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Introduction and Overview

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1.1 Introduction

Armed forces countries possess and use large quantities of munitions. Civil authorities, such as space agencies, also use quantities of energetic materials. The production, use, and disposal of these materials make a contribution to the overall environmental impact. Handling of munitions with energetic materials requires great care and considerable cost. The environmental impact of the processes must be acceptable to an increasingly critical general population to avoid public concern and be acceptable under environmental laws. Significant funds must be used to clean up and restore areas where military activities have polluted the ground or water. Past practices such as dumping at sea or into landfill sites are no longer generally acceptable. There is a need to know and minimize the environmental impact from munitions so that environmental management can be undertaken properly.

Governments have a duty of care to the members of their armed forces, and all reasonable precautions must be exercised to ensure safe use of munitions. For example, some weapons systems can spread over 70% of their energetic material, particularly propellant around the shooting range. This is a health risk with the hazard of fires after prolonged use of the shooting range and there is also a work environment hazard. It is also an environmental hazard since a propellant's environmental hazard assessment is usually based on the final combustion products and not on the propellant itself.

The design of new weapons should include disposal procedures and an environmental impact statement. The understanding of munitions disposal is still lagging behind this design requirement although progress has been made, as is noted in this volume. However, to better meet the requirement, it is important to fully understand the environmental issues so that they do not place undue constraints on the design of weapons. Such understanding can also reduce the costs.

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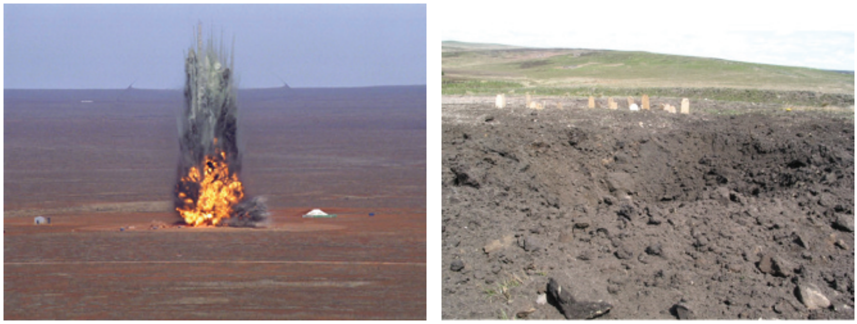

(a) (b)

Figure 1.1 Demonstration of (a) a large detonation and (b) the aftermath – residues left.

To be able to assess the environmental impact of the munitions, we need the right environmental assessment tools. To minimize the impact of manufacture and manage green munitions, it is important to look at all processes governing these activities.

This activity has been developing for many years and has been reported [1–6].

Finally, there is the need to understand, manage, and decontaminate after events such as those mentioned subsequently (Figure 1.1).

What we need to develop is a planned management method, and this is discussed later (Figure 1.2).

1.2 Legislative Impact

Public pressure has led to the implementation of legislation to manage environmental impact. This has gradually evolved from *ad hoc* national approaches to systematic regulations such as the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in the European Union (EU) where the law is limiting and controls the availability and use of materials.

While such legislation is of prime importance in the nations where it is directly applied, it has an effect elsewhere since import and export of materials is transnational and those imposing the legislation are usually the largest users and hence the largest market for the materials. For example the imposition of REACH terms affects the sales of energetic materials, etc. to EU nations from outside the EU [7].

The US Environmental Protection Agency (EPA) and the EU [7] have focused on minimizing impact, and in the EU legislation the control of chemicals is being introduced. Therefore, changing public perception and new legislation means that the environmental impact of munitions and their ingredients cannot be ignored. We require understanding of the problems if they are to be dealt with, simply:

(i) What is the impact of manufacturing processes as presently used and how may they be improved? Are there alternatives available or likely to become available?

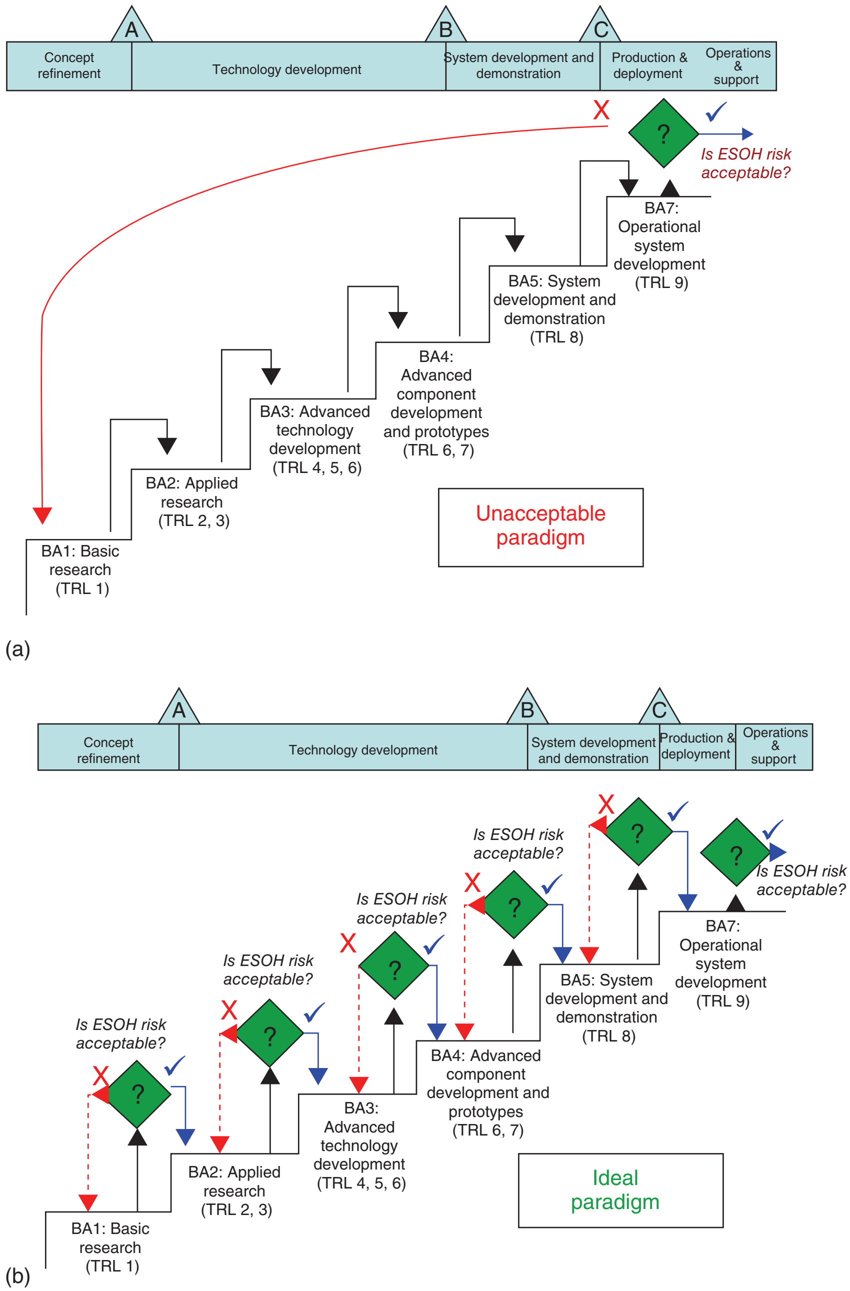

Figure 1.2 (a) Current and (b) proposed assessment practice – see Chapter 8.

(ii) What is the effect of use – on humans and on the environment?
  (a) What are the toxicity effects in handling and use?
  (b) What are the effects on land – that is managing contamination?

(iii) Are there disposal techniques available using safe methods?
(iv) Can improved disposal methods be devised?
(v) Finally, what are the costs involved? Are there spend-to-save options?

It is clear from examining the published literature that no one nation has all the answers and that no one nation has unique problems. While legal requirements do vary, there are common themes affecting all.

There is active work ongoing in the United States under the Strategic Environmental R&D Program (SERDP), a joint approach between Department of Defense (DoD), Department of Energy (DoE), and the EPA. There have been studies in the European Defence Agency and also studies in the North Atlantic Treaty Organization (NATO) – Science and Technology area.

These legislative requirements are driving research, as has been noted. However, they are discussed further in this book.

1.3 NATO Studies

Several activities have been completed or are in progress. Some have been openly reported [8, 9], but others may be available to NATO members and partners.

AVT 115: Environmental Impact of Munition and Propellant Disposal – study completed in 2009 and reported as an open document [10].
AVT 177: Symposium in Edinburgh 2011 – Munition and Propellant Disposal and its Impact on the Environment.
AVT 179: Design for Disposal of Present and Future Munitions and Application of Greener Munitions Technology (completed in 2013).
AVT 197: Munitions-Related Contamination – Source Characterization, Fate, and Transport (2012–2014).
AVT 269: Sea-Dumped Munitions and Environmental Risk (2016).

The first study, AVT 115, which was reviewed and discussed widely, produced the following conclusions:

- Open burning/open detonation (OB/OD) is not generally acceptable, although there are dissenting opinions and the use of amelioration technology is possible.
- Note that forensic studies have shown that residues do remain after detonation – these are used as court evidence. Whether these are meaningful in contamination terms needs discussion and examination.
- Technology exists for most current problems – current systems can generally be dealt with, although accidental failures or articles later discovered may need special treatment, and pyrotechnics can pose significant problems.
- Technology and needs are separated in many cases – e.g. the United States has technology/information and it is needed in, for example, Georgia.

- Availability of surplus systems must be considered as a target for terrorists as an easy source of materials.
- Surplus systems can also be targets for terrorist action, which may trigger an event.

There are therefore good safety and security reasons for dealing promptly with disposal.

1.4 New Ingredients and Compositions

It has been argued that changes in materials will answer the requirement and there is evidence that they can improve matters.

There is, however, a need to demonstrate that new materials offer significant advantages, and this is shown in several of the reports now in the open literature [5, 11–13]. An early example of this is the four-power programme on novel propellants [14]. Again, this is an illustration of the approach and, as detailed later, the area of focus is now materials such as ammonium dinitramide (ADN), etc (Figure 1.3) [15–21].

This was part of a multinational programme involving the United Kingdom, France, Germany, and the United States [14].

It involved joint studies on the formulation and testing of a smokeless propellant for tactical systems. The aim was proof of principle, but environmental issues did not play a major part in the study. It has interesting aspects, however, as elimination of acid smoke has been a first target for environmental improvement.

This is an improvement in many ways, but there are still products and these may be just as hazardous as the eliminated smoke. In some ways, an invisible product can be more hazardous.

Therefore, there is a need for clear demonstration of safety and proven ways of assessing true impact. This needs examination and experimental proof.

In short, simple answers can be in error and assumptions need testing before acceptance. These are the constraints that must be addressed.

There has also been considerable work on the replacement of metals in pyrotechnics and related systems [22–24]. The presence of metals, particularly Pb, is

(a) (b)

Figure 1.3 Comparison of (a) smoky and (b) smokeless propellants.

both undesirable and dangerous. Work has been under way for some time funded by the US Army with promising results [25]. Detailed toxicity studies are needed to avoid future problems of the kind found in the past and this is discussed in a later Chapters 8 and 10 in this book.

This is perhaps the most advanced study area, although small arms of all kinds are also being developed with the removal of ingredients of known toxicity. This is not as simple as might be supposed, as a recent Norwegian study [26] has shown. A round was introduced which seemed to offer improved environmental impact, but in use several Norwegian servicemen were taken ill prompting a detailed investigation. The results indicated that the new materials were less benign than originally thought. This illustrates the problems with the introduction of new materials where less is understood of their behaviour.

The development of national and international policies for the manufacture and use of less sensitive materials (insensitive munitions) led to the introduction and use of new polymer-bonded materials. While related to composite rocket propellants and themselves not possessing any significant problems, their manufacture make extensive use of isocyanates for curing the polymer. Many isocyanates are known carcinogens and therefore require careful handling, if not complete avoidance. To this can be added concerns over phthalates often used as plasticizers, which are now being banned in the EU.

Trinitrotoluene (TNT) has been used and is being used extensively and has been studied in depth by the US Army Corps of Engineers. It is toxic, but can be rendered non-available through immobilization in soils. It has useful explosive properties and ease of handing in preparation. This has prompted renewed research into similar materials to avoid some of the problems with polymer bonded explosive (PBX) while offering reduced sensitivity, and also to offer cost savings. However, recent studies have shown that it will leave more residues in use, and, more particularly, field disposal methods do not operate efficiently [27–29]. This is discussed in detail in later chapters.

1.5 Toxicology

It is hard to introduce new materials into use if there are uncertainties over their toxicity. Existing materials may well be toxic; but as the understanding of toxicity develops, their use may also be called into question [30–33]. For example, knowing how 1,3,5-trinitro-1,3,5-triazine (RDX) acts as a neurotoxin [31] helps manage the risk and should help devise treatment where possible.

This is a very active area and the likely main area of activity is in integrating this with other activities such as synthesis and formulation, as well as the study of the combustion and detonation products. It is often assumed that energetic materials are completely consumed when used in a design mode. However, forensic studies of explosives as detailed in the International Symposia on the Analysis and Detection of Explosives indicate that residues are left. An early paper [10] suggested that TNT could be trapped in explosives-generated carbon, for example. The question remains on the significance of those residues in health terms. Equally, the work by Walsh et al. indicates that significant residues are left by non-optimized function [30, 34, 35].

Contamination is of course not limited to the energetic materials, for metals in the system can be even more important and spread by explosive action [36].

First-generation tools now exist for modelling and predicting likely toxicity [37]. These have been developed for the speedier development of pharmaceuticals. These can be used to indicate bioactivity and hence estimate toxicity. Any such indication should reduce the testing and hence delays in introducing materials into use. It is important that they are used intelligently.

1.6 Life-Cycle Analysis

Environmental impact is part of the whole life of a munition and its ingredients. Experience elsewhere has shown that the whole life needs to be examined to understand and optimize the behaviour and so reduce the environmental impact. One of the areas identified for further immediate action within NATO was that of greener munitions. This formed the basis of a further study. Parts of the report are available and have been published [38].

At the outset of this study, the group identified several key issues that appeared to need examination:

Ingredients
Manufacturing
Use
Whole life-cycle management
Disposal
Impact on environment.

It became clear that the concept of greener munitions is far from simple. Not only are the individual aspects more complex but their interactions are also important and equally complex.

The approach and state of the art is discussed in later chapters.

1.7 Managing Contamination and Clean-Up

Land gets contaminated by use [2, 11, 14]. There is deposition from trials and tests as well as from impact and accidents. Often the use of ranges is poorly documented, and this is likely to be even more the case for battlefields. This is a prime source of contamination by hazardous materials, especially with incomplete functioning.

As reactive chemicals, energetic materials will have an effect on biology. This can be useful with nitrate esters being used to manage heart conditions, but on ranges, etc. it means that they can be bioavailable and therefore pose risks to health through incorporation into the food chain, perhaps through the water table.

For example, perchlorate is widely found in the water table, particularly in the United States, and as a bioactive material has provoked a series of programmes to understand its behaviour. Naturally, this has been extended to other energetic materials, with studies on behaviour and retention in soil and water. The behaviour depends on many factors including hydrogeology, soil structure, climate, and exposure. These all need consideration as do methods of assessing and managing any contamination.

Methods include bacteria and plants [39, 40] as well as more traditional chemical methods. Programmes on understanding the metabolism of energetics have been fairly successful and reported, with plants engineered to digest energetics. A problem arose in that energetic materials are not the preferred feedstock (other than ammonium nitrate) for bacteria; for example, energetic materials have less energy than more normal feedstock, although, of course, the energy that they have is released extremely rapidly in functional use.

As part of another multinational programme, there was a detailed study of ecotoxicology and land contamination. This work, involving the United Kingdom, United States, Canada, and Australia, was published in book form, but it forms a baseline for the assessment and management of land contaminated by energetic materials. It also includes a summation of the critical contamination levels as available at that point [35, 41, 42]. The first [41] report has produced a reference textbook on the Ecotoxicology of Explosives [43].

This publication [43] must mark the state of the art at the time, but requires updating on a regular basis to provide a measure of current understanding. However, the approach remains appropriate and the assessments and methods provide a sound basis for the necessary approach.

This is discussed in later Chapters 9 and 10.

1.8 Disposal Now and in the Future

The work by Walsh et al. indicates that there can be problems in disposing of new-generation materials as many of the existing tools for on-site disruption and disposal are insufficient for the task. This is specific for on-site disposal and would not affect the programmed demilitarization of surplus materials where a greater range of procedures can be employed. However, these are affected by legislation and the tightening of limits. The study in NATO indicated that most of the tools exist. These are being employed by various organizations to assist in the disposal of surplus materials worldwide. Some are being employed and developed by the NATO Support Agency under formal support agreements and are detailed in this book.

Unplanned disposal is not likely to diminish and cleaning up is certain to remain a live issue. The year 2018 also reminds us that material from the 1914 to 1918 war still requires handling!

These problems will continue and new variants will arise. The world situation means that tools for handling next-generation materials are needed, and tools must be applicable in a range of environments.

1.9 Recycling

Recycling is often seen as a way of covering the costs of disposal. However, experience has shown that at best it can be a disposal–cost offset. Metal parts can be recycled once certified free of explosives and the recovered energetics can possibly be reused for civil and military applications.

Techniques such as supercritical fluid extraction or liquid ammonia can produce recovered material which may be acceptable for use. However, a major drawback is the need to satisfy authorities of the consistency, and safety of the recovered materials. These materials need to be demonstrated to be safe in themselves and that no contaminants remain which will prevent safe use. This adds significantly to the cost. However, not all nations see this as an issue. It is likely to become more common especially with rare or expensive ingredients. It will require processes capable of producing a consistent product, or of making a consistent product from variable ingredients and hard evidence will be required to validate any such claims!

1.10 Conclusions

This is intended to provide an introduction to the technical area and to provide sufficient information to help manage environmental issues associated with munition systems.

In summary, to manage the potential environmental impact of energetic systems we need a range of approaches. Firstly, while it is not merely a matter of using new materials, they do offer sound options. However, they need to be understood well enough to deliver all the requirements placed upon them. This requires an understanding of likely toxicology and environmental and human impact as well as performance, ageing, and vulnerability. Since value for money also needs consideration, it may be that better specified and understood versions of existing materials will be more rapidly and effectively employed.

New processes can reduce manufacturing impact. Many processes were designed when there was less understanding of the effects and new approaches can be more efficient with reduced cost.

New-range management methods avoid damage and remove old damage. This is not limited to test ranges but also to manufacturing plants and storage facilities.

Overall, therefore, systems design for life minimizes overall impact!

These constraints and requirements should be considered a major driver for research and a scientific and engineering challenge. They require the following:

New methods for analysis.
New or re-engineered and well-characterized materials for use.
New methods for disposal.

References

1 Krause, H. and Fraunhofer ICT (1994). *Proceedings of the NATO ARW on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems*. Moscow: Kluwer Academic Publishers.

2 Cumming, A.S., Mostak, P., and Volk, F. (2001). Influence of sampling methodology and natural attenuation of analysis of explosives content in contaminated sites. In: *7th International Symposium on the Analysis and Detection Explosives*. Edinburgh: DERA.

3 Branco, P.C., Schubert, H., and Campos, J. (eds.) (2001). *Defense Industries: Science and Technology Related to Security – Impact of Conventional Munitions on Environment and Population*, NATO Science Series IV: Earth and Environmental Sciences, vol. 44. Kluwer.

4 Cumming, A.S. and Paul, N.C. (1998). Environmental issues of energetic munitions: a UK perspective. *Waste Manage.* 17: 129.

5 Cumming, A.S. et al. (2009). Environmental management of energetic materials. *1st Korean International Symposium on High Energy Materials*, Incheon.

6 Ruppert, W.H. et al. (2010). A history of environmentally sustainable energetics. In: *Insensitive Munitions and Energetic Technology Symposium*. Munich, Germany.

7 European Commission – Environment Directorate General (2007), REACH in brief.

8 Cumming, A.S. (2008). Recent and current NATO RTO work on munitions disposal. *Proceedings of the 11th International Seminar on New Trends and Research in Energetic Materials*, Pardubice, Czech Republic.

9 Research and Technology Organization (2010). Environmental Impact of Munition and Propellant Disposal. *RTO Technical Rep. RTO-TR-AVT-115*, open publication. NATO.

10 Clench, M.R., Cumming, A.S., and Park, K.P.. (1983). The analysis of post-detonation carbon residues by mass spectrometry. *Proceedings of the International Symposium on the Analysis and Detection of Explosives*, Quantico, USA.

11 Jenkins, T.F., Grant, C.L., Walsh, M.E. et al. (1999). Coping with spatial heterogeneity effects on sampling and analysis at an HMX-contaminated antitank firing range. *Field Anal. Chem. Technol.* 3 (1): 19–28.

12 Betzler, F.M., Boller, R., Grossmann, A., and Klapötke, T.M. (2013). Novel insensitive energetic nitrogen-rich polymers based on tetrazoles. *Z. Naturforsch.* 68b: 714–718.

13 Talawar, M., Sivabalan, R., Mukundan, T. et al. (2009). Environmentally compatible next generation green energetic materials (GEMs). *J. Hazard. Mater.* 161: 589–607.

14 Cumming, A.S. et al. (2017). Performance tests of next generation solid missile propellants. *NDIA 2007 Insensitive Munitions and Energetic Materials Technology Symposium*, Miami.

15 Eldsäter, C., de Flon, J., Holmgren, E. et al. (2009). ADN prills: production, characterisation and formulation. *40th International Annual Conference of ICT*, Karlsruhe, Germany (23–26 June 2009).

16 Larsson, A. and Wingborg, N. (2011). Green propellants based on ammonium dinitramide (ADN). In: *Advances in Spacecraft Technologies* (ed. J. Hall), 139–156. IntechOpen 978-953-307-551-8.

17 Weiser, V., Eisenreich, N., Baier, A., and Eckl, W. (1999). Burning behaviour of ADN formulations. *Propellants Explos. Pyrotech.* 24: 163–167.

18 Weiser, V. (2017). Combustion behaviour of aluminium particles in ADN/GAP composite propellants. In: *Chemical Rocket Propulsion*, 253–270. Springer.

19 Rosenbaum, K., Bachmann, M., Gold, S. et al. (2008). USEtox – the UNEP-SETAC toxicity model: recommended characterization factors for human toxicity and freshwater ecotoxicity in life-cycle impact assessment. *Int. J. Life Cycle Assess.* 13: 532–546.

20 Anderson, S.P., am Ende, D.J., Salan, J.S., and Samuels, P. (2014). Preparation of an energetic-energetic cocrystal using resonant acoustic mixing. *Propellants Explos. Pyrotech.* 39: 637–640.

21 Coguill, S.L. (2009). Synthesis of Highly Loaded Gelled Propellants. *Tech. Rep.*, Resodyn Corporation, Butte, MT.

22 Steinhauser, G. and Klapötke, T. (2008). "Green" pyro-technics: a chemists' challenge. *Angew. Chem. Int. Ed.* 47: 3330–3347.

23 Brinck, T. (ed.) (2014). *Green Energetic Materials*. Wiley.

24 Sabatini, J.J. and Shaw, A.P. (2014). Advances Toward the Development of "Green" Pyrotechnics. In: *Green Energetic Materials*, 9-1–9-12. NATO.

25 Klapotke, T.M., Piercey, D.G., Stierstorfer, J., and Weyrauther, M. (2012). The synthesis and energetic properties of 5,7-dintrobenzo-1,2,3,4-tetrazine-1,3-dioxide (DNBTDO). *Propellants Explos. Pyrotech.* 38: 527–535.

26 Moxnes, J.F., Jensen, T.L., Smestad, E. et al. (2013). Lead free ammunition without toxic propellant gases. *Propellants Explos. Pyrotech.* 38: 255–260.

27 Walsh, M.R., Walsh, M.E., Taylor, S. et al. (2013). Characterization of PAX-21 insensitive munition detonation residues. *Propellants Explos. Pyrotech.* 38: 399–409.

28 Walsh, M.R., Walsh, M.E., Ramsey, C.A. et al. (2014). Energetic residues from the detonation of IMX-104 insensitive munitions. *Propellants Explos. Pyrotech.* 39: 243–250.

29 Walsh, M.R., Walsh, M.E., Poulin, I. et al. (2011). Energetic residues from the detonation of common US ordnance. *Int. J. Energetic Mater. Chem. Propul.* 10 (2): 169–186.

30 Lima, D.R., Bezerra, M.L., Neves, E.B., and Moreira, F.R. (2011). Impact of ammunition and military explosives on human health and the environment. *Rev. Environ. Health* 26 (2): 101–110.

31 Braga, M.F.M. et al. (2011). RDX induces seizures by binding to the GABAA receptor convulsant site and blocking GABAA receptor-mediated currents in the amygdala. *Proceedings of 'Human and Environmental Toxicology of Munitions-Related Compounds – from Cradle to Grave'*, Amsterdam, The Netherlands.

32 Perkins, E. (2011). Molecular toxicology of munitions in environmental species. *Proceedings of 'Human and Environmental Toxicology of Munitions-Related Compounds – from Cradle to Grave'*, Amsterdam, The Netherlands.

33 Meuken, B. (2011). Effects of combustion products of small caliber munitions. *Proceedings of 'Human and Environmental Toxicology of Munitions-Related Compounds – from Cradle to Grave'*, Amsterdam, The Netherlands.

34 Walsh et al. (2012). Munitions propellants residue deposition rates on military training ranges. *Propellants Explos. Pyrotech.* 37: 393–406.

35 Thiboutot, S., Characterisation of residues from the detonation of insensitive munitions, SERDP ER-2219. www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Characterizing -Fate-and-Transport/ER-2219/ER-2219.

36 Leffler, P., Berglind, R., Lewis, J., and Sjöström, J. (2011). Munition related metals – combined toxicity of lead, copper, antimony. *Proceedings of 'Human and Environmental Toxicology of Munitions-Related Compounds – from Cradle to Grave'*, Amsterdam, The Netherlands.

37 Schultz, T.W., Cronin, M.T.D., and Netzeva, T.I. (2003). The present status of QSAR in toxicology. *J. Mol. Struct. THEOCHEM* 622 (1–2): 23–38.

38 Ferreira, C., Ribeiro, J., Mendes, R., and Freire, F. (2013). Life cycle assessment of ammunition demilitarisation in a static kiln. *Propellants Explos. Pyrotech.* 38: 296–302.

39 Bruce, N.C. (2011). Plant and microbial transformations of explosives. *Proceedings of 'Human and Environmental Toxicology of Munitions-Related Compounds – from Cradle to Grave'*, Amsterdam, The Netherlands.

40 French, C.E., Binks, P.R., Bruce, N. et al. (1998). Biodegradation of explosives by the bacterium *Enerobacter Cloacae* PB2. In: *Proceedings of the 6th International Symposium on Analysis and Detection of Explosives*. Prague.

41 Brochu, S., Williams, L.R., Johnson, M.S. et al. (2013), Assessing the Potential Environmental and Human Health Consequences of Energetic Materials: A phased Approach. Final Rep., *TTCP WPN TP-4 CP 4-42, DRDC Valcartier SL 2013-626*.

42 Brousseau, P., Brochu, S., Brassard, M., et al. (2010), Revolutionary insensitive, green and healthier training technology with reduced adverse contamination (RIGHTTRAC) technology demonstrator program, *41st International Annual Conference of ICT*, Karlsruhe, Germany (June 29–July 02 2010).

43 Sunahara, G. (2009). *Ecotoxicology of Explosives*. Wiley.