



# GUIDE TO EXPLOSIVE ORDNANCE POLLUTION OF THE ENVIRONMENT

#### ACKNOWLEDGEMENTS

The study was developed by Dr Tracey Temple PIEMA FHEA, Dr Melissa Ladyman MRSC, AIEMA, AFHEA and Roly Evans, Advisor at the GICHD. Illustrations were drawn by Clare Pratchett.

GICHD would like to thank Ole Feurer of the Swiss EOD Centre, Bob Seddon of Azide Ltd and Andy Duncan of the Halo Trust for their generous advice during the development of this guide. The GICHD would also like to thank Dr Michael Walsh and the Swiss EOD Centre for their kind permission to use their images.

Guide to Explosive Ordnance Pollution of the Environment, GICHD, December 2021 © GICHD

The content of this publication, its presentation and the designations employed do not imply the expression of any opinion whatsoever on the part of the Geneva International Centre for Humanitarian Demining (GICHD) regarding the legal status of any country, territory or armed group, or concerning the delimitation of its frontiers or boundaries. All content remains the sole responsibility of the GICHD.

GUIDE TO EXPLOSIVE ORDNANCE POLLUTION OF THE ENVIRONMENT

# TABLE OF CONTENTS

#### **INTRODUCTION**

Introduction

The Source Pathway Receptor Pollutant Linkage Model	11
Sources of contamination from explosive ordnance	13
Pathways of contamination from explosive ordnance	14
Effect on receptors of explosive ordnance contamination	15
Conceptual site diagrams to demonstrate pollutant linkages	16
Breaking the pollutant linkage	18
Summary and future considerations	18

7

9

9

ENVIRONMENTAL IMPACT OF ENERGETIC MATERIALS	21
Introduction	21
Environmental impact of Secondary Explosives	21
Environmental impact of propellants	24
Environmental impact of pyrotechnics	26
Environmental impact of explosives in the marine environment	27
Summary and future concerns	27

ENVIRONMENTAL IMPACT OF LEAD ANTIMONY	41
Introduction	41
The environmental impact of lead in the terrestrial environment	42
The environmental impact of antimony in the terrestrial environment	46
The environmental impact of lead and antimony in the marine environment	48
Summary and future concerns	50

## CONTAMINATION FROM HEAVY METAL TUNGSTEN ALLOY AND DEPLETED URANIUM

Introduction	55
Effect of Depleted Uranium on the environment	56
Effect of Heavy Metal Tungsten Alloy on the Environment	58
Summary and future concerns	60

#### MITIGATING CONTAMINATION FROM EXPLOSIVES AND METALS FOUND IN EXPLOSIVE ORDNANCE

Introduction	64
What can Mine Action Practically Do?	65
Approaches to mitigation	72
Conclusions and future considerations	77

#### A CASE STUDY: MITIGATION OF PROPELLANT CONTAMINATION FROM OPEN BURNING

Introduction	81
Context	81
Pollutant linkage	82
Source	82
Pathway	82
Receptors	83
Mitigation	84
Summary	86

#### CONCLUSION 88

#### LIST OF ABBREVIATIONS

90

55

64

81

# **INTRODUCTION**

The GICHD has developed this guide in order to inform those working in mine action about the research conducted to date concerning chemical pollution of the environment by explosive ordnance. The aim of this guide is to outline clearly what is known, and to at least suggest some specific measures by which such contamination may be mitigated.

It has not necessarily been fully appreciated in the past by the mine action sector that the explosives and metals found in explosive ordnance pose not only an immediate blast and fragmentation hazard, but also a potential long-term risk to the environment and human health. Nevertheless, it is easy to misrepresent the toxic hazard posed by certain explosives or metals such as lead. While there is a risk of significant pollution to the environment from explosives and metals, it should not be distorted. This guide will outline the risks as currently understood, and the means of mitigation available to mine action organisations.

The challenge for the mine action sector is to develop methods to mitigate pollution risks so that they can be said to be as low as reasonably practicable. Such mitigation might be as simple as better selection of a central demolition site, pH testing of soils, stricter burning procedures for small arms ammunition or stricter disposal procedures for slag residue from small arms ammunition (SAA) burning. Other courses of action might include better training to identify risk munitions such as kinetic penetrators and ordnance with insensitive fills, and improved explosive ordnance disposal training and procedures to minimise explosive residue. These measures, and others we are yet to develop, can offer limited ways of minimising the environmental impact of disposing of explosive ordnance. The key is to develop standard practices that the mine action sector readily adopts so we can continue to help those affected by explosive hazards, while not inadvertently damaging the environment any more than absolutely necessary.

It would be wrong to suggest that we fully understand the polluting effects of explosive ordnance on the environment. While there is a growing body of scientific evidence identifying how such contamination may arise, there is less research on practical mitigation methods we can adopt. Unfortunately, this is a problem with only a partial solution. What is possible, is for mine action organisations to try to mitigate the pollution risks inherent in clearing explosive ordnance. This guide will hopefully support those efforts.

This guide details the pollutant linkage model in Chapter 1, which is a conceptual framework within which contamination from explosive ordnance can be analysed. Chapter 2 covers the toxicity of traditional energetics such as TNT, and Chapter 3 the environmental impact of lead antimony. Small arms ammunition is often the item of ordnance disposed of most within mine action, but the pollution risk it presents is not as widely appreciated as it could be. Chapter 4 looks at the risk from ordnance containing depleted uranium and heavy metal tungsten alloys, while Chapter 5 focuses on potential ways that mine action operators can mitigate the range of pollution risks. Chapter 6 presents a case study of the successful mitigation of pollution during the disposal of double base gun propellant on a range.

Those who wish to have relatively detailed scientific explanations of the potential means by which explosive ordnance can pollute the environment may find more of interest in the earlier chapters. Those who wish to concentrate on how such pollution may be mitigated may wish to concentrate on the subsequent chapters.

## CHAPTER 1 THE POLLUTANT LINKAGE MODEL FOR EXPLOSIVE CONTAMINATION FROM EXPLOSIVE ORDNANCE

#### **INTRODUCTION**

Explosive Ordnance (EO) is a potential source of chemical pollution of the environment. Explosives, sometimes referred to as energetic materials, and metals, can be released into the environment leading to toxicological and ecological risks.<sup>1</sup> EO typically comprises a series of explosive components known as an explosive train, usually encompassing a detonator, a booster and a main charge (Figure 1). These components all have the potential to cause environmental contamination when either, a) initiated in their intended mode, b) abandoned in the environment, or c) disposed of by Open Burning Open Detonation (OBOD) techniques. The environmental impact of a single detonation of an individual item is minor. However, significant impact can be caused when multiple detonations or disposal activities are carried out in one place over a prolonged period of time, a scenario that can lead to residue loading in the environment. Equally, EO abandoned for long periods of time will corrode and potentially leach significant quantities of explosive into the environment. Table 1 is a summary of the most likely ways that EO and associated disposal activities can contaminate the environment.



Figure 1: Cross section of an M-19 AV mine, indicating the detonator, booster and main charge components of the explosive train. Image©CORD.

1	Energetic materials, metals and casing breaking down into soil- erosion of metals and plastics, solubilisation of energetic materials by weathering.	There may be secondary impacts on water e.g. surface and ground water from soil contamination.	Unlikely to cause impact to air quality or atmosphere in this form.
2	Residues from open burning, and from particulates falling to the ground, may comprise metals, explosives residues and ash that are solubilised or carried into soil by weathering.	There may be secondary impacts on water e.g. surface and ground water from soil contamination.	Emissions of greenhouse and toxic gasses to atmosphere causing temporary local air quality issues and contribution to climate change.
3	Physical land damage, and distribution of explosive and metal residue in the environment solubilised or carried into soil by weathering.	There may be secondary impacts on water e.g. surface and ground water from soil contamination.	Emissions of low levels of greenhouse and toxic gasses to atmosphere causing contribution to colmate change
4	Metals will corrode enabling energetic materials to leach into environment. Metals and energetic materials may accumulate in sediment.	Localised high concentration of metals and energetic materials potentially causing deoxygenation of water. Rapidly dilutes with distance from ERW.	No impact to air.

 Table 1: Summary of the most likely ways explosive ordnance and associated scenarios could contaminate the environment.

## THE SOURCE PATHWAY RECEPTOR POLLUTANT LINKAGE MODEL

To fully understand the environmental impact of EO as described in Table 1, it is necessary to understand how pollutants move through the environment, and what they will affect. The movement or transport mechanism of contaminants in the environment in the simplest form can be broken down into three linked component parts: the source, pathway and receptor (SPR). This is sometimes referred to as the Pollutant Linkage Model (PLM).<sup>2</sup> Typical routes are usually through land, air or water domains.

The SPR mechanism describes how a contaminant can enter the environment from a source, such as residues from disposal by open burning, or metals from corroding EO, and moves through the environment by air, soil or water (pathway) to a receptor.<sup>3</sup> A receptor is defined as an entity that may be adversely affected by interaction with a contaminant. An 'entity' can include flora and fauna, humans, the ecology of an area such as lake ecosystems and man-made structures and dwellings.

The point at which a contaminant reaches and affects a receptor is when the contaminant can be said to cause environmental impact. If the SPR linkages between the source and receptor are broken at any point, that is to say if the contaminant does not reach a receptor, then no environmental impact will be observed. SPR conceptual diagrams can therefore be used to illustrate the pathways between sources and potential receptors in and around training ranges to predict possible impacts on the environment (Figure 2).



Figure 2: Conceptual source-pathway-receptor diagram demonstrating pollutant linkages from a range of explosive ordnance activities

- 1. Buried explosive ordnance: contamination is leached from explosive filling and metal component casings. The potential receptors are personnel, groundwater and soil.
- Open burning of explosive ordnance: contamination is from burnt debris falling to the ground leaching into soil and groundwater. The potential receptors are personnel, local accommodation, groundwater and soil.
- **3.** Open detonation: contamination is distributed by explosive ordnance and metal component casings. The potential receptors are personnel, local accommodation, groundwater and soil.
- Underwater munitions from sea dumping: contamination is from corroding explosives and metal casings. The potential receptors are underwater ecosystems.

# SOURCES OF CONTAMINATION FROM EXPLOSIVE ORDNANCE

Pollutants from EO usually enter the environment by means of thermal or chemical shock, leading to rapid decomposition and emitting large amounts of heat and gas into the area surrounding the detonation. This is sometimes referred to as a 'high order' amongst explosive ordnance disposal personnel. It may also be through disposal activities such as open burning and incineration which produce emissions of gasses and waste metal or energetic residues, as well as visual pollution such as black smoke.<sup>4</sup> Finally, energetic materials and other EO components such as metals and plastic can transfer to the environment from the breakdown of the casings and subsequent leaching of energetic materials into the soil over time.<sup>5</sup>

Numerous compounds and compositions are classified as energetic compounds; however, secondary high explosives, such as 1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) at present pose the largest potential concern for the environment.<sup>6</sup> This is because they are produced and used in the greatest quantities around the world and they are the most studied for their toxicity characteristics.<sup>7</sup> Since the First World War, and until the recent advent of insensitive munitions, most high explosive ordnance has contained TNT or RDX, or a mixture of the two.8 Other potential contaminants from explosive ordnance include the casings and internal components which are likely to comprise plastic and heavy metals. The most common source of heavy metal contamination is lead, which is almost ubiquitously used in all small arms ammunition, and can also be found as a de-coppering agent in gun propellant. Lead is of particular note, as it is considered to be a contaminant of significant concern by many nations.<sup>9 10</sup> Other heavy metals of concern within EO are antimony, tungsten and bismuth.<sup>11</sup> In addition, some EO may contain specialist materials such as depleted uranium and cobalt.

#### PATHWAYS OF CONTAMINATION FROM EXPLOSIVE ORDNANCE

Contaminants from EO can enter the environment through the effect of weathering from rainfall, sunlight and other climatic conditions. There are three primary mechanisms for the transfer of contaminants from the soil surface: 1) gradual breakdown of solids by mechanical action into very small particles, known as erosion, 2) chemical transformation of metals into other metal compounds and complexes through corrosion; and 3) dissolution by water.<sup>12</sup> Generally, metals are eroded, or corroded and eroded, whereas energetic materials are more likely to be dissolved in water.<sup>13</sup> <sup>14</sup> These processes transform solids into smaller particles and chemical forms which are much more mobile in the environment, meaning that they are able to transport across the soil surface carried in water run-off and down through soil by infiltration with rainwater.

The speed at which contaminants travel through the environment depends on three factors: the chemical properties of the contaminant itself, the characteristics of the terrestrial environment, and the climate conditions.<sup>15</sup> Therefore, how far the same contaminant can travel in different environments can vary significantly and is affected by how rapidly it dissolves and how likely it is to interact with soil. For example, TNT and 2,4-dinitrotoluene (DNT) tend to bind to organic matter in the earth and therefore don't transport as readily as RDX, which has greater potential as a pollutant of groundwater.<sup>16</sup> If the soil contains less organic matter, such as sandy soil in a desert, the risk of TNT and DNT transportation increases. The rate of dissolution is also directly linked to temperature and rainfall, with most contaminants dissolving more rapidly in warm, wet climates. The acidity of the soil can also have a significant effect, with metals more readily dissolving under acidic conditions<sup>17</sup> than under alkaline conditions.<sup>18</sup> The interaction with soil is usually caused by two mechanisms, either sorption, wherein contaminants are attracted to components of soil, sediment or rock, and become immobilised;<sup>19 20</sup> or by degradation which is a chemical process that breaks down the contaminant into other, also potentially damaging, chemicals.<sup>21</sup> Where neither of these processes are particularly dominant, contaminants will continue to travel downwards through soil and spread outwards until they reach a receptor. While it is challenging to predict how far and how fast a contaminant will travel, it is necessary to understand the basic processes in order to make sensible assumptions for site management and remediation.

# EFFECT ON RECEPTORS OF EXPLOSIVE ORDNANCE CONTAMINATION

The impact a contaminant has on the environment depends on how much of the contaminant reaches a sensitive receptor, and the length of time the receptor is exposed to the contaminant. This depends on the pathway processes described above. However, it also depends on how the receptor is exposed to the contaminant and how sensitive the receptor is to the contaminant.<sup>22</sup> <sup>23</sup> For example, certain animals may be very sensitive to small quantities of energetic material, while plants may be able to degrade similar small quantities, ultimately removing them from the environment.

The toxicological effects of metals and energetic materials on microorganisms, plants and animals vary widely and can be significantly different depending on whether the exposure is acute (short term) or chronic (long term).<sup>24</sup> In some cases, the toxic effects may not be immediately apparent, but instead may be linked to an increased risk of cancer, or increased risk of mutation during pregnancy, which may not become evident for many years, if ever.<sup>25 26 27</sup> Contaminated soil and water may also have a toxic effect on plants and microorganisms, which over long periods of time may reduce the biodiversity in the area, and significantly reduce soil health, making it unsustainable for farming or other uses.28 For example, in Verdun, France, destruction of First World War artillery projectiles at a specific location on the Woëvre-Plain has led to long-term arsenic, copper, lead and zinc contamination, that is still present to this day.<sup>29</sup> Environmental impact is not limited to toxicological effects: other consequences such as discolouration of surface water and changes in acidity are strong indicators that there may be other hidden effects on the environment. For example, an alteration in acidity can change the form of immobilised contaminants, leading to the sudden release of a contaminant from the soil into groundwater.30

#### CONCEPTUAL SITE DIAGRAMS TO DEMONSTRATE POLLUTANT LINKAGES

A conceptional site diagram is an opportunity to develop a clear representation of an area or activity that has the potential to cause environmental contamination. As shown by the examples in Figure 2, the diagram can be very simple; however, it can be augmented with additional information depending on the circumstance. If practicable, SPR diagrams can be developed together with air, land and water sampling on the site to ensure a thorough understanding of the environment, or to highlight missing information about the site. When undertaking an SPR evaluation, the source is usually evident as it is directly related to activities at the site of interest. Receptors can be identified through observation of the site, particularly where there have been historic contamination incidents. Figure 2 outlines the most likely ways that explosive ordnance can contaminate the environment. Figure 2 also indicates the possible pathways along which the explosive ordnance is transported through the environment from either a land, water or air pathway, and the subsequent effect it has on the environmental receptors.



Anti-vehicle mines can degrade in situ and leach their explosive contents into the soil and groundwater over time. In this example, there are no impermeable layers to prevent leaching.

Figure 3: Magnified image of buried explosive ordnance



Explosive ordnance being burned on bare soil with no impermeable layers to protect the soil, therefore leaching chemicals into soil and groundwater. There are also emissions into the air from the burning process. The open burn reduces the heat, increasing the likelihood of post burn residues.

Figure 4: Magnified image of burning explosives in a pit



A bulk demolition resulting in emissions into the air and contamination of soil and groundwater. There are no impermeable layers to protect the soil, therefore there is potential of leaching into soil and groundwater.

Figure 5: Magnified image of a bulk demolition



Explosive ordnance buried at sea. The ordnance will become corroded over time and leach into the water causing potential contamination to the ecosystem and deoxygenation of the water.

Figure 6: Magnified image of explosive ordnance dumped into the sea

## **BREAKING THE POLLUTANT LINKAGE**

If the source, pathway and receptor are linked or connected, then a pollutant linkage exists. This means that contamination is present in the environment, and mitigation and management should be considered. In order to break this linkage, it is necessary to either reduce or modify the source, manage or break the pathway, or modify exposure to the receptor.

### SUMMARY AND FUTURE CONSIDERATIONS

Pollution by explosive ordnance can potentially lead to significant environmental impact, especially over long periods of time and use. Therefore, to assist with managing this type of contamination conceptual site diagrams can be used to outline the sources of contamination, the pathways and the receptors. The pollutant linkage process is a standard approach to map how pollution can occur. In terms of selecting appropriate mitigation, the SPR linkages need to be broken and this means ensuring that contamination does not reach a receptor via land, air or water pathways. It is not easy for mine action operators to develop SPR models, since invariably specialised knowledge is required to accurately develop such models in sufficient detail. For example, specific soil types interact differently with unique physiochemical properties of chemicals and explosives, and this requires expertise typically not available within the mine action sector. Nevertheless, with the use of conceptual site diagrams we are better able to visualise how pollution from mine action field operations may occur, and how we may minimise the effect activities causing the pollution.

- F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View," in *Eco-toxicology of Explosives and Unexploded Ordnance*, G. Sunahara, G. Lutofo, R. Kuperman, & J. Hawari, eds. (Boca Raton, FL.: CRC Press, Taylor and Francis Group LLC, 2009), 5–33.
- 2 C. W. Fetter, Thomas Boving & David Kreamer, Contaminant Hydrogeology, 3rd edn. (Long Grove, IL: Waveland Press, Inc., 2018), 647, <u>https://books.google.co.uk/books?hl=en&Ir=&id=ZXE8DwAAQBAJ&oi=fnd&p-g=PR1&dq=C+W+Fetter,+Contaminant+Hydrogeology&ots=RAU2kzRRpv&sig=sIOxKksrqhNJE1ZBrG6gb-7wL2BA#v=onepage&g#f=false.</u>
- <sup>3</sup> I. Bortone et al., "Scientific principles of environmental management," in *Global Approaches to Environmental Management on Military Training Ranges*, Tracey J. Temple and Melissa K. Ladyman, eds. (IOP Publishing Ltd, 2019), <u>doi.org/10.1088/978-0-7503-1605-7ch1</u>.
- 4 Carl Renan Estrellan & Fukuya lino, "Toxic emissions from open burning." Chemosphere 80, Issue 3 (2010): 193–207, doi.org/10.1016/j.chemosphere.2010.03.057.
- 5 Susan Taylor et al., "Underground UXO: Are They a Significant Source of Explosives in Soil Compared to Low-and High-Order Detonations?" Final report TR-04-23, (Hanover, NH: CRREL, 2004), <u>https://apps.dtic.</u> mil/dtic/tr/fulltext/u2/b308065.pdf.
- 6 J. Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 7 S. Chatterjee, et al., "Common explosives (TNT, RDX, HMX) and their fate in the environment: Emphasizing bioremediation." *Chemosphere* 184 (2017): 438–451, <u>doi.org/10.1016/j.chemosphere.2017.06.008</u>.
- 8 Paul W. Cooper, Explosives Engineering, (USA: Wiley-VCH, Inc., 1996).
- 9 M. L. Sall et al., "Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review," *Environ Sci Pollut Res* 27 (2020): 29927–29942, <u>doi.org/10.1007/</u> <u>s11356-020-09354-3</u>.
- 10 A. D. Hewitt et al., "Estimates for Explosives Residue from the Detonation of Army Munitions." Report TR-03-16, (Hanover, NH: CRREL, 2003), <u>http://65.175.100.54/uxofiles/enclosures/Residue\_Detonation\_TR03-16.</u> <u>pdf</u>.
- 11 Mathieu Laporte-Saumure, Richard Martel & Guy Mercier, "Characterization and metal availability of copper, lead, antimony and zinc contamination at four Canadian small arms firing ranges." *Environ Technol 32*, Issue 7 (2011): 767–781, doi.org/10.1080/09593330.2010.512298.
- 12 G. L. Baughman & L. A. Burns, "Transport and Transformation of Chemicals: A Perspective," in *The Handbook of Environmental Chemistry book series* (vol.2/2A), (Berlin, Heidelberg: Springer, 1980), 1–17, <u>doi.</u> org/10.1007/978-3-540-38519-6\_1.
- <sup>13</sup> Paul B. Tchounwou et al., "Heavy metal toxicity and the environment." *Exp Suppl* 101 (2012), 133–164, <u>doi.</u> <u>org/10.1007/978-3-7643-8340-4\_6</u>.
- 14 Steven L. Larson et al., "Dissolution, Sorption, and Kinetics Involved in Systems Containing Explosives, Water, and Soil." *Environ. Sci. Technol.* 42, Issue 3 (2008): 786–792, <u>doi.org/10.1021/es0717360</u>.
- 15 Xingtao Cao et al., "Influence of particle size and organic carbon content on distribution and fate of aliphatic and aromatic hydrocarbon fractions in chalks." *Environmental Technology & Innovation* 4 (2015): 227–239, doi.org/10.1016/j.eti.2015.09.001.
- <sup>16</sup> Neil C. Bruce et al., "Sustainable Range Management of RDX and TNT by Phytoremediation with Engineered Plants." Final Report, SERDP Project ER-1498 (Hanover, NH: ERDC-CRREL, 2016), 3.
- 17 L. Di Palma & R. Mecozzi, "Batch and column tests of metal mobilization in soil impacted by landfill leachate." Waste Manag. 30, Issues 8–9 (2010): 1594–1599, <u>doi.org/10.1016/j.wasman.2010.04.003</u>.
- 18 Rosalina González Forero, "Partitioning model of the adsorption of explosives from soils to determine its environmental fate." *Rev. Crim.* 56, Issue 3 (2014): 139–152, <u>http://www.scielo.org.co/pdf/crim/v56n3/ v56n3a10.pdf.</u>
- 19 Parya Broomandi, "Soil Contamination in Areas Impacted by Military Activities: A Critical Review." Sustainability 12, Issue 21 (2020): 1–35, doi.org/10.3390/su12219002.
- <sup>20</sup> T. Temple et al., "The effect of soil type on the extraction of insensitive high explosive constituents using four conventional methods." *Sci Total Environ* 668 (2019): 184–192, <u>doi.org/10.1016/j.scitotenv.2019.02.359</u>.
- 21 Carl Renan Estrellan & Fukuya lino, "Toxic emissions from open burning." Chemosphere 80, Issue 3 (2010): 193–207, doi.org/10.1016/j.chemosphere.2010.03.057.

- 22 Paul J. Lioy, "Assessing total human exposure to contaminants. A multidisciplinary approach." *Environ. Sci. Technol.* 24, Issue 7 (1990): 938–945, doi.org/10.1021/es00077a001.
- 23 F. A. Swartjes, "Human health risk assessment related to contaminated land: state of the art." *Environ Geochem Health* 37 (2015): 651–673, <u>doi.org/10.1007/s10653-015-9693-0</u>.
- 24 Paul J. Lioy, "Assessing total human exposure to contaminants. A multidisciplinary approach." *Environ. Sci. Technol.* 24, Issue 7 (1990): 938–945, doi.org/10.1021/es00077a001.
- <sup>25</sup> Mohamed Lamine Sall et al., "Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review." *Environ Sci Pollut Res.* 27 (2020): 29927–29942, <u>doi.</u> org/10.1007/s11356-020-09354-3.
- 26 Aaron J. Beck et al., "Spread, Behavior, and Ecosystem Consequences of Conventional Munitions Compounds in Coastal Marine Waters." *Front. Mar. Sci.* (2018): 5, <u>doi.org/10.3389/fmars.2018.00141</u>.
- 27 Mark S. Johnson, Gunda Reddy, Marc A. Williams, Michael J. Quinn Jr., eds., Wildlife toxicity assessments for chemicals of military concern. 1st edn. (Elsevier, 2015), 692.
- <sup>28</sup> Todd A. Anderson, "Environmental Toxicology of Munitions-Related Compounds," in *Wildlife Toxicology: Emerging Contaminant and Biodiversity Issues*, Ronald J. Kendall, Thomas E. Lacher, George C. Cobb, Stephen Boyd Cox, eds. (Boca Raton: CRC Press, 2010), 15–38.
- <sup>29</sup> Tobias Bausinger, Eric Bonnaire & Johannes Preuß, "Exposure assessment of a burning ground for chemical ammunition on the Great War battlefields of Verdun." *Science of the Total Environment* 382, Issues 2–3 (2007): 259–271, <u>doi.org/10.1016/j.scitotenv.2007.04.029</u>.
- 30 Jay Clausen & Nic Korte, "The Distribution of Metals in Soils and Pore Water at Three U.S. Military Training Facilities." Soil and Sediment Contamination: An International Journal 18, Issue 5 (2009): 546–563, doi. org/10.1080/15320380903085683.

## CHAPTER 2 ENVIRONMENTAL IMPACT OF ENERGETIC MATERIALS

#### **INTRODUCTION**

This chapter summarises some of the main environmental impacts of explosives, propellants and pyrotechnics. Traditional energetic materials can be grouped into categories based on the way they are used in explosive devices. Primary explosives are highly sensitive to initiation and are used in very small quantities; these are usually comprised of inorganic metal compounds. Secondary explosives are generally more powerful than primary explosives but are less sensitive to stimuli, and are therefore frequently used as the main explosive load of an explosive device and tend to be organic compounds. Propellants are designed to rapidly burn, rather than detonate, and produce large quantities of gas which is used for propulsion. Propellants also tend to be organic compounds. Finally, pyrotechnics are usually designed to produce a given effect - heat, light or smoke - and frequently use mixtures of metals and energetics.<sup>1</sup> Due to the diversity of the chemical composition of energetic materials, their behaviour and effect on the environment can significantly differ. Primary explosives will not be covered here as they are used in such small quantities that their impact is rarely significant.

### ENVIRONMENTAL IMPACT OF SECONDARY EXPLOSIVES

As the principal chemical component of an explosive device, secondary explosives present a significant risk to the environment, primarily from toxicity towards environmental receptors. The most commonly used secondary explosive is the nitro-aromatic 2,4,6- trinitrotoluene (TNT), which dissolves quickly when exposed to water (200 mg/L) or rainfall

and is characterised when in solution by a pink tint.<sup>2 3 4</sup> All similar compounds, such as picric acid, and TNT degradation products, such as a 2,4-dinitrotoluene (DNT), produce coloured solutions in water, which can sometimes be seen at sites of explosive contamination (Figure 1).<sup>5 6 7</sup> TNT and similar compounds are toxic to humans, animals and plants. A limit of 2.2 µg/L in drinking water has been designated by the United States Environmental Protection Agency (US EPA) indicating that even at very low concentrations long-term health effects can occur.<sup>8</sup> <sup>9</sup> However, this is dependent on TNT contaminating drinking water sources, which is often prevented by rapid degradation of TNT in soils containing high organic content.<sup>10</sup> <sup>11</sup> The risk of TNT contamination is higher if there is a higher groundwater risk. There is also a risk in sandy soil which does not contain significant organic material, as TNT will not be as rapidly degraded and may travel to groundwater or run off into surface water.<sup>12</sup> <sup>13</sup> TNT will typically biodegrade to a DNT isomer. DNT is highly toxic for humans,<sup>14 15</sup> since it can convert haemoglobin to methaemoglobin<sup>16</sup> at a relatively low threshold limit of 0.13 mg/L. It is therefore listed by the EPA as hazardous waste.<sup>17</sup>



Figure 1: Standing water contaminated with 2,4,6- trinitrotoluene (TNT) and TNT light-catalysed degradation products with the tell-tale pink tint. TNT and associated degradation products have a degree of toxicity, and in certain circumstances present a risk to humans, animals and plants. Image ©igem.org

The nitramine cyclotrimethylenetrinitramine (RDX) is another common secondary explosive, frequently used in combination with TNT, which has significantly different environmental properties. For example, RDX is significantly less soluble (30 mg/L) than TNT, but also much less susceptible

to degradation in soil and therefore more likely to leach through soil. It therefore may travel rapidly through all soil types to groundwater.<sup>18</sup> <sup>19</sup> <sup>20</sup> <sup>21</sup> <sup>22</sup> <sup>23</sup> RDX presents a degree of toxicity for humans, animals and plants, and particularly in humans has been linked to increased risk of cancer; the US EPA drinking water limit is therefore 0.61 µg/L.<sup>24</sup> <sup>25</sup> <sup>26</sup> <sup>27</sup> <sup>28</sup> Since RDX is less susceptible to degradation it may remain in the environment for long periods of time and the effect on a receptor (e.g. humans through potable water sources) may not materialise until tens of years after contamination has been released.<sup>29</sup> <sup>30</sup> <sup>31</sup> <sup>32</sup> 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX) has very similar properties to RDX, although it is less soluble and less toxic and therefore may present less of an impact to the environment.<sup>33</sup> <sup>34</sup>

Often TNT and RDX are used as a mixture in compositions such as Composition B. When combined in this way, it may affect how long it takes for the TNT and RDX to leach from an explosive device into the soil. Once in the soil it will behave as described above, since by that point the two explosives are unlikely to interact.<sup>35 36 37 38</sup>



Figure 2: A conceptual diagram illustrating the potential Pollutant Linkage Model for anti-vehicle mines left in the ground. Mines tend to be thin cased and prone to degradation over time. Most mines will contain TNT. In conditions where there is little organic matter, such as sandy soil, the risk of TNT polluting drinking water is greater. While removal of mines and their subsequent destruction may involve some environmental risk, the non-removal of mines can also present a long-term risk to the environment. Polymer-bonded explosives (PBX), which comprise traditional energetic materials suspended in a plastic (polymer) matrix,<sup>39</sup> are frequently used in aircraft munitions, and are increasingly found in land service ammunition. These behave somewhat differently in the environment. For example, due to the plastic matrix, leaching of the energetic component from the fill tends to take significantly longer, reducing the quantity of explosive exposed to the environment, particularly in bulk fills.<sup>40</sup> <sup>41</sup> However, after detonation, particularly when not in the intended design mode, such as a second order demolition in situ, or a low order mechanical break up or deflagration, significant pieces of PBX can be deposited in the area. These can present a toxicity risk to any foraging fauna. In addition, these PBXs can be carried by surface water to other environments where the explosive content may leach over long periods of time. As expected, the plastic component may take many years to degrade, although degradation, and subsequent explosive leachate, is more rapid in climates with significant temperature cycling and light.<sup>42</sup> In addition to its explosive constituents, PBX may also contain aluminium or oxidisers such as ammonium perchlorate which may also have an impact on the environment (see Table 1).

#### ENVIRONMENTAL IMPACT OF PROPELLANTS

Propellants can be subdivided into three chemical classes which each behave differently in the environment.<sup>43</sup> The most ubiquitous propellant constituent, used in both gun propellant and rocket propellant, is the fibrous polymer nitrocellulose.<sup>44</sup> Due to its structure, it has low solubility and though it may degrade through the loss of nitrogen atoms, the fibrous structure remains intact.<sup>45</sup> Therefore, nitrocellulose is most likely to move physically through the environment in larger pieces such as with water flow. In addition, nitrocellulose is one of the least toxic energetic materials and is often not considered to present a major concern.<sup>46 47</sup>

The second chemical class of propellants consists of nitroglycerine and nitroguanidine. Both are organic compounds, and similar to secondary explosives in their behaviour in the environment. Both are more soluble than TNT or RDX, and may rapidly transfer into soil and potentially to groundwater.<sup>48</sup> <sup>49</sup> <sup>50</sup> However, both are significantly less toxic than TNT or RDX, especially at the low concentrations often found in the environment.<sup>51</sup> <sup>52</sup> <sup>53</sup> However, nitroguanidine is not particularly susceptible to bio-degradation and therefore may persist in the environment travelling rapidly through soil to groundwater.<sup>54</sup> <sup>55</sup> <sup>56</sup> If located on the surface, nitroguanidine may undergo degradation from light, into ammonia and similar compounds which may contribute to other environmental impacts such as eutrophication.<sup>57</sup> <sup>58</sup> <sup>59</sup>

The third chemical class of propellants consists of salts such an ammonium perchlorate, which are known to be persistent in the environment in the form of their constituent ions i.e. perchlorate ions (negatively charged) and ammonium ions (positively charged).<sup>60</sup> <sup>61</sup> Ammonium perchlorate is readily soluble in water and does not degrade nor adsorb, and therefore tends to travel with the flow of water to groundwater where it may remain for decades.<sup>62</sup> Due to this, in areas where there has been extensive historic exposure to ammonium perchlorate, for example manufacturing facilities, or demolition areas, significant contamination of groundwater has been identified.63 64 65 66 67 Whilst not immediately fatal, exposure to perchlorate can cause negative health effects and therefore the US EPA has a recommended drinking water screening level of 11µg/L, though some US states have an enforced limit as low as 2 µg/L.68 69 70 The ammonium ion may also cause detrimental health effects to humans and terrestrial and aquatic species, and the World Health Organization recommends a drinking water limit of 0.5 mg/L.<sup>71</sup> It should be noted that perchlorate and ammonium ions may also arise from other sources such as pesticides and fertilisers, and in some areas occur naturally.<sup>72</sup> However, contamination from explosive activities is frequently in orders of magnitude higher than naturally occurring perchlorates.

#### ENVIRONMENTAL IMPACT OF PYROTECHNICS

Pyrotechnic devices can be tailored to produce desired effects such as emissions of light, smoke, noise or heat by optimising the chemical mixture in the fill.<sup>73</sup> Generally, the desired effect is achieved by use of metals and metal salts, therefore the primary environmental impact arises from deposition of metal residues or perchlorate residues from the oxidiser.<sup>74</sup> In particular, significant metal residues are deposited during intended use, as well as during disposal by open burning, which can cause respiratory distress in the short term such as an exacerbation of conditions such as asthma, as well as long-term growth and development impacts on soils and plants.<sup>75 76</sup> In addition, the form of the metal, whether as a metal solid, or as a metal ion, has a significant effect on its toxicity towards the environment and humans (see Chapter 4). For example, metal chromium is much less toxic than the chromium ion (Cr<sup>6+</sup>). Pyrotechnic devices frequently use metal salts (e.g. barium chromate) which can potentially result in the deposition of highly toxic metal ions in the environment.<sup>77 78</sup>

Many metals are now known to have severe health impacts at very low concentrations (toxic, mutagenic, carcinogenic) and are being increasingly controlled by legislation. Metal compounds of concern frequently used in pyrotechnic devices are lead (discussed in Chapter 3), aluminium, antimony, barium, boron, copper, manganese, and zinc, there are many more which are used less commonly, or have a less significant environmental impact.<sup>79</sup> <sup>80</sup> It is of interest to note that although aluminium is naturally occurring in the environment at high concentrations (10,000–300,000 mg/kg), as much as 10 g can be used in a single pyrotechnic.<sup>81</sup>

White phosphorus, frequently used in smoke-generating pyrotechnics, is an example of a particularly severe environmental impact.<sup>82</sup> <sup>83</sup> At Eagle River Flats (Fort Richardson), in Alaska, USA, white phosphorus at ordnance impact areas leached into the environment and caused the death of thousands of wildfowl per year.<sup>84</sup> <sup>85</sup> A thorough subsequent investigation revealed that white phosphorus, in toxic concentrations, had leached into water and sediments where the birds fed. The remediation effort has been expensive. <sup>86</sup> <sup>87</sup> <sup>88</sup>

### ENVIRONMENTAL IMPACT OF EXPLOSIVES IN THE MARINE ENVIRONMENT

While mine action is typically focused on the terrestrial environment, it is also important to note the contamination risk from explosive ordnance in the marine environment. There are significant guantities of abandoned ordnance in oceans worldwide, and of increasing relevance as they are being rediscovered during infrastructure developments such as the installation of windfarms.<sup>89 90</sup> In general, the environmental impact of ordnance at sea tends to be limited to the local area e.g. chemical compounds (organic and inorganic) reducing oxygen availability and subsequently driving marine organisms to other areas, or causing degrees of toxicity.91 92 93 94 95 96 Underwater noise from unintended detonations of unstable ordnance may also have an environmental impact, and recent research suggests that the impact from underwater noise is more significant than has previously been suspected.<sup>97</sup> 98 99 100 Metal corrosion is also more rapid in saline waters, and it is common to see elevated concentrations of metal near to underwater ordnance. At sea, contamination tends to dilute rapidly once beyond the immediate vicinity, however, this does not necessarily diminish the significance of marine contamination from explosive ordnance.<sup>101</sup>

## SUMMARY AND FUTURE CONCERNS

In recent years the drive for insensitive munitions has led to the development of Insensitive High Explosives (IHE) containing previously unused chemical compounds and compositions, which will increasingly be used in munitions. While, in the immediate future, the traditional energetics covered in this chapter, such as TNT, will remain the principal source of potential explosive contamination in the environment, it is likely that in years to come, increased research will be required to understand how these new compositions behave in the environment and, in particular, relevant mine action environments such as central demolition sites. The body of research currently underway suggests that some of the chemical compositions used as IHE are likely to differ considerably in their properties (solubility, acidity, charge, toxicity) and therefore, also in their effect and behaviour in the environment.<sup>102 103 104 105 107</sup>

 Table 1 summarises the chemical and environmental properties of the most common energetic materials

ENERGETIC MATERIAL	CHEMICAL CLASS <sup>108</sup>	TYPE OF EXPLOSIVE/ SOURCE <sup>109</sup>	SOLUBILITY (21°C) MG/L	ORAL REFERENCE DOSE (MG/KG/DAY)	COLOUR OF SOLUTION <sup>110</sup>	DEGRADATION (DEGRADATION PRODUCTS)	TRANSPORT	ENVIRONMENTAL LIMITS
2,4,6-trinitrotoluene (TNT)	Organic nitrobenzene	Secondary/ explosive fill	130111	0.0005 <sup>112</sup>	Pink/red	Rapid in soils with high organic content, rapid with exposure to light. (2-amino-4,6- dinitrotoluene, 4-amino- 2,6-dinitrotoluene) <sup>113</sup>	Dependent on degradation and sorption – often found in top layers of soil <sup>114</sup>	US EPA soil-to-groundwater risk-based soil screening level: 1.3 x 10-2 mg/kg <sup>115</sup>
2,4-dinitrotoluene (DNT)	Organic nitrobenzene	Secondary/ explosive fill or TNT degradation product	270 <sup>116</sup>	0.05117	Yellow	Rapid degradation in soils with high organic content, degrades on exposure to light. (2-amino-4- nitrotoluene, 2,4-diaminotoluene, 4-amino-2-nitrotoluene, 2,4-dinitrophenol) <sup>118</sup> <sup>119</sup>	Likely to degrade prior to transport to groundwater in organic soils. More likely to transport in sandy soil <sup>120</sup>	US EPA soil-to-groundwater risk-based soil screening level: 6.7 x 10-5 mg/kg <sup>121</sup>
Picric acid	Organic nitrobenzene	Secondary/ explosive fill	12,800 <sup>122</sup>	0.002 <sup>123</sup>	Yellow	Stable in water and less likely to degrade than TNT or DNT, however degradation will occur slowly and may produce more toxic and mutagenic degradation products <sup>124</sup>	Tends to be highly mobile in the environment due to its stability, which also means it can stay in the environment for a long time <sup>125</sup>	Not available
2,4,6-trinitrophenyl-methyl- nitramine (Tetryl)	Organic nitrobenzene	Secondary/ explosive fill	75126	0.1127	Pale yellow	Rapid degradation in soil, similar to other nitrobenzenes: within weeks in some soils <sup>128</sup>	If not degraded, may move through soils, and has been detected in groundwater where soil concentrations are very high <sup>129</sup>	Not available
Cyclotrimethylenetrinitramine (RDX)	Organic nitramine	Secondary/ explosive fill	38.4 <sup>130</sup>	0.003131	Colourless	Slow degradation more likely in highly organic soils (mono-, di-, and tri-nitroso products MNX, TNX and DNX) <sup>132</sup>	Likely to transport to groundwater and persist for long periods of time <sup>133</sup>	US EPA soil-to-groundwater risk-based soil screening limit: 2.3 x 10-4 mg/kg <sup>134</sup>

ENERGETIC MATERIAL	CHEMICAL CLASS <sup>108</sup>	TYPE OF EXPLOSIVE/ SOURCE <sup>109</sup>	SOLUBILITY (21°C) MG/L	ORAL REFERENCE DOSE (MG/KG/DAY)	COLOUR OF SOLUTION <sup>110</sup>	DEGRADATION (DEGRADATION PRODUCTS)	TRANSPORT	ENVIRONMENTAL LIMITS
1,3,5,7-tetranitro-1,3,5,7- tetrazoctane (HMX)	Organic nitramine	Secondary/ explosive fill	5-6.63135	0.05136	Colourless	Very slow/negligible degradation. (Degradation products not observed under environmental conditions) <sup>137</sup>	Likely to transport to groundwater and persist for long periods of time <sup>138</sup>	US EPA 10-day reference dose: 0.05 mg/kg/day <sup>139</sup>
Nitrocellulose	Polymer	Propellant	Insoluble <sup>140</sup>	5000141	Pale yellow	Degradation to nitrates and nitrites, also found from fertiliser run-off, though significant mass will not degrade <sup>142</sup>	Remains on top, or near to surface of soil with potential to be washed into surface water. Unlikely to transport through soil <sup>143</sup>	Not available
Nitroguanidine	Organic	Propellant	4,400144	316145	Colourless	Nitroguanidine degrades slowly in the environment, even in soils rich in organic materials, but will degrade to less harmful minerals <sup>146</sup>	High mobility in soils therefore may transport to groundwater	US EPA 10-day reference dose: 0.1 mg/kg/day <sup>147</sup>
Nitroglycerine	Organic	Propellant	Insoluble <sup>148</sup>	Not available.				Not available
Ammonium perchlorate	Inorganic salt	Propellant and pyrotechnics	200,000 <sup>149</sup>	0.007 (CIO4) <sup>150</sup>	Colourless	Found as ammonium and perchlorate ions once in water and persists for long periods of time <sup>151</sup>	Will move to groundwater, the time taken depends on soil characteristics as ions can be immobilised. Perchlorate groundwater contamination is common <sup>152</sup>	US EPA sets a drinking water limit of between 1 and 18 µg/L, depending on the State <sup>153</sup>
White phosphorus	Element	Pyrotechnic			Colourless	Does not degrade in the environment		US EPA reference dose: 0.00002 mg/kg/day <sup>154</sup>

- Jacqueline Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 2 James M. Brannon & Judith C. Pennington, "Environmental Fate and Transport Process Descriptors for Explosives." Final report, ERDC/EL TR-02-10. U.S. Army Engineer Research and Development Center, 2002.
- 3 Susan Taylor et al., "Outdoor weathering and dissolution of TNT and Tritonal." Chemosphere 77, Issue 10 (2009): 1338–1345, <u>doi.org/10.1016/j.chemosphere.2009.09.040</u>.
- 4 Kyoung S. Ro et al., "Solubility of 2,4,6-Trinitrotoluene (TNT) in Water." J. Chem. Eng. Data 41, Issue 4 (1996): 758–761, <u>http://doi.org/10.1021/je950322w</u>.
- <sup>5</sup> Sally L. Yost et al., "Environmental process descriptors for TNT, TNT-related compounds and picric acid in marine sediment slurries." *Marine Pollution Bulletin* 54, Issue 8 (2007): 1262–1266, <u>doi.org/10.1016/J.</u> <u>MARPOLBUL.2007.03.019</u>.
- <sup>6</sup> Ronald T. Checkai et al., "Transport and Fate of Nitroaromatic and Nitramine Explosives in Soils from Open Burning/Open Detonation Operations: Anniston Army Depot (AAD)," Report, 1993, <u>https://www.researchgate.net/publication/235010194</u> Transport and Fate of Nitroaromatic and Nitramine Explosives in Soil from Open BurningOpen Detonation Operations. Anniston Army Depot AAD.
- 7 Mohammad Nazrul Islam et al., "TNT and RDX degradation and extraction from contaminated soil using subcritical water." *Chemosphere* 119 (2015): 1148–1152, <u>doi.org/10.1016/j.chemosphere.2014.09.101</u>.
- 8 United States Environmental Protection Agency (EPA), "Technical Fact Sheet 2,4,6-Trinitrotoluene (TNT)." January 2014, <u>https://www.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet\_contaminant\_tnt\_january2014\_final.pdf</u>.
- <sup>9</sup> Gunda Reddy et al., "Toxicity of 2,4,6-Trinitrotoluene (TNT) in Hispid Cotton Rats (*Sigmodon hispidus*): Hematological, Biochemical, and Pathological Effects." *International Journal of Toxicology* 19, Issue 3 (2000): 169–177, <u>doi.org/10.1080%2F10915810050074937</u>.
- Prasesh Sharma, Melanie A. Mayes & Guoping Tang, "Role of soil organic carbon and colloids in sorption and transport of TNT, RDX and HMX in training range soils." *Chemosphere* 92, Issue 8 (2013): 993–1000, doi.org/10.1016/j.chemosphere.2013.03.028.
- 11 Hiroshi Yamamoto et al., "Fate and Transport of High Explosives in a Sandy Soil: Adsorption and Desorption." Soil and Sediment Contamination: An International Journal 13, Issue 4 (2004): 361–379,doi. org/10.1080/10588330490500419.
- 12 Ghasem Alavi et al., "The fate and transport of RDX, HMX, TNT and DNT in the volcanic soils of Hawaii: A laboratory and modeling study." *Journal of Hazardous Materials* 185, Issues 2–3 (2011): 1600-1604, <u>doi.</u> org/10.1016/j.jhazmat.2010.10.039.
- <sup>13</sup> Elly P. H. Best et al., "Environmental behavior of explosives in groundwater from the Milan Army Ammunition Plant in aquatic and wetland plant treatments. Uptake and fate of TNT and RDX in plants." *Chemosphere* 39, Issue 12 (1999): 2057–2072, <u>doi.org/10.1016/S0045-6535(99)00117-4</u>.
- 14 Paul B. Tchounwou et al., "Environmental Toxicology and Health Effects Associated with Dinitrotoluene Exposure," *Reviews on Environmental Health* 18, Issue 3, (2003), 203–229, <u>doi.org/10.1515/</u> <u>REVEH.2003.18.3.203</u>.
- 15 https://www.epa.gov/sites/production/files/2016-09/documents/2-4-dinitrotoluene.pdf.
- 16 Methaemoglobin is unable to bind with oxygen. An abnormal amount of methaemoglobin formation causes the blood to be unable to release oxygen effectively to body tissues.
- 17 United States Environmental Protection Agency (EPA) 40 CFR § 261.30.
- <sup>18</sup> Judith C. Pennington & James M. Brannon, "Environmental fate of explosives." Thermochimica Acta 384, Issues 1–2 (2002): 163–172, doi.org/10.1016/S0040-6031(01)00801-2.
- <sup>19</sup> William A. Tucker, Gerald J. Murphy & Eric D. Arenberg, "Adsorption of RDX to Soil with Low Organic Carbon: Laboratory Results, Field Observations, Remedial Implications." *Soil and Sediment Contamination: An International Journal* 11, Issue 6 (2002): 809–826, <u>doi.org/10.1080/20025891107104</u>.
- <sup>20</sup> Muhammad Imran Khan, Jaejin Lee & Joonhong Park, "Microbial Degradation and Toxicity of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine." J. Microbiol. Biotechnol 22, Issue 10 (2012): 1311–1323, <u>doi.org/10.4014/</u> <u>imb.1203.04002</u>.
- 21 Mark Johnson et al., Wildlife Toxicity Assessments for Chemicals of Military Concern, 1st edn. (Elsevier, 2015), 692.

- 22 J. Singh et al., "Long-Term RDX Sorption and Fate in Soil." *Journal of Environment Quality* 27, Issue 3 (1998): 572-577, <u>doi.org/10.2134/jeq1998.00472425002700030014x</u>.
- <sup>23</sup> Thomas A. Douglas et al., "Investigating the Fate of Nitroaromatic (TNT) and Nitramine (RDX and HMX) Explosives in Fractured and Pristine Soils." *Journal of Environment Quality* 38, Issue 6 (2009): 2285-2294, doi.org/10.2134/jeq2008.0477.
- 24 Muhammad Imran Khan, Jaejin Lee & Joonhong Park, "Microbial Degradation and Toxicity of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine." J. Microbiol. Biotechnol 22, Issue 10 (2012): 1311–1323, <u>doi.org/10.4014/</u> <u>jmb.1203.04002</u>.
- <sup>25</sup> United States Environmental Protection Agency (EPA). "Technical Fact Sheet Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)." January 2014, <u>https://www.epa.gov/sites/production/files/2014-03/documents/</u> <u>ffrrofactsheet\_contaminant\_rdx\_january2014\_final.pdf</u>.
- <sup>26</sup> Sharon A. Meyer et al., "Up-and-down procedure (UDP) determinations of acute oral toxicity of nitroso degradation products of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)." *Journal of Applied Toxicology* 25, Issue 5 (2005): 427–434, <u>doi.org/10.1002/jat.1090</u>.
- 27 Dennis T. Burton, Steven D. Turley & Gregory T. Peters, "The acute and chronic toxicity of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) to the fathead minnow (Pimephales promelas)." *Chemosphere* 29, Issue 3 (1994): 567–579, <u>doi.org/10.1016/0045-6535[94)90444-8</u>.
- <sup>28</sup> Michael Simini et al., "Evaluation of soil toxicity at joliet army ammunition plant." Environmental Toxicology and Chemistry 14, Issue 4 (1995): 623–630, doi.org/10.1002/etc.5620140410.
- 29 Elly P. H. Best et al., "Environmental behavior of explosives in groundwater from the Milan Army Ammunition Plant in aquatic and wetland plant treatments. Uptake and fate of TNT and RDX in plants." *Chemosphere* 39, Issue 12 (1999): 2057–2072, doi.org/10.1016/S0045-6535(99)00117-4.
- <sup>30</sup> William A. Tucker, Gerald J. Murphy & Eric D. Arenberg, "Adsorption of RDX to Soil with Low Organic Carbon: Laboratory Results, Field Observations, Remedial Implications." *Soil and Sediment Contamination: An International Journal* 11, Issue 6 (2002): 809–826, <u>doi.org/10.1080/20025891107104</u>.
- 31 Marianne E. Walsh et al., "Sampling for Explosives Residues at Fort Greely, Alaska. Reconnaissance Visit July 2000. "November 2001, <u>https://clu-in.org/characterization/technologies/pdf/FortGreely\_Sampling\_TR-01-15.pdf.</u>
- 32 Jay Clausen et al., "A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA." Environmental Pollution 129, Issue 1 (2004): 13–21, doi.org/10.1016/j.envpol.2003.10.002.
- 33 Lei Wang et al., "Investigation of the Solubility of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine and 1,3,5-Triacetyl-hexahydro-s-triazine." *J. Chem. Eng. Data* 58, Issue 3 (2013): 737–740, © American Chemical Society, <u>doi.org/10.1021/je301237t</u>.
- 34 P. Gong et al., "Toxicity of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) to Soil Microbes." Bull. Environ. Contam. Toxicol. 69, Issue 1 (2002): 97–103, doi.org/10.1007/s00128-002-0014-9.
- 35 J. H. Lever et al., "Dissolution of Composition B Detonation Residuals." *Environ. Sci. Technol.* 39, Issue 22 (2005): 8803–8811, <u>doi.org/10.1021/es050511r</u>.
- <sup>36</sup> Marianne E. Walsh et al., "Field observations of the persistence of Comp B explosives residues in a salt marsh impact area." *Chemosphere* 78, Issue 4 (2010): 467–473, <u>doi.org/10.1016/j.chemosphere.2009.10.021</u>.
- 37 Susan Taylor et al., "Simulated rainfall-driven dissolution of TNT, Tritonal, Comp B and Octol particles." Chemosphere 75, Issue 8 (2009): 1074–1081, doi.org/10.1016/j.chemosphere.2009.01.031.
- 38 Susan Taylor et al., "Characteristics of Composition B particles from blow-in-place detonations." Chemosphere 65, Issue 8 (2006): 1405–1413, doi.org/10.1016/j.chemosphere.2006.03.077.
- 39 P. P. Vadhe et al., "Cast aluminized explosives (review)." Combust Explos Shock Waves 44 (2008): 461–477, doi.org/10.1007/s10573-008-0073-2.
- 40 M. Kumar et al., "Release of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) from polymer-bonded explosives (PBXN-109) into water by artificial weathering." *Chemosphere* 169 (2017): 604–608, <u>doi.org/10.1016/j.</u> <u>chemosphere.2016.11.107</u>.
- 41 F. W. DuBois & J. F. Baytos, "Weathering of Explosives for Twenty Years." (New Mexico: Los Alamos National Laboratory, 1991), <u>http://permalink.lanl.gov/object/tr?what=info</u>:lanl-repo/lareport/LA-11931.

- 42 Tracey Temple et al., "Optimised Accelerated Solvent Extraction of Hexahydro-1,3,5-Trinitro-1,3,5 Triazine (RDX) from Polymer Bonded Explosives." *Propellants, Explosives, Pyrotechnics* 43, Issue 11 (2018): 1171-1177, <u>doi.org/10.1002/prep.201800185</u>.
- 43 Jacqueline Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 44 John Pichtel, "Distribution and Fate of Military Explosives and Propellants in Soil: A Review." Applied and Environmental Soil Science volume 2012, Article ID 617236, doi.org/10.1155/2012/617236.
- <sup>45</sup> Welford C. Roberts, "Data summary for nitrocellulose." (Frederick, MD: U.S. Army Medical Bioengineering Research & Development Laboratory, 1986), <u>https://apps.dtic.mil/sti/pdfs/ADA186413.pdf</u>.
- 46 Michael J. Quinn Jr., "Wildlife Toxicity Assessment for Nitrocellulose," in Wildlife Toxicity Assessments for Chemicals of Military Concern, Chapter 11 (Elsevier, 2015), 217–226, <u>doi.org/10.1016/B978-0-12-800020-5.00011-9</u>.
- 47 Denise K. MacMillan et al., "A reproducible method for determination of nitrocellulose in soil." *Talanta* 74, Issue 4 (2008): 1026–1031, <u>doi.org/10.1016/j.talanta.2007.08.013</u>.
- 48 Jennifer D. Arthur et al., "Dissolution and transport of insensitive munitions formulations IMX-101 and IMX-104 in saturated soil columns." *Science of The Total Environment* 624 (2018): 758–768, <u>doi.org/10.1016/j.</u> <u>scitotenv.2017.11.307</u>.
- 49 Geneviève Bordeleau et al., "Biodegradation of Nitroglycerin from Propellant Residues on Military Training Ranges." *Journal of Environment Quality* 43, Issue 2 (2014): 441-449, <u>doi.org/10.2134/jeq2013.06.0241</u>.
- 50 Geneviève Bordeleau et al., "The fate and transport of nitroglycerin in the unsaturated zone at active and legacy anti-tank firing positions." J Contam Hydrol 142–143 (2012): 11–21, <u>doi.org/10.1016/j.jconhyd.2012.09.001</u>.
- 51 Alan J. Kennedy et al., "Aquatic toxicity of photo-degraded insensitive munition 101 (IMX-101) constituents." Environmental Toxicology and Chemistry 36, Issue 8 (2017): 2050–2057, <u>doi.org/10.1002/etc.3732</u>.
- 52 B. Ho et al., "The Fate of Nitroguanidine in the Rat." Toxicological Sciences 10, Issue 3 (1988): 453–458. doi. org/10.1093/toxsci/10.3.453.
- <sup>53</sup> Marc A. Williams, Bradley E. Sample & Glenn J. Leach, "Wildlife Toxicity Assessment for Nitroglycerin," in Wildlife Toxicity Assessments for Chemicals of Military Concern, Chapter 13 (Elsevier, 2015): 239–255, doi. org/10.1016/B978-0-12-800020-5.00013-2.
- <sup>54</sup> Thomas Richard & Jennifer Weidhaas, "Dissolution, sorption, and phytoremediation of IMX-101 explosive formulation constituents: 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine." *Journal of Hazardous Materials* 280 (2014): 561–569, <u>doi.org/10.1016/i.jhazmat.2014.08.042</u>.
- 55 T. Temple et al., "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 (2018): 1264–1271, doi.org/10.1016/j.scitotenv.2017.12.264.
- 56 Rosalina González Forero, "Partitioning model of the adsorption of explosives from soils to determine its environmental fate." *Rev. Crim.* 56, Issue 3 (2014): 139–152, <u>http://www.scielo.org.co/pdf/crim/v56n3/ v56n3a10.pdf.</u>
- 57 June E. Mirecki, Beth Porter & Charles A. Weiss Jr., "Environmental transport and fate process descriptors for propellent compounds," ERDC/EL TR-06-7 (Hanover, 2006).
- 58 N. Pal, "Eutrophication An Ecological Menace." Biotica Research Today (2020), <u>www.bioticainternational.</u> <u>com</u>.
- <sup>59</sup> E. Kän-man & H. Jönsson, "Including oxidisation of ammonia in the eutrophication impact category." Int. J. LCA 6 (2001): 29–33, doi.org/10.1007/BF02977592.
- 60 C. Oommen & S. R. Jain, "Ammonium nitrate: a promising rocket propellant oxidizer." Journal of Hazardous Materials 67, Issue 3 (1999): 253–281, doi.org/10.1016/S0304-3894(99)00039-4.
- 61 Edward Todd Urbansky, "Perchlorate as an environmental contaminant." Environ Sci & Pollut Res 9 (2002): 187–192, doi.org/10.1007/BF02987487.
- 62 Gilbert M. Brown & Baohua Gu, "The chemistry of Perchlorate in the Environment" in *Perchlorate. Environmental Occurrence, Interactions and Treatment*, B. Gu, J. D. Coates, eds. (Boston, MA: Springer, 2006), 17–47, doi.org/10.1007/0-387-31113-0\_2.

- 63 Michael R. Walsh et al., "Perchlorate contamination from the detonation of insensitive high-explosive rounds." *Journal of Hazardous Materials* 262 (2013): 228–233, doi.org/10.1016/j.jhazmat.2013.08.045.
- 64 Geneviève Bordeleau et al., "Environmental Impacts of Training Activities at an Air Weapons Range." Journal of Environment Quality 37, Issue 2 (2008): 308–317, doi.org/10.2134/jeq2007.0197.
- 65 Feifei Cao et al., "Sources and behavior of perchlorate in a shallow Chalk aquifer under military (World War I) and agricultural influences." *Journal of Hazardous Materials* 398 (2020), 123072, <u>doi.org/10.1016/j.</u> jhazmat.2020.123072.
- 66 Katherine R. Weeks et al., "A study of treatment options to remediate explosives and perchlorate in soils and groundwater at Camp Edwards, Massachusetts." *Remediation* 13, Issue 2 (2003): 131–143, <u>doi.</u> org/10.1002/rem.10068.
- 67 Richard W. Gullick, Mark W. Lechevallier, Twila S. Barhorst, "Occurrence of perchlorate IN DRINKING WATER SOURCES." *JournalAWWA* (American Water Works Association) 93, Issue 1 (2001): 66–77, <u>doi.</u> org/10.1002/j.1551-8833.2001.tb09100.x.
- <sup>68</sup> R. G. York et al., "Two-generation reproduction study of ammonium perchlorate in drinking water in rats evaluates thyroid oxicity." *International Journal of Toxicology* 20, Issue 4 (2001): 183–197, <u>https://pubmed.ncbi.nlm.nih.gov/11563414/</u>.
- <sup>69</sup> Joseph C. Siglin et al., "A 90-day drinking water toxicity study in rats of the environmental contaminant ammonium perchlorate." *Toxicol Sci.* 57, Issue 1 (2000): 61–74, <u>doi.org/10.1093/toxsci/57.1.61</u>.
- 70 United States Environmental Protection Agency (EPA), "Technical Fact Sheet Perchlorate," January 2014, https://www.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet\_contaminant\_perchlorate\_january2014\_final.pdf.
- Vorld Health Organization Europe, "Support to the revision of Annex I Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption (Drinking Water Directive). Recommendations." September 2017: 1–240, http://ec.europa.eu/environment/water/water-drink/pdf/20171215\_EC\_project\_report\_final\_corrected.pdf.
- 72 Clayton W. Trumpolt et al., "Perchlorate: Sources, uses, and occurrences in the environment." *Remediation* 16, Issue 1 (2005): 65–89, <u>doi.org/10.1002/rem.20071</u>.
- <sup>73</sup> Jacqueline Akhavan, *The Chemistry of Explosives*, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 74 Jay Clausen et al., "Metal Residue Deposition from Military Pyrotechnic Devices and Field Sampling Guidance." U.S. Army Corps of Engineers, Engineer Research and Development Center, May 2012, file:///C:/ Users/UTILIS~1/AppData/Local/Temp/Metal\_Residue\_Deposition\_from\_Military\_Pyrotechnic.pdf.
- <sup>75</sup> Georg Steinhauser & Thomas M. Klapötke, "Using the chemistry of fireworks to engage students in learning basic chemical principles: A lesson in eco-friendly pyrotechnics." *J. Chem. Educ.* 87, Issue 2 (2010): 150–156, © 2010 The American Chemical Society and Division of Chemical Education Inc., <u>doi.org/10.1021/</u> ed800057x.
- <sup>76</sup> Vaishali V. Khaparde et al., "Influence of burning of fireworks on particle size distribution of PM10 and associated Barium at Nagpur." *Environ Monit Assess* 184 (2012): 903–911, <u>doi.org/10.1007/s10661-011-2008-8</u>.
- 77 M. L. Sall et al., "Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review." *Environ Sci Pollut Res* 27, (2020): 29927–29942, <u>doi.org/10.1007/</u> <u>s11356-020-09354-3</u>.
- <sup>78</sup> J. S. Rieuwerts et al., "Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals." *Chemical Speciation & Bioavailability* 10 (2015), <u>doi.</u> org/10.3184/095422998782775835.
- 79 Monisha Jaishankar et al., "Toxicity, mechanism and health effects of some heavy metals." Interdisciplinary Toxicology 7, Issue 2 (2014): 60–72, doi.org/10.2478/intox-2014-0009.
- 80 Paul B. Tchounwou et al., "Heavy metal toxicity and the environment." *Exp Suppl* 101 (2012): 133–164, <u>doi.</u> org/10.1007/978-3-7643-8340-4 6.
- 81 Jay Clausen et al., "Metal Residue Deposition from Military Pyrotechnic Devices and Field Sampling Guidance." U.S. Army Corps of Engineers, Engineer Research and Development Center, May 2012, file:///C:/ Users/UTILIS~1/AppData/Local/Temp/Metal\_Residue\_Deposition\_from\_Military\_Pyrotechnic.pdf.

- <sup>82</sup> Øyvind Albert Voie et al., "Environmental risk assessment of white phosphorus from the use of munitions – A probabilistic approach." *Science of The Total Environment* 408, Issue 8 (2010): 1833–1841, <u>doi.</u> org/10.1016/j.scitotenv.2010.01.002.
- 83 Ernst-Christian Koch, "Special Materials in Pyrotechnics: V. Military Applications of Phosphorus and its Compounds." *Propellants, Explosives, Pyrotechnics* 33, Issue 3 (2008): 165–176, <u>doi.org/10.1002/</u> prep.200700212.
- 84 M.E. Walsh et al., "White Phosphorus Contamination of an Active Army Training Range." Water Air Soil Pollut 225 (2014): 2001, doi.org/10.1007/s11270-014-2001-2.
- 85 Charles H. Racine et al., "White Phosphorus Poisoning of Waterfowl in an Alaskan Salt Marsh." J Wildl Dis 28, Issue 4 (1992): 669–673, doi.org/10.7589/0090-3558-28.4.669.
- <sup>86</sup> Donald W. Sparling et al., "Toxicity of white phosphorus to waterfowl: acute exposure in mallards." J Wildl Dis 33, Issue 2 (1997): 187–197, doi.org/10.7589/0090-3558-33.2.187.
- B. D. Roebuck et al., "Predation of ducks poisoned by white phosphorus: Exposure and risk to predators." Environmental Toxicology and Chemistry 13, Issue 10 (1994): 1613–1618, <u>doi.org/10.1002/etc.5620131010.</u>
- <sup>88</sup> Donald W. Sparling, D. Day & P. Klein, "Acute Toxicity and Sublethal Effects of White Phosphorus in Mute Swans, *Cygnus olor.*" Arch. Environ. Contam. Toxicol. 36 (1999): 316–322, <u>doi.org/10.1007/s002449900477</u>.
- 89 T. Missiaen & J-P. Henriet, "Chemical munition dump sites in coastal environments: a border-transgressing problem." 2002.
- 90 "Chemical Weapons Material Dumped at Sea," Google My Maps., accessed 21 March 2021, <u>https://www.google.com/maps/d/viewer?ll=54.831198475830774%2C-3.61369416997103348z=58mid=1ALnvOrN-5J08H50znwJdl Si8lwE.</u>
- 91 Margo Edwards & Jacek Bełdowski, "Chemical munitions dumped at sea." Deep-Sea Research Part II: Topical Studies in Oceanography 128 (2016): 1–3, doi.org/10.1016/j.dsr2.2016.04.008.
- 92 Jacek Bełdowski et al., "Sea-dumped ammunition as a possible source of mercury to the Baltic Sea sediments." Science of the Total Environment 674, (2019): 363–373, doi.org/10.1016/i.scitotenv.2019.04.058.
- <sup>93</sup> Jacek Bełdowski et al., "Chemical Munitions Search & Assessment–An evaluation of the dumped munitions problem in the Baltic Sea." *Deep-Sea Research Part 2: Topical Studies in Oceanography* 128 (2016): 85–95, <u>doi.org/10.1016/j.dsr2.2015.01.017</u>.
- 94 Aaron J. Beck et al., "Spread, Behavior, and Ecosystem Consequences of Conventional Munitions Compounds in Coastal Marine Waters." Front. Mar. Sci. (2018): 141, <u>doi.org/10.3389/fmars.2018.00141</u>.
- <sup>95</sup> Daniel Appel et al., "Bioaccumulation of 2,4,6-trinitrotoluene (TNT) and its metabolites leaking from corroded munition in transplanted blue mussels (*M. edulis*)." *Marine Pollution Bulletin* 135 (2018): 1072–1078, <u>doi.</u> org/10.1016/j.marpolbul.2018.08.028.
- 96 Øyvind A. Voie & Espen Mariussen, "Risk Assessment of Sea Dumped Conventional Munitions." Propellants, Explosives, Pyrotechnics 42, Issue 1 (2017): 98–105, doi.org/10.1002/prep.201600163.
- 97 Sven Koschinski, "Underwater noise pollution from munitions clearance and disposal, possible effects on marine vertebrates, and its mitigation." *Marine Technology Society Journal* 45, Issue 6 (2011): 80–88, <u>doi.</u> org/10.4031/MTSJ.45.6.2.
- 98 Geert Aarts et al., "Harbour porpoise movement strategy affects cumulative number of animals acoustically exposed to underwater explosions." *Mar Ecol Prog Ser* 557 (2016): 261–275, <u>doi.org/10.3354/meps11829</u>.
- <sup>99</sup> Janne K. Sundermeyer et al., "Effects of underwater explosions on presence and habitat use of harbor porpoises in the German Baltic Sea," in *The Effects of Noise on Aquatic Life*. Advances in Experimental Medicine and Biology series, vol 730 (2012): 289–291, <u>doi.org/10.1007/978-1-4419-7311-5 64</u>.
- 100 Peter H. Dahl et al., "Physical effects of sound exposure from underwater explosions on Pacific sardines (Sardinops sagax)." The Journal of the Acoustical Society of America 147, Issue 4 (2020): 2383–2395, doi. org/10.1121/10.0001064.
- 101 Jennifer S. Strehse & Edmund Maser, "Marine bivalves as bioindicators for environmental pollutants with focus on dumped munitions in the sea: A review." *Marine Environmental Research* 158 (2020): 105006, <u>doi.</u> org/10.1016/j.marenvres.2020.105006.
- 102 Alan J. Kennedy et al., "Aquatic toxicity of photo-degraded insensitive munition 101 (IMX-101) constituents." Environmental Toxicology and Chemistry 36, Issue 8 (2017): 2050–2057, <u>doi.org/10.1002/etc.3732</u>.

- 103 Thomas Richard & Jennifer Weidhaas, "Dissolution, sorption, and phytoremediation of IMX-101 explosive formulation constituents: 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine." *Journal of Hazardous Materials* 280 (2014): 561–569, <u>doi.org/10.1016/j.jhazmat.2014.08.042</u>.
- 104 T. Temple et al., "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 (2018): 1264–1271, doi.org/10.1016/j.scitotenv.2017.12.264.
- <sup>105</sup> Susan Taylor et al., "Outdoor dissolution of detonation residues of three insensitive munitions (IM) formulations." *Chemosphere* 134 (2015): 250–256, <u>doi.org/10.1016/j.chemosphere.2015.04.041</u>.
- <sup>106</sup> Mark S. Johnson, William S. Eck & Emily M. Lent, "Toxicity of Insensitive Munition (IMX) Formulations and Components." *Propellants, Explosives, Pyrotechnics* 42, Issue 1 (2016): 9–16, <u>doi.org/10.1002/</u> prep.201600147.
- 107 Wilfred C. McCain, Larry Williams & Gunda Reddy, "In Vitro Dermal Absorption of Insensitive Munitions Explosive 101 (IMX-101) and Components." US Army Public Health Command, Technical Report, (2013): 1–9, <u>https://apps.dtic.mil/sti/citations/ADA584068</u>.
- 108 Jacqueline Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 109 Jacqueline Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 110 Jacqueline Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 111 F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in *Eco-toxicology of Explosives and Unexploded Ordnance*, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, doi. org/10.1201/9781420004342.ch2.
- 112 Hyerim Ryu et al., "Human health risk assessment of explosives and heavy metals at a military gunnery range." *Environ Geochem Health* 29 (2007): 259–269, <u>doi.org/10.1007/s10653-007-9101-5</u>.
- 113 Judith C. Pennington & James M. Brannon, "Environmental fate of explosives." Thermochimica Acta 384, Issues 1–2 (2002): 163–172, doi.org/10.1016/S0040-6031(01)00801-2.
- 114 J. C. Pennington et al., "Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 1." Report ERDC TR 01-13, September 2001, <u>https://www.researchgate.net/publication/265599138 Distribution and Fate of Energetics on DoD Test and Training Ranges Interim Report 1</u>.
- 115 United States Environmental Protection Agency (EPA), "Technical Fact Sheet 2,4,6-Trinitrotoluene (TNT)." January 2014, <u>https://www.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet\_contaminant\_tnt\_january2014\_final.pdf</u>.
- 116 F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in Ecotoxicology of Explosives and Unexploded Ordnance, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, doi. org/10.1201/9781420004342.ch2.
- 117 "Toxicological Profile for Dinitrotoluenes," ATSDR (Agency for Toxic Substances and Disease Registry). Toxic Substance Portal. <u>https://wwwn.cdc.gov/TSP/ToxProfiles/ToxProfiles.aspx?id=847&tid=165</u>.
- 118 T. Temple et al., "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 (2018): 1264–1271, doi.org/10.1016/j.scitotenv.2017.12.264.
- 119 Smruthi Karthikeyan & Jim C. Spain, "Biodegradation of 2,4-dinitroanisole (DNAN) by Nocardioides sp. JS1661 in water, soil and bioreactors." Journal of Hazardous Materials 312 (2016): 37–44, <u>doi.org/10.1016/j.</u> jhazmat.2016.03.029.
- 120 Jennifer D. Arthur et al., "Batch soil adsorption and column transport studies of 2,4-dinitroanisole (DNAN) in soils." *Journal of Contaminant Hydrology* 199 (2017): 14–23, <u>doi.org/10.1016/j.jconhyd.2017.02.004</u>.
- 121 United States Environmental Protection Agency (EPA), "Technical Fact Sheet Dinitrotoluene (DNT)," September 2017, <u>https://19january2017snapshot.epa.gov/sites/production/files/2015-05/documents/9530566.pdf</u>.
- 122 F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in *Eco-toxicology of Explosives and Unexploded Ordnance*, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, doi. org/10.1201/9781420004342.ch2.

- 123 Q. Jay Zhao, et al., "Provisional Peer-Reviewed Toxicity Values for Picric Acid (2,4,6-Trinitrophenol) and Ammonium Picrate." US Environmental Protection Agency, September 2020.
- 124 Sally L. Yost et al., "Environmental process descriptors for TNT, TNT-related compounds and picric acid in marine sediment slurries." *Marine Pollution Bulletin* 54, Issue 8 (2007): 1262–1266, <u>doi.org/10.1016/J.</u> <u>MARPOLBUL.2007.03.019</u>.
- 125 Rachel M. Hebert & Allison M. Jackovitz, "Wildlife Toxicity Assessment for Picric Acid (2,4,6-Trinitrophenol)," in Wildlife Toxicity Assessments for Chemicals of Military Concern, Chapter 15, (Elsevier, 2015): 271–277, doi. org/10.1016/B978-0-12-800020-5.00015-6.
- 126 F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in *Eco-toxicology of Explosives and Unexploded Ordnance*, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, <u>doi.org/10.1201/9781420004342.ch2</u>.
- 127 John C. Lipscomb et al., "Provisional Peer-Reviewed Toxicity Values for Trinitrophenylmethylnitramine." US Environmental Protection Agency, 2013.
- 128 David DeTata, Peter Collins & Allan McKinley, "An investigation into the fate of organic explosives in soil." Australian Journal of Forensic Sciences 45, Issue 1 (2013): 71–84, <u>doi.org/10.1080/00450618.2012.691548</u>.
- 129 ATSDR (Agency for Toxic Substances and Disease Registry), "Tetryl: Potential for Human Exposure," <u>https://www.atsdr.cdc.gov/toxprofiles/tp80-c5.pdf</u>.
- 130 Hyerim Ryu et al., "Human health risk assessment of explosives and heavy metals at a military gunnery range." Environ Geochem Health 29 (2007): 259–269, <u>doi.org/10.1007/s10653-007-9101-5</u>.
- 131 Idem.
- 132 Judith C. Pennington & James M. Brannon, "Environmental fate of explosives." Thermochimica Acta 384, Issues 1–2 (2002): 163–172, doi.org/10.1016/S0040-6031(01)00801-2.
- <sup>133</sup> F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in *Eco-toxicology of Explosives and Unexploded Ordnance*, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, <u>doi.org/10.1201/9781420004342.ch2</u>.
- 134 United States Environmental Protection Agency (EPA). "Technical Fact Sheet Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)." January 2014, <u>https://www.epa.gov/sites/production/files/2014-03/documents/</u> <u>ffrrofactsheet contaminant rdx january2014 final.pdf</u>.
- <sup>135</sup> Hyerim Ryu et al., "Human health risk assessment of explosives and heavy metals at a military gunnery range." *Environ Geochem Health* 29 (2007): 259–269, <u>doi.org/10.1007/s10653-007-9101-5</u>.
- 136 Idem.
- 137 Judith C. Pennington & James M. Brannon, "Environmental fate of explosives." Thermochimica Acta 384, Issues 1–2 (2002): 163–172, doi.org/10.1016/S0040-6031(01)00801-2.
- 138 F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in *Eco-toxicology of Explosives and Unexploded Ordnance*, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, <u>doi.org/10.1201/9781420004342.ch2</u>.
- 139 United States Environmental Protection Agency, Office of Water, "2018 Edition of the Drinking Water Standards and Health Advisories" (EPA 822-F-18-001), March 2018, <u>https://www.epa.gov/sites/default/ files/2018-03/documents/dwtable2018.pdf</u>.
- 140 F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in *Eco-toxicology of Explosives and Unexploded Ordnance*, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, <u>doi.org/10.1201/9781420004342.ch2</u>.
- 141 Michael J. Quinn Jr., "Wildlife Toxicity Assessment for Nitrocellulose," in Wildlife Toxicity Assessments for Chemicals of Military Concern, Chapter 11 (Elsevier, 2015), 217–226, <u>doi.org/10.1016/B978-0-12-800020-5.00011-9</u>.
- 142 John Pichtel, "Distribution and Fate of Military Explosives and Propellants in Soil: A Review." Applied and Environmental Soil Science, volume 2012, Article ID 617236, doi.org/10.1155/2012/617236.
- 143 Idem.
- 144 F. Monteil-Rivera et al., "Fate and Transport of Explosives in the Environment: A Chemist's View" in *Eco-toxicology of Explosives and Unexploded Ordnance*, 1st Edn. (Boca Raton, FL.:CRC Press, 2009): 5–33, doi. org/10.1201/9781420004342.ch2.
- 145 United States Environmental Protection Agency (EPA), "Nitroguanidine" (CASRN 556-88-7), IRIS Assessments, <u>https://iris.epa.gov/ChemicalLanding/8substance\_nmbr=402</u>.
- 146 T. Temple et al., "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 (2018): 1264–1271, doi.org/10.1016/j.scitotenv.2017.12.264.
- 147 United States Environmental Protection Agency, Office of Water, "2018 Edition of the Drinking Water Standards and Health Advisories" (EPA 822-F-18-001), March 2018, <u>https://www.epa.gov/sites/default/ files/2018-03/documents/dwtable2018.pdf</u>.
- 148 Jacqueline Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 149 United States Environmental Protection Agency (EPA), "Technical Fact Sheet Perchlorate," January 2014, https://www.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet contaminant perchlorate january2014 final.pdf.
- 150 United States Environmental Protection Agency (EPA), "Perchlorate and Perchlorate Salts" CASRN 7790-98-9, IRIS Assessments, <u>https://iris.epa.gov/AtoZ/?list\_type=alpha</u>.
- 151 M. R. Sijimol et al., "Review on Fate, Toxicity, and Remediation of Perchlorate." *Environmental Forensics* 16, Issue 2 (2015): 125–134, <u>doi.org/10.1080/15275922.2015.1022914</u>.
- 152 Edward Todd Urbansky, "Perchlorate as an environmental contaminant." Environ Sci & Pollut Res 9 (2002): 187–192, <u>doi.org/10.1007/BF02987487</u>.
- 153 United States Environmental Protection Agency (EPA), "Technical Fact Sheet Perchlorate," January 2014, https://www.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet\_contaminant\_perchlorate\_january2014\_final.pdf.
- 154 United States Environmental Protection Agency, Office of Water, "2018 Edition of the Drinking Water Standards and Health Advisories" (EPA 822-F-18-001), March 2018, <u>https://www.epa.gov/sites/default/ files/2018-03/documents/dwtable2018.pdf.</u>

## CHAPTER 3 ENVIRONMENTAL IMPACT OF LEAD ANTIMONY

#### **INTRODUCTION**

While there are many different definitions of metals, generally they can be defined as materials that are able to conduct electricity or heat. As such, metals can be a single chemical element such as lead, or an alloy containing two chemical elements such as lead antimony.<sup>1</sup> As metals naturally occur in the Earth's crust, their behaviour is highly dependent on their geographical location in the environment and their chemical form.<sup>2</sup> <sup>3</sup> In addition, metals are often deposited in the environment by human activities, including disposal activities, as a solid mass like a bullet or slag from burning, for example, but over time these will be eroded (small particles physically removed from the bulk) and corroded (reaction with atmospheric water and oxygen) making them much more able to move through the environment.<sup>4</sup> Movement through soil and water is highly dependent on the form of the metal. For example, small metal particles may be more likely to be transported by surface water, whereas corrosion complexes (metal in combination with carbon, oxygen and hydrogen) may be more likely to dissolve in water and interact with chemicals in the soil.<sup>5</sup> <sup>6</sup> In addition, the chemical form of the metal has a significant effect on toxicity.7 Environmental impact is often discussed and investigated in terms of the overall metal concentration, as it can be assumed that once corroded and dissolved the metal is more likely to be in a form that is more toxic to environmental receptors - soil microorganisms, flora and fauna.

Lead antimony is a metal alloy commonly used in small arms ammunition (SAA).<sup>8</sup> Once transferred to the environment in a bioavailable form, the impact of the alloy can generally be considered in terms of the impacts of the individual metals: lead and antimony. This is also true of the source, for example, regardless of whether the metal is deposited from intentional

use, from abandoned munitions, the residue of burning, e.g. slag residue, or erroneously deposited by inappropriate detonation methods. Once transferred into the environment in a bioavailable form the potential impacts are the same. Generally, the severity of the impact of lead and antimony contamination will depend on how much contamination there is, how bioavailable the contamination is, and the duration of exposure of receptors to the lead or antimony.<sup>9</sup> Metals do not chemically or biologically degrade like organic energetic materials, and whilst such energetic materials can remain for long periods of time, metals will remain in the environment theoretically forever.

### THE ENVIRONMENTAL IMPACT OF LEAD IN THE TERRESTRIAL ENVIRONMENT

Lead contamination is common at shooting ranges and demolition sites, <sup>10</sup> <sup>11</sup> <sup>12</sup> <sup>13</sup> <sup>14</sup> partially due to the ubiquity of lead in munitions, including in bullets in the form of a metal alloy. Lead is also found in primary explosives as an inorganic compound e.g. lead azide, although the volume used in primers is so small as to have a negligible impact on the environment in comparison with SAA.<sup>15</sup> <sup>16</sup> Lead is globally recognised as a chemical of major public health concern, according to the World Health Organization,<sup>17 18</sup> and is currently under scrutiny by the European Chemical Hazards Agency (ECHA) for inclusion on the Restriction Evaluation Assessment and Regulation of Chemical Hazards (REACH).<sup>19</sup> Lead chromates have already been added to the Authorisation List,<sup>20</sup> which means that the use of lead chromate within the European Union must be authorised by ECHA. In 2018, bulk metal lead was recommended for inclusion in the Authorisation List and may in time require authorisation for use. Currently, the use of lead for defence purposes is exempt from the REACH regulation in the EU, and therefore can continue to be used in explosive ordnance. Lead has also been recognised as a priority substance in the US where it is listed second on the Agency for Toxic Substances and Disease Registry substance priority list, due to its toxicity and frequent occurrence in the environment.<sup>21</sup>

Handling a bullet containing lead carries a low risk of toxic effects. This is because lead metal absorption through the skin is generally limited and it does not release fumes that can be inhaled. Conversely, soil containing corrosion complexes of lead may be ingested or inhaled relatively easily, and the form of the metal is much more accessible for the biological organs of flora and fauna, therefore causing much higher toxicity.<sup>22</sup> As lead is not an essential element for life, it is detrimental to the health of most living organisms, from soil bacteria to humans, however individual organism tolerance to lead varies greatly. In humans, the tolerable daily intake has been estimated at 3.5  $\mu$ g/kg of bodyweight, with a lead level of greater than 10  $\mu$ g/dl considered as the threshold for lead blood poisoning in children.<sup>23</sup> Lead is particularly toxic for children and may cause irreversible health effects, although even low levels of exposure may cause central nervous system effects such as irritability, poor attention and hallucinations with convulsions, or comas developing in cases of high exposure (> 100  $\mu$ l/ dl).<sup>24 25</sup> Soil contaminated with lead is thought to be the second most likely cause of exposure to lead in children, behind paints containing lead, with an estimate of up to 0.2 g of soil per day ingested by children on average.<sup>26</sup>

Other organisms are also affected by lead, which may reduce enzymatic activity in soil, subsequently reducing other essential processes such as degradation of waste.<sup>27</sup> It may also reduce the growth of plant species, ultimately reducing the biodiversity of plant and insect species with a subsequent effect on entire localised ecosystems.<sup>28</sup> For example, at a site in Verdun where 200,000 World War I artillery projectiles were disposed of by open burning in the 1920s, there is an area of approximately 70 m in diameter where vegetation and growth is limited, and with no vegetation growth at all in the central area where the concentration of lead in the soil averages 12,690 mg/kg (> 10% soil mass is lead) (Figure 1).<sup>29</sup> Disposal of the artillery projectiles was carried out directly on the soil, with ash and residue left in place. Lead contamination tends to be highly localised due to the limited mobility of lead in clay soil. It sorbs into organic content and is essentially immobilised in low acidity (> pH 5) soils with greater than 5% organic content.<sup>30 31</sup> In the case of the Verdun burning site, the correlation to soil acidity can clearly be seen with lead contamination transmitting through the acidic surface soils, but being immobilised at 1.8 m (36 mg/ kg) deep where the pH becomes neutral (pH 7.1).<sup>32</sup> As in this example, lead tends to accumulate in the top layers of soil where it can be taken up by plants and is unlikely to leach into groundwater unless there is a significant change to the soil pH.<sup>33 34 35 36 37</sup> However, areas where there is significant surface water are particularly sensitive to lead contamination, with use of lead shot banned in these areas in the UK since 1999.38



Figure 1: 'Place du Gaz' in Verdun, France, where World War I artillery projectiles were disposed of by open burning, remains unable to support growth of vegetation at the epicentre of the burn where there are high concentrations of lead. Even in areas of lower concentration, vegetation cover is limited to mosses that can withstand the increased metal concentrations.<sup>39</sup> Image © Eric Bonnaire

Pollution from lead does not only come from SAA. There have also been instances of lead contamination following open burning of artillery propellants. Lead and tin foil strips were used in smokeless gun propellants as a de-coppering agent but have since been phased out by a number of nations for reasons of lead toxicity. Open burning of propellants containing de-coppering agents and other additives will in all likelihood lead to direct heavy metal contamination of the soil. This has been recently observed in the field.



Figure 2: An open burn of old Soviet gun propellant in an arid environment, March 2016. Image© Swiss EOD Centre



Figures 3 and 4: Heavy metal de-coppering agents and other residues deposited on the soil surface following an open propellant burn, March 2016. Open burning of propellant on the soil surface can present a significant pollutant risk. Image© Swiss EOD Centre

#### THE ENVIRONMENTAL IMPACT OF ANTIMONY IN THE TERRESTRIAL ENVIRONMENT

Antimony is typically described as a metalloid which can exist in two forms: 1) a silvery metal form, and 2) a grey powder, and is increasingly used in alloys with lead as a hardener (~2%) in small arms ammunition rounds.<sup>40</sup> While antimony has been identified as a potential substance of concern, the only antimony compound currently on the REACH candidate list is antimony lead oxide (antimony lead yellow) used in coatings, inks and toners.<sup>41</sup> However, due to the toxicity of antimony the U.S. Environmental Protection Agency has advised an oral reference dose of 0.4  $\mu$ g/kg bodyweight per day.<sup>42</sup> and the World Health Organization (WHO) has estimated the tolerability in water for humans to be 6  $\mu$ g/kg bodyweight per day.<sup>43</sup>

The toxicity of antimony varies depending on the chemical form of the element that is produced during weathering and corrosion. For example, in well oxygenated environments (soil surfaces)  $Sb(OH_6)^-$  (V) is the most common form, whereas in low oxygen environments (underwater, in peat soils) the more toxic  $Sb(OH_3)$  (III) is more likely to be formed.<sup>44</sup> However, in the environment the less toxic  $Sb(OH_6)^-$  has been shown to be more mobile than other forms as it is less likely to be absorbed into the soil, whereas the more toxic forms are likely to remain immobilised near the soil surface, though both forms transmit more readily than lead.<sup>45</sup> <sup>46</sup> This means that while contamination of groundwater by antimony is possible, and has been observed,<sup>47</sup> there remains a significant exposure risk from inhalation or ingestion of contaminated soil particles.

Exposure to compounds containing antimony can cause irritation of the gastric system at lower concentrations, and continued exposure to antimony can lead to an accumulation in the organs resulting in cardiovascular, liver and respiratory diseases.<sup>48</sup> Inhalation of antimony causes skin rashes, as well as irritation to eyes and skin (> 9 mg/m<sup>3</sup> in air).<sup>49 50</sup> Flora, fauna and other microorganisms are also susceptible to antimony toxicity, though the toxic response is highly dependent on the chemical form of the antimony and the length of exposure.<sup>51 52</sup>

Concentrations of antimony at firing ranges are frequently reported in the range of 100s–1000s of mg/kg, which is much higher than the naturally expected concentration (measured in ng or  $\mu$ g/kg). For example, concentrations up to 517 mg/kg were reported at a Texas firing range<sup>53</sup> and a maximum of 17,500 mg/kg reported at stop-butts at the Swiss Quartino shooting range.<sup>54 55</sup> These concentrations significantly exceed recommended antimony levels in soil in Germany [3.5 mg/kg] and the Netherlands [5 mg/ kg].<sup>56</sup> In addition, due to the solubility of antimony, periods of intense rainfall can exacerbate surface run-off, or transmission of antimony through soil to groundwater resulting in a temporary peak in antimony concentration. In a study from Norway, antimony concentrations peaked at 9  $\mu$ g/L in a stream due to run-off from a firing berm during a storm, showing the potential to reach the recommended WHO drinking water limit (20  $\mu$ /L) and demonstrating that potentially harmful concentrations can be generated rapidly.<sup>57</sup>

It is worth noting that current examples of antimony contamination from explosive ordnance in soil and water tend to originate from shooting ranges, or areas where there has been intensive use of small arms ammunition containing lead antimony.<sup>58</sup> However, it can be expected that disposal by open burning of large quantities of small arms ammunition, or long-term erosion of small arms ammunition in soil, will also lead to increased concentrations of antimony in soil and water. While there are currently few legislative controls and recommendations for concentrations of antimony in soil, antimony is increasingly recognised as a contaminant of concern and therefore the introduction of additional controls is likely in the future.

#### THE ENVIRONMENTAL IMPACT OF LEAD AND ANTIMONY IN THE MARINE ENVIRONMENT

The main environmental concern for lead and antimony in the marine environment is the potential for bio-accumulation and subsequent contamination of the human food chain.<sup>59 60 61</sup> The potential for toxicity from fish and shellfish contaminated with heavy metals not originating from EO has been extensively studied in the case of mercury, where consumption of fish with high levels of mercury caused Minamata disease in Japan and is now thought to have effected over 20,000 people.<sup>62 63</sup> With levels of other heavy metal pollution also increasing in the oceans, there is now a concern that levels of lead in fish will affect human populations.<sup>64 65 66 67</sup> Antimony is not yet such a risk due to the lower global concentrations in seawater, and may not have the same potential for magnification through the food chain.<sup>68</sup>

While the impact of lead and antimony are of concern, it is challenging to determine the extent of impact from a particular source. For example, lead and antimony both occur naturally, though most studies conclude that elevated levels of lead and antimony in the environment derive from human sources. Underwater ordnance has repeatedly been shown to increase the concentration of lead in the local environment through corrosion of metal projectiles, with multiple munition dump sites (Labrador, Canada; the Baltic Sea; Kiel, Germany) exhibiting elevated levels of lead in sediment and water samples.<sup>69 70 71 72 73</sup> However, other sites such as a munitions dump site off the coast of Hawaii have not recorded significant impacts despite recording elevated concentrations of heavy metals, including lead.<sup>74</sup> However, the Hawaiian study is ongoing due to concerns about gaps in the data and may yet be shown to present a risk. Determining the risk of antimony and lead contamination from explosive ordnance underwater is particularly challenging, as it is difficult to predict the rate of corrosion of different types of ordnance; one study estimated that significant corrosion could take anywhere between 25 and 250 years.<sup>75</sup> To demonstrate, underwater mines in the Kiel Fjord (Germany) suspected to have been dumped at approximately the same time, have been found in various states of corrosion, with some in almost pristine condition (Figure 5).<sup>76</sup> Ultimately this means that the most significant environmental impacts will not be realised until many years after explosive ordnance is deposited in marine environments, by which time it may too dangerous to bring to the surface for disposal.<sup>77</sup>



Figure 5: (left) a significantly corroded naval mine found at the munitions dump site in Kolberger Heide, at the entrance to Kiel Fjord in Germany; (right) a mine with no evidence of corrosion found in the same location. This demonstrates how varied the condition of ordnance can be even in very limited geographical environments and highlights how difficult it can be to predict environmental impact. Image© Jana Ulrich, FTZ Uni Kiel

Due to safety concerns, underwater munitions are frequently detonated in situ, however a study of an underwater demolition at Pointe Amour, Canada, demonstrated that after detonation the concentration of lead and antimony in the local environment increased by a factor of ten.<sup>78</sup> Deposition of contamination and the effect of noise from detonations on aquatic species have recently been highlighted as issues of underwater demolition as a disposal method, particularly in ecologically sensitive areas.<sup>79 80 81</sup>

## SUMMARY AND FUTURE CONCERNS

Lead antimony is a common alloy used in small arms ammunition, however, once in the environment the lead and antimony will behave independently of one another. Both metals have been highlighted as contaminants of significant concern due to their toxicity towards flora, fauna and biota, and while lead is currently undergoing significant legislative and regulatory restriction, it is likely that the regulation of antimony will also increase in the future. The impact of lead and antimony is challenging to predict due to corrosion of the metals in different forms, which differ in their transport and behaviour in the environment. Figure 6 summarises the major pathways for lead and antimony in the environment; however, these pathways are highly dependent on the receiving environment and therefore an individual assessment should be made for each contaminated site.



Figure 6: Overview of how lead and antimony behave and move in the natural environment via natural processes such as erosion (physical wear), corrosion (chemical transformation) and transport (movement through soil and water). Metal exposure may also occur through inhalation of particles suspended in the air, but this will only be during disposal processes. Metals will rapidly deposit on soil and follow the pathways outlined in this figure.

- Hazrat Ali, Ezzat Khan & Ikram Ilahi, "Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation." *Journal of Chemistry*, Article 6730305 (2019), <u>doi.</u> org/10.1155/2019/6730305.
- 2 Idem.
- 3 Raymond A. Wuana & Felix E. Okieimen, "Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation." *International Scholarly Research Notices*, Article 402647 (2011), <u>doi.org/10.5402/2011/402647</u>.
- 4 Caleb D. Scheetz & J. Donald Rimstidt, "Dissolution, transport, and fate of lead on a shooting range in the Jefferson National Forest near Blacksburg, VA, USA." *Environ Geol* 58 (2009): 655–665, <u>doi.org/10.1007/</u> <u>s00254-008-1540-5</u>.
- <sup>5</sup> Espen Mariussen, Ida Vaa Johnsen & Arnljot Einride Strømseng, "Distribution and mobility of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) from ammunition residues on shooting ranges for small arms located on mires." *Environ Sci Pollut Res* 24 (2017): 10182–10196, <u>doi.org/10.1007/s11356-017-8647-8</u>.
- 6 Peter Sanderson et al., "Contamination, Fate and Management of Metals in Shooting Range Soils—a Review." Curr Pollution Rep 4, (2018): 175–187, doi.org/10.1007/s40726-018-0089-5.
- 7 Paul B. Tchounwou et al., "Heavy metal toxicity and the environment." in A. Luch (eds) *Molecular, Clinical and Environmental Toxicology*. Experientia Supplementum, vol 101 (2012): 133–164, <u>doi.org/10.1007/978-3-7643-8340-4\_6</u>.
- 8 Espen Mariussen, Ida Vaa Johnsen & Arnljot Einride Strømseng, "Distribution and mobility of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) from ammunition residues on shooting ranges for small arms located on mires." *Environ Sci Pollut Res* 24 (2017): 10182–10196, <u>doi.org/10.1007/s11356-017-8647-8</u>.
- 9 Raymond A. Wuana & Felix E. Okieimen, "Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation." *International Scholarly Research Notices*, Article 402647 (2011), doi.org/10.5402/2011/402647.
- 10 Caleb D. Scheetz & J. Donald Rimstidt, "Dissolution, transport, and fate of lead on a shooting range in the Jefferson National Forest near Blacksburg, VA, USA." *Environ Geol* 58 (2009): 655–665, <u>doi.org/10.1007/</u> <u>s00254-008-1540-5</u>.
- 11 Jay Clausen & Nic Korte, "The Distribution of Metals in Soils and Pore Water at Three U.S. Military Training Facilities." *Soil and Sediment Contamination: An International Journal* 18, Issue 5 (2009): 546–563, <u>doi.</u> org/10.1080/15320380903085683.
- S. Thiboutot et al., "Evaluation of Heavy Metals Contamination at CFAD Dundurn Resulting from Small-Arms Ammunition Incineration." Defence Research and Development Canada – Valcartier, Technical Report, 2001.
- <sup>13</sup> Donald W. Hardison et al., "Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering." *Science of the Total Environment* 328, Issues 1–3 (2004): 175–183, <u>doi.org/10.1016/j.</u> <u>scitotenv.2003.12.013</u>.
- 14 Mathieu Laporte-Saumure, Richard Martel & Guy Mercier, "Characterization and metal availability of copper, lead, antimony and zinc contamination at four Canadian small arms firing ranges." *Environmental Technology* 32, Issue 7 (2011): 767–781, doi.org/10.1080/09593330.2010.512298.
- 15 Espen Mariussen, Ida Vaa Johnsen & Arnljot Einride Strømseng, "Distribution and mobility of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) from annunition residues on shooting ranges for small arms located on mires." *Environ Sci Pollut Res* 24 (2017): 10182–10196, doi.org/10.1007/s11356-017-8647-8.
- 16 Jacqueline Akhavan, The Chemistry of Explosives, 3rd edn. (Cambridge: The Royal Society of Chemistry, 2011).
- 17 World Health Organization. "Exposure to Lead: A major public health concern," Preventing Disease Through Healthy Environments, (Geneva, 2019).
- <sup>18</sup> Zeeshanur Rahman & Ved Pal Singh, "The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview." *Environ Monit Assess* 191, Article 419 (2019): 1–21, <u>doi.org/10.1007/s10661-019-7528-7</u>.
- <sup>19</sup> European Chemicals Agency (ECHA). "Inclusion of substances of very high concern in the Candidate List for eventual inclusion in Annex XIV" (Decision of the European Chemicals Agency). Helsinki, 2018.
- 20 ECHA Authorisation List List of substances included in Annex XIV of REACH ("Authorisation List"), accessed 11 April 2021, <u>https://echa.europa.eu/authorisation-list</u>.

- 21 ATSDR (Agency for Toxic Substances and Disease Registry) Substance Priority List 2019. Accessed 11 April 2021, <u>https://www.atsdr.cdc.gov/spl/index.html</u>.
- 22 Hilary Arnold Godwin, "The biological chemistry of lead." Current Opinion in Chemical Biology 5, Issue 2 (2001): 223–227, doi.org/10.1016/S1367-5931(00)00194-0.
- 23 Idem.
- 24 Swaran J. S. Flora, Govinder Flora & Geetu Saxena, "Environmental occurrence, health effects and management of lead poisoning," in *Chemistry, Analytical Aspects, Environmental Impact and Health Effects*, José S. Casas and José Sordo, eds. (Elsevier, 2006): 158–228, <u>doi.org/10.1016/B978-044452945-9/50004-X</u>.
- <sup>25</sup> Gagan Flora, Deepesh Gupta & Archana Tiwari, "Toxicity of lead: A review with recent updates." Interdisciplinary Toxicology 5, Issue 2 (2012): 47–58, doi.org/10.2478/v10102-012-0009-2.
- <sup>26</sup> European Commission Directorate-General Health and Consumer Protection. Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE), "Opinion on Lead – Danish Notification 98/595/DK," Brussels, 2000.
- 27 Brett H. Robinson et al., "Plant uptake of trace elements on a Swiss military shooting range: Uptake pathways and land management implications." *Environmental Pollution* 153, Issue 3 (2008): 668–676, <u>doi.org/10.1016/j.</u> envpol.2007.08.034.
- 28 Michael J. Lawrence et al., "The effects of modern war and military activities on biodiversity and the environment." *Environmental Reviews* 23, Issue 4 (2015): 443–460, doi.org/10.1139/er-2015-0039.
- <sup>29</sup> Tobias Bausinger, Eric Bonnaire & Johannes Preuß, "Exposure assessment of a burning ground for chemical ammunition on the Great War battlefields of Verdun," *Science of the Total Environment* 382, Issues 2–3 (2007): 259–271, doi.org/10.1016/j.scitotenv.2007.04.029.
- <sup>30</sup> European Commission Directorate-General Health and Consumer Protection. Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE), "Opinion on Lead – Danish Notification 98/595/DK," Brussels, 2000.
- 31 Caleb D. Scheetz & J. Donald Rimstidt, "Dissolution, transport, and fate of lead on a shooting range in the Jefferson National Forest near Blacksburg, VA, USA." *Environ Geol* 58 (2009): 655–665, <u>doi.org/10.1007/</u> s00254-008-1540-5.
- <sup>32</sup> Tobias Bausinger, Eric Bonnaire & Johannes Preuß, "Exposure assessment of a burning ground for chemical ammunition on the Great War battlefields of Verdun," *Science of the Total Environment* 382, Issues 2–3 (2007): 259–271, <u>doi.org/10.1016/j.scitotenv.2007.04.029</u>.
- 33 Peter Sanderson et al., "Contamination, Fate and Management of Metals in Shooting Range Soils—a Review." Curr Pollution Rep 4, (2018): 175–187, doi.org/10.1007/s40726-018-0089-5.
- 34 Jay Clausen et al., "A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA." Environmental Pollution 129, Issue 1 (2004): 13–21, doi.org/10.1016/j.envpol.2003.10.002.
- <sup>35</sup> Jay Clausen & Nic Korte, "The Distribution of Metals in Soils and Pore Water at Three U.S. Military Training Facilities." Soil and Sediment Contamination: An International Journal 18, Issue 5 (2009): 546–563, <u>doi.</u> org/10.1080/15320380903085683.
- 36 Amy Dale, "Climate model uncertainty in impact assessments for agriculture: A multi-ensemble case study on maize in sub-Saharan Africa." *Earth's Future* 5, Issue 3 (2017): 337–353, doi.org/10.1002/2017EF000539.
- 37 Philip de Lasson, "Metal and energetics survey of the Borris shooting range, Denmark," in *Global Approaches to Environmental Management on Military Training Ranges* (IOP Publishing Ltd, 2019): 1–30, doi. org/10.1088/978-0-7503-1605-7ch10.
- <sup>38</sup> UK Government, "The Environmental Protection (Restriction on Use of Lead Shot) (England) Regulations 1999," <u>https://www.legislation.gov.uk/uksi/1999/2170/contents/made</u>.
- <sup>39</sup> Tobias Bausinger, Eric Bonnaire & Johannes Preuß, "Exposure assessment of a burning ground for chemical ammunition on the Great War battlefields of Verdun," *Science of the Total Environment* 382, Issues 2–3 (2007): 259–271, <u>doi.org/10.1016/j.scitotenv.2007.04.029</u>.
- 40 Peter Sanderson et al., "Distribution and availability of metal contaminants in shooting range soils around Australia," in 19th World Congress of Soil Science, Brisbane, August 2010.
- 41 European Chemicals Agency (ECHA), "Pyrochlore, antimony lead yellow" Brief Profile, accessed 11 April 2021, <u>https://echa.europa.eu/brief-profile/-/briefprofile/100.029.436</u>.

- 42 United States Environmental Protection Agency (EPA), "Antimony (CASRN 7440-36-0)." Integrated Risk Information System, 1987.
- 43 Fengchang Wu et al., "Health risk associated with dietary co-exposure to high levels of antimony and arsenic in the world's largest antimony mine area." *Science of the Total Environment* 409, Issue 18 (2011): 3344–3351, doi.org/10.1016/j.scitotenv.2011.05.033.
- 44 Mengchang He et al., "Antimony speciation in the environment: Recent advances in understanding the biogeochemical processes and ecological effects." *Journal of Environmental Sciences* 75 (2019): 14–39, <u>doi.</u> org/10.1016/j.jes.2018.05.023.
- <sup>45</sup> Jeffrey Lewis et al., "Distribution, Chemical Speciation, and Mobility of Lead and Antimony Originating from Small Arms Ammunition in a Coarse-Grained Unsaturated Surface Sand." *Journal of Environmental Quality* 39, Issue 3 (2010): 863–870, <u>doi.org/10.2134/jeq2009.0211</u>.
- 46 Thomas Trainor, "Lead and Antimony Speciation in Shooting Range Soils: Molecular Scale Analysis, Temporal Trends and Mobility." Final Report (SERDP Project ER-1770), 2017.
- 47 W. Andy Martin, Linda S. Lee & Paul Schwab, "Antimony migration trends from a small arms firing range compared to lead, copper, and zinc." *Science of the Total Environment* 463–464 (2013): 222–228, <u>doi.org/10.1016/j.</u> <u>scitotenv.2013.05.086</u>.
- 48 Indika Herath, Meththika Vithanage & Jochen Bundschuh, "Antimony as a global dilemma: Geochemistry, mobility, fate and transport." *Environmental Pollution* 223 (2017): 545–559, <u>doi.org/10.1016/j.envpol.2017.01.057</u>.
- 49 Idem.
- 50 Ross G. Cooper & Adrian P. Harrison, "The exposure to and health effects of antimony." Indian Journal of Occupational and Environmental Medicine 13, Issue 1 (2009): 3–10, doi.org/10.4103/0019-5278.50716.
- <sup>51</sup> Fengchang Wu et al., "Health risk associated with dietary co-exposure to high levels of antimony and arsenic in the world's largest antimony mine area." *Science of the Total Environment* 409, Issue 18 (2011): 3344–3351, <u>doi.org/10.1016/j.scitotenv.2011.05.033</u>.
- 52 Irina Shtangeeva, Roza Bali & Andrew Harris, "Bioavailability and toxicity of antimony." Journal of Geochemical Exploration 10, Issue 1 (2011): 40–45, doi.org/10.1016/j.gexplo.2010.07.003.
- 53 Shamsuzzoha Basunia & Sheldon Landsberger, "Contents and leachability of heavy metals (Pb, Cu, Sb, Zn, As) in soil at the pantex firing range, Amarillo, Texas." *Journal of the Air and Waste Management Association* 51, Issue 10 (2001): 1428–1435, doi.org/10.1080/10473289.2001.10464374.
- 54 Andreas C. Scheinost et al., "Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy." Geochimica et Cosmochimica Acta 70, Issue 13 (2006): 3299–3312, doi.org/10.1016/j.gca.2006.03.020.
- 55 Stéphanie Lafond et al., "Chemical leaching of antimony and other metals from small arms shooting range soil." Water, Air, and Soil Pollution 224, Article no. 1371 (2013): 1–15, <u>doi.org/10.1007/s11270-012-1371-6</u>.
- Jiayu Li et al., "Antimony contamination, consequences and removal techniques: A review." Ecotoxicology and Environmental Safety 156 (2018): 125–134, doi.org/10.1016/j.ecoenv.2018.03.024.
- 57 Arnljot Einride Strømseng et al., "Episodic discharge of lead, copper and antimony from a Norwegian small arm shooting range." J. Environ. Monit. 11, Issue 6 (2009): 1259–1267, doi.org/10.1039/b823194j.
- <sup>58</sup> W. Andy Martin, Linda S. Lee & Paul Schwab, "Antimony migration trends from a small arms firing range compared to lead, copper, and zinc." *Science of the Total Environment* 463–464 (2013): 222–228, <u>doi.org/10.1016/j.</u> <u>scitotenv.2013.05.086</u>.
- 59 Derya Çamur et al., "Heavy Metals and Trace Elements in Whole-Blood Samples of the Fishermen in Turkey: The Fish/Ermen Heavy Metal Study (FHMS)." *Environmental Management* 67, Issue 3 (2021): 553–562, <u>doi.</u> org/10.1007/s00267-020-01398-y.
- 60 Jae-Wook Lee et al., "Equilibria and dynamics of liquid-phase trinitrotoluene adsorption on granular activated carbon: Effect of temperature and pH." *Journal of Hazardous Materials* 14, Issue 1 (2007): 185–192, <u>doi.</u> org/10.1016/J.JHAZMAT.2006.06.110.
- 61 P. V. Krishna, Madhusudhana Rao Kotte & V. Jyothirmayi, "Human health risk assessment of heavy metal accumulation through fish consumption, from Machilipatnam Coast, Andra Pradesh, India." *International Research Journal of Public and Environmental Health* 1, Issue 5 (2014): 121–125, <u>https://www.researchgate.net/</u> publication/276290217. Human health risk assessment of heavy metal accumulation through fish consumption from Machilipatnam Coast Andhra Pradesh India.

- Fion C. W. Davies, "Minamata disease: A 1989 update on the mercury poisoning epidemic in Japan." *Environ Geochem Health* 13, Issue 1 (1991): 35–38, doi.org/10.1007/BF01783494.
- <sup>63</sup> Kenji Yoshino et al., "Food sources are more important than biomagnification on mercury bioaccumulation in marine fishes." *Environmental Pollution* 262 (2020): 113982, <u>doi.org/10.1016/j.envpol.2020.113982</u>.
- 64 Zhe Hao et al., "Heavy metal distribution and bioaccumulation ability in marine organisms from coastal regions of Hainan and Zhoushan, China." *Chemosphere* 226 (2019): 340–350, doi.org/10.1016/j.chemosphere.2019.03.
- <sup>65</sup> Oana Jitar et al., "Bioaccumulation of heavy metals in marine organisms from the Romanian sector of the Black Sea." *New Biotechnology* 32, Issue 3 (2015): 369–378, <u>doi.org/10.1016/j.nbt.2014.11.004</u>.
- 66 Levent Bat & Elif Arici, "Heavy Metal Levels in Fish, Molluscs, and Crustacea From Turkish Seas and Potential Risk of Human Health," in *Food Quality: Balancing Health and Disease*, Chapter 5 (Elsevier Inc., 2018): 159–196, <u>doi.org/10.1016/B978-0-12-811442-1.00005-5</u>.
- 67 Isidro José Tamele & Patricia Vázquez Loureiro, "Lead, Mercury and Cadmium in Fish and Shellfish from the Indian Ocean and Red Sea (African Countries): Public Health Challenges." J. Mar. Sci. Eng. 8, Issue 5 (2020): 344, doi.org/10.3390/jmse8050344.
- 68 Maximilian Obinna Obiakor et al., "Bioaccumulation, trophodynamics and ecotoxicity of antimony in environmental freshwater food webs." *Critical Reviews in Environmental Science and Technology*, 47, Issue 22 (2017): 2208–2258, <u>doi.org/10.1080/10643389.2017.1419790</u>.
- 69 G. Ampleman et al., "Evaluation of underwater contamination by explosives and metals at Point Amour Labrador and in the Halifax Harbour area." Defence Research and Development Canada – Valcartier, Technical Report, 2004.
- 70 Jacek Bełdowski et al., "Chemical Munitions Search & Assessment An evaluation of the dumped munitions problem in the Baltic Sea." Deep-Sea Research Part II: Topical Studies in Oceanography 128 (2016): 85–95, doi. org/10.1016/j.dsr2.2015.01.017.
- 71 Rafał Mitkiewicz, "Dumped conventional warfare (munition) catalog of the Baltic Sea." Marine Environmental Research 161 (2020): 105057, doi.org/10.1016/j.marenvres.2020.105057.
- 72 Jacek Bełdowski , Matthias Brenner & Kari Lehtonen, "Contaminated by war: A brief history of sea-dumping of munitions." *Marine Environmental Research* 162 (2020): 105189, <u>doi.org/10.1016/j.marenvres.2020.105189</u>.
- <sup>73</sup> Alexander Callaway et al., "Trace metal contamination of Beaufort's Dyke, North Channel, Irish Sea: A legacy of ordnance disposal." *Marine Pollution Bulletin* 62, Issue 11 (2011): 2345–2355, <u>doi.org/10.1016/j.marpolbul.2011.08.038</u>.
- 74 Sonia Shjegstad Garcia et al., "Discarded military munitions case study: Ordnance Reef (HI-06), Hawaii." Marine Technology Society Journal 43, Issue 4 (2009): 85–99, doi.org/10.4031/MTSJ.43.4.13.
- 75 Hans Sanderson et al., "Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea." Journal of Hazardous Materials 154, Issues 1–3 (2008): 846–857, <u>doi.org/10.1016/j.jhaz-</u> mat.2007.10.117.
- 76 Jennifer S. Strehse & Edmund Maser, "Marine bivalves as bioindicators for environmental pollutants with focus on dumped munitions in the sea: A review." *Marine Environmental Research* 158 (2020): 105006, <u>doi.</u> org/10.1016/j.marenvres.2020.105006.
- 77 G. Ampleman et al., "Evaluation of underwater contamination by explosives and metals at Point Amour Labrador and in the Halifax Harbour area." Defence Research and Development Canada – Valcartier, Technical Report, 2004.
- <sup>78</sup> Gary Fisher, "Metal Content of Ocean Sediment in Support of UXO Clearance HMS Raleigh." Defence R&D Canada, Technical Memorandum, December 2003.
- <sup>79</sup> Edmund Maser & Jennifer S. Strehse, "Don't Blast": blast-in-place (BiP) operations of dumped World War munitions in the oceans significantly increase hazards to the environment and the human seafood consumer." *Archives of Toxicology* 96, Issue 6 (2020): 1941–1953, <u>doi.org/10.1007/s00204-020-02743-0</u>.
- 80 Sven Koschinski, "Underwater noise pollution from munitions clearance and disposal, possible effects on marine vertebrates, and its mitigation." *Marine Technology Society Journal* 45, Issue 6 (2011): 80–88, <u>doi.org/10.4031/MTSJ.45.6.2</u>.
- 81 Janne K. Sundermeyer et al., "Effects of underwater explosions on presence and habitat use of harbor porpoises in the German Baltic Sea," in *The Effects of Noise on Aquatic Life*. Advances in Experimental Medicine and Biology series, vol 730 (2012): 289–291, <u>doi.org/10.1007/978-1-4419-7311-5\_64</u>.

## CHAPTER 4 CONTAMINATION FROM HEAVY METAL TUNGSTEN ALLOY AND DEPLETED URANIUM

#### **INTRODUCTION**

Heavy Metal Tungsten Alloy (HMTA) has been introduced as a replacement for Depleted Uranium (DU) armour piercing rounds used in multiple conflicts since 1991.<sup>1</sup> <sup>2</sup> DU is a heavy metal by-product of the Uranium 235 (<sup>235</sup>U) enrichment process used to produce fuel for nuclear reactors. DU consists primarily of the Uranium 238 (<sup>238</sup>U) isotope (99.977%), which differs from the 235 isotope by having three additional neutrons in the atomic nucleus. Generally, chemical isotopes have very similar properties. In the case of Uranium, <sup>235</sup>U is much more readily split to generate energy than the <sup>238</sup>U isotope and therefore nuclear reactor fuels are enriched to 3–5% <sup>235</sup>U. This enrichment produces <sup>238</sup>U as a by-product with high density and an ability to ablate as it passes through armour, ensuring a continually sharp nose and highly effective penetration.<sup>3</sup> However, concerns around the radioactivity and long-term impacts of <sup>238</sup>U led to the development of weapons containing HTMA.<sup>4</sup>

HMTA is a heavy metal alloy usually consisting of 80–98% tungsten in combination with a mixture of Nickel, Iron, Copper and Cobalt. It is usually produced by sintering – forming a solid mass by compaction at high temperatures.<sup>5 6</sup> HMTA's are used as armour penetrating rounds due to their high density and strength, as well as their improved environmental profile. HMTAs do not ablate on impact, therefore have a lower risk of aerosolized pollutants, and tend to be more resistant to corrosion. The environmental impact of DU and Tungsten is characterised by their properties as heavy

metals, which is highly dependent on the receiving environment. Although the radioactivity of DU is an added complication, the decay by-products are produced in such low concentrations that they can be discounted, and the environmental impact focused primarily on the exposure to Uranium.<sup>7</sup>

# EFFECT OF DEPLETED URANIUM ON THE ENVIRONMENT

DU has been extensively studied due to its widespread use in conflicts from the 1990s through to the early 2000s and its link to increased risk of cancer and Gulf War Syndrome. However, DU is significantly less radioactive than natural Uranium, which is ingested daily through food (2 µg g<sup>-1</sup> per day) and water (1.5 µg L<sup>-1</sup>).<sup>8</sup> In areas where there is a high natural concentration of Uranium such as Norway, potable groundwater has been shown to contain up to 34 µg L-1 Uranium, which is above the U.S. Environmental Protection Agency (US EPA) drinking water limit of 30 µg L<sup>-1</sup> and yet no ill effects have been reported in the population.9 10 While this comparison is to natural Uranium, it is reasonable to compare exposure limits, as the only difference between natural Uranium and DU is the percentage of isotope content, reflected by the lower radioactivity of DU.<sup>11</sup> For example, the World Health Organization's (WHO) recommended drinking water limit for DU is 2 µg L-1 based on the limit for Uranium.12 This is lower than the US EPA limit, and may frequently be lower than natural background levels; the average concentration of uranium in the ocean is 3 µg L<sup>-1.13 14</sup>

The environmental impact of DU is highly dependent on the source of the DU, the form of the DU and the environmental conditions. In its metallic form, toxicity from DU is very unlikely as there is limited transmission of metal through the skin, and radiation in the form of alpha particles cannot penetrate the skin. There is a higher risk when DU particles enter through broken skin, or become embedded in flesh.<sup>15</sup> <sup>16</sup> The more likely form of exposure to DU is from inhalation or ingestion of particles produced either during use or long-term weathering.<sup>17</sup> When impacting a hard target (metal) or when involved in a fire, the outer surface of the DU projectile ignites producing very small (< 20  $\mu$ m) aerosolised UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> particles, which may form larger particles (200–500  $\mu$ m) with materials from the incident target e.g. iron.<sup>18</sup> These particles will settle on vehicles or the soil surface

where they may be washed away by rainfall into local surface water, or become immobilised in soil. Alternatively, upon impact with a soft target, i.e. soil, the projectile may be embedded up to 50 cm beneath the soil surface where weathering will erode and corrode the DU, mainly forming  $UO_3$  and complexes (> 500  $\mu$  m) with water and soil minerals.<sup>19 20 21</sup>

When considering the environmental impact of DU it is important to note that it has both chemical toxic properties and radiological properties. However, as discussed, DU is less radioactive compared to its natural isotopes, and while any exposure to radiation increases the risk of cancer, this must be offset against an individual's general risk of developing cancer, which averages 1 in 5.22 Several reports into the use of DU projectiles in Kosovo concluded that there is minimal radiological or toxicological risk from areas where DU projectiles were used, even in localised areas of high concentration.<sup>23 24 25</sup> A subsequent investigation of post-conflict sites in Bosnia and Herzegovina did identify low levels of DU in groundwater, and although contamination levels were lower than WHO recommended limits, it highlights the potential mobility of DU in soil.<sup>26</sup> The highest cancer risk to an individual from DU is likely to be from inhalation of high concentrations of insoluble forms of DU which can remain in the lungs for extended periods of time.<sup>27</sup> Exposure to high concentrations is possible, and is most likely from enclosed spaces such as vehicles or buildings damaged by DU projectiles, or from inhalation of DU loaded soils in very localised areas. Children are especially likely to be exposed through playing in areas with DU contaminated soil.<sup>28</sup> It is therefore recommended that these areas are decontaminated or made inaccessible to civilian populations.<sup>29</sup>

While radioactive, DU is a heavy metal and may pose more of a risk from its chemical toxicology than its radiological toxicology.<sup>30</sup> DU toxicity primarily affects the kidneys, and may cause renal failure in high-enough concentrations.<sup>31</sup> <sup>32</sup> Though there have not been enough human cases to definitely provide a fatal dose figure, it is thought that serious renal effects are observable within a few days of exposure to 50 µg g<sup>-1</sup> of kidney mass.<sup>33</sup> These levels could easily be exceeded in soil beneath DU projectiles, where levels of up to 45 g kg<sup>-1</sup> soil have been identified. Ingestion of only a few grammes could result in serious kidney damage.<sup>34</sup> <sup>35</sup> This poses more of a risk to children, who are more likely to handle soil, but highlights the need for good housekeeping when working in proximity to corroded DU

projectiles. Less serious effects are likely to be felt at lower exposures, and it has been shown that kidneys may recover from minor DU toxicity.<sup>36</sup>

While, in general, the radiological and toxicological risk of DU to the general population is low, there remains a risk of exposure from highly concentrated point sources such as corroding DU projectiles buried in soil, and vehicles or buildings involved in a DU projectile strike. In these cases, the most likely exposure pathway to humans and animals is by direct inhalation or ingestion of aerosolised particles or soil within the localised area. DU projectiles remaining in the environment will take hundreds of years to fully corrode, therefore providing a continued source of high DU concentration unless removed.<sup>37</sup> <sup>38</sup> While DU, like many metals, is not highly mobile in neutral pH soils, in the long-term DU will migrate to the wider environment and if not removed from soil may cause long-term health impacts.

#### EFFECT OF HEAVY METAL TUNGSTEN ALLOY ON THE ENVIRONMENT

HMTA's were introduced as a replacement to DU as they were thought to be less damaging toward the environment, and less toxic.<sup>39</sup> However, as their use has increased there has been growing concern around the potential environmental impacts which may be far more complex than for other heavy metals. For this reason, Tungsten has been identified as an emerging toxicant by the US EPA.<sup>40</sup> Although there are currently no regulatory European or US limitations on Tungsten concentration in the environment, Russia has enforced a 0.05 mg L<sup>-1</sup> limit in drinking water.<sup>41</sup> Preliminary work by the US has suggested an oral reference dose of 0.1 mg kg<sup>-1</sup>; this is the daily dose considered safe for lifetime exposure and is notably lower than for lead and antimony, as described in Chapter 3.42 The same report recommends risk-based concentrations for soil and water at 7821 mg kg<sup>-1</sup> and 3.65 mg L<sup>-1</sup> respectively. While these numbers are significantly higher in comparison to other heavy metals of concern, these are only preliminary findings and it is acknowledged that the environmental impacts and toxicity of Tungsten warrant further investigation.43

Due to the relatively recent interest in HMTA as an environmental contaminant, there are relatively few studies that quantitatively assess the

release of Tungsten metal from HMTA kinetic energy penetrators. However, in a military context, entry to the environment will be when the penetrator rods either strike a hard target and deposit fragments up to 2 mm in size, or are embedded in soil upon striking the ground.<sup>44</sup> Within the mine action context, it is conceivable that abandoned HMTA ordnance could be inadvertently added to a logistic demolition, or mistakenly destroyed in situ by high order. These scenarios could also entail entry into the environment of HMTA slivers.

One of the reasons HMTA was cited as being preferential to DU was due to its resistance to corrosion. However, research has shown that HMTA may be more soluble than other heavy metals, particularly under alkali conditions (pH > 7) resulting in the transfer of Tungsten to the environment.<sup>45 46</sup> In addition, it has since been suggested that corrosion resistance is highly dependent on the pH level, with corrosion more likely in acidic environments.<sup>47</sup> Similarly, solubility may be variable and has been found to increase when alloyed with iron, but decreased when alloyed with Cobalt.<sup>48</sup> This effect highlights the complexity of the environmental impact of HMTA, which tends to contain varying concentrations of Nickel, Iron or Cobalt, given that the properties of tungsten can be significantly altered by co-deposited materials.

The variability of the Tungsten's properties extends to the toxicity, which may have additive effects on other materials. For example, evidence suggests that the toxicity of Tungsten and Cobalt combined may be greater than either metal alone.<sup>49</sup> This is also true of the carcinogenic properties of Tungsten, which have been shown to exacerbate the carcinogenic properties of other metals e.g. Cobalt, and which may even preferentially increase cancer risk in those with a genetic predisposition.<sup>50 51 52</sup> HMTA was shown to have particularly concerning carcinogenic properties when aggressive tumours developed in rodents implanted with tungsten, mimicking subcutaneous shrapnel injuries.<sup>53</sup> While this may seem to be exclusive to conflict scenarios, the likelihood of exposure to fragments of tungsten via injuries during demolition activities cannot be ignored.<sup>54</sup>

Though environmental behaviour studies of Tungsten are limited, there are early indications that the non-lethal effects of Tungsten on soil organisms may be more significant than those from Lead. While the non-lethal impacts may not be as striking, the long-term impacts on soil health and the subsequent ability to use the land for pasture or agriculture may be affected.<sup>55</sup> Tungsten is taken up by vegetation through root systems, and may accumulate in roots and plants, for example, snails fed on lettuce leaves grown on contaminated soil were exposed to higher doses than if they were fed exclusively on the contaminated soil.<sup>56</sup> This suggests that transfer through the food chain is possible, and though significant consumption is required to have a toxic effect there may be milder effects from long-term exposure. In addition, tungsten loading of soil of over 1% (10 g kg<sup>-1</sup>) is likely to kill soil bio-organisms, resulting in degradation of soil health and potentially limiting the ability of soil to produce crops.<sup>57</sup> While this may seem like a high soil loading, it is reasonable to assume that where HMTA penetrators are left in the environment for long periods of time, this level of contamination may be realised.

#### SUMMARY AND FUTURE CONCERNS

While HMTA was heralded as the replacement for DU in kinetic energy penetrators, recent scrutiny into its environmental impact has demonstrated that it is not environmentally benign, as first thought. There is an initiative to remove Cobalt from HMTA alloys [40],<sup>58</sup> due to concerns that Tungsten exacerbates Cobalt toxicity and carcinogenic properties, but this alone will not necessarily eliminate the environmental impact of HMTA. The environmental impacts of both DU and HMTA present significant long-term concerns, and it is likely that similar to DU, the removal of bulk sources of HMTA from the environment will also be recommended. It is also crucial that during demolition operations, DU penetrators in particular are not included in open burning, as this is likely to distribute more environmentally mobile DU dust particles into the environment. Detonation should be used to dispose of HMTA ammunition. Finally, the environmental impact of Tungsten in isolation may be less severe than for other heavy metals associated with Mine Action activities, yet the presence of Tungsten in already contaminated soil may exacerbate existing issues. For example, Tungsten may increase the acidity of soil, which in turn may result in the release of previously immobilised heavy metals such as lead and antimony from the soil and enable their transport to groundwater.<sup>59</sup>

- Sidney A. Katz, "The Chemistry and Toxicology of Depleted Uranium." Toxics 2, Issue 1, (2014): 50–78, (Heavy Metals Toxicology Collection), <u>doi.org/10.3390/toxics2010050</u>.
- 2 Anish Upadhyaya, "Processing strategy for consolidating tungsten heavy alloys for ordnance applications." Materials Chemistry and Physics 67, Issues 1–3 (2001): 101–110, doi.org/10.1016/S0254-0584(00)00426-0.
- 3 Albert C. Marshall, "Gulf war depleted uranium risks." Journal of Exposure Science and Environmental Epidemiology 8, Issue 1 (2008): 95–108, doi.org/10.1038/si.jes.7500551.
- 4 Monique van Hulst, Jan P. Langenberg & Wim P. C. de Klerk, "Hazard assessment of exposure to ammunition-related constituents and combustion products," in *Global Approaches to Environmental Management on Military Training Ranges*, (IOP Publishing Ltd, 2019): 1–18, <u>doi.org/10.1088/978-0-7503-1605-7ch6</u>.
- 5 Anish Upadhyaya, "Processing strategy for consolidating tungsten heavy alloys for ordnance applications." Materials Chemistry and Physics 67, Issues 1–3 (2001): 101–110, doi.org/10.1016/S0254-0584(00)00426-0.
- 6 N. Senthilnathan, A. Raja Annamalai & G. Venkatachalam, "Sintering of Tungsten and Tungsten Heavy Alloys of W–Ni–Fe and W–Ni–Cu: A Review." *Transactions of the Indian Institute of Metals* 70 (2017): 1161–1176, doi.org/10.1007/s12666-016-0936-2.
- 7 Sidney A. Katz, "The Chemistry and Toxicology of Depleted Uranium." *Toxics* 2, Issue 1, (2014): 50–78, (Heavy Metals Toxicology Collection), <u>doi.org/10.3390/toxics2010050</u>.
- 8 A. Bleise, P. R. Danesi & W. Burkart, "Properties, use and health effects of depleted uranium (DU): a general overview." *Journal of Environmental Radioactivity* 64, Issues 2–3 (2003): 93-112, <u>doi.org/10.1016/S0265-931X(02)00041-3</u>.
- 9 Idem.
- Bjørn Frengstad et al., "The chemistry of Norwegian groundwaters: III. The distribution of trace elements in 476 crystalline bedrock groundwaters, as analysed by ICP-MS techniques." *Science of the Total Environment* 246, Issue 1 (2000): 21–40, <u>doi.org/10.1016/S0048-9697(99)00413-1</u>.
- 11 A. Bleise, P. R. Danesi & W. Burkart, "Properties, use and health effects of depleted uranium (DU): a general overview." *Journal of Environmental Radioactivity* 64, Issues 2–3 (2003): 93-112, <u>doi.org/10.1016/S0265-931X(02)00041-3</u>.
- Barry Smith, "Depleted Uranium. Sources, Exposure and Health Effects." World Health Organization, Geneva (2001), http://apps.who.int/iris/bitstream/handle/10665/66930/WHO\_SDE\_PHE\_01.1.pdf;jsessionid=E2B432AE38E0F2FD0A66B98AECDB1864?sequence=1.
- <sup>13</sup> Teh-Lung Ku, Keven G. Knauss & Guy G. Mathieu, "Uranium in open ocean: concentration and isotopic composition." *Deep Sea Research* 24, Issue 11 (1977): 1005–1017, <u>doi.org/10.1016/0146-6291(77)90571-9</u>.
- 14 M. Konstantinou & I. Pashalidis, "Speciation and spectrophotometric determination of uranium in seawater." Mediterranean Marine Science 5, Issue 1 (2004): 55–60: doi.org/10.12681/mms.210.
- <sup>15</sup> Yong-Chao Yue et al., "The toxicological mechanisms and detoxification of depleted uranium exposure." Environ Health Prev Med 23, Article 18 (2018), doi.org/10.1186/s12199-018-0706-3.
- S. Keith et al., "Potential for Human Exposure," in *Taxicological Profile for Uranium*. Agency for Toxic Substances and Disease Registry (US), 2013, <u>https://www.ncbi.nlm.nih.gov/books/NBK158799/</u>.
- 17 Yong-Chao Yue et al., "The toxicological mechanisms and detoxification of depleted uranium exposure." Environ Health Prev Med 23, Article 18 (2018), doi.org/10.1186/s12199-018-0706-3.
- <sup>18</sup> Mustafa Sajih et al., "Physicochemical characterisation of depleted uranium (DU) particles at a UK firing test range." *Science of The Total Environment* 408, Issue 23 (2010): 5990–5996, <u>doi.org/10.1016/j.scitotenv.2010.07.075</u>.
- 19 Yuheng Wang et al., "Products of in Situ Corrosion of Depleted Uranium Ammunition in Bosnia and Herzegovina Soils." *Environ. Sci. Technol.* 50, Issue 22 (2016): 12266–12274, © 2016 American Chemical Society, doi.org/10.1021/acs.est.6b03732.
- 20 Stephanie Handley-Sidhu et al., "Corrosion and fate of depleted uranium penetrators under progressively anaerobic conditions in estuarine sediment." *Environ. Sci. Technol.* 43, Issue 2 (2009): 350–355, © American Chemical Society, <u>doi.org/10.1021/es8021842</u>.
- 21 Stephanie Handley-Sidhu et al., "Corrosion and transport of depleted uranium in sand-rich environments." Chemosphere 77, Issue 10 (2009): 1434–1439, doi.org/10.1016/j.chemosphere.2009.08.053.
- 22 The Royal Society, "The health hazards of depleted uranium munitions Part I," May 2001.

- 23 International Atomic Energy Agency (IAEA), "Depleted Uranium in Kosovo: Post conflict environmental assessment," 2000.
- 24 United Nations Environment Programme (UNEP), "Depleted Uranium in Serbia and Montenegro: Post-Conflict Environmental Assessment in the Federal Republic of Yugoslavia," 2002, <u>https://wedocs.unep.org/xmlui/ handle/20.500.11822/8251</u>.
- <sup>25</sup> Umberto Sansone et al., "Radioecological survey at selected sites hit by depleted uranium ammunitions during the 1999 Kosovo conflict." *Science of the Total Environment* 281, Issues 1–3 (2001): 23–35, <u>doi.</u> org/10.1016/S0048-9697(01)01034-8.
- 26 United Nations Environment Programme (UNEP), "Depleted Uranium in Bosnia and Herzegovina Post conflict Environmental Assessment, 2003.
- 27 Sidney A. Katz, "The Chemistry and Toxicology of Depleted Uranium." *Toxics* 2, Issue 1 (2014): 50–78, (Heavy Metals Toxicology Collection), <u>doi.org/10.3390/toxics2010050</u>.
- 28 S. Keith et al., "Potential for Human Exposure," in *Toxicological Profile for Uranium*. Agency for Toxic Substances and Disease Registry (US), 2013, <u>https://www.ncbi.nlm.nih.gov/books/NBK158799/</u>.
- 29 Steve Fetter & Frank von Hippel, "The hazard posed by depleted uranium munitions." Science & Global Security 8, Issue 2 (2000): 125–161, doi.org/10.1080/08929880008426473.
- <sup>30</sup> Fernando P. Carvalho & João M. Oliveira, "Uranium isotopes in the Balkan's environment and foods following the use of depleted uranium in the war." *Environment International* 36, Issue 4 (2010): 352–360, <u>doi.</u> org/10.1016/j.envint.2010.02.003.
- 31 Yong-Chao Yue et al., "The toxicological mechanisms and detoxification of depleted uranium exposure." Environ Health Prev Med 23, Article 18 (2018), doi.org/10.1186/s12199-018-0706-3.
- 32 Guoying Zhu et al., "Renal dysfunction induced by long-term exposure to depleted uranium in rats." Archives of Toxicology 83 (2009): 37–46, doi.org/10.1007/s00204-008-0326-6.
- <sup>33</sup> The Royal Society Working Group on the Health Hazards of Depleted Uranium Munitions, "The health effects of depleted uranium munitions: A summary." *J. Radiol. Prot.* 22, Issue 2 (2002): 131–139, doi/10.1088/0952-4746/22/2/301.
- <sup>34</sup> United Nations Environment Programme (UNEP), "Depleted Uranium in Serbia and Montenegro: Post-Conflict Environmental Assessment in the Federal Republic of Yugoslavia," 2002, <u>https://wedocs.unep.org/xmlui/ handle/20.500.11822/8251</u>.
- <sup>35</sup> United Nations Environment Programme (UNEP), "Depleted Uranium in Bosnia and Herzegovina Post conflict Environmental Assessment," 2003.
- <sup>36</sup> Sidney A. Katz, "The Chemistry and Toxicology of Depleted Uranium." *Toxics* 2, Issue 1, (2014): 50–78, (Heavy Metals Toxicology Collection), <u>doi.org/10.3390/toxics2010050</u>.
- 37 Stephanie Handley-Sidhu et al., "Corrosion and fate of depleted uranium penetrators under progressively anaerobic conditions in estuarine sediment." *Environ. Sci. Technol.* 43, Issue 2 (2009): 350–355, © American Chemical Society, <u>doi.org/10.1021/es8021842</u>.
- 38 Stephanie Handley-Sidhu et al., "Corrosion and transport of depleted uranium in sand-rich environments." Chemosphere 77, Issue 10 (2009): 1434–1439, doi.org/10.1016/j.chemosphere.2009.08.053.
- 39 A. Koutsospyros et al., "A review of tungsten: From environmental obscurity to scrutiny." Journal of Hazardous Materials 136, Issue 1 (2006): 1–19, doi.org/10.1016/j.jhazmat.2005.11.007.
- 40 Alicia M. Bolt & Koren K. Mann, "Tungsten: an Emerging Toxicant, Alone or in Combination." Curr Envir Health Rpt 3 (2016): 405–415, doi.org/10.1007/s40572-016-0106-z.
- 41 Nikolay Strigul et al., "Effects of tungsten on environmental systems." Chemosphere 61, Issue 2 (2005): 248–258, doi.org/10.1016/j.chemosphere.2005.01.083.
- 42 John D. Schell & Michael J. Pardus, "Preliminary risk-based concentrations for tungsten in soil and drinking water." *Land Contamination & Reclamation* 17, Issue 1 (2009), <u>https://www.itia.info/assets/files/ACGIH/28</u> <u>Schell Land Contam Reclam 2009 V17 P179.pdf</u>.
- 43 Alicia M. Bolt & Koren K. Mann, "Tungsten: an Emerging Toxicant, Alone or in Combination." Curr Envir Health Rpt 3 (2016): 405–415, doi.org/10.1007/s40572-016-0106-z.

- 44 B. Pedersen & S. Bless, "Behind-armor debris from the impact of hypervelocity tungsten penetrators." International Journal of Impact Engineering 33, Issues 1–12 (2006): 605–614, <u>doi.org/10.1016/j.jjim-peng.2006.09.007</u>.
- <sup>45</sup> Alicia M. Bolt & Koren K. Mann, "Tungsten: an Emerging Toxicant, Alone or in Combination." Curr Envir Health Rpt 3 (2016): 405–415, <u>doi.org/10.1007/s40572-016-0106-z</u>.
- 46 Nikolay Strigul et al., "Effects of tungsten on environmental systems." Chemosphere 61, Issue 2 (2005): 248–258, doi.org/10.1016/j.chemosphere.2005.01.083.
- 47 Li Lu, Liu Zhu & Liu Yuxiang, "Corrosion Performance of W-Ni-Cu and W-Ni-Fe Alloys." Rare Metal Materials and Engineering 47, Issue 6 (2018): 1708–1715, doi.org/10.1016/s1875-5372(18)30154-1.
- 48 Alicia M. Bolt & Koren K. Mann, "Tungsten: an Emerging Toxicant, Alone or in Combination." Curr Envir Health Rpt 3 (2016): 405–415, doi.org/10.1007/s40572-016-0106-z.
- 49 Idem.
- 50 Eric Q. Roedel et al., "Pulmonary toxicity after exposure to military-relevant heavy metal tungsten alloy particles." *Toxicology and Applied Pharmacology* 259, Issue 1 (2012): 74–86, <u>doi.org/10.1016/j.taap.2011.12.008</u>.
- 51 Alexandra C. Miller et al., "Neoplastic transformation of human osteoblast cells to the tumorigenic phenotype by heavy metal-tungsten alloy particles: Induction of genotoxic effects." *Carcinogenesis* 22, Issue 1 (2001): 115–125, <u>doi.org/10.1093/carcin/22.1.115</u>.
- 52 Alexandra C. Miller et al., "Effect of the military-relevant heavy metals, depleted uranium and heavy metal tungsten-alloy on gene expression in human liver carcinoma cells (HepG2)." *Mol Cell Biochem* 255 (2004): 247–256, doi:org/10.1023/8:MCBI.0000007280.72510.96.
- <sup>53</sup> John F. Kalinich et al., "Embedded weapons-grade tungsten alloy shrapnel rapidly induces metastatic highgrade rhabdomyosarcomas in F344 rats." *Environmental Health Perspectives* 113, Issue 6 (2005): 729–734, <u>doi.org/10.1289/ehp.7791</u>.
- 54 Roly Evans & Andy Duncan, "Disposal of Explosive Ordnance and Environmental Risk Mitigation." The Journal of Conventional Weapons 24, Issue 1 (2020), <u>https://commons.lib.imu.edu/cisr-journal/vol24/iss1/5</u>.
- <sup>55</sup> Amanda J. Barker et al., "Environmental impact of metals resulting from military training activities: A review." Chemosphere 265 (2021): 129110, doi.org/10.1016/j.chemosphere.2020.129110.
- James H. Lindsay et al., "Uptake Kinetics and Trophic Transfer of Tungsten from Cabbage to a Herbivorous Animal Model." *Environmental Science and Technology* 51, Issue 23 (2017): 13755–13762, <u>doi.org/10.1021/</u> acs.est.7b04376.
- 57 Nikolay Strigul et al., "Effects of tungsten on environmental systems." Chemosphere 61, Issue 2 (2005): 248–258, doi.org/10.1016/j.chemosphere.2005.01.083.
- <sup>58</sup> Rafael Cury et al., "Evolution of cobalt-free tungsten heavy alloys for kinetic energy penetrators." *Powder Metallurgy* 56, Issue 5 (2013): 347–350, doi.org/10.1179/0032589913Z.00000000137.
- <sup>59</sup> Gijsbert B. van der Voet et al., "Metals and Health: A Clinical Toxicological Perspective on Tungsten and Review of the Literature." *Military Medicine* 172, Issue 9 (2007): 1002–1005, <u>doi.org/10.7205/</u> <u>MILMED.172.9.1002</u>.

## CHAPTER 5 MITIGATING CONTAMINATION FROM EXPLOSIVES AND METALS FOUND IN EXPLOSIVE ORDNANCE

#### **INTRODUCTION**

In 1978, the Council on Environmental Quality in the United States produced regulations to complement the National Environmental Policy Act (1969). These regulations define what, for the purposes of that Act, is meant by mitigation and it can be summarised as follows:

- Minimising impacts by limiting the magnitude of the action and its implementation;
- Rectifying the impact by repairing or remediating the affected area;
- **3.** Reducing or eliminating the impact over time by preservation and maintenance during the life of the activity;
- 4. Compensating for or offsetting the impact by replacing or providing substitute resources.<sup>1</sup>

Mitigating may therefore be defined as reducing, avoiding or offsetting any potential adverse environmental consequences of specific activities.<sup>2</sup>

# WHAT CAN MINE ACTION PRACTICALLY DO?

Mine action clearance operations damage the environment. Such damage is to a degree inherent to such operations. Clearance of mines and explosive remnants of war is typically an intrusive process that inevitably entails a degree of damage to the environment.<sup>3</sup> <sup>4</sup> Destruction of Explosive Ordnance (EO), including SAA, by either Open Burning, or Open Detonation entails a potential pollution risk in certain circumstances. This is especially true in areas such as Central Demolition Sites, where Open Burning Open Detonation (OBOD), often over decades, can increase the risk of residue loading.<sup>5</sup> What can mine action operators do that does not inhibit their operations to an impractical degree? What can mine action operators do that enables them to make all reasonable effort to reduce pollution to a level that is no more than absolutely necessary? There is no comprehensive answer to these questions as yet, and more research is required. However, there are some practical measures that operators can consider as outlined below:

# **SCENARIO 1:** MITIGATION FOR DISPOSAL OF EXPLOSIVE ORDNANCE BY DEMOLITION IN SITU.

MINE ACTION SCENARIO	POTENTIAL ENVIRONMENTAL CONSEQUENCES	MITIGATION
Disposal of Composition-B filled EO on a demolition range. Source: Residue loading of RDX, TNT on soil surface in a Central Demolitions Site over a prolonged period. Pathways: TNT: Air- Soil RDX: Air- Soil RDX: Air- Soil Metal: Air- Soil Receptor: RDX and TNT exposure to animals and humans from soil ingestion / inhalation.	Physical soil damage restricting land use for agriculture. Low quantities of metal and explosive particulate deposited on soil and surface water; some larger fragments may also be deposited. Long-term reduction in soil health. Long-term toxicity to receptors if exposed either through soil (or water), ingestion or inhalation. Secondary impacts on surface and groundwater from soil contamination.	Ascertain soil type and pH using a basic testing kit. Avoid locations with acidic soil if possible. If possible, avoid areas near water courses, and saturated land, or land prone to flooding. Avoid areas near known aquifers. Sandy sites prone to flooding or with a high-water table present a particular risk for TNT main fills. If possible, try to identify likely receptors including sensitive areas or species. <sup>6</sup> Consider long-term impacts from contamination for future land use e.g. development, such as farming or housing. <sup>7</sup> Select a detonation method that transforms energetics within EO to detonation products as effectively as practicable. <sup>8</sup> Consider use of extra donor charge, ensure demolition stacks maximise sympathetic detonation, try to use first order (fuze well) initiation where possible, only use low order techniques where necessary. Ensure pit inspections and daily post range clearance are stringent in order to minimise EO left on the ground. Consider regular BAC of demolitions range to reduce ongoing EO contamination. CFFE and remove scrap metal. After final remediation of site used for a prolonged period, such as a demolitions range, consider a professional assessment, including soil sampling, to determine whether levels of contamination pose an ongoing risk. <sup>10</sup> <sup>11</sup> <sup>12</sup>





# **SCENARIO 2:** MITIGATION FOR DISPOSAL OF EXPLOSIVE ORDNANCE BY OPEN BURNING.

<ul> <li>Deen-burning disposal of explosive natures, propellant, and SAA.</li> <li>Source: Propellant, explosive and metal particulates deposited from fire.</li> <li>Soli contamination by airborne particulates and fragments of explosive, propellant and metals deposited from fire.</li> <li>Soli contamination by explosives and metal particulates deposited from fire.</li> <li>Soli contamination by explosives and fragments of explosive, propellant and metals deposited from fire.</li> <li>Soli contamination by explosives and fragments of explosive, propellant and metals deposited from fire.</li> <li>Soli contamination by explosives and fragments of explosive, propellant and metals deposited from fire.</li> <li>Subsurface contamination by explosives and metals reducing soil health.</li> <li>Long-term traxify to receptors if expose either through soil (or water), ingestion or inhalation.</li> <li>Long-term traxify to receptors of explosive contamination to water source for through soil (or water), ingestion or and inhalation.</li> <li>Burning invariably creates visible pollution which may or may not be environmentally significant, but may surely lead to a negative perception of the population.</li> <li>Burning invariably creates the population.</li> </ul>	MINE ACTION SCENARIO	POTENTIAL ENVIRONMENTAL CONSEQUENCES	MITIGATION
	ordnance including high explosive natures, propellant, and SAA. Source: Propellant, explosive and metal particulates deposited from open burning, metal slag and explosive residue from open burning, projectiles expelled from fire. Pathway: Propellant: Air-Soil Explosive: Air- Soil (TNT)- Water (RDX) Metal: Air- Soil (immobilisation > pH4) Receptor: Exposure to animals, plants and humans from soil and/ or water	<ul> <li>preventing growth of flora and with exposure risk to humans and animals in the immediate vicinity.</li> <li>Fire damage from uncontrolled burning ignited by spark.</li> <li>Soil contamination by airborne particulates and fragments of explosive, propellant and metals deposited in the wider area.</li> <li>Subsurface contamination by explosives and metals reducing soil health.</li> <li>Long-term toxicity to receptors if exposed either through soil (or water), ingestion or inhalation.</li> <li>Long-term transport of explosive contamination to water, contaminating water table that may be used as a potable water source for humans and animals.</li> <li>Burning invariably creates visible pollution which may or may not be environmentally significant, but may surely lead to a negative perception of the</li> </ul>	<ul> <li>products e.g. use burn tables to raise pile, use ventilated incinerators for SAA, remove SAA from boxes.<sup>13 14 15</sup></li> <li>Use intercepting burn trays to capture residue and slag directly beneath burn pile and dispose of as hazardous waste, breaking source-pathway linkage.<sup>16</sup></li> <li>Use incinerators to dispose of SAA and dispose of slag residue as hazardous waste.<sup>17</sup> Remove slag residue for industrial processing.</li> <li>For open propellant burns consider burning on a thin unreinforced temporary concrete pad if burn tables unavailable or impractical.</li> <li>Visual check of surrounding area after each burn serial to collect any projected fragments (removing</li> </ul>



## **SCENARIO 3:** MITIGATION FOR DISPOSAL OF UNDERWATER EXPLOSIVE ORDNANCE.

MINE ACTION SCENARIO	POTENTIAL ENVIRONMENTAL CONSEQUENCES	MITIGATION
Underwater detonation of EO. <b>Source</b> : Corroding EO that is unsafe to remove. <b>Pathway:</b> Propellant: Dissolution and suspension, deposition in sediment. Explosive: Dissolution and suspension, deposition in sediment. Metal: Corrosion, suspended solids, deposition in sediment. <b>Receptors</b> : Exposure to animals and humans from sediment and or water ingestion.	Accumulation of toxic dissolved and eroded metals in sediment. Localised areas of deoxygenation forcing flora and fauna to other environments. Noise and peak pressure of underwater detonation damaging to mammals at long distances due to blast waves. Physical disturbance of marine ecosystems forcing migration of species.	Raise the previously dumped EO to the surface where safe to do so, although in many cases it may not be safe. Where safety is in question, advanced techniques could be used to render them safe such as freezing, using robotic equipment, disposal in static detonation chamber and chemical destruction by light. <sup>18</sup> Detonate underwater using deflagration methods to reduce the sound. <sup>19</sup> Use novel techniques such as the 'Bubble curtain ©' Hydrotechnik Lübeck; this creates a wall of bubbles from a bottom-resting nozzle pipe connected to a compressor which cushions the detonation by absorbing much of the energy of the blast and sound waves. <sup>20</sup> Test detonations can be used to ascertain potential levels of disturbance and contamination to help decide on most appropriate mitigation. Consider use of small precursor detonations (e.g. NONEL detonator) to chase away fish and water mammals with reduced impact.





### **APPROACHES TO MITIGATION**

The above scenarios describe three brief examples of activities that have the potential to cause environmental impacts. The examples include clear Source Pathway Receptor (SPR) pollutant linkages that may occur and suggestions for mitigation that can support environmental best practice. Figure 1 presents a useful hierarchy of how to consider mitigation when undertaking mine action activities and it is based on the United States National Environmental Policy Act<sup>21</sup> as mentioned in Section 5.1.



Figure 1: Hierarchy of mitigation to support mine action decision-making for environmental best practice, with avoidance or removal of the source as the preferential option and remediation of contamination as the least preferential.

The preferred option is removing the source, which is the main aim of mine action in any case, although the intrusive and physical nature of this removal process can itself affect the environment. During OBOD activities, the full force of detonating a munition in situ propels explosive residues, metal fragments, dust and so forth into the environment landing on soil surfaces and in water courses.<sup>22</sup> If repeated at the same location over a prolonged period, energetic materials and metal fragments may cumulatively build up in the environment and directly and indirectly effect environmental receptors, leading to contamination that may need remediation. This build-up over time is sometimes referred to as residue loading. Use of burning tanks for small arms ammunition is also an option, with the slag residue removed from the site afterwards. Burn tanks for fuzes have also been used although these can be ineffective in consuming energetic components enclosed within the fuze, for example on a rotor.



Figure 2: Burn tanks for Small Arms Ammunition (SAA) can be a useful way of minimising the environmental impact of SAA disposal. However, the issue of onward disposal of slag residue remains a challenge. Operators should commission specialist removal, ideally for processing and recycling.

The next preferred option is minimising the impact of the source. This is often a challenge for mine action. For activities like open burning, simple measures such as taking SAA out of storage boxes for burning, can increase the burn temperature and minimise incomplete combustion and deposition of energetic materials in by-products such as burnt ash and slag mixtures.<sup>23</sup> SAA should never be burnt within packaging and should certainly never be destroyed by bulk demolition, unless in exceptional circumstances where the proportion of SAA within a stack is minimal. Other items of high explosive ordnance included in bulk demolitions should also be removed from packaging as much as practicable prior to being included

in a stack. Burning regimes, including plastic wastes and other municipal materials, should also be planned so that the release of black smoke into the atmosphere is minimised.<sup>24</sup> Demolition techniques can also be used to maximise the efficient detonation of the explosive within an item of EO. For example, use of more donor charge, especially if part of a sensible priming plan, can assist in maximising the potential of breaching the case so that the explosive inside is also consumed. If possible, fuze wells should be primed in order to utilise the explosive train inherent within the munition design. This technique is sometimes referred to as a 'first order' or 'stores own' detonation. Use of low order techniques, such as a mechanical breakup, implicitly carries the risk of greater residue deposition on the ground. While low order techniques should remain as a key set of techniques for EOD operators, they should only be used if really necessary, since they arguably carry a greater pollution risk.



Figure 3: A bulk demolition primed by making maximum use of empty fuze wells. This enables more *First Order* detonations that have a higher probability of consuming the explosive fill compared to *Second Order* detonations. Liberal use of donor charge for *Second Order* detonations also reduces the risk of residue deposition and, over time, cumulative residue loading on locations such as Central Demolition Sites.

The third preference for mitigation is to use simple methods to break or reduce the link between the source and pathway for example, using impermeable surfaces when burning, such as metal burn trays in cages when disposing of EO by open burning, to avoid contamination leaching into the environment by pathways that can reach receptors.<sup>25</sup> The use of open pit burning will increase the risk of residue loading and should ideally be avoided. Open burning of propellant on the ground should also be avoided, if possible, especially if the propellant is old (incomplete combustion) and there is a risk of a de-coppering agent such as lead or tin foil being present. One practical possibility for mitigation is the creation of a temporary concrete pad on which a series of burns can be conducted. The thin concrete layer would form a barrier for contaminants such as lead and tin, and for explosive residues. After each burn the pad could be swept for metal and explosive residues, which could be removed from the site for specialist disposal. The technique could be particularly appropriate in very hot climates where metal burning tables can be difficult or hazardous to use, or areas where a burn table cannot be retrieved from the field and might be stolen. Once all burning serials are complete, the unreinforced temporary pad can be broken up and removed for disposal elsewhere (e.g. specialised landfill).



Figure 4: Open burning of propellant can present significant contamination risks. One idea to avoid this is to burn on a temporary concrete pad.

Mine action operators are also advised to avoid siting CDS in areas of sandy soil near water courses, or areas with high water tables, or sandy areas prone to flooding. 2,4,6-trinitrotoluene (TNT) will not be as rapidly degraded in areas of sandy soil where there is little organic material. This increases the risk of TNT travel to groundwater or run-off into surface water,<sup>26 27 28</sup> especially in circumstances where residue loading over time is a risk, such as with a demolition range.

Pollutant linkages that are created by EO underwater are also difficult to deal with, as removing them is often unsafe due to partial degradation and the effects of the water. Therefore, if the source of contamination has no way of reaching a receptor, it may be that a justifiable decision could be made that the risk involved in moving the source does not outweigh the risk of leaving it in place.<sup>29</sup> In addition to safety issues associated with EO underwater, removing EO by physical or chemical means may disturb the marine environment or sensitive habitats. There are several mitigation options available that will reduce sound and blast waves for detonating EO underwater. However, these methods are often dependant on the EO size rather than the charge size.<sup>30</sup> Many of these approaches are under review as they have not been widely tested on diverse explosive ordnance. In addition, these techniques are often expensive, complicated and produce additional environmental impacts.<sup>31 32 33</sup> Therefore, if no particular safety issue is evident, it may be preferable to leave underwater EO in situ.

The least preferable mitigation option is remediation. Basic CDS remediation, by means of BAC of the site should be routine for most mine action operators in any case. This will typically involve disposal on the range of items still containing energetics, and removal of scrap metal once it has been Certified Free From Explosives (CFFE). The actual removal of contaminated soil is expensive, time consuming and may cause a degree of further environmental harm. Therefore, the potential benefits of soil removal should be balanced with any potential harm such a process may cause. There are some natural processes that can be used to remediate areas such as phytoremediation, bioremediation and the use of chemical additives on soil.<sup>34</sup> <sup>35</sup> <sup>36</sup> <sup>37</sup> <sup>38</sup> These processes are naturally useful, although they are labour intensive as they require continuous aeration, and they are slow to revert back to their original state. How useful processes such as phytoremediation are for areas such as a heavily contaminated CDS is

unclear? For water remediation there are also options, such as absorptive methods, although they require high maintenance, involve continuous monitoring and replenishment of consumable materials, and are also expensive.<sup>39 40</sup>



Figure 5: Long-standing procedures such as doing basic Battle Area Clearance (BAC) after a demolition serial on a range, while by no means a comprehensive solution, can assist in reducing the risk of residue loading and metal contamination. Scrap metal found during BAC should be subject to rigorous Certification Free From Explosives procedures.

### CONCLUSIONS AND FUTURE CONSIDERATIONS

Environmental mitigation during actual mine action activities is challenging. Using the SPR pollutant linkage model as a way of identifying contamination and associated pathways can help identify options for breaking the pollutant linkages. The removal of the immediate blast and fragmentation hazard of EO will inevitably take priority over environmental considerations. The primary aim is to avoid loss of life amongst the local population and those charged with clearing EO. However, the lack of incorporating mitigation measures for chemical contamination may cause long-term environmental impacts for the affected areas in the immediate and long-term future. The key is to avoid pollution from mine action field operations where possible, mitigate where practicable, and to only accept it where no viable alternative exists.
- 1 United States Council on Environmental Quality: "Regulations for Implementing the Procedural Provisions of the National Environmental Policy Act," Reprint 40 CFr Parts 1500-1508 (2005) 28, <u>https://www.energy.gov/ sites/default/files/NEPA-40CFR1500\_1508.pdf</u>.
- 2 SOAS (University of London), "Introduction to Environmental Impact Assessment (EIA) Mitigation," <u>https://www.soas.ac.uk/cedep-demos/000\_P507\_EA\_K3736-Demo/unit1/page\_22.htm</u>. 1996.
- 3 Roly Evans & Andy Duncan, "Disposal of Explosive Ordnance and Environmental Risk Mitigation," The Journal of Conventional Weapons 24, Issue 1, Article 5 (2020).
- 4 GICHD, A Guide to Mine Action. Fifth Edition (Geneva: GICHD, March 2014).
- 5 Roly Evans & Andy Duncan, "Disposal of Explosive Ordnance and Environmental Risk Mitigation," The Journal of Conventional Weapons 24, Issue 1, Article 5 (2020).
- 6 I. Bortone et al., "Scientific principles of environmental management," in *Global Approaches to Environmental Management on Military Training Ranges*, Tracey J. Temple and Melissa K. Ladyman, eds. (IOP Publishing Ltd, 2019), <u>doi.org/10.1088/978-0-7503-1605-7ch1</u>.
- 7 Pytrik Reidsma et al., "Impacts of land-use change on biodiversity: An assessment of agricultural biodiversity in the European Union," *Agriculture, Ecosystems & Environment* 114, Issue 1 (2006): 86–102, <u>https://doi.org/10.1016/j.agee.2005.11.026</u>.
- 8 United States Environmental Protection Agency. National Environmental Policy Act. <u>https://www.soas.ac.uk/</u> cedep-demos/000 P507 EA K3736-Demo/unit1/page 22.htm. <u>https://www.energy.gov/sites/prod/files/</u> nepapub/nepa\_documents/RedDont/Req-NEPA.pdf.
- 9 Michael R. Walsh et al., "Physical Simulation of Live-Fire Detonations using Command-Detonation Fuzing," Propellants, Explosives, Pyrotechnics 43, Issue 6 (2018): 602–608, <u>doi.org/10.1002/prep.201700316</u>.
- <sup>10</sup> Thomas F. Jenkins et al., "Representative Sampling for Energetic Compounds at Military Training Ranges," *Environmental Forensics* 6, Issue 1 (2005): 45–55, accessed 10 August 2016, <u>doi.</u> org/10.1080/15275920590913912.
- 11 Jean Crépin & Richard L. Johnson, "Soil sampling for Environmental Assessment," in Soil Sampling and Methods of Analysis, Martin R. Carter (ed.) (Lewis Publishers, CRC Press LLC, 1993) 823, <u>https://</u> books.google.co.uk/books?hl=en&tr=Bid=E4IYLsV492IC&oi=fnd&pg=PA5&dq=soil+sampling+methods&ots=K3eF\_IM4yP&sig=P1xxM-VVIU1IM6FLF3MDkIj0RpM#v=onepage&gdf=false.
- 12 Tobias Bausinger, Eric Bonnaire & Johannes Preuß, "Exposure assessment of a burning ground for chemical ammunition on the Great War battlefields of Verdun," *Science of the Total Environment* 382, Issues 2–3 (2007): 259–271, doi.org/10.1016/j.scitotenv.2007.04.029.
- <sup>13</sup> Brian D. Woodall et al., "Emissions from Small-Scale Burns of Simulated Deployed U.S. Military Waste," *Environ. Sci. Technol.* 46, Issue 20 (2012): 10997–11003, © American Chemical Society, <u>doi.org/10.1021/</u> <u>es3021556</u>.
- 14 Nico van Ham & Henk Bartelds, "Environmentally acceptable disposal of munition and explosives," in 22nd International Annual Conference on ICT 1991, (Karlsruhe, Germany: Internationale Jahrestagung – Fraunhofer-Institut fuer Treib-und Explosivstoffe, 1991): 16.1–16.9.
- <sup>15</sup> Paul M. Lemieux, Christopher C. Lutes & Dawn A. Santoianni, "Emissions of organic air toxics from open burning: a comprehensive review," *Progress in Energy and Combustion Science* 30, Issue 1 (2004): 1–32, <u>http://www.sciencedirect.com/science/article/pii/S0360128503000613</u>.
- 16 Guy Ampleman et al., "New range design and mitigation methods for sustainable training," in *European Conference of Defence and the Environment 2013*, (Finland: Finnish Ministry of Defence, 2013), <u>https://www.defmin.fi/files/2608/Conference proceedings web 2013.pdf#page=91</u>.
- 17 James Stratta et al., "Alternatives to Open Burning/Open Detonation of Energetic Materials. A Summary of Current Technologies," 29, Figure 1. X-Y Table. USACERL Technical Report 98/104 (1998), <u>https://www.epa.gov/sites/production/files/2015-03/documents/9545928.pdf</u>.
- S. Koschinski & K-H. Kock, "Underwater Unexploded Ordnance Methods for a Cetacean-friendly Removal of Explosives as Alternatives to Blasting." Report of the International Whaling Commission (2009), SC/61/ E21: 1–13.
- 19 Stephen P. Robinson et al., "Underwater acoustic characterisation of unexploded ordnance disposal using deflagration," *Mar Pollut Bull* 160 (2020): 111646, <u>doi.org/10.1016/j.marpolbul.2020.111646</u>.

- 20 S. Koschinski & K-H. Kock, "Underwater Unexploded Ordnance Methods for a Cetacean-friendly Removal of Explosives as Alternatives to Blasting." Report of the International Whaling Commission (2009), SC/61/ E21: 1–13.
- 21 United States Environmental Protection Agency. National Environmental Policy Act. <u>https://www.soas.ac.uk/</u> cedep-demos/000\_P507\_EA\_K3736-Demo/unit1/page\_22.htm. <u>https://www.energy.gov/sites/prod/files/</u> nepapub/nepa\_documents/RedDont/Req-NEPA.pdf.
- I. Bortone et al., "Scientific principles of environmental management," in *Global Approaches to Environmental Management on Military Training Ranges*, Tracey J. Temple and Melissa K. Ladyman, eds. (IOP Publishing Ltd, 2019), <u>doi.org/10.1088/978-0-7503-1605-7ch1</u>.
- 23 Paul M. Lemieux, Christopher C. Lutes & Dawn A. Santoianni, "Emissions of organic air toxics from open burning: a comprehensive review," *Progress in Energy and Combustion Science* 30, Issue 1 (2004): 1–32, http://www.sciencedirect.com/science/article/bii/S0360128503000613.
- 24 James Stratta et al., "Alternatives to Open Burning/Open Detonation of Energetic Materials. A Summary of Current Technologies," 29, Figure 1. X-Y Table. USACERL Technical Report 98/104 (1998), <u>https://www.epa.gov/sites/production/files/2015-03/documents/9545928.pdf</u>.
- <sup>25</sup> Guy Ampleman et al., "New range design and mitigation methods for sustainable training," in *European Conference of Defence and the Environment 2013*, (Finland: Finnish Ministry of Defence, 2013), accessed 23 April 2021, https://www.defmin.fi/files/2608/Conference proceedings web 2013.pdf#page=91.
- <sup>26</sup> Ghasem Alavi et al., "The fate and transport of RDX, HMX, TNT and DNT in the volcanic soils of Hawaii: a laboratory and modeling study," *J Hazard Mater* 185, Issues 2–3 (2011): 1600–1604, <u>doi.org/10.1016/j.</u> jhazmat.2010.10.039.
- 27 A. Thenmozhi & M. Devasena, "Remediation of 2,4,6-trinitrotoluene Persistent in the Environment A review," Soil and Sediment Contamination: An International Journal 29, Issue 1 (2020), http://doi.org/10.1080/ 15320383.2019.1664394.
- 28 Elly P. H. Best et al., "Environmental behavior of explosives in groundwater from the Milan Army Ammunition Plant in aquatic and wetland plant treatments. Uptake and fate of TNT and RDX in plants," *Chemosphere* 39, Issue 12 (1999): 2057–2072, <u>doi.org/10.1016/S0045-6535(99)00117-4</u>.
- 29 Sven Koschinski, "Underwater noise pollution from munitions clearance and disposal, possible effects on marine vertebrates, and its mitigation," *Marine Technology Society Journal* 45, Issue 6 (2011): 80–88, <u>doi.org/10.4031/MTSJ.45.6.2</u>.
- 30 Stephen P. Robinson et al., "Underwater acoustic characterisation of unexploded ordnance disposal using deflagration," *Mar Pollut Bull* 160 (2020): 111646, <u>doi.org/10.1016/j.marpolbul.2020.111646</u>.
- 31 Aaron J. Beck et al., "Spread, Behavior, and Ecosystem Consequences of Conventional Munitions Compounds in Coastal Marine Waters", Front. Mar. Sci. (2018): 5, doi.org/10.3389/fmars.2018.00141.
- 32 Peter H. Dahl et al., "Physical effects of sound exposure from underwater explosions on Pacific sardines (Sardinops sagax)," The Journal of the Acoustical Society of America 147, Issue 4 (2020): 2383–2395, doi. org/10.1121/10.0001064.
- <sup>33</sup> Janne K. Sundermeyer et al., "Effects of underwater explosions on presence and habitat use of harbor porpoises in the German Baltic Sea," Adv Exp Med Biol 730 (2012): 289–291, <u>doi.org/10.1007/978-1-4419-7311-5 64</u>.
- 34 Harry D. Craig, "Review of remediation technologies for energetics contamination in the US," in *Global Approaches to Environmental Management on Military Training Ranges*, Tracey J. Temple and Melissa K. Ladyman, eds. (IOP Publishing Ltd, 2019), <u>https://iopscience.iop.org/book/978-0-7503-1605-7/chapter/bk978-0-7503-1605-7ch7</u>.
- <sup>35</sup> Elizabeth L. Rylott & Neil C. Bruce, "Right on target: using plants and microbes to remediate explosives," International Journal of Phytoremediation 21, Issue 11 (2019): 1051–1064, <u>doi.org/10.1080/15226514.2019.1</u> <u>606783</u>.
- <sup>36</sup> Panagiotis Misaelides, "Application of natural zeolites in environmental remediation: A short review," *Microporous and Mesoporous Materials* 144, Issues 1–3 (2011): 15–18, <u>https://doi.org/10.1016/j.micromeso.2011.03.024.</u>
- 37 Saumik Panja, Dibyendu Sarkar & Rupali Datta, "Vetiver grass (Chrysopogon zizanioides) is capable of removing insensitive high explosives from munition industry wastewater," *Chemosphere* 209 (2018): 920–927, doi.org/10.1016/J.CHEMOSPHERE.2018.06.155.

- <sup>38</sup> Jeffrey D. Kiiskila et al., "Phytoremediation of Explosive-Contaminated Soils," *Current Pollution Reports* 1 (2015): 23–25, <u>doi.org/10.1007/s40726-015-0003-3</u>.
- L. Le Campion, A. Vandais & J. Ouazzani, "Microbial remediation of NTO in aqueous industrial wastes," FEMS Microbiol Lett 176, Issue 1 (1999): 197–203, doi.org/10.1111/j.1574-6968.1999.tb13662.x.
- 40 Lynne Wallace et al., "Electrochemical Method Applicable to Treatment of Wastewater from Nitrotriazolone Production," *Environ. Sci. Technol.* 43, Issue 6 (2009): 1993–1998, © American Chemical Society, <u>doi.</u> org/10.1021/es8028878.

# CHAPTER 6 A CASE STUDY: MITIGATION OF PROPELLANT CONTAMINATION FROM OPEN BURNING

### **INTRODUCTION**

The purpose of this chapter is to describe an example of successful environmental mitigation of open burning of propellant in Petawawa, Canada. Although this example is not specific to mine action, the disposal methods used can also be employed by mine action organisations. The case study describes how the disposal activity causes contamination, including the potential source-pathway-receptor linkages and describes the mitigation that was implemented.

# CONTEXT

Canadian Forces Base (CFB) / Area Support Unit (ASU) Petawawa in Canada is used for live-fire military training and regularly requires disposal of unused propellant by open burning.<sup>1</sup> Soil sampling at the site identified residues of 2,4-dinitrotoluene (13.5  $\mu$ g kg<sup>-1</sup>), a common component of propellant, which exceeded regulatory limits and therefore required remediation and the introduction of mitigation to prevent further accumulation.<sup>2</sup> The training range is predominantly sandy, and the eastern limit is defined by Chalk Bay and the Ottawa River. Although no in-depth hydrogeological studies had been conducted at the time, it was suspected to overlay an aquifer.<sup>3</sup> There is a residential area downstream from the site which may use the aquifer as a potable water source, and the northern area of the range consists of sensitive marshlands. Wildlife common to the site are white-tailed deer, moose, black bear and red fox, beaver, muskrat grouse and cottontail rabbit. While other energetic contamination was found at this site, this case study focusses on 2,4-dinitrotoluene.

# **POLLUTANT LINKAGE**

### SOURCE

Residues of unburnt 2,4-dinitrotoluene propellant, an organic compound with a chemical structure similar to 2,4,6- trinitrotoluene are deposited from open burning disposal of propellant, directly on the soil surface.

#### PATHWAY

2,4-dinitrotoluene solubilises in rainwater (270 mg/L), which at Patawawa averages 985 mm / year,<sup>4</sup> which is enough to dissolve 265 g per m<sup>2</sup> of contaminated land. In reality, the maximum quantity dissolved per year may be slightly lower depending on the size and distribution of residue particles.<sup>5</sup> Once dissolved, the 2,4-dinitrotoluene will infiltrate into the soil. At Petawawa, the primary soil type is sand from sediment deposition resulting in a neutral soil high in organic matter.<sup>6</sup> Without experimentation it was not possible to determine how rapidly degradation of 2,4-dinitrotoluene will occur, however it is likely that it will be biologically degraded. The rate at which 2,4-dinitrotoluene transports through the soil is therefore a balance between the rate of degradation, the rainwater infiltration and the depth to groundwater. Groundwater at Petawawa is likely to flow downstream to the local rivers, and towards the nearby residential area. However, tests of Petawawa groundwater sources have not detected 2,4-dinitrotoluene.

An alternative pathway of concern is surface run-off during rainfall directly into local surface water sources, however, during site characterisation no 2,4-dinitrotoluene was detected in surface water.

### RECEPTORS

There are multiple potential receptors at the Petawawa site. Direct exposure to 2,4-dinitrotoluene is possible by ingestion or inhalation by local fauna while grazing, such as deer, moose and rabbits, as well as by humans using the area. The minimum safe daily dose for humans determined by the U.S. EPA is 2 µg kg<sup>-1</sup> per day, where kg represents the body weight of humans exposed to the source. This is equivalent to the ingestion of approximately 200 g of soil per kg, which is very unlikely to occur; therefore, the risk of direct exposure is low. Other receptors include on-site flora which take up water and nutrients from the soil, although affected flora would be that found in the direct vicinity of the site which is limited, due to the use of the area as a training range. Finally, human and animal receptors may also be affected by the consumption of contaminated drinking water from the aquifer, or local rivers. While 2,4-dinitrotoluene has not been detected in groundwater, the high concentration in the soil and planned continued use of the site to dispose of propellant, means that the risk of transmission to groundwater remains a concern.

The conceptual Pollutant Linkage Model for this case study can be seen in Figure 1.



Figure 1: Conceptual Pollutant Linkage Model for contamination from munitions burning.

## **MITIGATION**

Due to the risk posed to receptors from the accumulation of unburned propellant including 2,4-dinitrotoluene at Petawawa, as well as other heavily used training areas, mitigation measures were introduced. In this case, the issue identified was the open burning of propellant directly on the soil. Using the hierarchy introduced in Chapter 5, a plan for mitigation was proposed. The preferable option would be to avoid the practice of open burning of propellant, and where possible pristine propellant bags were to be sent back to stores for re-use. However, it was not always possible to return all propellant and therefore the next preferable option was to minimise the contamination from its disposal and break the source-pathway linkage.

The solution was to intercept the link between the source and the pathway (Figure 1) by using burn trays constructed of high-temperature stainless steel or aluminium, measuring  $3 \text{ m} \times 5 \text{ m} \times 0.1 \text{ m}$  (Figure 2).<sup>7</sup> The depth of the trays was deliberately low to reduce the risk of transition from combustion to detonation, and the size was limited by the requirement to be portable. The trays enabled the collection and appropriate disposal of the burnt residue, which when analysed was shown to contain high quantities of lead but significantly reduced quantities of unburnt propellant, compared to burning on the ground. In total, less than 0.001% of the total mass of 2,4-dinitrotoluene was deposited on the ground outside of the tray during disposal; this is a negligible amount that does not constitute an environmental hazard. This demonstrates that use of the trays not only prevented deposition of residue, but actually increased the efficiency of the burn.

Dissolution in rainwater, transport through sand to aquifer

Unburned 2,4-dinitrotoluene Human and animal consumption of contaminated water

Figure 2: The burn trays mitigated the risk to human and animal receptors by breaking the link between the source and pathway for the DNT pollutant linkage



Figure 3: Prototype of the burn tray developed by Canada and the US, a) loaded with propellant prior to burn, and b) during disposal. The trays surrounding it were put in place to capture the mass of propellant deposited outside of the tray (*Images* ©Dr Michael Walsh)

#### Successful outcomes:

- The construction proved resistant to warping and the removal of residues for disposal was easy;
- Ash contained so little explosive residue that it could be disposed of as hazardous waste rather than explosive contaminated waste;
- Full loading of the tray (150 kg) resulted in the most efficient combustion and least residue deposited around the tray;
- Multiple trays could be set up simultaneously to increase the quantity of propellant disposed of;
- The trays cooled down within 45 minutes and could be reused;
- The trays were portable using a forklift.

#### What could be improved:

- Ignition cords tended to fuse to the metal burn table itself and were difficult to remove;
- Screens could be added to reduce the ejection of propellant from the burn tray and further minimise land contamination;
- Use of less costly materials could be investigated for construction of the burn tray;
- Being portable and made of potentially recyclable metals means the trays may be stolen; securing the trays could be considered.

### **SUMMARY**

This type of burn tray design has been successfully introduced at multiple training ranges in Canada for the disposal of unwanted propellant. This has enabled the continued disposal of excess gun propellant on the ranges with very limited environmental impact. Although gaseous emissions from the burning are emitted into the atmosphere and will contribute to pollution and climate change, this is mitigated by the remote locations of the burns and the significant dilution of gaseous products by the time receptors are encountered. Meanwhile, the risk of contamination of the potable water sources from 2,4-dinitrotoluene at the Petawawa training range has been effectively eliminated by interruption of the link between the source and pathway, through the use of the portable burn trays.

This case study demonstrates use of the hierarchy principle (Chapter 5) to determine preferential mitigation options. The use of burn trays minimised the contamination produced from the combustion as well as severing the source-pathway linkage. This means that the least preferential option of costly soil and water remediation will be prevented in the future.

- 1 Director Infrastructure and Environment, Department of National Defence. Army Bases Range and Training Area Characterization. Canada, 2012.
- 2 United States Environmental Protection Agency (EPA), Land and Emergency Management, "Technical Fact Sheet – Dinitrotoluene (DNT)," September 2017.
- 3 Marc-André Lavigne et al., "Initial study of terrestrial forces training sites potentially contaminated by energetic materials." Study prepared for Defence Research Establishment Valcartier (DREV) and CFB Petawawa (Sainte-Foy, Québec: INRS-ETE, 2003).
- 4 "Climate Petawawa, average temperature Petawawa, weather by month Petawawa, weather averages Petawawa." <u>Climate-Data.org</u>, accessed 29 April 2021, <u>https://en.climate-data.org/north-america/canada/ontario/ petawawa-48386/.</u>
- 5 Susan Taylor et al., "Outdoor weathering and dissolution of TNT and Tritonal." *Chemosphere* 77, Issue 10 (2009): 1338–1345, <u>https://doi.org/10.1016/j.chemosphere.2009.09.040</u>.
- 6 J. E. Gillespie, R. E. Wicklund & B. C. Matthews, "Soil Survey of Renfrew County." Report no. 37 of the Ontario Soil Society 1964, <u>https://sis.agr.gc.ca/cansis/publications/surveys/on/on37/on37\_report.pdf</u>.
- 7 Michael R. Walsh, et al., "Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Interim Report 2." ESTCP Project ER-1481, 2010: 1–337, file:///C:/Users/UTILIS~1/AppData/Local/Temp/ERDC-CRREL-TR-10-13-withESTCPcover.pdf.

# CONCLUSION

Mine action affects the environment. Whether it is the removal of vegetation and topsoil during demining, or the chemical contamination left behind during Open Burning Open Detonation disposal activities, or even the carbon footprint inherent in a sector that works around the globe, mine action will have an impact. The question is not whether there is an impact, but how such an impact can be mitigated responsibly, in a practical way that does not inhibit the immediate task of removing explosive hazards that cause harm.

The guide provides a brief survey of the scientific research conducted to date, mostly conducted in the defence sector. This guide does not have complete answers to the issue of chemical contamination of the environment by explosive ordnance. This is principally due to the fact that there is still significant amount for scientists to discover about the subject. While military research dates back decades, there is a consensus that there is still a great deal more to learn and fully understand, not least since certain environmental effects are not apparent until many years after the original contamination.

Within this context of ongoing research, what are the implications for mine action? At present mine action lags equivalent sectors such as industrial demilitarisation when it comes to active mitigation of environmental risks. For example use of Open Burning Open Detonation has been significantly reduced in many countries but remains standard practice in mine action. There are often good reasons for this, not least the lack of viable alternatives in many of the locations where mine action operations occur. However the direction of travel of greater regulation concerning explosive ordnance and the environment is clear. By the same token we must be careful not to suddenly over-regulate clearance and disposal activities to a point where we inhibit the immediate need to remove explosive ordnance endangering civilians.

The real challenge for mine action operators is to develop reasonable risk management practices concerning chemical contamination from explosive ordnance. The hierarchy of mitigation and identification of the potential Pollutant Linkage Models gives frameworks within which such risk management can be developed. What *"As Low As Reasonably Practicable"* looks like when it comes to management of chemical contamination in mine action is yet to be defined. It is hoped this guide provides a starting point for that process.

# **LIST OF ABBREVIATIONS**

BAC	Battle area clearance
CFFE	Certified Free From Explosives
DNT	2,4-dinitrotoluene
DU	Depleted uranium
EO	Explosive ordnance
MA	Mine action
HMTA	Heavy metal tungsten alloy
PBX	Polymer-bonded explosives
RDX	1,3,5-trinitro-1,3,5-triazine
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SAA	Small arms ammunition
SPR	Source-pathway-receptor
TNT	2,4,6-trinitrotoluene
US EPA	United States Environmental Protection Agency
WHO	World Health Organization



Geneva International Centre for Humanitarian Demining (GICHD) Maison de la paix, Tower 3, Chemin Eugène-Rigot 2C PO Box 1300, CH – 1211 Geneva 1, Switzerland info@gichd.org gichd.org

