed by the activated carbon were extracted by Soxhlet [83–87]. From each canister (overall activated carbon mass of 100 g) two samples of 8 g were extracted. Each sample was placed in one glass crucible and Soxhlet extraction with acetone was carried out for 4 h. Each sample was extracted twice to assess the extraction efficiency. The extracts were analysed by HPLC and GCMS.

5.2.2.4.2 Accelerated solvent extraction

The chemicals adsorbed by the activated carbon were also extracted by ASE using a Dionex ASE 350 device (Thermo Fisher Scientific) [88]. Samples were extracted using acetone/water (3:2) at 100 °C and ambient pressure, with a heating time of 5 min, a static time of 10 min and a 100-second purge interval. The extracts were analysed by HPLC and GCMS.

5.2.3 Experimental setup

5.2.3.1 Laboratory small-scale setup

In the laboratory, small-scale open burning was carried out using four setup variations (Figure 5-1): (1) heating on a tray, (2) heating on a tray with accelerant, (3) combustion on a tray with accelerant, and (4) combustion on a metal sieve. First, the burning was carried out on top of a 10 x 10 cm carbon-steel tray (2 mm thick), heated from beneath using a handheld butane torch (Figure 5-2). A collection funnel was suspended above the burning materials and connected to a 10 cm^3 headspace vial modified to include two taps. A BACOENG 4.2 CFM two-stage vacuum pump (operating at 3.4 L min^{-1}) was connected to the end of the modified headspace vial to draw the gaseous flow from the burning materials into the canister.

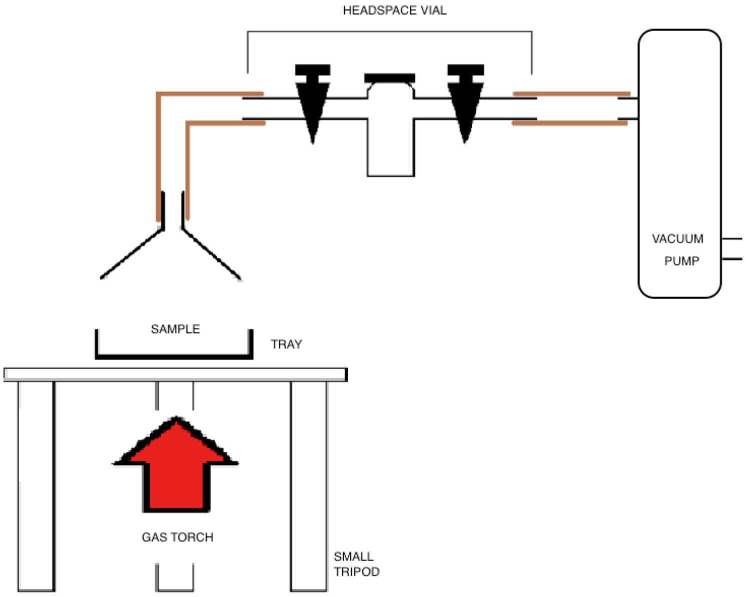


Figure 5-2 **Schematic of the experimental method for the laboratory-scale fast heating open burning setup**

The setup shown in Figure 5-2 was modified for the second variation of the experiment by adding 10 mL acetone to the tray as an accelerant, and by the removal of the constant heat flow for the third variation. For the fourth and final setup, a metal sieve was placed on top of the metal tray to hold the explosive sample above any burning fuel. The experimental series is summarized in Table 5-3.

We also used a modified 10 cm^3 headspace vial with a single tap as a mobile canister to capture gases during different burning phases. Prior to the experiments, we applied the vacuum to these vials for 30 s to maximize their efficiency as a collection device.

Table 5-3 Summary of the laboratory small-scale experiments

Configuration	Sample mass	Sample type	Replicates
Heating on a tray	0.3–0.5 g	DNAN	3
		NTO	3
		RDX	6
		Formulation 1	6
Heating on a tray with accelerant	0.3–0.5 g	DNAN	1
		NTO	1
		RDX	6
		Formulation 1	6
Combustion on a tray with accelerant	0.3–0.5 g	DNAN	3
		NTO	3
		RDX	6
		Formulation 1	6
Combustion on a metal sieve	0.3–0.5 g	DNAN	1
		NTO	1
		RDX	1
		Formulation 1	6

5.2.3.2 Medium-scale burning setup

Prior to the burning of the explosive samples, the canisters were filled with 100 g activated charcoal as a sorbent and connected to three live sensors (ClairAir Alphasense sensors CO-AF [89], NO-A1 [90], NO2-A1 [91] and IRC-A1 CO2 [92]). Charcoal does not adsorb CO and CO_2 and does not desorb NO and NO_2, so the live sensors were used to detect these gases. The sensors for CO, NO and NO_2 were integrated with a PicoLoger DC24 using circuit boards that we designed and constructed in-house specifically for this purpose (blueprint shown as Figure 1-18 and Figure 1-19 after the references) whereas we used a commercially available IRC-A1 4–20 mA transmitter board [93] for CO_2. Before the vacuum pump, a flow meter was integrated to establish an air flow rate of 3.4 L min^{-1}. The setup is shown in Figure 1-3.

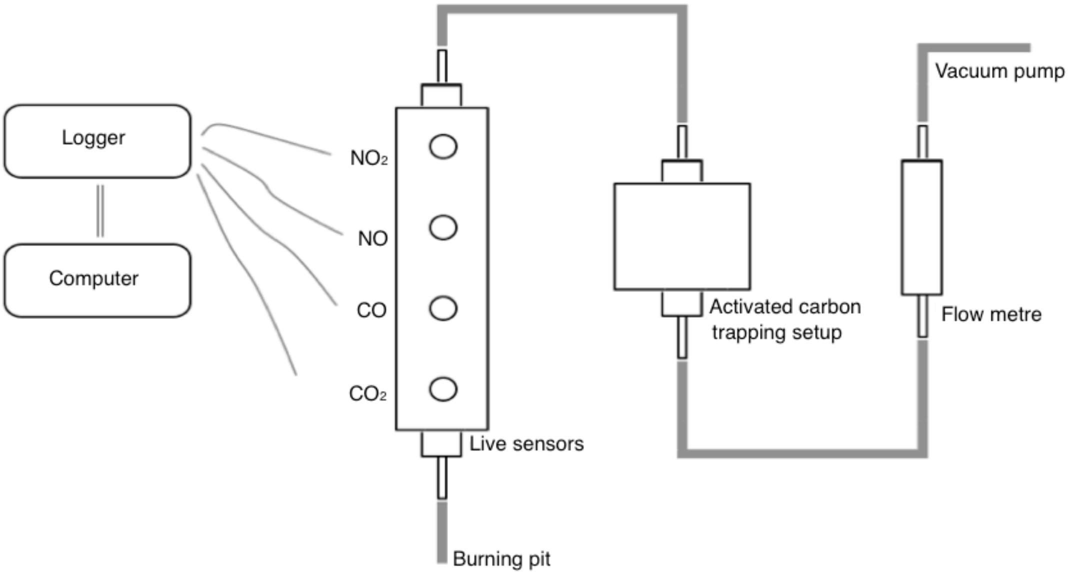


Figure 5-3 **Schematic of the in situ analytical setup for monitoring the open burning experiments**

Natural levels (baseline) for the concentration of the four gases were monitored by recording the concentration for at least 15 min before the first burning experiment. The experimental details are summarized in Table 1-4.

Table 5-4 **Summary of the medium-scale experiments**

Configuration	Sample mass	Sample type	Replicates
Heating on a tray with accelerant/fuel	10–20 g	DNAN	3
		NTO	3
		RDX	3
		Formulation 1	6
Combustion on a tray with accelerant/fuel	10–20 g	DNAN	3
		NTO	3
		RDX	3
		Formulation 1	6
Combustion on a metal sieve	5–10 g	DNAN	3
		NTO	3
		RDX	3
		Formulation 1	6

5.2.3.3 Large-scale open burning setup

Burning on a realistic scale was conducted in a disposal area operated by an ordnance industry partner. The 8 x 5 m burning area was concreted and bordered by three concrete-block walls, 2 m in height. A mobile metal roof could be moved to cover the burning area but was not used during our trials. The burning area was surrounded by soil traverses and was covered in a metal mesh.

The collection apparatus consisted of a steel funnel (50 x 30 cm) that was placed either (1) to the side, or (2) directly above the fire and was connected to a vacuum pump via a plastic tube (D: 2.5 cm, L: 5.7 m). The position of the funnel could be changed to minimize weather effects, e.g. strong gusts of wind. The vacuum pump ensured a constant flow (3.4 L min^{-1}) of smoke from the fire over the three sensors which were set up along the length of the plastic tube, as near to the source as possible (17 m). The concentration of CO, NO and NO_2 was recorded live on site using a laptop adjacent to the burn pit, in a protective enclosure. Unfortunately, the CO_2 sensor malfunctioned during the tests. Data were gathered for 2 h and the system was shut down before nightfall and all cables and wires were packed away to ensure animals and adverse weather would not damage the setup. Baseline levels of the three gases were monitored by recording the concentration for at least 15 min prior to burning.

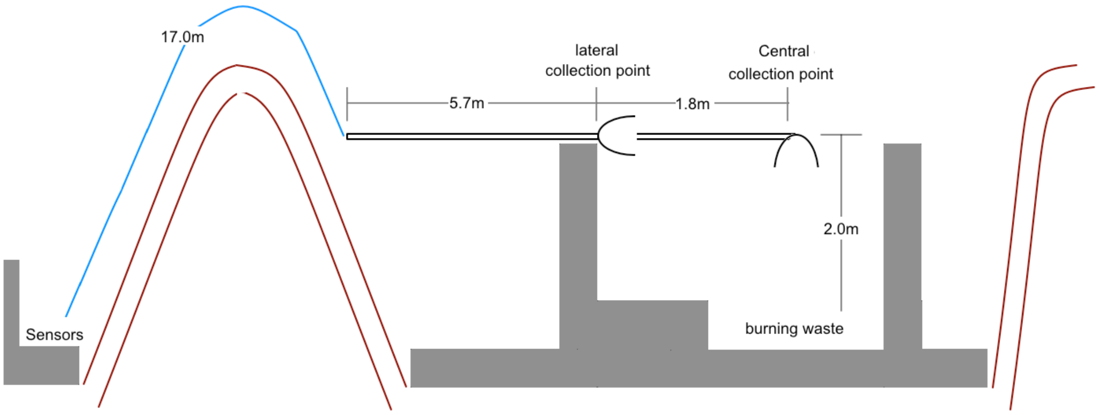


Figure 5-4 **Schematic of the experimental method for the monitoring of realistic-scale open burning, with two funnel positions shown – the blue line is the plastic tube running from the funnel to the sensors over the surrounding mound (brown line)**

In a typical burning experiment, the explosives (5 kg of PBX1 per event) were placed in position and surrounded with combustible material. The combustible material (~100 kg) included cardboard boxes, plastic, paper, and other waste contaminated with solvents (~30 L), fuel and explosives.

5.3 Results and Discussion

Before starting the open burning experiments, we designed an overall plan that would, once implemented, allow us to monitor real, larger-scale burning at an operational burning site. As part of this overall plan, we gathered information regarding the procedures adopted by the industry partner, which showed that they burn explosives on top of common contaminated waste (such as cardboard, gloves and tissues) with added waste solvents (mostly acetone) which helps the materials to ignite by acting as an accelerant. Therefore, prior to the open burning experiments, we used the closed system setup previously tested for RDX [77] to build a baseline data library for the decomposition and burning of these common materials. The gases captured in the headspace vial were analysed by GCMC and the results are shown in Figure 5-5.

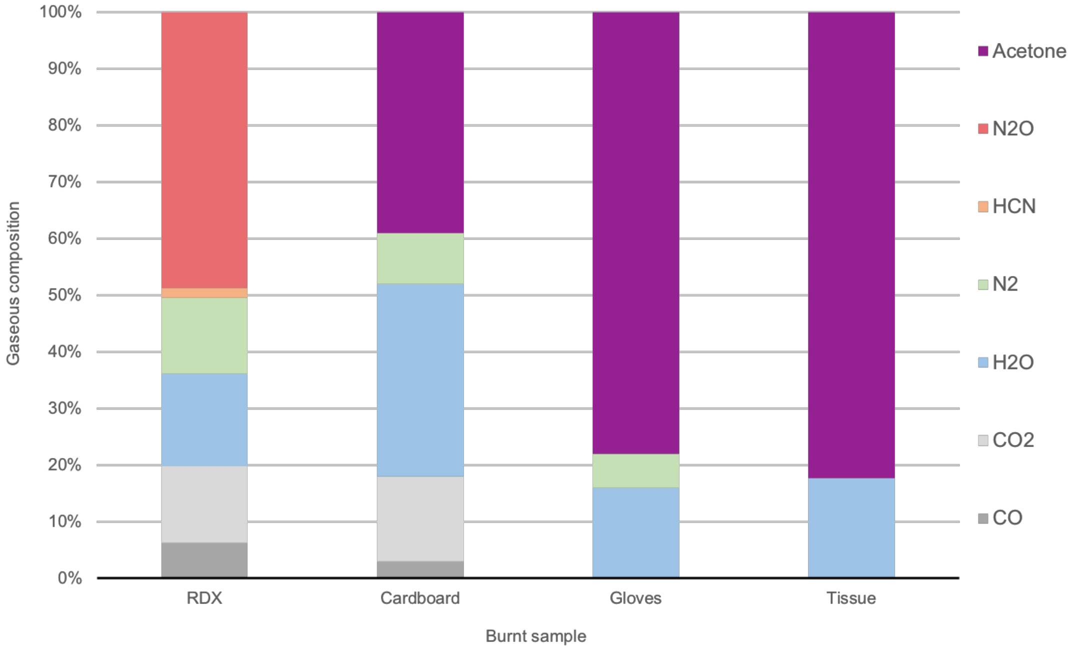


Figure 5-5 Percentage composition of the gases captured during the small-scale burning of RDX and other consumables compared to air

Our tests showed that, for the common waste materials (Figure 5-5), most of the gaseous emissions were acetone, which is consistent with its low boiling point and high volatility. Another interesting observation was the release of H_2 from the decomposition of cardboard. Gloves and tissues were very resilient to burning, which is shown by the lack of carbon-based gases produced. The data showed that testing common waste-type materials (cardboard, gloves and tissues) in our small-scale setup would produce enough gases for analysis. Moreover, it suggested that we should expect some amount of unburnt acetone in our gaseous samples.

5.3.1 Laboratory small-scale burning

During these experiments we tested NTO, RDX and DNAN both as individual components and as a formulation. The tests were conducted using four different setups: initially the samples were placed on a metal tray and heated from beneath, then we added an accelerant and repeated the heating cycle. After examining the effect of heating on the samples, we added accelerant into the metal tray and ignited it. Finally we put a metal sieve on the metal tray, with the explosive on top and solid fuel (paper) with acetone on the metal tray beneath the sieve.

First, we assessed the behaviour of these materials when they were placed on the metal tray and heated from beneath using an open flame. Interestingly, each compound displayed a different behaviour. NTO was the most resilient to combustion, absorbing the heat, partially melting, but producing no flame or smoke, whereas DNAN melted and evaporated, indicating that no chemical reaction took place. In contrast, both RDX and Formulation 1 underwent an intense chemical reaction, involving the release of vivid white-yellowish smoke. The effect was more intense for Formulation 1 than pure RDX.

The residues were weighed, and the mass balance leftovers were 67 % for NTO, 35 % for RDX, and 12 % for Formulation 1 (Figure 5-6). When tested alone, almost no DNAN residues were detected, suggesting most of the compound had melted, vaporized and sublimated. Formulation 1 and RDX burnt, whereas DNAN melted, followed by evaporation. NTO proved its insensitive behaviour by showing great resilience to burning, remaining mostly unreacted after a heating cycle of 10 min (achieving ~350 °C).

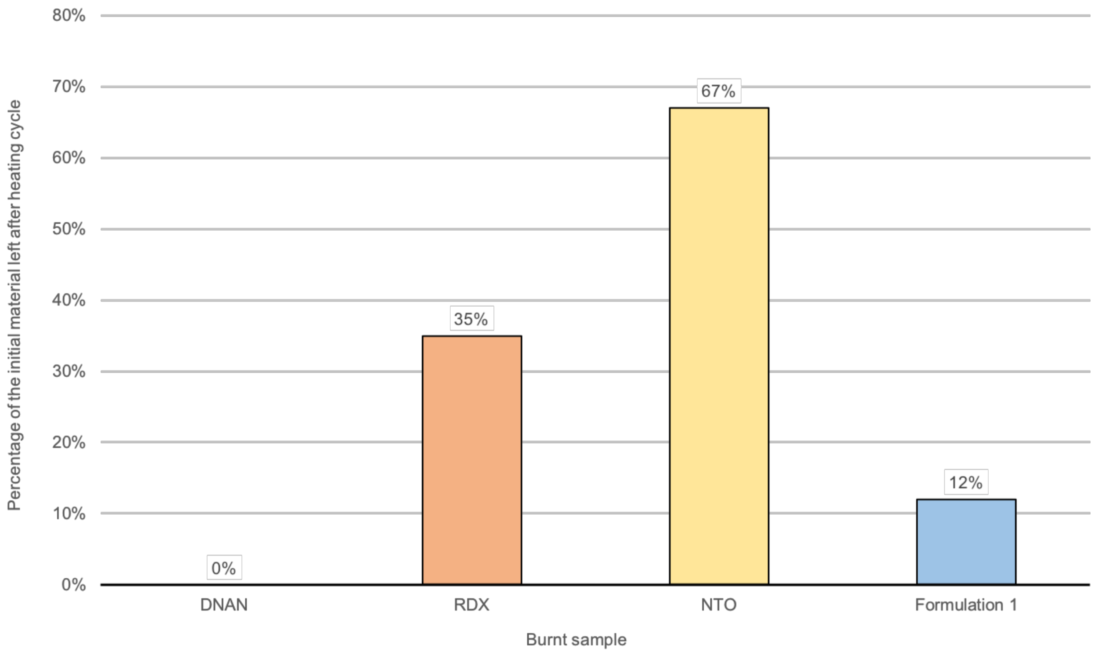


Figure 5-6 **Remaining masses of DNAN, RDX, NTO and Formulation 1 on the metal tray after the heating cycle (average of all samples)**

When heated alone, DNAN left zero residues on the metal tray (Figure 5-6) due to the constant source of heat provided by the torch placed beneath the tray, allowing all the DNAN to melt, evaporate and sublimate away from the tray.

In the case of Formulation 1, we determined the composition of its residues by HPLC and the percentage of the initial mass (Figure 5-7). This showed that most of the remaining material was DNAN (loss of 6 %), which was expected based on previous work [77]. The interesting result was the massive loss of NTO from the burning of Formulation 1 compared with the 67 % NTO left when heated alone. This suggests that NTO uses some of the enthalpy of combustion from the RDX to react, which is more efficient (due to the mix and particle sizes) than the energy provided by the torch when tested alone. In particular for DNAN, the difference between the results shown in Figure 5-6 (zero DNAN left when heated alone) and Figure 5-7 (14 % out of 20 %, which means 70 % left unburnt) is due to the constant source of heat supplied by the torch contrasting with the limited energy provided by the burning of RDX and NTO in Formulation 1.

Due to the open nature of the experiment, a full mass balance was not possible, but we accounted for the remaining masses of materials left on the burning tray after the experiment.

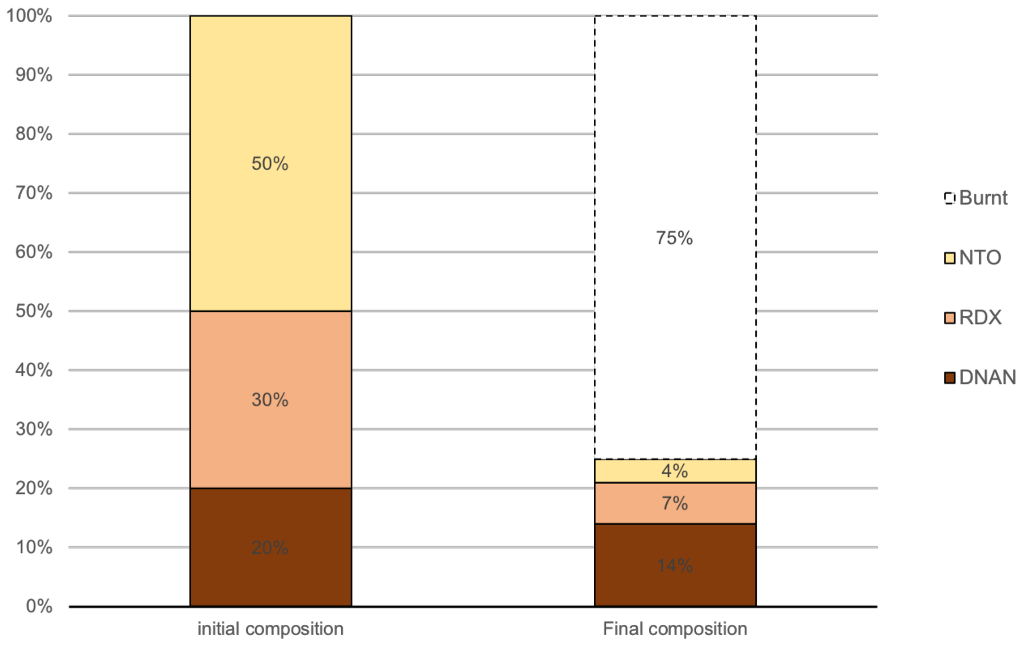


Figure 5-7 **Average composition of Formulation 1 on the metal tray before and after the heating cycle**

Interestingly, when we tested Formulation 1 and DNAN, we observed some solids condensing in the modified headspace vials (Figure 5-8), which we identified as DNAN by HPLC.

Figure 5-8 Example of DNAN condensed within the modified headspace vial

Given that between the burning tray and the headspace vial there was a metal funnel and 25 cm of rubber tubing, the presence of solid DNAN inside the headspace vial supports earlier results [77] showing that, when disposed of by open burning, DNAN becomes mobile and moves away from the burning area, spreading to surrounding locations. Calculating the mass balances including the DNAN recovered in headspace vial and the remaining masses on the tray, it is interesting to observe that the unaccounted mass of DNAN (20 %) in this experiment is very similar to the loss of DNAN reported in closed-system experiments (~30 %) [77]. The more DNAN unaccounted for in the closed-system experiment reflects the higher temperature achieved in the small vial, causing more DNAN to decompose, in contrast to its mobility and solidification in the open system.

Second, we added solvents and accelerants to the mix, which caused a change in the overall behaviour from burning and decomposition towards a steady phase transition (melting, evaporation and sublimation). The accelerants were heated to boiling point, inducing the samples to undergo a phase transition or remain unreacted. The solid residues of Formulation 1 after burning were ~60 % of the original mass, compared with 12 % in the first setup. This shows that acetone as the accelerant boiled and evaporated, removing most of the energy from the system and leaving more unreacted explosive behind.

Next, we changed the setup so that an open flame was used to ignite the solvent and accelerant on the tray directly, instead of indirect heating from beneath the tray. In this case, the solvent completely burnt, leaving most of the explosive samples behind, unreacted. This result is consistent with the surface burning of liquids, while the bulk liquid remains unreacted (and cooler) closer to the bottom of the container where the explosive was located. Once the solvent finished burning, there was not enough energy to ignite (and sustain combustion) of the explosive. We therefore observed explosive residual masses close to the initial values.

Finally, we introduced a metal sieve saddle holding the explosive sample above the accelerant placed on the metal tray. This modified setup was introduced to increase the O_2 availability near the burning site, as well as raising the explosive above the solvents and fuels, holding the explosive above the flames rather than immersed in liquid.

In this modified setup, we observed an increase in the efficiency of burning, leaving almost no solid residues for any of the test materials. At the same time, the burning cycle was reduced from 5–6 min to 30 s, which strongly suggests that the use of boreholes for the open burning of explosives on military ranges and in theatre is likely to be inefficient due to poor oxygenation, and that raising the explosives above the burning fuel would be a more effective disposal strategy if safety could be ensured.

Each experiment was recorded on video and the differences between the decomposition behaviour of Formulation 1 when it is heated on the tray (video available here [94]) and the bright burning when ignited on the sieve (video available here [95]) are shown as a series of images in Figure 5-10.

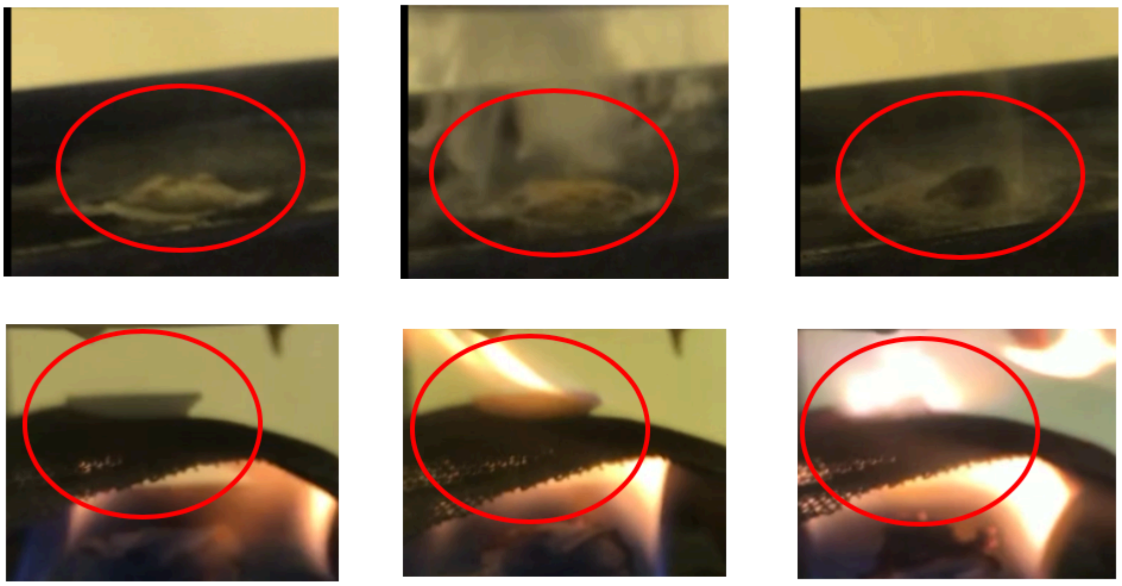


Figure 5-9 The top row shows different stages of the burning of Formulation 1 without an accelerant: melting at 25 s (left), massive gaseous production from decomposition and burning at 1 min 47 s (centre) and residues (right); the bottom row shows three stages of burning on top of a sieve saddle: early/12 s (left), middle/19 s (centre) and full burning/30 s (right)

Regardless of the setup (heating on a tray with and without accelerant, combustion on a tray with accelerant or combustion on a metal sieve) the gases were collected in the modified headspace vials and analysed by GCMS (Figure 5-11). The analysis of the samples trapped within the modified headspace vials showed the presence of N_2 and O_2 in all samples, which comes from the air that dilutes the gaseous emissions (due to the experimental setup), whereas the CO_2 and H_2O observed across samples should be generated by the burning materials. The amounts of CO_2 did not vary much across samples (~50 % of the gaseous emissions were CO_2 for each sample), suggesting a mechanism leaning towards full oxidation of the carbon, in contrast to the outcome of closed-system burning

[77]. Only when testing on a saddle was CO detected, which could have been produced by the fuel or by the conversion of CO_2 into CO due to the higher temperatures generated by the open flame. Unfortunately, the experimental setup did not allow us to confirm the burning mechanism. Acetone was also detected in the gaseous emissions, which was expected considering that the acetone accelerant not only burns but also volatilizes. Burning with acetone also produced more H_2O, originated from the acetone itself.

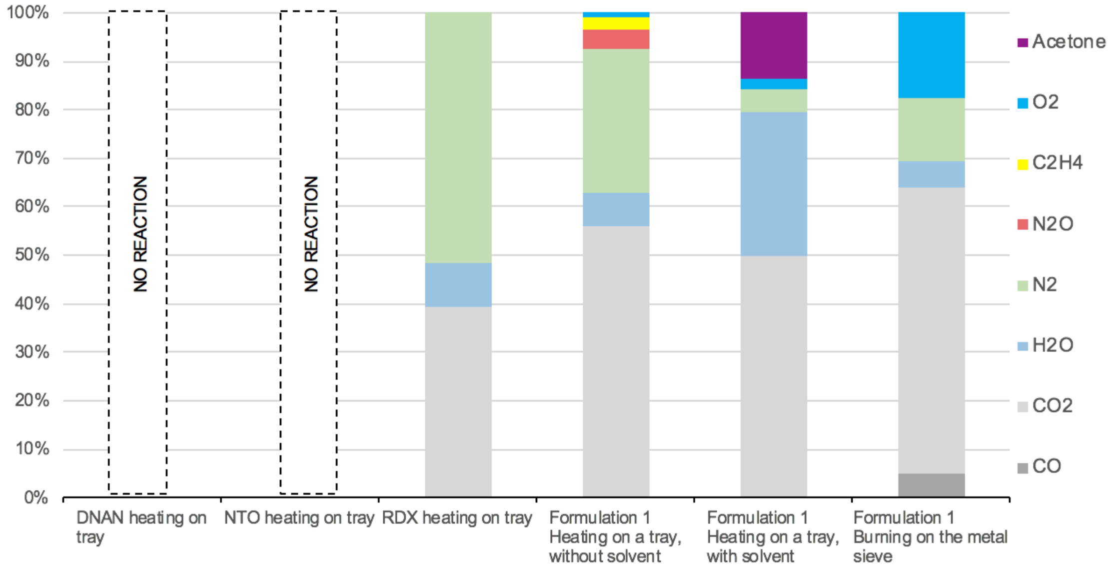


Figure 5-10 GCMS analysis of the small-scale open-burning experiments

Previous thermal decomposition studies of RDX and NTO [42,44,60] showed that the decomposition of these substances by pyrolysis produces N_2O before forming other species such as H_2O, HCN and NO. In our experiment (Figure 5-11) we observed the formation of N_2O when testing Formulation 1 without an accelerant or the metal saddle, suggesting that although some burning was observed, both pyrolysis and combustion may also have occurred. The same mechanism may explain the presence of C_2H_4 in the gaseous emissions. Unfortunately, our setup does not reveal the reaction mechanism, but when RDX was tested individually in the same setup, no N_2O or C_2H_4 was produced, which suggests that NTO, being the more resilient of the two, undergoes partial pyrolysis whereas RDX burns. N_2O and C_2H_4 was not detected when NTO was tested alone.

When these results are compared against previous works (Table 1-5) for other energetic materials [14][13], it is possible to observe a higher production of CO per mass of explosive when TNT is burnt, which is consistent with its lower oxygen balance. From the tested materials, only DNAN has an oxygen balance close to TNT, but its chemical properties [77] reduced the amount burnt, thus producing less CO. For the other materials the emission of CO was below the emission limit [14,96] of 50 mg.m^{-3} for CO, which on its own does not assure compliance due to the massive amounts of solid residues produced.

Table 5-5 Emission Factors (kg/tonne) for observed compared against published values from TNT

	RDX(1)	Formulation 1(1)				**TNT** [13]
		Heating on a tray, without solvent	Heating on a tray, with solvent	Burning on the metal sieve		
CO	0	0	0	25		398
CO_2	766	1120	1002	1061		
H_2	0	0	0	0		
H_2O	72	56	241	0		
N_2	650	375	63	325		
HCN	0	0	0	24		13
N_2O	0	79	0	314		
C_2H_4	0	0	0	0		
Acetone	0	0	0	0		

1 – Values calculates (stoichiometrically) from Figure 1-11

Interestingly, we only observed CO when burning on a metal saddle, which provides the brightest and strongest flame (Figure 1-11). This suggests either that the CO is derived from the fuel rather than the explosive, or that it represents the reduction of CO_2 to CO due to the high temperatures.

5.3.2 Medium-scale burning

The medium-scale setup was designed to replicate as accurately as possible a confinement profile similar to our industrial-scale process. We therefore used a burning tray and closed three sides with two layers of thermo-resistant bricks and a custom-made aluminium funnel on the top, as shown in Figure 1-12.

Figure 5-11 Medium-scale burning setup

The medium-scale burning experiments featured three different configurations (Figure 5-1): (1) Heating on a tray with accelerant, (2) combustion on a tray with accelerant, and (3) combustion on a metal sieve. Initially we tested non-explosive material to determine the emissions baseline before testing with explosive samples. As described for the small-scale burning setups (Section 5.3.1) we first heated the explosive samples on a metal tray with fuel and accelerant, then we ignited the accelerant and finally we burned pure explosive samples on a metal sieve.

We burned samples of Formulation 1 as well as pure RDX, NTO and DNAN, using common waste materials (paper) as fuel and acetone as an accelerant. During these experiments, we attached sensors for NO, NO_2, CO and CO_2 to the top funnel, followed by an activated carbon canister and a vacuum pump. The cumulative results for the sensors are shown in Figure 5-13.

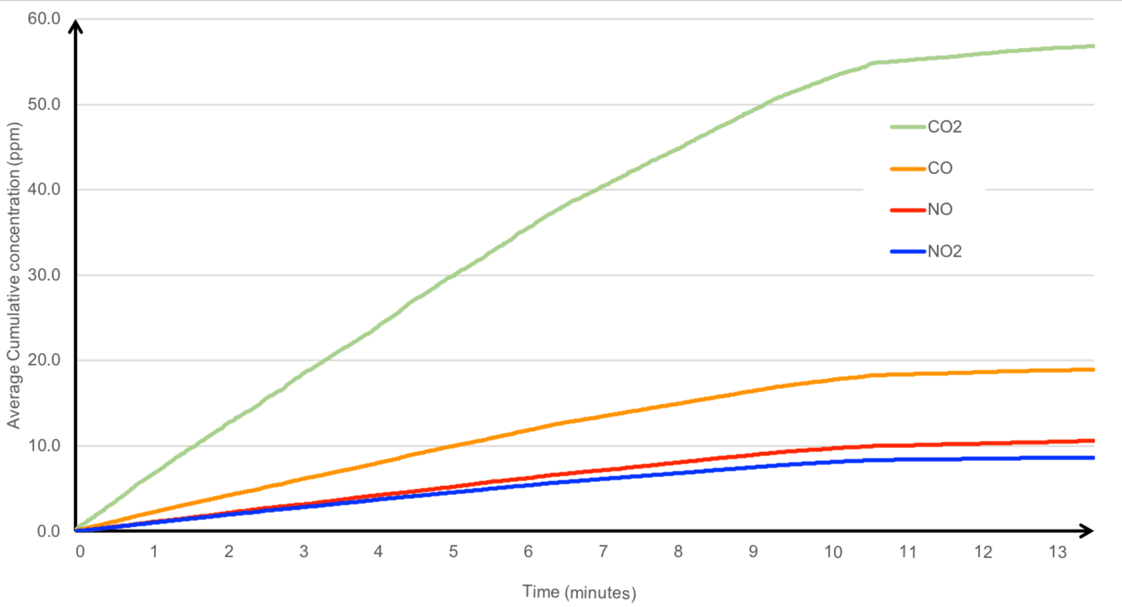


Figure 5-12 Cumulative readings for NO, NO_2, CO and CO_2 (averaged over six samples); this medium-scale open burning experiment involved Formulation 1 burning on top of common waste material (paper)

The 1:10 ratio of explosives to solid waste was enough to ensure that the explosives did not affect the overall characteristics of the gaseous emissions, indicating that burning explosives do not produce emissions that differ significantly from those of general waste materials. The values reported in Figure 5-13 are above the baseline, but in the same order of magnitude.

We therefore re-sized the experiment and removed the waste materials entirely. In this new setup, we implemented the approach already demonstrated for the small-scale open-burning experiment (Section 5.3.1 above), increasing the mass of the explosive sample and using both activated carbon canisters and live sensors instead of modified headspace vials to capture the gases.

As expected, the overall behaviour was similar to that observed in the small-scale experiment: the materials were resilient to burning and leaned towards phase transition from solid to liquid and, for DNAN, into vapour and gas. When the metal saddle was used, the formulation burnt in less than 1.5 min, in contrast to the 5 – 8 min duration without the saddle.

When placed in the same setup as before (in-line between the vacuum pump and the metal funnel), the sensors reported levels of NO, NO_2, CO and CO_2 close to the baseline (Figure 5-14 and Figure 5-15), which probably reflects the dilution of the small samples with air from the environment. Therefore, we re-arranged the sensors by attaching them to the brick walls that confined the experiments, but the results were similar, indicating that both setups work correctly (sensors directly assessing the gases vs forcing gases through the sensors using a pump).

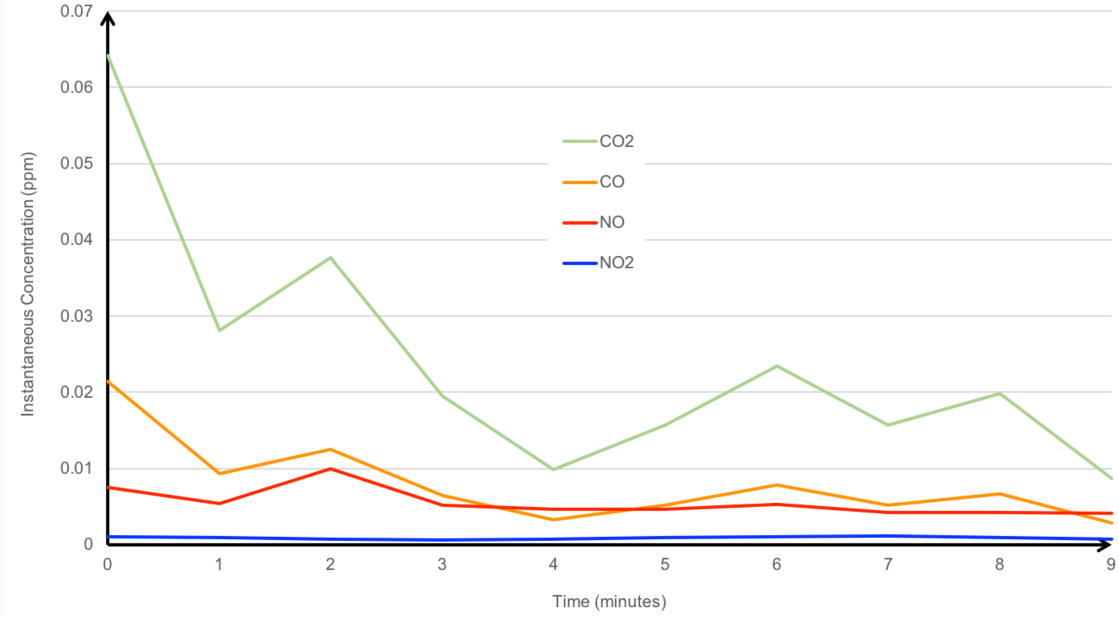


Figure 5-13 Time-dependant readings for NO, NO_2, CO and CO_2 averaged over six Formulation 1 samples (air background values subtracted) burnt alone in the metal sieve saddle configuration; the accelerant was acetone (10 mL) on the metal tray

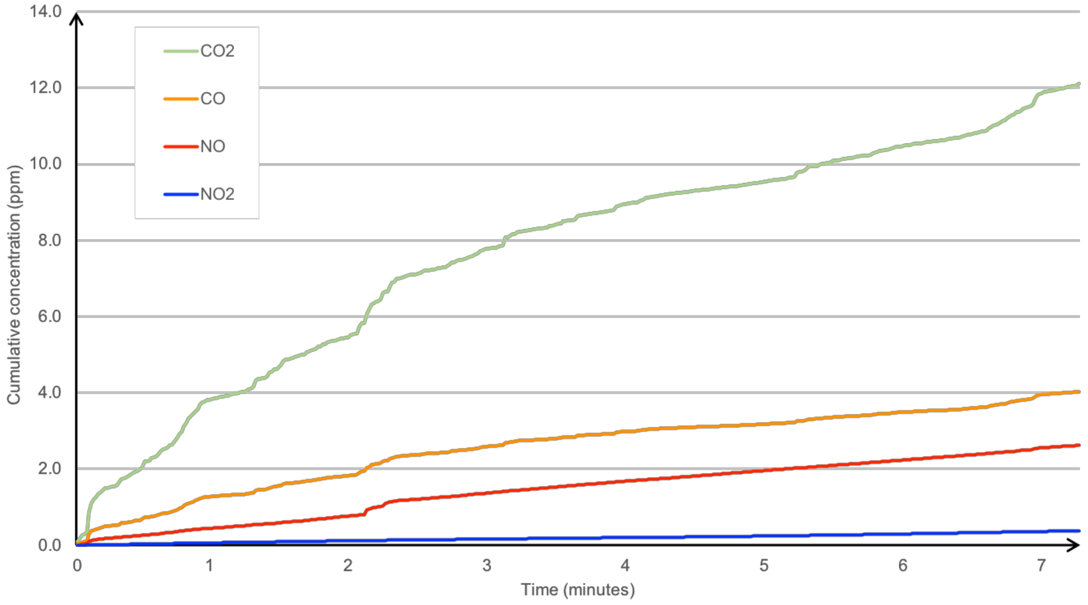


Figure 5-14 Cumulative readings for NO, NO_2, CO and CO_2 averaged over six Formulation 1 samples (air background values subtracted) when burning alone in the metal sieve saddle configuration; the accelerant was acetone (10 mL) on the metal tray

Finally, we extracted the activated carbon from each active and passive canister. We took two 8-g samples per canister for Soxhlet extraction (using acetone) and another 20-g sample for ASE, followed by HPLC analysis. As expected, all samples were clean, which is consistent with the scale of the experiment.

Comparing the cumulative data for the gases emitted when Formulation 1 was burnt with waste material (Figure 5-13) or alone (Figure 5-15), we found that the explosive produces less than 25 % CO_2 and other gases than the waste material, which suggests that the explosive emissions are masked by the baseline emissions from the common waste.

5.3.3 Large-scale open burning

The real-size burning was hosted by an ordnance company in Europe. Unfortunately, due to their production schedule, it was not possible to monitor the disposal of the same formulation discussed above, but we were able to monitor the disposal of RDX-based PBX mixed with contaminated waste. To account for the waste interference, we relied on preliminary closed-burning trials (Section 5.3, Figure 5-5), which indicated that CO_2 and CO are the main gases emitted during the open burning of cardboard and RDX, so these were monitored during open burning.

Materials included as fuel during the *in situ* incineration included cardboard, personal protective equipment, acetone and other miscellaneous industrial and laboratory consumables. The collected waste differed each day, but usually contained 150–300 kg of solid waste such as cardboard boxes, and general laboratory consumables such as gloves and paper. In addition, hard plastic and rubber was frequently added to the burn, including rubber shoes, rubber face masks and other personal protective equipment. Up to 5 kg of explosive was also incinerated, along with explosive-contaminated materials (~100 kg). Particularly unexpected was the disposal of contaminated wastewater (~60 L) from the wash-down of areas that use explosives, which was poured directly onto the dry consumable and explosive waste.

The burning was monitored for 6 days, and the site was monitored before and after the burn. For the first three burns only contaminated waste was placed in the burning area for disposal, but on the fourth day PBX1 (~4 kg) was placed on top of the waste material. No extra PBX1 was added on the fifth and sixth days. Regardless of the burning composition, we made use of activated carbon canisters to adsorb the gases and vapours both passively (two canisters hanging 0.80 m and 1.60 m from the collection funnel) and actively (in line with a vacuum pump). We placed live sensors for NO, NO_2, CO and CO_2 between the collection funnel and the activated carbon canister, but unfortunately the CO_2 sensor malfunctioned and the data was not collected.

Due to the ambient temperature at the site, the safety protocol includes the dampening of the soil traverses with water before each burn. The water runs down the slopes and collects in a chamber beneath the concrete shelter. This water is assumed to be uncontaminated and is periodically removed and shipped off site for treatment. The waste was stacked to distribute the cardboard, bagged waste and the explosive samples were spread on top of the waste piles. The waste was stacked in the burn pit on top of the ashes of previous burns. The ash waste is also periodically shipped off site as non-explosive hazardous waste, assuming that all explosive traces have been destroyed by burning.

During the early phase of the burn, black smoke was generated, most likely due to the solid plastics and rubber. The burn continued for several hours, with the thick black smoke mostly concentrated during the early phase (first hour). Examination of the remains of the burn revealed that the explosive materials were not completely consumed, and in some cases remained almost intact (Figure 5-16). Subsequent examination showed that the 'dog-bones' generated in the quality control process were frequently not incinerated. This may reflect the way the waste is stacked, the ignition process or the fact that the burning temperature may be lower than that required to destroy RDX or PBX1 (which has an auto-ignition temperature of 200 °C, related to its high RDX content). It is therefore likely that the temperature around the explosives does not reach 200 °C [97–99]. It is possible that additional material is obscured beneath the soot, or that very small pieces of the explosive are not detected before the soot is sent for disposal.

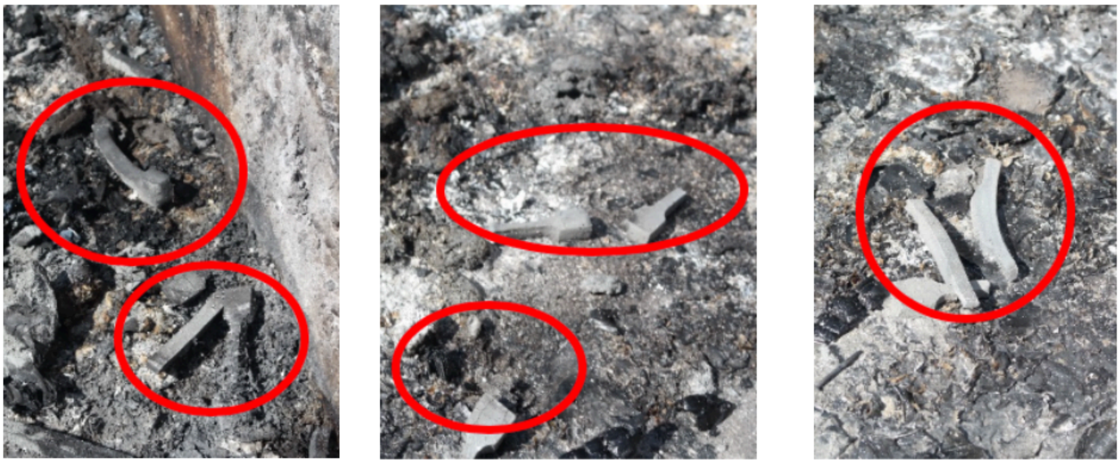


Figure 5-15 Photographs of the waste after burning with the remaining 'dog bone' samples of explosive: explosive residues after the first burning (left – day 4), second burning (centre – day 5) and third burning (right – day 6) – no explosive was added after the first burning (day 4)

The open burn was monitored for CO, NO and NO_2 *in situ* using two different collection locations (lateral and central to the burn). When the collection funnel was placed laterally to the burn, monitoring was impeded by the wind, which directed the smoke away from the funnel. The centrally located funnel was more effective at collecting the smoke, and achieved a more consistent record of CO, NO and NO_2 emissions (Figure 5-17). CO was the most abundant gas among the three we monitored, although both NO and NO_2 were also detected. Due to time constraints for access to the burning ground, it was not possible to monitor the open burning to completion. The equipment was packed away overnight, and final access to the burning ground was approximately 2 h after the waste was ignited.

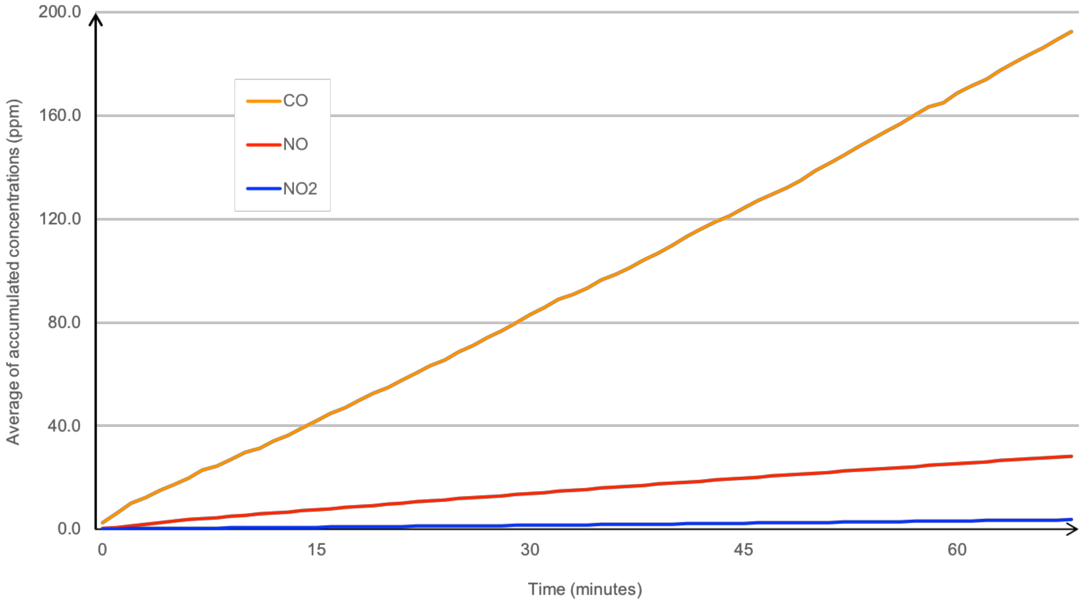


Figure 5-16 Cumulative values of CO, NO and NO_2, averaged across the real-size burnings with explosives (days 4–6)

Finally, the activated carbon was extracted as described above for the medium scale burning. HPLC analysis revealed peaks of the same intensity as equipment background noise. Like the medium-scale burning, this supported the conclusions of previous studies involving the burning of TNT [63], in which it was shown that the solids left over on the soil are the primary environmental concern and the effect of gaseous emissions was negligible.

In summary, the majority of the waste burnt at the industrial site was laboratory waste such as cardboard, contaminated tissue, plastics and rubber. The emissions generated from the small quantity of explosives were minor (~5 kg of explosive against ~150 kg of solid waste, on average) compared to the emissions from the bulk waste, and were therefore almost completely masked by the burning non-explosive waste materials. Small-scale laboratory experiments showed that the gaseous emissions from the waste were mainly CO_2, CO, NO_2 and NO, and *in situ* experiments confirmed that these gases were indeed produced. The main concern with the current open burning method is that the temperature is lower than the decomposition temperature of the explosives, which is not high enough to ensure complete destruction of the explosive waste. This may reflect a combination of factors such as the enclosed burn area (which reduces oxygen availability, favouring the less exothermic formation of incompletely oxygenated combustion products compared full oxidation) the proximity of waste to damp soot, and the addition of contaminated water to the waste (which, on its own, reduces the burning temperature).

As a result of this large-scale monitoring experiment, the ordnance industry partner has decided to discontinue its burning procedures and, to the best of our knowledge, is studying newer and more efficient options to dispose of explosive waste. At this stage, the industry is leaning towards a robust closed-system incinerator equipped with sensors to monitor the exhaust gases and a constant heat flow to improve the burning efficiency. This incinerator can be considered as an industrially-confined version of the experimental setup b.4 and c.3 (combustion on a metal sieve) presented in Figure 1-1. This outcome shows the relevance of our research, even though the gaseous emissions mainly consisted of greenhouse gases.

5.4 Conclusion

In all our tests, we observed the emission of greenhouse gases, which agrees with previous studies reporting the thermal decomposition of explosives [38,39,48–52,57–59,40–47] and experiments assessing the open burning of TNT [63]. Moreover, we found that the fuel and other materials added to the explosives to facilitate burning are the primary source of gases.

The small-scale open burning setup showed similar behaviour to the closed-system tests for the same IHE [77], including the gaseous emissions being mainly greenhouse gases and the large amount DNAN left unburnt within the solid residues. Moreover, the solidification of DNAN within the headspace vial indicates its mobility in the vapour phase. Our experiments also showed that, due to its thermodynamic characteristics, DNAN takes energy from the burning RDX and NTO to melt, evaporate and sublimate, reducing the energy available to sustain the combustion reaction, which increases the amounts of RDX and NTO in the solid residues.

The medium-scaled tests, In summary, showed that the analysis of gases and vapours released by the open burning of DNAN, NTO, RDX and Formulation 1 yielded similar results to previous closed-system tests [77] and to the BangBox study using TNT [63]. Gaseous emissions lean toward greenhouse gases and are of less concern than the residual solids and the condensation of particles that have spread to surrounding locations.

Overall, regardless of the scale of our tests with Formulation 1, DNAN was always resistant to burning and instead favoured melting, evaporation and sublimation, as confirmed by its tendency to leave solid residues on the tray and in other parts of the apparatus, such as the gas sampling vial. When tested individually, DNAN first melted and then evaporated, with no evidence of any chemical decomposition or reaction. NTO was also resilient to combustion and thermal decomposition when heated alone, with no visual indication of decomposition or chemical reaction. In contrast, RDX and Formulation 1 behaved as previously reported in closed-system experiments [77], absorbing energy from the heat source and burning. Whereas RDX burnt to completion, Formulation 1 left residues behind (~12 %), in particular DNAN (~70 % of the initial mass). This behaviour is undesirable when disposing of IHE material by open burning. As the scale increased, the more the gaseous products of the IHEs were masked by the baseline of the other materials used to facilitate burning. These results indicate that the gaseous products generated by the open burning of IHEs are not a significant environmental issue, in contrast to the solid residues left on the burning area as well as the unreacted explosives spread to the surroundings.

The real-size experiment showed almost 100 % of explosives are left unburnt, whereas the medium-scale experiment showed that the gaseous emissions form the explosive are masked by the fuels added to facilitate burning. Moreover, both the laboratory small-scale and medium-scale tests showed that the efficiency of burning depends on the setup in terms of heat transfer and oxygen availability (which improved when a metal sieve was introduced). The laboratory-scale experiments supported a mass balance, which showed solid residues close to zero when a metal sieve was used, in contrast to up to 35 % for RDX, 67 % for NTO and 12 % for Formulation 1 (with a final composition of 70 % DNAN, 23 % RDX and 7 % NTO). Moreover, DNAN was found to melt, evaporate and sublimate as long as energy was available, which explains why DNAN left zero residues when heated alone from beneath.

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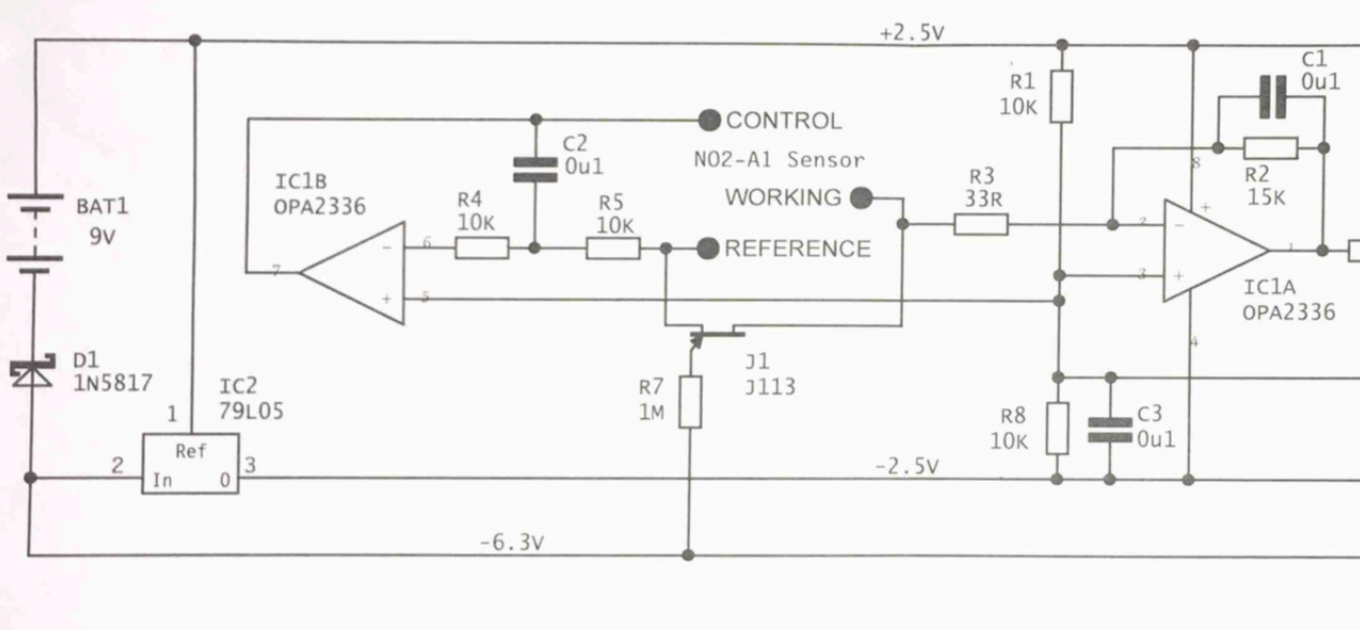
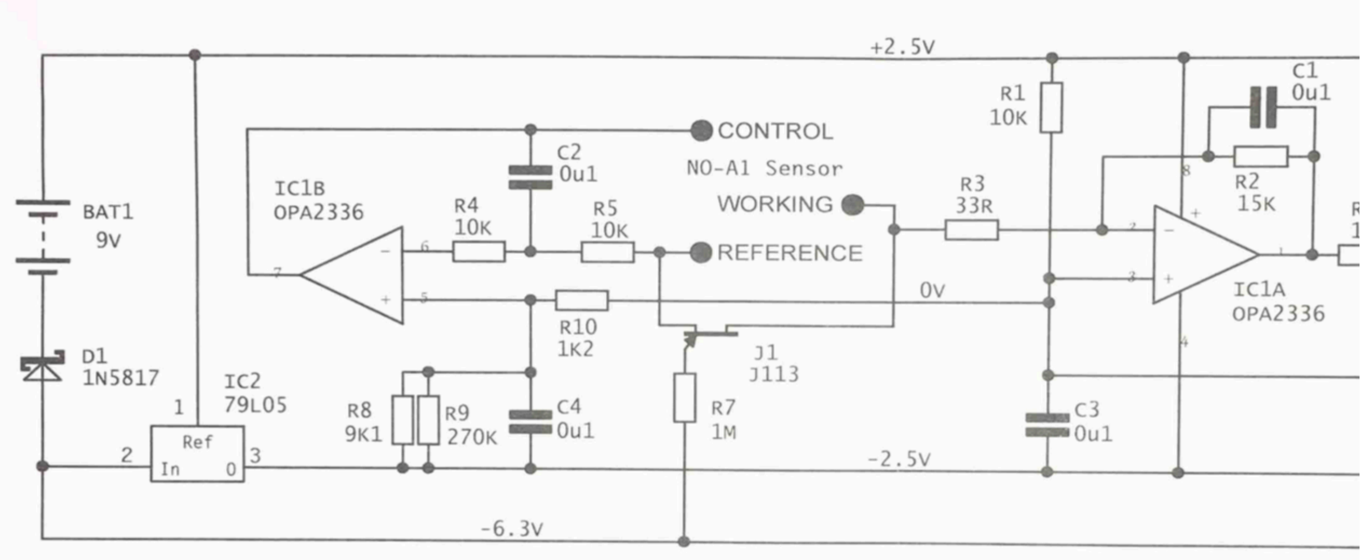


Note: Battery must be isolated from all ground connections.

Figure 5-17 Integration circuit boards – CO and NO_2



Note: Battery must be isolated from all ground connections.

Cell bias voltage = -0.3V
For unbiased condition, replace R10 with
link, replace R8 with 10K and remove R9.

Figure 5-18 Integration circuit boards – NO

6 SIMULATION OF THE TRANSPORTATION OF DNAN AND NTO THROUGH SOIL USING HYDRUS 1D

Abstract

Military training using ammunition containing trinitrotoluene (TNT) has caused environmental contamination over many decades. Time consuming and costly remediation is now required, which interrupts military use. An environmentally aware society expects military training ranges to be well managed and to minimize environmental damage. Contamination from TNT-based compositions has already occurred in some ranges and can be measured, but such compositions are currently being replaced with new insensitive high explosive (IHE) formulations containing 2,4-dinitroanilisole (DNAN) as a melt-castable energetic material and binding agent, e.g. when combined with 3-nitro-1,2,4-triazol-5-one (NTO) and nitroguanidine (NQ) in IMX-101. The lack of experimental data concerning the environmental impact of these materials may compromise training and future disposal procedures. We therefore simulated the dispersion of IHE chemical components through the soil using HYDRUS 1D, a modelling tool for the analysis of water flow and solute transport. Primary data were generated in soil column experiments, in which the soil was spiked with DNAN, NTO and NQ. The aim of this research was to test whether HYDRUS 1D can be used to predict environmental contamination on military ranges, as well as address which variables and material properties should be relevant in said simulations. We found that the code it uses relies solely on diffusivity data which are not yet fully available for our samples. Ultimately, we found that HYDRUS 1D yields promising results when modelling the flow of water and relatively inert chemicals, but it must be modified to accurately simulate the dissolution of energetic compounds from IHE formulations in order to correctly predict the leaching of NTO and DNAN through loamy and sandy soils.

Keywords: Gaseous emissions; open burning; energetic materials; diffusivity

6.1 Introduction

Insensitive high explosives (IHEs) have been developed to replace legacy materials such as trinitrotoluene (TNT), offering safer alternatives that do not detonate accidentally [1–4] Because IHEs are relatively new and many of their components have only been in service for a short time, little is known about their environmental impact, especially when open burning is used for disposal. IHE materials include 3-nitro-1,2,4-triazol-5-one (NTO) [5–7], 2,4-dinitroanilisole (DNAN) [8] and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) [9].

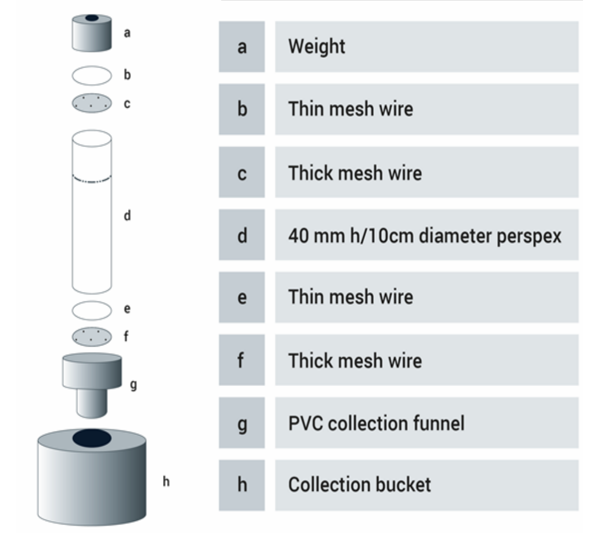
Although the behaviour of IHE materials in the environment has been investigated in a small number of studies [10–12], open burning has received little attention, even though this is the primary means by which munitions and ordnance are destroyed when they are no longer needed. The absence of such studies is important because IHEs are more likely than legacy explosives to undergo lower-order detonations, leaving unreacted materials on the ground [13]. If IHE formulations are left unattended in the environment, NTO will quickly dissolve when exposed to rain, leaving some DNAN and most of the RDX behind. Whereas DNAN is rapidly degraded into less toxic products by soil microbes, particularly if the organic content of the soil is high, RDX is much more stable and is therefore likely to leach into groundwater, as already reported on several training ranges *[14–16]*. Previous studies have addressed the emissions produced during the open burning of TNT-based explosives [17,18], but not IHE materials such as RDX, DNAN and NTO. This means that damage caused by environmental contamination can only be assessed after the event, when it is too late to prevent negative impacts on the ecosystem and humans.

The environmental impact of IHEs has been tested empirically in fate and transport studies using soil columns spiked with single or mixed ingredients. These studies have shown that DNAN and NTO do not interact with each other when deposited as mixed residues in soil [19]. NTO in particular has a significant environmental impact because although NTO itself has a low toxicity, its degradation products are much more potent [19]. Soil column experiments provide useful and accurate information, but they are expensive and time-consuming, and the results are only relevant to the specific types of soils that are tested [20]. These limitations can be addressed by conducting simulations using mathematical models of the contaminant and the environment. If all the variables are known or can be estimated, simulations can provide results more quickly and with much lower costs than empirical experiments, or can be used to reduce the number of empirical experiments needed to validate the simulation results.

Here we used HYDRUS 1D [21–23], a software platform originally developed to predict the dispersion of solids and liquids through soil in an agricultural context. Although it was originally designed to model the dispersion of pesticides and fertilizers, it has also been used to model the fate and transport of explosives and energetic materials in soil, specifically TNT, RDX and Comp B [24], 2,4 DNT and 2,6 DNT from M1 propellant [25], and more recently NTO [26], IMX101 and IMX104 [11]. In these earlier studies, HYDRUS 1D was only used to calculate the adsorption coefficient (K_d) but the values predicted for TNT and RDX were very close to the experimentally determined values [24]. Interestingly, the correct K_d value was predicted for solid Comp B but was underestimated for Comp B in solution, which suggests that the absorption of chemicals in solution was not fully accounted for during the experiments, potentially making it difficult to predict what happens with explosives exposed to rain. The previous studies indicated that HYDRUS 1D could be used to predict the fate of energetic materials and their transport through soil with some limitations (such as an inability to accommodate the decomposition of explosives in the soil environment), but they did not consider the details of the transportation mechanisms. We have addressed this omission by using HYDRUS 1D to replicate the empirical results reported earlier for DNAN and NTO in loamy and sandy soils [19].

6.2 Materials and methods

We used the previously reported empirical data for the fate and transport of IHE components as the source data for our calculations [19]. In this earlier report, samples of DNAN (0.423 g), NQ (0.367 g) and NTO (0.215 g) were dissolved in 1.5 L of deionized water and dispersed into six vertical Perspex soil columns (10 x 40 cm). The columns were fitted with polyvinyl chloride (PVC) collection funnels and stainless-steel wire meshes. They were then placed into collection containers and filled with soil to a depth of 20 cm (Figure 6-1). The experiment used loamy soil (density = 1.27 ± 0.03 kg L^{-1}) and sandy soil (1.81 ± 0.02 kg L^{-1}) exposed to 9.11 L of spiked water per column for 5 weeks, resulting in an artificial watering scheme representative of a full year's rainfall (1160 mm). Specifically, this is the average annual rainfall in South West England and Wales from 1995 to 2015 [27].



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

Figure 6-1 Schematic showing the construction of the soil columns used by Temple et al. [19]

For the simulations, we used HYDRUS 1D, a finite element model that simulates the one-dimensional movement of water, heat and multiple solutes in variably saturated media [21–23]. HYDRUS 1D calculates Richard’s equation (Equation 12) for both saturated and unsaturated water flows, as well as Fickian-based advection–dispersion equations for heat and solute transport. The main processes considered by HYDRUS 1D are water flow, solute transport, heat transport, and inverse parameter optimization.

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\left(\frac{\partial h}{\partial z} + 1\right)\right] \qquad \textbf{1}$$

where K is the hydraulic conductivity, h is the matric head induced by capillary action, z is the elevation above a vertical datum, θ is the volumetric water content, and t is time.

6.3 Results and discussion

The results section is divided into three parts. First, we present the empirical data generated by Temple at al. [19] because this is relevant to our work. Second, we use HYDRUS 1D to calculate the quantity of DNAN and NTO that leaches through the same soils. Finally, we refine the calculations and determine the absorption coefficient and hydraulic conductivity, comparing them to the empirical values reported by Temple at al. [19].

6.3.1 Empirical results

The static and soil column experiments reported by Temple at al. [19] confirmed that soils with a high content of organic material degrade DNAN and NTO more quickly than sandy soils. NTO itself has minimal toxicity, but it rapidly degrades into potentially toxic products, whereas DNAN degradation products are less toxic than the original compound. In their experiments, the explosives were introduced into the soil columns in solution, followed by the addition of 150 cm^3 water, which was then subtracted from the initial dose of water to ensure water delivery was consistent with the average annual rainfall in the UK.

The results for the sandy soil column static experiments indicated that DNAN, NTO and NQ were neither adsorbed nor degraded by sandy soil, and the recovery of explosive constituents was thus expected from both the liquid and solid phases. This was indeed the case for NTO and NQ, which were fully eluted during the first 7 days, but the recovery of DNAN from the sandy soil column leachate was incomplete (Table 1-1). The concentration of DNAN in the eluent gradually declined, with a cumulative total of 38 %. None of the expected degradation products were identified in the leachate. In contrast, only NQ was detected in the leachate of the loamy soil columns during the 5-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 (Table 6-1). However, given the high solubility of NTO and its low attenuation in soil (as revealed by the static experiments), we expected to detect some NTO in the leachate during the first few weeks before significant degradation took place. The lack of NTO in the leachate suggested that degradation is much quicker in dynamic systems than static environments, which may reflect the much higher quantity of soil compared to explosive materials in the soil columns, allowing greater exposure to the microbes responsible for biodegradation.

Table 6-1 Recovery of explosives over time from sandy and loamy soil column leachate as reported by Temple et al. [19]

	Percentage recovery			
	Sandy soil		Loamy soil	
Week	**DNAN**	**NTO**	**DNAN**	**NTO**
1	12.3	97.0	12.0	0
2	24.1	97.3	24.0	0
3	31.7	97.3	29.0	0
4	35.9	97.5	33.0	0
5	38.0	97.6	35.0	0

6.3.2 Simulation results

HYDRUS software packages implement a Marquardt-Levenberg type parameter estimation technique [21,22] for the inverse estimation of soil hydraulic parameters, solute transport, and/or heat transport based on measured transient or steady-state flow and/or transport data. For this purpose, the programs are written in such a way that almost any application that can be implemented in direct mode (i.e., when all parameters and initial and boundary conditions are specified, and predictions are made) can be implemented equally well in the inverse mode, providing an effective strategy for model calibration and parameter estimation. Because of its generality, the inverse option has proven very popular with many users.

For our simulations in HYDRUS 1D, we implemented the same constant water flux equivalent of 3.31 cm^2 day^{-1} used by Temple et al. [19]. We also set up the software to model the initial condition of the explosive as solid deposits on the surface of the soil at the top of the column. The simulation predicted that all explosives should be fully recovered after 3–4 weeks, and that the rate at which they travel through the column should increase over time due to the time taken for the contaminants to dissolve.

The simulations for both DNAN and NTO suggested that all the initial material would be transported through the column by the time the experiment concluded, but this was not consistent with the empirical data shown in Table 1-1. The calculations indicated that the leaching rate would be inversely proportional to the column density (the denser the column, the slower the leaching rate). Hence the DNAN should travel more slowly through sandy soil (density = 1.8 kg L^{-1}) than loamy soil (density = 1.27 kg L^{-1}).

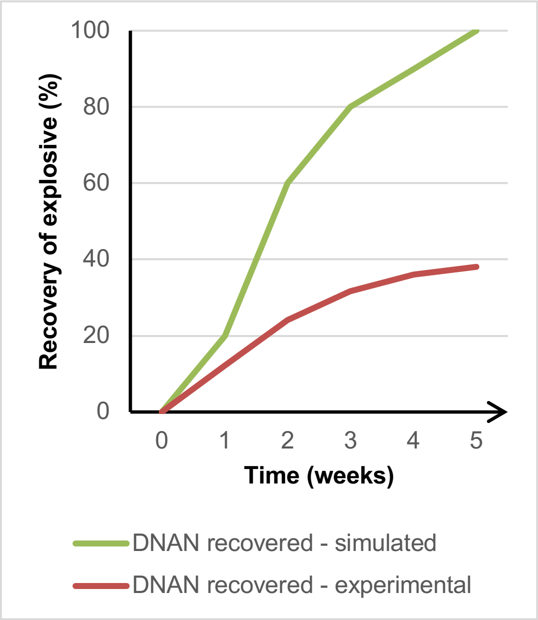


Figure 6-2 Concentration of DNAN at the base of the sandy soil column

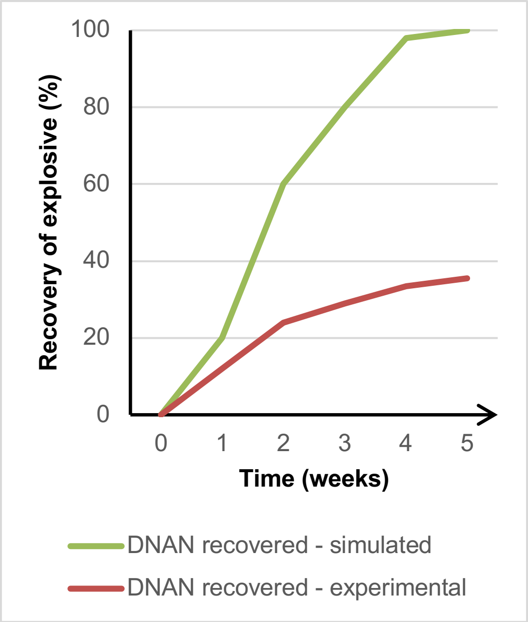


Figure 6-3 Concentration of DNAN at the base of the loamy soil column

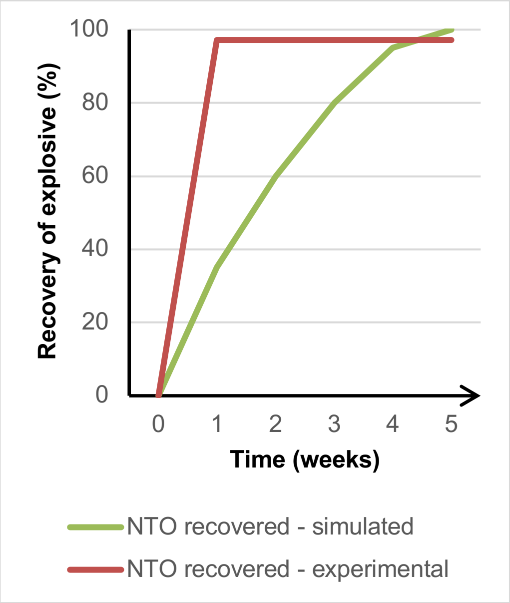


Figure 6-4 **Concentration of NTO at the base of the sandy soil column**

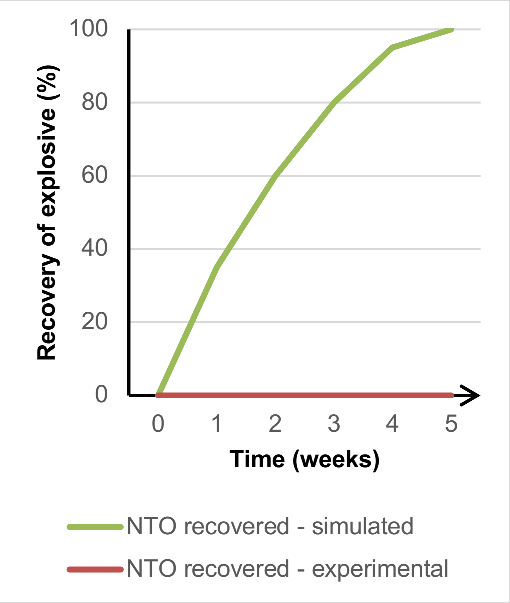


Figure 6-5 **Concentration of NTO at the base of the loamy soil column**

The empirical experiments [19] revealed different leaching rates for DNAN and NTO (Figures 6-2 – 6-5), whereas the simulations in HYDRUS 1D predicted that 100 % of the DNAN and NTO should pass through the column during the same time frame. Similar behaviour has been reported for other explosives, which confirms that Fick’s law of dispersion and Richard’s variation cannot capture all the phenomena taking place. The soil column experiments therefore provide strong evidence of further interactions between the explosives and the soil, which are not included in the simulation.

HYDRUS 1D models the movement of dissolved substances in soil but does not account for their degradation or decomposition. Initially we assumed that degradation, decomposition and binding to soil particles, all of which compromise the transport of chemicals through soil and thus their recovery from the leachate, could be addressed by modifying *K*, representing the hydraulic conductivity, or *h*, representing the matric head induced by capillary action, but the simulation did not show this behaviour. In previous studies, the authors used empirical data to calculate the hydraulic conductivity, absorption coefficient and dissolution rates [11,24,25,28], and we adopted the same approach based on the soil column experiments conducted by Temple et al. [19] for the same explosive materials in two different soils. As previously reported, the HYDRUS 1D code was used to simulate the one-dimensional movement of water, heat and multiple solutes in variably saturated porous media.

HYDRUS 1D was applied in the inverse mode to analyse breakthrough curves obtained in the column experiments, and was modified to account for the dissolution of constituents from solids. Similar modifications have been used previously to estimate the dissolution rates of energetic materials, explosives and propellants [11,24,25,28].

Although there were major differences in the soil column setups described by Temple et al. [19] and earlier studies [11,24,25,28], the overall results are very similar, confirming the strength of Richard's equation. Temple et al. [19] set up a soil column holding ~3 kg of soil (10 cm diameter x 20 cm height) whereas the earlier studies used much smaller soil columns (1.18 cm diameter x 7 cm height) [11,24,25,28].

Moreover, the HYDRUS 1D calculates fate and transport through Richard's equation, which depends on material properties and interactions with soils, which is not fully know for explosives, specially IHE's, such as DNAN, NTO and RDX mix. Hence, aiming to improve accuracy of the calculations, more research is required to determine material properties, such as diffusion, and degradation and decomposition mechanisms. Finally, it is paramount to comment that, whilst this work addresses DNAN-based IHE, it is not the only type of IHE currently under investigation. This formulation has been selected since it is a candidate for replacing composition B [2,3] in artillery rounds, thus with potential for massive amounts being used on ranges.

6.4 Conclusion

HYDRUS 1D relies on diffusivity data to estimate the quantity of contaminants leaching through soil. This adds an extra layer of complexity when modelling the transport of explosives because the diffusivity coefficients of the IHE components are not yet known. We were able to approximate the diffusivity coefficients using empirical data [14], but Richard’s equation always provided an outcome of 100 % leaching for each solute at the end of the 5-week experiment, which was not consistent with the observed results. This indicates that the explosive materials are reacting or interacting with the soil matrix in a manner that cannot be incorporated into the HYDRUS 1D model. Previous studies have shown that HYDRUS 1D can be used to characterize the fate and transport of energetic materials through soil, but with limitations. The input data must include the full physical characterization of the soil to ensure that the correct parameters are used in the simulations. HYDRUS 1D therefore yields promising results when modelling the flow of water and relatively inert chemicals, but it must be modified to accurately simulate the dissolution of energetic compounds from IHE formulations in order to correctly predict the leaching of NTO and DNAN through loamy and sandy soils. Moreover, we have shown that, regardless the soil column designs, HYDRUS 1D can be used to determine soil-based parameter values and that these values should be a function of the soil and explosive, not the soil column geometry.

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7 OVERALL DISCUSSION

The body of work reported in this thesis was initiated by analysing the literature (Chapter 2) concerning environmental management systems (EMS), the environmental fate and impact of legacy explosives and more recent IHE formulations, in particular regarding the disposal of explosives by open burning. This literature survey demonstrated the existence of data regarding environmental impacts caused by the disposal of TNT-based explosives by open burning, but almost no information addressing newer DNAN-based IHE materials. This gap in knowledge was explored throughout this thesis, initially by analysing a realistic case study (Chapter 3) which places the need for environmental impact information for disposal of explosives into context with an EMS.

A standard EMS includes several stages of a material or process life cycle. The ISO 14001 and 14040 series provide the basis for a civilian and industrial EMS. But given the specific challenges of military applications, such as the short time at a particular location, the lack of fixed infrastructure, the need for mobility, and the threat of hostile environments, implementing an EMS based solely on ISO guidelines is not possible. This is why the UK Process Oriented Environmental Management System (POEMS) is required as a military-oriented EMS.

As discussed in Chapter 3, POEMS is a UK MOD military-oriented EMS that is compatible with ISO 14001:1996 [1], ISO 14040:2006 [2] and Mil Std 882-E [3] when applied to military scenarios. In order to demonstrate the POEMS method, a case study was developed concerning the routine firing of 105-mm howitzer artillery rounds on a 640 km^2 training range in the southwest of England. Because the technical specifications of the 105-mm howitzer artillery round vary among different manufacturers [4–8], the 105-mm HE lightgun was selected for the case study [9]. This device weighs 15.1 kg and the payload is 2.5 kg TNT/RDX (L31 type) with a lead azide-based L116 multi-role fuze. The training regime was based on the assumption that the range could serve four artillery battalions, each carrying out two training sessions per year. Each artillery battalion consists of three artillery batteries, each with 6–8 howitzers, making a total of 18–24 howitzers per battalion. Each howitzer fires up to 100 rounds per training session, i.e. 1800–2400 rounds per battalion, making a total of 14,400–19,200 105-mm rounds fired per year.

The POEMS case study considered all aspects of the product life cycle, but the in-service stage was the most relevant in the context of this case study because this required the identification of all activities associated with the deployment of the 105-mm round during training, the embodied and emitted aspects, and anticipated environmental impacts. Aspects were identified for the detonation of the round, such as the gaseous detonation products, blast wave and noise, and the residues left behind. The quantities of emitted aspects such as heavy metals, explosive residues and gases were calculated through a risk matrix according to the reaction conditions (confinement, pressure, reaction rate, oxygen availability) using values for TNT and RDX available in the literature (as shown in Table 3-4). These were then used to construct a spreadsheet to calculate the environmental impact, and this study was published to provide a template for the use of POEMS in other scenarios.

One of the most important conclusions from the POEMS case study was that correct implementation requires reliable data, which includes information regarding the environmental impact of ordnance during all six stages of the explosives life cycle: concept, assessment, development, manufacture, in service and disposal. For TNT-based ordnance, there is enough information available to implement POEMS in a comprehensive manner, but there is little data available for DNAN-based ordnance, particularly concerning the environmental impacts related to the last two stages: in service and disposal. This is an egregious omission given that open burning is the recommended disposal method for explosives and ordnance that have reached the end of their in-service phase. Some work has been done for in-service environmental impact, as discussed in Chapter 2 of this thesis, which has been complemented by research on the fate and transport of Formulation 1 components (RDX, NTO and DNAN) in the soil, at least in cases of incomplete detonation. However, there is still a significant knowledge gap when it comes to understanding all the environmental impacts of open burning, its mechanisms, emissions and pollutants. In order to progress to the next stage, it was therefore necessary to collect data for the environmental behaviour of IHE formulations during open burning so that the data could be applied to the POEMS template, thus allowing the environmental impacts of components such as RDX, NTO and DNAN to be investigated and quantified in detail.

Obtaining new data to determine the environmental impact of IHEs clearly requires robust and reliable methods to replicate the conditions encountered during the open burning of explosives, combined with suitable analytical approaches for the detection of specific products. The military setup described in the introduction (Chapter 1) limits the efficiency of burning, and therefore influences the gases that are emitted and the residues that are left behind. Specifically, the lack of oxygen means that the initial materials are not fully converted into CO_2, H_2O and other stable compounds. Moreover, residual explosives remain in detonated ordnances, so similar behaviour during open burning was expected. Furthermore, the borehole setup favours the formation of plumes, and promotes soil contamination because the material is in direct contact with the soil at the base and along the sides of the hole.

Ideally, one would assess the efficiency of open burning in a real military environment, but this would be expensive, technically challenging, and dependent on the timing of authorized burning activities. Therefore a small-scale laboratory experiment was developed to replicate the conditions of open burning, and an exhaustive investigation of the materials was conducted in a 10 cm^3

closed system, which allowed the analysis of all the gases produced and accounted for the entire mass balance of the burning reaction (Chapter 4).

The closed system experiments were conducted testing an explosive mix of RDX, NTO and DNAN, since this formulation is being considered as a promising candidate for replacing a mix of RDX and TNT in artillery rounds in the near future [10,11]. The experiments mimicked the open burning mechanism for both RDX and NTO. However, DNAN required more oxygen than is present in 10 cm^3 of air (the volume of the headspace vial). DNAN was resilient to burning, instead undergoing melting, evaporation and sublimation rather than full combustion. This observation was supported by detailed thermal analysis, which showed that DNAN undergoes prompt sublimation at the same temperatures used in the burning experiments. The thermal analysis also confirmed that DNAN evaporates at 270 °C, which raises additional environmental concerns if open burning is used for the disposal of IHEs containing this substance. The closed system experiment showed that 1 % solid residues remained when burning pure NTO, but this increased to 13 % in the presence of DNAN. Similarly, 2 % solid residues remained after burning pure RDX, but these increased to 20 % when DNAN was also present. When tested alone, ~70 % of the DNAN remained as solid residues, the same order of magnitude observed when it was mixed with NTO and RDX. The reason for the more abundant solid residues of NTO and RDX when combined with DNAN relates to the thermodynamic properties of DNAN, which allow it to draw energy from the burning reaction to achieve sublimation, thus reducing the energy available for the combustion of NTO and RDX.

In the case of DNAN, open burning is thought to generate vapours at temperatures below the ignition point. These vapours are not energetic enough to ignite, so there is minimal decomposition. Moreover, the convection of gases and density-induced fluid movements draws the volatilized DNAN away from the burning area, and once DNAN cools down, it returns to the stable solid form at ambient temperatures and precipitates on the soil. When DNAN is mixed with

RDX and NTO, this process draws energy from the mixture, reducing the energy available for the combustion of RDX and NTO, thus increasing the amount of residual explosive and potentially moving these two unreacted components away from the burning reaction, expanding the contamination area. When all this information is considered in concert with the fate and transport of DNAN in soil, the inescapable partial conclusion from the closed-burning experiments is that open burning should be avoided as a method to dispose of DNAN-based IHEs because DNAN increases the residual masses of other materials with which it is mixed, including NTO and RDX.

When this work moved from a closed experimental setup to the laboratory small-scale open burning, the same macro-behaviour was observed for RDX and Formulation 1 (burning and decomposition with vivid gas production), whereas DNAN and NTO (tested individually) behaved differently in the metal tray heating test. NTO partially melted, but produced no flame or smoke, and DNAN melted and sublimated, with no signs of any chemical reaction. Table 1-1 compares the residual explosives after closed- system burning (Chapter 4) and the laboratory small-scale heating test reported in Chapter 5.

Table 7-1 **Summary of the residual explosive masses after each experiment**

	Tested individually (w/w %)				**Remaining masses within Formulation 1 (F1) (w/w %)**		
	NTO	**RDX**	**DNAN**	**F1**	**NTO**	**RDX**	**DNAN**
Percentage of unburnt explosives remaining after combustion by closed-system small-scale burning (Chapter 4)	1	2	75	23	13	20	67
Percentage of unburnt explosives remaining on the metal tray after the heating cycle (Chapter 5) in the small-scale experiment without accelerants	67	35	0	12	8	22	70

Based the data shown in Table 1-1, the first interesting point is that the massive difference in the residual mass of DNAN between the two experimental setups is due to its sublimation: when tested in the closed system, DNAN sublimated but remained confined (solidification at the top of the vial) (Figure 1-1) and was recovered in the solvent, whereas in the open experiment it sublimated and moved away from the metal tray (and was recovered in the modified headspace vial) (Figure 1-1), which is consistent with the sublimation observed.

Figure 7-1 Recovered DNAN in the closed-system experiment (left) and open-system experiment (right)

The higher remaining masses of NTO and RDX observed in the open system are consistent with the unconfined nature of the experiment, which allows heat to be transferred away from the reaction by the gases, lowering the temperature of the explosive. In contrast, when tested in the closed system, the gases remained confined, which maintained a higher temperature within the system. In the case of Formulation 1, a similar proportion of DNAN, NTO and RDX was observed in the solid residues, which suggests that the sublimation of DNAN plays a more significant role than the oxygen availability (given the similar values observed for both the closed and open systems) in terms of reducing the burning efficiency of NTO and RDX. It is very interesting to compare the 12–23 % solid residues found for the IHEs tested herein (Table 1-1) with the ~0.5–1.5 % observed by Walsh [12] when the same IHE formulation was detonated as an 81-mm mortar round.

When an accelerant was added, which is closer to real open-burning scenarios, a change was observed in the overall behaviour from burning and decomposition towards melting. The temperature of the bulk of the accelerant (acetone) did not exceed its boiling point, inducing the explosives to undergo a phase transition (melting, evaporation and sublimation). In summary, the accelerant evaporated, leaving most the explosive behind, unreacted. This alone indicated that current open burning methods may need to be revised, because the accelerant or fuel controls the reaction while it lasts, shutting the reaction down once all the fuel is consumed. Taking these results into consideration, soaking the explosives in fuel would not be the best approach, so a metal sieve “saddle” was introduced to elevate the explosive and make sure it was touched by the flame, which allows better heat transfer and more oxygenation for the explosive. This facilitated tests with different alternatives to current disposal methods.

The inclusion of the metal sieve saddle increased the efficiency of burning, leaving almost no solid residues for any of the test materials. At the same time, the burning cycle was reduced from 5–6 min to 30 s, which strongly suggests that the use of fuel-filled boreholes for the open burning of explosives on military ranges and in theatre is likely to be inefficient due to poor oxygenation and the dousing of the explosives in fuel. The process would be more efficient if burning was carried out in the open air and the explosives were elevated above the fuel. Currently, the fuel and accelerants that are used for open burning are generally liquids, and as such they burn on the surface, leaving any submerged material untouched by the flames. The same phenomenon was observed for the IHE materials tested herein.

In terms of real environmental impacts, the experiments reported in both Chapter 4 and Chapter 5 demonstrated high masses of explosives unburnt left on the soil, which increases environment awareness regarding soil and groundwater contaminations. These explosives will be transported through the soil and eventually contaminate the underground water, becoming mobile. Among the three materials considered, NTO (20 % remaining) is the most soluble and, as such, is more likely to be quickly dissolved and transported through both soil and water [13,14], where it increases the soil pH and promotes the leaching and migration of heavy metals [14], accelerating the spread of metals originating from discarded ordnance in soil and groundwater.

DNAN, whilst is much less soluble than NTO (0.21 g/L), is left in higher masses (70 % of initial masses) and is likely to adsorb to the organic components of soil [13] which prompts its degradation, whose products are also more likely to adsorb irreversibly to soil and therefore are less likely to enter groundwater [15].

Finally, the remaining RDX (orders of 20 % of initial masses) is highly mobile in soil environments and likely to contaminate groundwater as seen at several training ranges [16–19]. Where RDX does remain in soil, it can be taken up by plants and can have a damaging effect at concentrations >1.5 mg.L^{-1} [20]. In addition, RDX bioaccumulates in edible plant species such as lettuce, corn and tomato even at approved post-remediation concentrations (5.8 mg.kg^{-1}) [21], which suggest that the threshold value of 5.8 mg.kg^{-1} for RDX contamination should be reduced.

The gaseous products from both closed-system burning (Chapter 4) and the laboratory small-scale open-burning tests (Chapter 5) were analysed by GCMS and the results are summarized in Table 1-2.

However, the GCMS analysis summarized in Table 1-2 refers to gas composition and, as such, does not have an environmental meaning on its own. Therefore, the gaseous emission factor, which is environmentally and toxicologic meaningful were calculated from the GCMS data (Table 1-3). The emission factor is expressed in expressed in kg of gaseous from tonne of explosive and can be compared against EU Directive 2000/76/EC [22,23], that regulates maximum concentration of pollutants.

For the particular gaseous composition observed from the experiments reported in this thesis, only CO generated from the incineration of hazardous wastes has a maximum concentration (50 $mg.m^{-3}$) under EU Directive 2000/76/EC [22,23]. Furthermore, this directive addresses other pollutants, including particulate material (PM) and metals which were not measured as part of the experiments reported here.

Table 7-2 Comparative GCMS analysis of closed-system burning (Chapter 4) and small-scale open burning (Chapter 5)

	NTO		RDX		DNAN		Formulation 1			
	Burning in the closed system	Heating on a tray, without solvent	Burning in the closed system	Heating on a tray, without solvent	Burning in the closed system	Heating on a tray, without solvent	Burning in the closed system	Heating on a tray, without solvent	Heating on a tray, with solvent	Burning on the metal sieve
CO	2%	No reaction	6%	-	-	No reaction, only melting and sublimation	3%	-	-	2%
CO_2	54%		14%	39%	1%		52%	57%	51%	54%
H_2	-		-	-	-		-	-	-	-
H_2O	-		16%	9%	1%		-	7%	30%	-
N_2	26%		14%	52%	82%		21%	30%	5%	26%
HCN	2%		2%	-	16%		7%	-	-	2%
N_2O	16%		49%	-	-		17%	4%	-	16%
C_2H_4	-		-	-	-		-	2%	-	-
Acetone	-		-	-	-		-	-	14%	-

Table 7-3 Emission Factors (kg/tonne) calculated from the GCMS analysis of closed-system burning (Chapter 4) and small-scale open burning (Chapter 5)

	NTO		RDX		DNAN		Formulation 1			
	Burning in the closed system	**Heating on a tray, without solvent**	**Burning in the closed system**	**Heating on a tray, without solvent**	**Burning in the closed system**	**Heating on a tray, without solvent**	**Burning in the closed system**	**Heating on a tray, without solvent**	**Heating on a tray, with solvent**	**Burning on the metal sieve**
CO	25	No reaction	75	-	-	No reaction, only melting and sublimation	38	-	-	25
CO_2	1061		275	766	20		1021	1120	1002	1061
H_2	-		-	-	-		-	-	-	-
H_2O	-		129	72	8		-	56	241	-
N_2	325		175	650	1025		263	375	63	325
HCN	24		24	-	193		84	-	-	24
N_2O	314		963	-	-		334	79	-	314
C_2H_4	-		-	-	-		-	-	-	-
Acetone	-		-	-	-		-	-	-	-

The data consolidated in Table 1-2 show that NTO and DNAN only reacted in the closed-system experiments. For DNAN, this is consistent with the observation that it sublimes, melts and evaporates, not achieving temperatures high enough to undergo any reaction. The presence of NCH and N_2O among the gaseous products generated by NTO suggests some level of decomposition [24–40] when tested in the closed system, which might be related to the heat transfer between NTO and the open air dissipating heat away from the explosive faster than its temperature can increase to achieve ignition. Similar to NTO, the emission of N_2O by RDX in the closed burning system suggests some degree of thermal decomposition, because N_2O has consistently been identified as part of the decomposition kinetics of RDX [24–40].

Comparing the results for Formulation 1 across all the small-scale tests (both open and closed) (Table 1-2), the first observation is that it reacted in all configurations, producing 52–57 % CO_2, which indicates combustion. CO was only observed for the closed system (oxygen deficient when compared to the open system) and when burning above an open flame, which produces higher temperatures and reduces some of the CO_2 into CO. Unreacted acetone was detected in the gases, which is consistent with its volatility and low vapour pressure. Moreover, it is likely that some CO_2 came from the acetone and not from the Formulation 1, because this setup resulted in the largest quantity of solid residues on the metal tray. Furthermore, the HCN and N_2O observed for the tests with Formulation 1 indicate that some RDX (and possibly some NTO) not only burnt, but also underwent thermal decomposition. This decomposition may occur before or during burning, but the experimental setup did not allow the kinetics of the reaction to be determined.

Moving on from small-scale tests, the work reported in this thesis tested larger sample sizes (the medium and larger scale experiments reported in Chapter 5), so it was necessary to consider the limitations of capturing gases in larger open-burning setups. Therefore, the gas-capturing GCMS analysis approach was replaced by sensors and sorbent materials. For the medium-scale setup, the explosive samples (RDX, NTO and Formulation 1) were burnt mixed with other oxygen-deficient solid waste at a 1:10 mass ratio, which caused no significant change in the readings recorded by the NO, NO_2, CO and CO_2 sensors when compared with the tests without explosives added. DNAN was not tested in this setup, because previous experiments have shown that it would sublimate and melt. This indicates that gaseous emissions from burning explosives do not cause a significant additional environmental impact compared with the fuel and other waste materials that are added to facilitate burning. Similar findings were reported for TNT in the previously-described BangBox study [41] and the EPA aerostat study [42], i.e. that burning explosives emits greenhouse gases and particulates indistinguishable from those emitted by the fuel and waste materials, hence the real environmental threat caused by the open burning of explosives is the solid residues left behind, containing unreacted chemicals.

The captured chemicals were extracted from the activated carbon canisters by Soxhlet (using acetone) and accelerated solvent extraction (ASE), and characterized by HPLC. As expected from previous studies involving formulations containing TNT, every sample was negative for contaminants, which strongly suggests that most of the burning residues are either solids or gases and, as such, are not captured by the activated carbon.

Overall, the behavioural pattern observed in the small-scale open burning experiment (RDX and IHE burning, NTO showing high resilience to burning and DNAN sublimating and melting) was observed at both the medium and large scales, which is particularly interesting because the medium-scale setup was designed to replicate as accurately as possible a confinement profile similar to real burning scenarios.

Next the disposal of explosive materials and explosive-contaminated waste was tested in a real-size scenario. The findings from the smaller-scale tests suggested that the gaseous emissions would be virtually hidden by the vast excess of gases generated by the simultaneous burning of waste and fuel, but the sensor recordings and activated carbon extraction were repeated nevertheless. As described in Chapter 5, the real-size burning experiment was hosted by an ordnance company in Europe. Unfortunately, due to their production schedule, it was not possible to monitor Formulation 1, but it was possible to monitor the disposal of an RDX-based PBX formulation mixed with contaminated waste.

The burning composition was different on each day but was qualitatively consistent and usually contained 150–300 kg of solid waste such as cardboard boxes, and general laboratory consumables such as gloves and paper. In addition, hard plastic and rubber was frequently added to the burn, including rubber shoes, rubber face masks, and other personal protective equipment. Up to 5 kg of explosive material was also included for burning, along with explosive-contaminated waste. Particularly unexpected was the disposal of contaminated wastewater from the wash-down of areas that use explosives, which was poured directly onto the dry consumables and waste. The burning itself occurred in phases. During the early phase of the burn, black smoke was generated, most likely due to the solid plastics and rubber. The burn continued for several hours, with the thick black smoke mostly concentrated during the early phase (first hour).

The inclusion of contaminated wastewater caused some of the energy to be used for evaporation, reducing the temperature of the burning reaction. This is one of the most likely reasons for the poor efficiency of disposal observed. Visual inspection revealed that almost every piece of explosive remained unburnt, reflecting the low temperature and the inability of the flame to spread due to the presence of wet soot. Other potential reasons include the way in which the waste was stacked (piled up instead of spread out, which reduces the oxygenation), and the efficiency of the ignition process. The auto-ignition temperature of the PBX was dominated by the RDX at ~200 °C, and it is likely that the temperature around the explosive did not become this high due to the factors listed above [43–45]. It is also possible that additional material was obscured beneath the soot, or that very small pieces of the explosive were not detected before the soot was sent for its final disposal as non-hazardous solid waste.

The open burn was monitored for CO, NO and NO_2 *in situ*. CO was the most abundant gas of the three tested, although both NO and NO_2 were also detected. The emissions generated from the small quantity of explosives were minor compared to the emissions from the bulk waste and therefore cannot be isolated. Small-scale laboratory experiments showed that the gaseous emissions from the waste were mainly CO_2, CO, NO_2 and NO, and *in situ* experiments confirmed that these gases were indeed produced.

The activated carbon was extracted as described in Chapter 5 and the HPLC analysis revealed a clean profile. This result is supported by the conclusions of previous studies involving the burning of TNT [41], which showed that the solid residues left on the soil are the primary environmental concerns.

In summary, the array of burning experiments conducted at various scales led to the conclusion that gaseous emissions from the burning of IHEs are primarily greenhouse gases, as previously reported for formulations based on TNT [41,42]. Therefore, I believe that solid residues are the real environmental issue raised by the open burning these newer IHE formulations, again in common with previous experiments involving TNT [41,42]. The particulates may be unreacted explosives, ashes or other materials that are dragged away from the burning area by the hot gases and are deposited on the soil once the gases have cooled. The in-laboratory tests indicated that DNAN will sublimate, melt, and evaporate, being carried away in the plume of hot gases, landing on the soil at a distance from the burning site. The travel capacity was not tested, but the finding that DNAN solidifies within the modified headspace vial indicates that, in the open environment, it may spread widely to surrounding areas through sublimation and later solidification.

Given that open burning of explosives appears to have a greater impact on the soil than the air (if for no other reason, the shear mass of solid residues is a strong indication), the next step is to determine how the IHE components behave in the environment. As discussed in Chapter 2, some experimental work has already been published, but only in a limited number of soil types. The ability to predict the transport of DNAN and NTO though more diverse soils using computer codes is therefore an alternative worth investigating. Hence, available empirical data [46] were used to test the suitability of HYDRUS 1D as a tool to predict the way in which IHE components are transported through soil.

As shown in Chapter 6, HYDRUS 1D relies on diffusivity data to estimate the quantity of contaminants leaching through soil. This adds an extra layer of complexity when modelling the transport of explosives, because the diffusivity coefficients of the IHE components are not yet known. The diffusivity coefficients were approximated using empirical data [46] but Richard's equation always predicted 100 % leaching for each solute at the end of the 5-week experiment, which was not consistent with the observed results: 38 and 35 % of DNAN leached from the sandy and loamy soils, respectively, whereas the corresponding figures for NTO were 97 % and 0 %, respectively (Table 6-1). This indicates that the IHE materials react or interact with the soil matrix in a manner that cannot be incorporated into the HYDRUS 1D model. Previous studies have shown that HYDRUS 1D can be used to characterize the fate and transport of energetic materials through soil, but not without limitations given the drawbacks of the underlying equations, as discussed above.

Finally, this body of work has shown that the closed-system burning setup could be used to conduct a preliminarily assessment of the gaseous products from the burning of explosives. This closed system provided the data needed to select appropriate sensors and develop suitable methods for larger-scale open-system burning. In particular, it was observed that the gaseous products emitted by burning IHEs are mainly greenhouse gases and the main environmental issues are particulates and solid residues, as previously shown for TNT. Throughout the tests, DNAN-based IHEs were very resilient to burning. This is desirable as a safety feature (as discussed in Chapters 1 and 2) but hinders effective disposal. The tests indicated that, during open burning, ~70 % of the original mass of DNAN is left as solid residues, and the presence of DNAN can increase the residual mass of NTO and RDX from negligible quantities to 10–20 % of the initial mass. Considering that the tests were conducted on bare explosives, the quantity of residual explosive materials left after the open burning of normal military rounds may be even higher, because they are commonly burnt with the metal shell in place, which has even worse oxygenation and conducts heat from the explosive into the metal parts. Ultimately, this suggests that the military should revise their procedures for disposal once newer rounds filled with IHE come into service to account for the sublimation of DNAN, which generates even more solid residues deposited on the soil than has been observed for TNT-based rounds.

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8 CONCLUSIONS AND FURTHER WORK

The work reported in this thesis identified and addressed a knowledge gap concerning the collection of environmental impact data for the disposal of DNAN-based IHEs. Such data are required for environmental assessment as well as POEMS implementation. The gap was addressed through a series of experiments indicating that small-scale, closed-system laboratory experiments can be used to some extent to represent open burning. These experiments showed that the burning of RDX, NTO and DNAN, both individually and combined, generated mainly greenhouse-type gases and that solid residues and particulates are the main environmental concern from open burning, which agrees with previous studies focusing on TNT. Interestingly, the second key conclusion from the experiments is that DNAN is resistant to burning and less reactive than the other materials. In the IHE formulation, DNAN increased the quantity of solid residues from NTO and RDX probably by taking energy from the burning reaction to achieve sublimation, melting and evaporation. These same patterns were observed in all experiments: the gaseous emissions were mainly greenhouse gases, while the solid residues from RDX and NTO became more abundant in the presence of DNAN, which sublimates (closed system), or melts and evaporates (open system), moving away from the burning area.

Overall, the results indicate that the gaseous products generated by the open burning of IHEs are not a significant environmental issue because they are similar to emissions from other solid waste. The main concern is therefore the solid residues left on the burning area as well as unreacted explosives, which can be carried by smoke and hot gases, thus spreading to surrounding areas.

8.1 Principal conclusions

The principal conclusions from the work described in this thesis can be summarized as follows:

1. The application of POEMS was demonstrated in a case study using a 105-mm howitzer by collecting the necessary data and developing a risk matrix to address environmental impacts and aspects (Chapter 3). However, POEMS can only be applied when accurate data are available for all stages of the product life cycle. In the case of insensitive high explosives (IHEs), little information is available about the in-service and disposal stages because such formulations do not have an established track record and fewer studies have been carried out.

2. To address the lack of data concerning the disposal of IHEs, a small-scale closed system was developed for the burning of IHE components and formulations (Chapter 4). The results obtained were followed by a series of small, medium and large-scale open burning experiments (Chapter 5). Combined, the experiments showed that burning IHEs release primarily greenhouse gases and leave significant amounts of solid residues (particularly the DNAN component).

3. The tests in both the closed and open systems revealed that DNAN is highly resistant to burning, leaving ~70 % of its original mass behind. The presence of DNAN also inhibits the burning of NTO and RDX, increasing the residual mass from near 0 % when each component is burned alone to 10–20 % when burned in the presence of DNAN. The principal mechanism appears to be DNAN's sublimation, for which it draws energy from the burning reaction and inhibits the burning of NTO and RDX. The

poor efficiency of burning is exacerbated at larger scales and in more realistic scenarios when (a) the burning is constrained in a trench or pit, which limits oxygen availability, and (b) ‘unhelpful’ materials such as explosive-contaminated wastewater are included in the mix of waste materials, taking heat away from the reaction. Ultimately, DNAN is excellent as an insensitive component to prevent the accidental detonation of munitions but this is a drawback when it comes to the efficient disposal of IHEs by open burning, and the military should consider developing more efficient disposal methods.

4. The take home message from the above experiments is that the open burning of explosives leaves more solid residues than anticipated in and around the burning site due to unburned residues in the fire ashes and the deposition of smoke particles at a variable distance from the principal burning site. This means that environmental analysis to permit effective application of POEMS should concentrate on the residues deposited in the soil.

5. The experiments in Chapter 4 and 5 demonstrated that burning DNAN-based IHEs leaves significant quantities of solid resides, making it necessary to characterize their transportation through soil. Addressing this issue, empirical data were fed into HYDRUS 1D to check whether the code can predict the transport of IHEs through soil (Chapter 6). The empirical data showed less than 50 % recovery of DNAN in the leachate collected from the soil column, whereas the computer simulations always showed 100 % recovery. DNAN is likely to degrade, and there is not enough data available to properly account for this aspect in the model. However, as more empirical and experimental data become available, it should be possible to adjust the code to yield more accurate predictions.

In summary, the overall conclusion for the experiments reported in this thesis is that particulates and solid residues are the main environmental issue caused by the open burning of IHEs, not gases (which are mainly greenhouse gases). Moreover, for DNAN-based IHEs, the thermodynamic properties of DNAN make it more likely to sublimate and melt, instead of combusting during open burning. This causes DNAN to become mobile and to spread to surrounding areas via smoke and hot gases moving from the burning area. Overall from an RDX/NTO/DNAN mixture, ~70 % of DNAN is left unburnt. DNAN also reduces the efficiency of the burning of RDX and NTO, increasing the solid residues of these materials from minimal amounts (near zero solid residues) to figures in the order of 10–20 % of their initial masses.

Going back to the POEMS case study in Chapter 3, typical training on a range, using only 105-mm rounds, consumes an average of ~16,800 (14,400–19,200) rounds every year. Considering that the payload of said rounds is likely to move from TNT to IHE without changing the shell design, the overall explosive mass of 42,000 kg (2.5 kg per round) is likely to remain unchanged. Following standard protocols, if anything happens and the training is interrupted, the rounds would be destroyed by burning. From the experiments reported in this thesis (Chapters 4 and 5), it is likely that 12–20 % (Chapter 7, Table 7-1) of this payload would be unburnt, which means a minimum of ~5,000 kg of IHEs would be left on the soil. Based on the composition of ~70 % DNAN, ~10 % NTO and ~20 % RDX in the solid residues described herein, the real-life training and burning scenario outlined above would leave 3,500 kg of DNAN, 500 kg of NTO and 1,000 kg RDX on the soil (and this considers just one exercise, on one training range, not including residues from detonated rounds). Such massive amounts of uncontrolled deposits represent a huge environmental threat. Other reports (summarized in Chapter 2) show that DNAN is likely to undergo chemical degradation, forming toxic compounds, whereas NTO is soluble and is likely to travel through soil, contaminating the groundwater. The work in this thesis therefore leads to a final conclusion that traditional open burning methods, validated for TNT-based rounds over many years, should not be used for the disposal of DNAN-based rounds, and new procedures should be designed and implemented. These new procedures need to consider the tendency of DNAN to undergo sublimation, which reduces the energy available for the burning and increases the solid residues from NTO and RDX to 10–20 % of the initial mass, not to mention also leaving 70 % of the DNAN unreacted. Moreover, as demonstrated in Chapter 6, the use of computer simulations to predict the fate and transport of these huge masses of explosives is still not possible, which reinforces the importance in avoiding standard open burning procedures for DNAN-based IHE formulations.

Hence, this thesis has demonstrated that disposal process for newer IHE rounds needs to be reviewed to avoid and minimize critical environmental issues.

8.2 Further work

The principal conclusions from the work described in this thesis lead to the following suggestions for further work:

1. To better understand the chemistry behind open burning, it would be interesting to scale up the closed-burning system (Chapter 4) trying to achieve a size closer to the BangBox study conducted in America for TNT-based explosives and survey the behavior of larger masses of IHEs during open burning. This could be used to replicate the closed-system experiments shown in Chapter 4 with a different air-to-explosive ratio. Initially, the next scale of this BangBox could be in the order of 10 L (a 1000-fold increase compared to Chapter 4). This box could be made of metal or high-density glass (allowing observation of the reaction) and could be connected to canisters for gas analysis. Moreover, this

experiment should be designed considering oxygen and heat flow variation, thus allowing determining the optimum configuration for disposing of IHE materials.

2. To prepare for the disposal of IHE filled ammunition, engineering options to fully burn DNAN should be designed to provide an external heat source and more oxygen. Such options would include the following: (1) Change the borehole approach and introduce a metal mesh to hold the ordnance above the fuel source (a real-size version of the medium-scale experiment reported in Chapter 5) then evaluate the burning of ammunition filled with IHEs; (2) Investigate new accelerants that could increase the burning temperature to above 300 ºC (to account for heat losses) that would increase the chances of achieving proper burning; (3) Address the science and engineering foundations to develop a deployable incinerator suitable for disposing of large rounds filled with IHE materials. The incinerator would provide constant heat flow to the explosives, increasing the decomposition temperature, as well as burning within a chamber, thus controlling the emissions. The biggest challenge would be engineering an incinerator light enough to be deployable, but robust enough to withstand possible detonations and ensure operator safety.

3. The degradation kinetics of DNAN should be studied in more detail, and more soil column studies using DNAN-based formulations should be carried out aiming to determine absorption and degradation coefficients to update HYDRUS 1D equations and constants, making the latter a tool suitable for predicting the transport of DNAN-based IHEs though soils.

4. Assess the safety aspects of IHE ordnance after exposure to the environment during operations to verify whether they are safe to transport back for disposal, which would remove the need for disposal in situ. For

TNT-based ordnances, the common understanding is that, after being exposed to weather during deployment, ammunitions are not safe for transport, and in situ disposal is therefore necessary. However, if IHE-based rounds are safer to transport, the *in situ* disposal of deployed ordnances may be unnecessary, which would reduce and maybe eliminate the impact of open burning on ranges and/or in theatres of operation.

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