Carlos Miguel Baptista Ferreira

EXTENDED ENVIRONMENTAL LIFE-CYCLE ASSESSMENT OF MUNITIONS:
ADDRESSING CHEMICAL TOXICITY HAZARD ON HUMAN HEALTH

PhD thesis in Mechanical Engineering, area of Industrial Ecology, supervised by Professor José Manuel Baranda M. Silva Ribeiro
and Professor Fausto Miguel Cereja Seixas Freire, presented to the Department of Mechanical Engineering,
Faculty of Sciences and Technology, University of Coimbra

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Abstract

Despite of the increasing awareness to the environmental impact associated with munitions, the research efforts done in this area are mainly related to safety and performance improvements, while a holistic perspective of the environmental impacts of their production, use, and disposal are not covered. To utterly comprehend those impacts is necessary to quantify the potential environmental and toxicological impacts associated with the life-cycle of ammunition. The use of the Life-Cycle Assessment (LCA) methodology for that purpose will not only allow the quantification of the impacts, but also indicate the path to enhance the environmental profile of ammunition.

Environmental legislation is a main driver to enforce industry, including military industry, to develop new approaches to mitigate the environmental impacts of their products. An example of legislation pressure is the REACH regulation that is restricting the use of substances of very high concern (SVHC) that are classified based on limits established for selected physicochemical properties. The interpretation drawn from this classification system is that the potential consequences to human health are essentially dependent on a restricted number of a substance's properties, and that the limits imposed are equivalent from that point of view. However, it is necessary to understand if those issues are verified in order to enhance the classification of hazardous substances.

This thesis provides insights about two main goals associated with the life-cycle environmental impacts of ammunition. Firstly, LCA is presented to assess the environmental and toxicological impacts of ammunition in order to highlight the principal burdens associated with the production, use, and disposal of ammunition. The scarcity of life-cycle studies regarding this issue reflects its importance, novelty, and contribution to the scientific community to facilitate future studies about this issue. Secondly, this thesis aims to improve the hazard classification system of chemical substances, and to strength the reliability of the identification of SVHC. For that purpose, a conceptual framework was developed based on USEtox to calculate toxicological characterization factors (CFs) associated with virtual substances: hypothetical substances whose properties are based on the regulatory limits established by REACH. A hazard classification system based on the aforesaid toxicological CFs for virtual substances is proposed to assist in the evaluation of safer toxicological alternatives.

The life-cycle inventories for energetic materials contributed to complete the gap and facilitate future studies associated with the environmental impact assessment of ammunition. Comprehensive LCA studies referent to the whole life-cycle of ammunition helped to assess and highlight the main hotspots for this product. In particular, LCA studies demonstrated the importance of a life-cycle approach to ammunition by illustrating that the information obtained from these studies outweighs the effort needed to overcome the difficulties stemming from data collection. The employment of a life-cycle perspective shed some light in some unexpected consequences or trade-offs related to "green" paths for ammunition. These findings will allow shooting range managers, ammunition producers or others, to become more aware of the main environmental impacts of ammunition as well as defining strategies to manage or mitigate ammunition burdens and carry out tailored modifications to decrease the impacts.

The calculation and comparison of the toxicological CFs for the virtual substances allowed to conclude that: i) the different regulatory limits established by REACH are equivalent from the point of view of their ability to evaluate the human health impact; ii) the combinatory effect of the different physicochemical properties is not negligible when evaluating the hazard potential of a substance; iii) parameters such us water solubility or Henry´s law coefficient (not included in the SVHC classification) are as relevant as others presently included in REACH to evaluate hazard to human health; iv) the CFs of the virtual substances may be seen as a reference of what is an acceptable toxicological impact, and can be employed in a hazard classification of chemical substances.

The aforesaid hazard classification system can be used to evaluate the significance of potential toxicological impacts and to provide additional information to screen the substances according to their toxicity hazard. This hazard classification system not only incorporates more properties than the ones considered in REACH regulation, but also takes in consideration the combinatory effect to calculate toxicological impacts on humans. This new framework intends to improve the toxicological assessment of substances, helping the industry to classify SVHC and understand the significance of the toxicological impacts related to conventional or new products.

Keywords: energetic materials; hazard classification system; life-cycle assessment; REACH regulation; USEtox method.

Resumo

Apesar de uma maior perceção para os impactes ambientais associados a munições, os esforços da investigação feitos nesta área são sobretudo relacionados com a melhoria da segurança e performance, enquanto uma perspetiva holística aos impactos ambientais da sua produção, uso e eliminação não são abrangidos. Para compreender esses impactes é necessário quantificar os impactes ambientais e toxicológicos associados ao ciclo de vida de munições. A aplicação da metodológica de Avaliação de Ciclo de Vida (ACV) para esse propósito permitirá a quantificação dos impactes, e indicar o caminho para melhorar o perfil ambiental das munições.

A legislação ambiental é um precursor para forçar a indústria, incluindo a indústria militar, a desenvolver novas abordagens para mitigar os impactes ambientais dos seus produtos. Um exemplo da pressão da legislação é o regulamento REACH que tem restrito o uso de substâncias de integração progressiva (SIP) que são classificadas tendo em conta limites estabelecidos para certas propriedades físico-químicas. A interpretação a partir deste sistema de classificação é que as potenciais consequências para a saúde humana são basicamente dependentes de um número restrito de propriedades de uma substância, e que os limites impostos são equivalentes desse ponto de vista. No entanto, é necessário perceber se esses pressupostos verificam-se e desta forma melhorar a classificação de substâncias perigosas.

Esta tese faculta uma maior clareza sobre dois objetivos associados ao impacte ambiental do ciclo de vida de munições. Primeiro, a ACV é apresentada para avaliar os impactes ambientais e toxicológicos de munições de forma a esclarecer os principais problemas associados à produção, uso e eliminação de munições. A escassez de estudos de ciclo de vida sobre este assunto reflete a importância, a novidade e o contributo para a comunidade científica para facilitar futuro estudos sobre este assunto. Em segundo, com esta tese pretende-se melhorar o sistema de classificação de substâncias perigosas, e consolidar a identificação das SIP. Com esse propósito, foi desenvolvido um enquadramento conceitual baseado no método USEtox para calcular os fatores de caracterização (FCs) toxicológicos associados a substâncias virtuais: substâncias hipotéticas em que as propriedades baseiam-se nos limites regulatórios determinados pelo REACH. É proposto um sistema de classificação de perigo, baseado nos FCs toxicológicos para as substâncias virtuais, para auxiliar na avaliação de alternativas mais seguras.

Os inventários de ciclo de vida de materiais energéticos contribuem para completar a lacuna e auxiliar futuros estudos referentes à avaliação dos impactes ambientais de munições. Estudos de

ACV referentes ao ciclo de vida total de munições ajudam a avaliar e realçar os "hotspots" deste produto. Nomeadamente, os estudos de ACV indicam a importância de uma perspetiva de ciclo de vida para munições, ilustrando que a informação obtida destes estudos supera o esforço requerido para superar as dificuldades na obtenção de dados. A perspetiva de ciclo de vida indicou que algumas soluções amigas do ambiente podem originar consequências inesperadas. Estes resultados permitem que gestores de campo de tiro, produtores de munições ou outros, estejam mais cientes dos principais impactes ambientais de munições, além de ajudar a definirem estratégias para gerir ou mitigar os problemas ambientais de munições e realizar modificações para reduzir esses impactes.

O cálculo e comparação dos FCs toxicológicos das substâncias virtuais permitiu concluir que i) os diferentes limites regulatórios estabelecidos pelo REACH são equivalentes em relação à sua aptidão para avaliar os impactes na saúde humana; ii) o efeito combinatório das diferentes propriedade físico-químicas não pode ser negligenciado quando são avaliados os potenciais perigos de uma substância; iii) propriedades como solubilidade e coeficiente da lei de Henry (não incluídas na classificação de SIP) são igualmente relevantes que as outras propriedades atualmente incluídas no REACH para avaliar os perigos na saúde humana; iv) os FCs das substâncias virtuais podem ser vistas como uma referência de um nível aceitável de impacte toxicológico, podendo ser utilizados num sistema de classificação de substâncias químicas perigosas.

O sistema de classificação de perigo pode ser utilizado para avaliar a magnitude do potencial impacte toxicológico e fornecer informação adicional para selecionar substâncias de acordo com o seu perigo tóxico. Este sistema de classificação de perigo incorpora mais propriedades que os considerados atualmente pelo regulamento REACH, além de incluir também o efeito combinatório no cálculo dos impactes toxicológicos. Com este enquadramento novo pretende-se melhorar a avaliação do impacte toxicológico de substâncias, ajudando a indústria a classificar as SIP e entender a significância dos impactes toxicológicos relacionados com produtos novos ou convencionais.

Palavras-chave: Avaliação de ciclo de vida; materiais energéticos; método USEtox; regulamento REACH; sistema classificação de risco.

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Acronyms

1,4-DB: 1,4 dichlorobenzene

AAS: Atomic Absorption Spectrometry

Acid: Acidification

AD: Abiotic depletion

AVT: Applied vehicle technology

BAF_{fish}: Bioaccumulation factor in fish

C4 PBX: Composition 4, polymer-bonded explosive

CFs: Characterisation factors

CFC: Chlorofluorocarbon

CMRs: Carcinogens, mutagens, toxic to reproduction

CO_2: Carbon dioxide

CTUe: Comparative toxic unit for ecosystems

CTUh: Comparative toxic unit for human health

DDNP: Diazodinitrophenol

DNAN: 2,4-Dinitroanisole

EC_{50}: Half maximum effective concentration

ECHA: European Chemical Agency

ED_{50}: Median effective dose

EDA: European Defence Agency

EPi suite: Estimation Programs Interface suite

ERM: Environmentally Responsible Munitions

Eut: Eutrophication

GW: Global warming

H_2O_2: Hydrogen peroxide

HCl: Hydrogen chloride

HF: Hydrogen fluoride

HMX: Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (octogen)

HT: Human toxicity

idD: *Plataforma das Indústrias de Defesa Nacional*

$\mathbf{k_{doc}}$: Dissolved organic carbon-water partition coefficient

$\mathbf{k_H}$: Henry’s law coefficient

$\mathbf{k_{oc}}$: Organic carbon-water partition coefficient

$\mathbf{k_{ow}}$: Octanol-water partition coefficient

LCA: Life-Cycle Assessment methodology

LCIA: Life-Cycle Impact Assessment

LCI: Life-Cycle Inventory

LDPE: Low density polyethylene

MIDAS: Munition Item Disposition Action Systems

MW: Molecular mass

NATO: North Atlantic Treaty Organization

NMVOC: Non-methane volatile organic compounds

NOx: Nitrogen oxides

OLD: Ozone layer depletion

PBT: Persistent, bioaccumulative, toxic

PETN: Pentaerythritol tetranitrate

PO: Photochemical oxidation

POEMS: Project Oriented Environmental Management System

$\mathbf{P_{vap}}$: Vapour pressure

QSAR: Quantitative structure–activity relationship

RDX: 1,3,5-Trinitroperhydro-1,3,5-triazine (hexogen)

REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals

SCR: Selective catalytic reduction

SEM-EDX: Scanning Electron Microscopy **-** Energy-dispersive X-ray spectroscopy

$\mathbf{SO_2}$: Sulphur dioxide

$\mathbf{SO_3}$: Sulphur trioxide

$\mathbf{Sol_{25}}$: Water solubility

SVHC: Substances of Very High Concern

$\mathbf{t_{1/2}}$ **air**: Half-life in air

$\mathbf{t_{1/2}}$ **water**: Half-life in water

$\mathbf{t_{1/2}}$ **soil**: Half-life in soil

$t_{1/2}$ sediment: Half-life in sediment

TNR-Pb: Lead styphnate

TNT: 2,4,6-trinitrotoluene

TNT eq: 2,4,6-trinitrotoluene equivalent

UXO: Unexploded ordnance

VOC: Volatile Organic Compounds

vPvB: Very persistent, Very bioaccumulative

Chapter 1 - Introduction

1.1 Background and motivation

Environmental and toxicological consequences associated with ammunition have been away from the concern of general population and authorities due to their intended application in war/conflict scenarios. However, the perception and the relevance of the problem can change completely considering that only a small percentage of ammunitions are used in war scenarios. In fact, the majority of ammunitions are demilitarised or used in live-fire training, contributing significantly to soil, water and air contamination with (unburned or partially burned) energetic materials and heavy metals.

The awareness to the relevance of contamination associated with ammunition is noticeable when their market is considered. Despite the fact that is challenging to ascertain the global production of ammunition, SIPRI – Stockholm International Peace Research Institute – estimated that in 2014 (last year with published data) at least 94.5 billion dollar of ammunition were exported (SIPRI, 2016). However, these values are underestimated due to the opacity of the market, as many countries failed to report the imports or exports of munitions. Solely considering the production of small arms ammunition for military forces, the global production is estimated to approximately 13 billion rounds (Anders and Weidacher, 2006).

For disposal more than half a million tons of excess stockpile just in western countries is estimated (Wilkinson and Watt, 2006). The main demilitarisation contractors are established in United States, which is the largest market representing approximately a sixth of the total stockpile (around 450 000 metric ton), and Western Europe (Small Arms Survey, 2013). Beyond the western countries, other parts of the world also have significant amounts of munitions to decommission where they are a safety hazard and present a potential risk for terrorist activities (Wilkinson and Watt, 2006).

Research about munitions is usually related to the safety and performance improvement (e.g. detonation velocity, insensitive munitions), involving different but complementary fields of research. However, due to the environmental awareness, the emissions of heavy metals and unreacted, or partial reacted, energetic materials associated with ammunition use and the amount of those contaminants in the soil and water have recently started to be measured (Hewitt *et al.*, 2005; Clausen and Korte, 2009; Walsh *et al.*, 2012; Walsh *et al.*, 2013a; Walsh *et al.*, 2014a; Perroy *et al.*, 2014; Thiboutot *et al.*, 2015). Those measurements even include the amount of lead intake by birds (Fisher *et al.*, 2006; Helander *et al.*, 2009) and human exposure to lead by direct inhalation at small calibre ammunition shooting ranges (Bonanno *et al.*, 2002).

The aforesaid studies are based on monitoring individual aspects and lack a holistic view that is possible to address with the life-cycle perspective. Surely the evaluation of heavy metals toxicity (e.g. lead) to some species helps to understand the importance and increase the awareness associated with ammunition contamination, but that can be insufficient to comprehend the potential environmental burdens as other substances poses a significant influence to different environmental impacts. To utterly comprehend the consequences related to the use of ammunition it is required the quantification of potential impacts on human health and ecosystems. Therefore, it is important to move forward and use the data from the characterisation of those emissions to quantify the potential burdens. In order to assess the environmental impacts of ammunition is relevant to address all emissions of heavy metals, energetic materials and other substances as well as, beyond the impacts on human health and different individual species that exist in ecosystems, other potential environmental impacts (e.g. global warming, acidification).

It is important to note that the production and disposal of ammunition have been mainly discussed from a risk and safety perspective, so environmental and toxicological issues are usually not covered despite the importance of the impacts associated with these life-cycle phases (Ferreira *et al.*, 2013; Ferreira *et al.*, 2016; Ferreira *et al.*, 2017). Sources of contamination from ammunition production are usually associated with explosives manufacture processes (casting, curing, and machining), inadequate storage practices, and inadequate disposal of contaminated wastewaters (Pichtel, 2012). With respect to ammunition decommission the main environmental burdens are reported to open burning/open detonation. Substantial residues are dispersed associated mostly with low order detonations or ammunitions throw out from the burn pits (resulting in unexploded ordnances – UXO) (Pichtel, 2012). Decommission of ammunition by incineration can also present some environmental concerns, mainly due to indirect emissions resulting from the consumption of energy to clean the flue gases from the energetic material combustion or thermal treatment (Ferreira *et al.*, 2013).

The relevance of addressing the environmental issues in military systems is also observed in the several activities that are promoted in NATO – Science and Technology Organization. For the last ten years NATO has been organized several technical groups to combine the knowledge of industry and academic institution of many countries to discuss the environmental problems associated with military systems (RTO 2010; RTO 2014; RTO 2015). In fact, the AVT-179 report on "Design for disposal of present and future munitions and application of greener ammunition technology" has received a Scientific Achievement Award recognizing the effort, quality, and originality of these technical groups in the scientific and technical content in terms of military benefit.

Environmental legislation has also been a driver to enforce industry to develop new approaches to mitigate or at least decrease the environmental impacts of their products, and ammunition production actives are not an exception. An evident example of legislation pressure is the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation that is restricting the production and use of harmful substances (European Commission, 2006). Harmful substances, named as substances of very high concern (SVHC), are classified accordingly with criteria outlined in Annex XIII of REACH, in which limits are established for the physicochemical properties of the substances that are assumed to characterize its hazard to human health and ecosystems. These restrictions to certain chemical substances are pushing both the research labs and the industry to develop safer alternatives.

Underlying the employment of this classification system are the following ideas: i) the potential consequences to human health and ecosystems associated with the emission of a certain substance are essentially dependent on a restricted number of the substance's properties, and ii) the regulatory limits are equivalent from the perspective of the potential consequences to human health and ecosystems. However, it is necessary to understand if the aforesaid issues are verified in order to enhance the classification of hazardous substances.

It is also relevant to mention that safer alternatives, with the same performance and safety requirements than the substance banned by REACH, should show lower toxicological impact in a life-cycle perspective. In order to enable an appropriate mitigation of the environmental impacts of ammunition and to ensure that all potential consequences are taken into account, it is important to consider a life-cycle perspective. Therefore, when a life-cycle perspective is employed, it is possible to evaluate whether there is any shift of impacts from one life-cycle phase to another (Azapagic, 2004). For instance, the shifting of impacts can be associated with the selection of a substance that presents lower toxicity but has a higher impact in the production phase (when compared with conventional substances).

The toxicological assessment reflects the influence of the different parameters to the toxicological impact ascertaining the magnitude of the contribution of fate, exposure, and effect parameters to those impacts. The toxicological assessment can also assist in the search for safer alternatives for substances banned by REACH. The alternatives can present unexpected consequences that can be avoided if a preliminary evaluation is considered, so presenting additional information, such as a screening or raking chemicals hazard toxicity, can enhance the capability to comprehend and predict potential unintended consequences or trade-offs. The toxicological assessment can be carried out with life-cycle impact assessment methods, such as USEtox (Rosenbaum *et al.*, 2008).

A gap to assess the environmental and toxicological impacts related to the whole life-cycle of ammunition is evident, and this have been pressuring the Armed Forces and military stakeholders to find a methodology to assist in the enhancement of the environmental profile of ammunition. The strategies as well legal instruments that need to be adopted to protect the environment from military activities have also been discussed, and the ecologist Robert Francis stated that the principal research priorities for warfare contamination are (Francis, 2011): “(1) the prediction and communication of risk to freshwater ecosystems from warfare; (2) the determination and quantification of impacts associated with warfare; (3) establishment of methods and techniques to mitigate impacts or improve recovery of freshwater systems; and (4) examination of how legislative instruments may be strengthened to ensure greater environmental responsibility to parties involved in conflict”. These priorities were established for freshwater contamination from warfare activities; however the aforementioned priorities can be extrapolated for all the life-cycle phases of ammunition to cover similar problems in a life-cycle perspective.

Several attempts have been made to address the aforesaid gaps associated with the evaluation of environmental impacts of ammunition and military systems. Among those attempts, UK has developed the POEMS methodology (UK MOD, 2011) to assess the environmental impacts of military platforms; whilst USA has developed the MIDAS (Chemical Compliance Systems, 2011) to provide a score of the environmental performance of munitions. However, the results delivered by these methodologies are very broad, qualitative, and do not allow an assessment of the eventual environmental benefits from different specific production or disposal options as well the identification of eventual burdens associated with ammunition use.

Life-Cycle Assessment methodology to ammunition can be an appropriate tool to help to improve the environmental profile of ammunition, as it might contribute to close the gap observed in the quantification of life-cycle environmental consequences from ammunition. Therefore, the main goal of this thesis is to present a life-cycle assessment of ammunition in order to highlight the principal environmental and toxicological concerns associated with the production, use, and disposal of ammunition. The Life-Cycle Assessment methodology has been employed to a large range of products (and systems) and can also be applied to quantify the potential impacts of the ammunition life-cycle. Consequently, LCA can help decision makers in the procurement and design of environmentally responsible ammunitions, reducing the impacts of their manufacture, the impacts on ecosystems near shooting ranges or training areas, and the impacts associated with its disposal.

A few studies attempted to implement a life-cycle approach to improve the environmental performance of military activities. Hochschorner *et al.* (2006) assessed life-cycle of a grenade; Alvebro *et al.* (2009) presented a comparative assessment of two demilitarisation paths (open detonation and incineration in a static kiln); and an LCA to compare a standard grenade with a “greener” grenade was also performed using an ecodesign approach for the production phase of the ammunition (Hägvall and Tryman, 2010). These two articles and the report mentioned above are the only ones known. One of the reasons to explain that scarcity is the difficulty to obtain real data to perform this type of studies.

Collection of data is the most time-consuming phase in a LCA study, and for military systems this difficulty is increased as the databases are not properly adapted for ammunition, and the literature is either scarce, rather outdated, or might be protected by military trade secret. These difficulties tend to hinder LCA studies significantly. This thesis aims to demonstrate that the information obtained from Life-Cycle Assessment studies outweigh the effort needed to overcome the difficulties stemming from data collection. As a result, it is intended to contribute to the scientific community with different environmental and toxicological assessments associated with ammunition life-cycle to facilitate future studies about this issue.

The life-cycle approach employed in this thesis can help to adopt the appropriate strategies to predict and ascertain the environmental problems associated with the whole life-cycle of ammunition; and also improve the hazard classification system of chemical substances. In fact, this thesis partially cover the four research priorities stated by Francis (2011) in order to provide an assessment to predict, quantify and enhance the environmental profile of ammunition (priorities 1, 2 and 3) with the employment of LCA methodology to ammunition. In addition, it is intended to address the priority 4 by strengthening the legislation related to toxicological compliance with the creation of a new framework to present recommendations and improve the existing legislation.

1.2 Research questions

This PhD thesis is carried out to give an answer to two main objectives, which are independent but complementary, associated with the life-cycle environmental impacts of ammunition. Firstly, the novel study about the implementation of life-cycle assessment to munitions is addressed, with real applications related to the main environmental and toxicological burdens associated with production, use, and disposal of ammunition. Secondly, the toxicological assessment of substances is improved with the inclusion of regulatory limits into the life-cycle impact assessment method USEtox in order to comprehend the importance of the combinatory effect of different physicochemical properties and the environment characteristics to the toxicological consequences on human health. Ultimately, the overall purpose of this later research topic is to develop and implement an extended life-cycle model to improve the toxicological assessment of products. Thus, assist the industry with the creation of toxicological thresholds that can be employed to classify substance of very high concern (SVHC).

To accomplish the main objectives presented above, three research questions were formulated and the inherent specific objectives were defined to answer these research questions, as presented in Table 1.1.

Table 1.1 Research questions and specific objectives.

Research questions	Specific objectives	Chapter
1) What are the life-cycle environmental impacts (and hotspots) associated with the production and use phase of ammunition? Are those impacts significant?	i) To create life-cycle inventories related with production of common energetic materials and assess the life-cycle environmental impacts. To provide a comprehensive understanding of these impacts with common chemicals; ii) to assess the life-cycle environmental impacts of ammunitions as well as evaluate which life-cycle stages significantly contributes to the total impact. iii) to assess and comprehend the effects/consequences of replacing lead by alternative materials (ecodesign for ammunition); iv) to provide a comprehensive understanding of the magnitude of the impacts assessed for ammunition.	3
2) What is the appropriate technology, from an environmental life-cycle perspective, to disposal ammunition?	i) To develop life-cycle models related with ammunition disposal; ii) to assess the life-cycle environmental impacts associated with ammunition disposal by incineration in a static kiln; iii) to assess the life-cycle environmental impacts associated with ammunition disposal by open detonation; iv) to assess the potential benefits, with the employment of the system expansion method, from the valorisation of energetic material from ammunition into civil explosives v) to determine which disposal technique presents lower environmental impacts.	4
3) How to improve the toxicological hazard classification system of chemical substances and strengthen the reliability of the identification of substances of very high concern?	i) To develop the concept of virtual substance, mainly based on limits defined by REACH regulation, and a conceptual framework for the calculation of its toxicological characterisation factors; ii) to comprehend the influence of the combinatory effect of different physicochemical properties on the potential impact calculation: iii) to evaluate which physicochemical property contributes most for the calculated toxicological characterisation factors; iv) to provide a new tool to classify substances according with their chemical hazard, and assist in the evaluation of safer toxicological alternatives for substances banned by REACH.	5

For the first topic, life-cycle models to assess the environmental impacts associated with ammunition were developed. The scarcity of life-cycle studies regarding this issue reflects the importance and novelty to assess the life-cycle environmental and toxicological impacts related to ammunition. Hence, this thesis aims to deliver the baseline for the environmental impact assessment of ammunition in order to simplify the application of LCA studies to other military products not covered in this research. For that purpose, life-cycle inventory and impact assessment for common energetic materials (TNT, RDX, powders, primers) production is developed as well as recommendations to overcome the problem of data absence.

Life-cycle models of different types and calibres of ammunition and of different disposal techniques were also addressed: production and use of generic 155 mm ammunition; comparison of four different 9 mm small calibre ammunition; comparison of three techniques to disposal ammunitions – open detonation, incineration in static kiln with gas treatment and, valorisation of energetic material by incorporation into civil explosives. The application of LCA to ammunition enabled us to answer questions such as: are new "green" ammunitions presenting lower environmental impacts than standard ones? Does the use of alternative materials raise new environmental concerns? Are the impacts significant and why? What further steps should be taken to improve ammunitions from a toxicological and environmental point of view? What technology shows lower environmental and toxicological impact to disposal ammunition?

To improve the toxicological assessment of substances centred on regulatory limits and to enhance the classification of substance of very high concern, a concept framework to calculate, with the use of USEtox method, the toxicological characterisation factors associated with virtual substances defined based on the regulatory limits imposed by REACH regulation was developed. A virtual substance is a hypothetical substance which physicochemical properties are determined by the limits establish by REACH. That toxicological CFs were used: i) to assess the equivalence between the limits established for the different physicochemical properties; ii) to evaluate the significance of the combinatorial effect from different physicochemical properties into potential impacts; iii) to provide a new tool to assist in the evaluation of safer toxicological alternatives for substances banned (or restricted) by REACH; and iv) to present recommendations to improve, support, and facilitate the classification of substance of very high concern (SVHC) in REACH regulation. This approach for toxicological evaluation can also be extrapolated to other systems or products beyond military systems.

1.3 Contribution

This thesis contributes to understanding the importance and magnitude of environmental burdens of ammunition as well improving the toxicological assessment of organic substances, in particular by:

1. Creating "gate-to-gate" life-cycle inventories for energetic materials and recommendations on how to compile information for energetic materials not included in this analysis in order to facilitate future studies associated with environmental impact of ammunition;

2. Shedding light in which are the most important hotspots and life-cycle phases that shows a higher environmental and toxicological significance for ammunition.

3. Demonstrating the importance of a life-cycle approach to assess the environmental impacts associated with ammunition, illustrating "green" approaches that originated unexpected trade-offs or adverse consequences.

4. Enhancing our understanding of the demilitarisation burdens with the analysis of three disposal techniques (incineration in a static kiln with flue gas treatment; open detonation; and valorisation of energetic material from ammunition via incorporation in civil explosives) and determining which one shows lower life-cycle environmental and toxicological impacts.

5. Providing recommendations to enhance and support the classification of substance of very high concern in REACH regulation, and determine if the physicochemical properties, including the properties not addressed in the current classification, present similar importance to the toxicological impact. Moreover, allowing determining the influence of combining different physicochemical properties in toxicological impacts.

6. Improving the toxicological assessment of organic substances via the integration of regulatory limits from REACH in the life-cycle impact assessment method USEtox. The toxicological characterisation factors can be seen as a reference (threshold) to understand the significance of the potential toxicological impact and to help selecting safer alternatives.

Most of the research in this PhD thesis is based on the following core articles published or under review in ISI-indexed journals (abstracts and keywords of the articles are presented in Appendix I):

Ferreira C, Ribeiro J, Mendes R, Freire F (2013) Life-Cycle Assessment of Ammunition Demilitarization in a Static Kiln, *Propellants, Explosives, Pyrotechnics* 38, 2: 296 - 302. doi: 10.1002/prep.201200088. JCR Impact Factor® (2014): 1.604; Citation: 5

Ferreira C, Freire F, Ribeiro J (2015) Life-cycle assessment of a civil explosive, *Journal of Cleaner Production* 89, 1: 159 - 164. doi: 10.1016/j.jclepro.2014.11.027. JCR Impact Factor® (2016): 4.959; Citation: 4

Ferreira C, Ribeiro J, Almada S, Rotariu T, Freire F (2016) Reducing impacts from ammunitions: A comparative life-cycle assessment of four types of 9mm ammunitions, *Science of The Total Environment* 566-567, 1: 34 - 40. doi: 10.1016/j.scitotenv.2016.05.005. JCR Impact Factor® (2016): 3.976; Citation: 2

Ferreira C, José R, Almada S, Freire F (2017) Environmental Assessment of Ammunition: the importance of a life-cycle approach, *Propellants, Explosives, Pyrotechnics* 42, 1: 44 - 53. doi: 10.1002/prep.201600158 JCR Impact Factor® (2016): 1.604; Citation: 0

Ferreira C, José R, Freire F (2017) A hazard classification system based on incorporation of REACH regulation limits in the USEtox method (submitted)

In addition, more than twelve articles related to this PhD research were published in conference proceedings with scientific refereeing. The full list of publications is presented in Appendix II.

1.4 Thesis outline

This thesis is composed of six chapters, including this introductory chapter, and is structured as follows:

Chapter 2 reviews the literature on the two main topics for which this research will contribute: i) implementation of a Life-Cycle Assessment for military systems, and ii) improvement of the toxicological assessment based on regulatory limits defined by REACH regulation. Firstly, a review of the recent literature addressing the environmental concerns regarding ammunition, and methodologies employed to **evaluate the environmental impacts associated with military systems**, principally the Life-Cycle Assessment methodology, is provided and research gaps are identified. Secondly, an overview of the legislation in European Union related to toxicological issues, focusing on the recently implemented **REACH regulation and the inherent concerns** is reviewed.

Finally, a detailed description of the **USEtox method**, a Life-Cycle Impact Assessment method dedicated to assess toxicological impacts, is also presented.

Chapter 3 describes the assessment of the main hotspots associated with the production and use phase of ammunition. The novel **life-cycle inventories of energetic material** are provided, as well as recommendation to create the inventories to any energetic material not covered in this work. The main **environmental and toxicological concerns related to the production and use phase of ammunition are highlighted**, in which LCA is employed to the production and use of generic large calibre ammunition, and four types of small calibre ammunitions. Furthermore, it is also presented the most important life-cycle phases to this aforesaid case studies. The magnitude and significance of the impacts assessed for ammunition is evaluated with the employment of normalisation factors based on the domestic emissions for Europe.

Chapter 4 presents a **comprehensive LCA of ammunition disposal** in order to ascertain which ammunition disposal technique shows lower environmental and toxicological impacts. The LCA compares three different disposal techniques to ammunition: **incineration in static kiln with flue gas treatment; open detonation; and valorisation of energetic material from ammunition via incorporation in civil explosives.** The latter technique, an industrial ecology approach to ammunition decommission, is evaluated with the employment of the system expansion method.

Chapter 5 analyses the creation of a new conceptual framework that **integrates regulatory limits from REACH regulation in the life-cycle impacts assessment method USEtox** in order to calculate toxicological characterisation factors, aiming to improve the classification of substance of very high concern. The toxicological characterisation factors permit to comprehend the potential toxicological effects of combining different physicochemical properties, evaluate which property contributes most to the toxicological impact, and act as a toxicological reference (threshold) to help evaluating safer alternatives. **Recommendations to improve, support, and facilitate the classification of substance of very high concern (SVHC) in REACH regulation** are also addressed.

Chapter 6 summarises the main findings related to the main research questions of this thesis and provides recommendations for future research.

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Chapter 2 - State-of-the-Art

Summary: The literature review intends to provide an overview of the two main topics for which this research will contribute: i) implementation of a Life-Cycle Assessment for ammunition, and ii) improvement of the hazard classification system of chemical substances as well as strengthen the reliability of the identification of substances of very high concern. Section 2.1 covers a review of the literature about the environmental concerns regarding ammunition, and methodologies employed to evaluate the environmental impacts associated with the military systems, principally Life-Cycle Assessment methodology. Section 2.2 aims at presenting the legislation in European Union for toxicity issues, focusing on the recently implemented REACH regulation. A detailed description of the USEtox method, a Life-Cycle Impact Assessment method, to assess toxicological impacts is also presented in section 2.3.

2.1 Environmental impact of ammunition

The awareness of the general population from the consequences of warfare activities are essentially focused on devastation and causalities, in some cases lasting for long periods. However, the effects of other military activities (e.g. live-firing training) on the environment are also negative and they need to be addressed. In fact, ammunition contaminants are found, beyond the battlegrounds, on military bases, artillery firing ranges, and industrial sites (Via and Zinnert, 2016). In training facilities high levels of heavy metal and explosive residues associated with ammunition usage was encountered, which can lead to the close of facilities. For instance, the Massachusetts Military Reservation (US) in 2001 was closed due to surface and groundwater contamination (Francis, 2011).

The main residues associated with the use of ammunitions in training facilities and hunting areas are energetic materials and heavy metals (Tsuji *et al.*, 2008). The major residues were metallic substances, mainly associated with bullets. The projectile of small calibre ammunition in time releases lead that progressively dissolves and originates new minerals (mostly oxides). Moreover, other metals are usually released to the soil by bullets such as chromium, antimony, arsenic, cadmium, copper, mercury, nickel, and zinc (Certini *et al.*, 2013). Energetic materials are the other source of contamination that normally has high soil persistence which can contaminate groundwater or accumulate in edible plants (Certini *et al.*, 2013).

The motivation to characterise and quantify the emissions (and subsequent level of contamination) related to military activities has been increasing. Some studies focused on emissions from live-firing or detonation of specific ammunitions, measuring concentrations of PETN (Thiboutot *et al.*, 2015); RDX and TNT (Hewitt *et al.*, 2005); propellant deposition rates (Wash *et al.*, 2010; Wash *et al.*, 2014a); and white phosphorus from smoke rounds (Wash *et al.*, 2014c). Emissions from the particular case of sensitive ammunitions were also studied (Wash *et al.*, 2013a; Wash *et al.*, 2013b; Wash *et al.*, 2014b).

The characterisation and measurement of heavy metals concentrations has also been conducted. Clausen *et al.*, (2004) analysed the concentration of metals in soils and waters at nine small arms training ranges from three military installations in the U.S. They concluded that the major substances found were lead, antimony, copper, and zinc. Despite this information, the majority of the studies are related with lead contamination from small calibre ammunition (Clausen *et al.*, 2004). In fact, in shooting ranges can be found concentrations of lead ranging from 7.3 mg/kg up to 54 000 mg/kg, depending on different soil and weather conditions. (Hardison *et al.*, 2004; Cao *et al.*, 2003; Manninen and Tanskanen, 1993). Antimony contained in Swiss shooting ranges was also quantified (Ackermann *et al.*, 2009) as well as monitored the mobility and leached concentration of this element (Hockmann *et al.*, 2015).

The information and data collected from the measurement of energetic materials and heavy metals are of great importance for Life-Cycle Assessment studies about ammunitions. However, it is difficult to connect the mass deposition rates on soils for specific munitions or military activities. In fact, the link between the contamination and the items used are even out of the research scope (Wash *et al.*, 2012a). Training facilities were used for long periods of time and the majority of the items used were not recorded. Therefore, it becomes difficult to select a functional unit and quantify the environmental impacts related to the contamination of a specific type of ammunition.

The exposure of animals and humans to ammunition contamination has been also conducted. That studies were mainly focused on lead poisoning due to unintentional consumption of lead fragments or animals contaminated (Fisher *et al.*, 2006; Green and Pain, 2012). The consumption of meat contaminated with lead and other heavy metals by humans (Green and Pain, 2012), and human exposure to lead by direct inhalation at small calibre ammunition shooting ranges (Bonanno *et al.*, 2002) was also assessed. In addition, some studies have been focusing in the assessment of fate of energetic materials - monitoring dissolution rates of composition B on soils (Lever *et al.*, 2005), and the fate of TNT in marine ecosystems (Smith *et al.*, 2015) -, and the toxicity effect of new energetic material for some species - for instance, the ecotoxicological effects of DNAN for bacteria, algae, terrestrial plants, and earthworms (Dodard *et al.*, 2013; Liang *et al.*, 2013).

The aforesaid studies are based on monitoring individual aspects and lack a holistic view that is possible to address with the life-cycle perspective. Therefore, the evaluation of ammunition contamination carried out only for some substances and on some toxicity parameters is insufficient to ascertain all the potential toxicity burdens. It is important to move forward and use all the data from the characterisation and quantification of the emissions to quantify the potential toxicity impacts. Beyond the impacts regarding the use of ammunition, is important to note that the production and disposal of ammunitions can present significant environmental burdens. However, usually only the risk and safety issues are addressed for these life-cycle phases of ammunition, and the environmental and toxicological issues are not covered.

A scientific gap to assess the environmental and toxicological impacts related to the life-cycle of ammunition is evident. The employment of Life-Cycle Assessment methodology to ammunition can provide an appropriate tool to improve the environmental profile of ammunitions in order to close the gap observed in the quantification of environmental consequences from ammunition contamination. Employment of life-cycle impact assessment methods can also improve the environmental and toxicological assessment of ammunition. Predict the behaviour on the environment and the inherent toxicity effects of energetic materials (or other substances) by experimental studies is time consuming and costly. The employment of models that calculates their physicochemical properties – EPi suite (Estimation Programs Interface developed to estimate the physical/chemical property and environmental fate) or QSAR (Quantitative structure–activity relationship) – coupled with other models that relies on that information, and average environmental characteristics, to determine the fate and exposure of substances, is a solution to facilitate the determination of the substance behaviour on the environment. USEtox method, based on the physicochemical properties and environmental characteristics, can provide the information required to assess the potential toxicological impacts, which is described in more detail in Section 2.3.

2.1.1 Life-Cycle Assessment of ammunition

The main problem opposing the pursuit of the environmental assessment of munitions is the absence of a suitable methodology to evaluate these impacts and rank the different alternatives from an environmental point of view. Several attempts have been made to overcome this problem. The UK has developed the POEMS methodology (UK MOD, 2011) to assess the impacts for the procurement and acquisition of new military platforms. This methodology includes the life-cycle perspective so all the life-cycle phases are considered. The evaluation of the importance of a certain impact is carried out by calculating a priority score based on the attribution of a value to the severity and to the frequency to that impact. The priority score is obtained by multiplying the severity and frequency, in which values range from zero to six and are defined by the experts involved in the evaluation. Values of the score above twelve classify the impact as medium priority and above twenty four it is classify as high priority. The prioritisation of the environmental impacts presents some limitations associated with the generalisation of processes. This methodology is focused on the impact evaluation of platforms (e.g. ships, aeroplanes), so small items as munitions usually obtain a low value score, even if they are used in large quantities because that cumulative effect is not considered. Moreover, the comparison of scores between projects is not possible and the scoring, even attributed by experts, is generally subjective.

MIDAS (Chemical Compliance Systems, 2011) is also a method that provides a score of the environmental performance of munitions. This method enables the selection of the parts that constitutes the ammunitions and then provides a final score related to three normalised criteria: ecological score, health score, and safety score. However, the results provided are very broad, subjective, and presented as a black-box. It is not possible to know what is contributing to the impact as well as ascertain the reasons that a “green” alternative has a lower score. Therefore, the assessment of the eventual environmental benefits from different specific production, use, or disposal options is difficult to evaluate.

The studies considering environmental issues associated with ammunition are very scarce. In 2001, six different techniques for ammunition decommission, considering safety issues but also including, for the first time, environmental issues, were compared (Duijm and Market, 2002). Duijm and Market (2002) employed a multi-criteria decision analysis in which air emissions and solid waste were the environmental topics addressed. LCA studies that cover military systems are even scarcer mostly due to lack of data. Collection of data is the most time-consuming phase in a LCA study, and for military systems this difficulty is increased as the databases used in LCA studies (such as Ecoinvent) are not properly adapted for ammunition as none information regarding the production of military explosives and propellants exists. Furthermore, the information on literature is either scarce, rather outdated, or might be protected by military trade secret. These difficulties tend to hinder LCA studies significantly. Nevertheless, since 2004 were published some Life-Cycle Assessment studies about military systems, demonstrating the feasibility of this methodology.

Hochschorner (2004) carried out a thesis with the aim to provide suggestions on how to consider environmental issues for the acquisitions of defence material in Sweden, taking into account the full life-cycle of those products. In his thesis Hochschorner (2004) stated that an environmental life-cycle perspective is important in order to contemplate the most significant environmental aspects. Hochschorner *et al.* (2006) also assessed the environmental impacts of a pre-fragmented high explosive grenade. One objective of the study was to demonstrate the applicability of LCA to military systems, showing the most significant environmental burdens of the grenade. Hägvall and Tryman (2010) also conducted a LCA to grenades, in which was compared a typical smoke grenade with a "greener" grenade using an eco-design approach for the production phase. They concluded that the new design will reduce the impacts by approximately 50%, mainly due to the use of lighter and reusable materials in production.

Alvebro *et al.* (2009) assessed two decommission paths for grenades (open detonation and incineration in a static kiln) identifying the environmental advantages and disadvantages for each process. Alvebro and co-authors (2009) concluded that disposal by incineration in a static kiln with emission controls presents lower impacts in comparison with the other techniques. Nevertheless, due to its very broad scope, this study has some significant limitations: it considered values based on the maximum legally permitted emissions rather than real emissions, and did not take into account the equipment manufacture, transport, and use.

The definition of the functional unit is of major importance in LCA studies. The functional unit is a reference relating the system inputs and outputs, which is required to ensure that different LCA studies can be compared (ISO 14040, 2006). A detailed observation of the LCA studies related to ammunition mentioned above allows to conclude that they adopted the ammunition under analysis as the functional unit (Hochschorner (2006) - 100 grenades; Hägvall and Tryman (2010) - 80 grenades; Alvebro *et al.*, (2009) – 100 grenades). Selecting this type of functional unit narrows the possibility to relate the results from the LCA studies with other types of ammunition significantly different in concept. It is relevant to provide a functional unit which delivers an appropriate indication of the ammunition function, such as the ammunition energy content (TNT equivalent) or the efficiency to destroy a specific target.

For the last ten years NATO has been organized some technical groups to combine the knowledge of industry and academic institution of many countries to discuss the environmental problems associated with the military systems (RTO 2010; RTO 2014; RTO 2015). Moreover, the European Defence Agency (EDA) has been supporting European projects with the same purpose. The participation on one EDA project - Environmentally Responsible Munitions (ERM) – and several AVT technical groups provided essential information to conduct the life-cycle assessment studies. The information acquired with the participation of different countries was an asset to overcome the limitation of data and assess the life-cycle environmental impacts associated with munitions. It is important to demonstrate that the potential conclusions drawn from these studies outweigh the effort needed to overcome the difficulties stemming from data collection, and contribute to facilitate future studies about ammunition.

2.2 Overview of toxicity legislation in EU

War scenarios are not the focus of this PhD thesis; however it is important to recognise that exists legislation to protect environmental resources from formal war conflicts. The Geneva Convention has imposed some laws that prohibit “widespread’, ‘long-term’ and ‘severe’ damage to the natural environment (Hulme, 2008). Moreover, the Protocol I from the Geneva Convention states that targets should be solely related to military objectives excluding political, economic or civilian targets – which include the environment (Francis, 2011).

Nowadays, REACH regulation can pose a significant concern for the European defence capabilities and industrial base regarding the full life-cycle of the military systems (design, procurement, production, use, and disposal). Substances as dibutyl phthalate (a plasticizer used in gun propellants) already need an authorization to be produced or imported to Europe, and others (e.g. RDX; 2,4-dinitrotoluene; di-isobutyl-phthalate) are also in risk to be restricted. The restrictions to the production, importation, and use of these substances can seriously impact the operability of the defence industry, as is difficult to comply with REACH regulation and present alternatives that maintain the required performance level (EDA, 2016).

Before REACH was implemented, chemical substances were classified for their toxicity in the form of a legal imposition or the producers delivered a self-classification (Oltmanns, 2014); thus an overview of the legislation prior to REACH is presented. Warhurst (2006) described in detail the regulatory system before REACH, stating that the system could be divided into four types of regulation: i) Council Directive 67/548/EEC was the first regulation published in Europe, which created a standardised system for classification, packaging and labelling of dangerous substances. Since its publication this directive has been revised many times, and in 2008 it was replaced by the Regulation (EC) No 1272/2008 – Classification, labelling and packaging of substances and mixtures – which is a complement to REACH regulation; ii) Directive 76/769/EEC – Restrictions on the marketing and use of certain dangerous substances and preparations – provided restrictions for specific uses of chemicals. This regulation only restricted the use of substance in the market, instead of banning their use; iii) Directive 79/831/EEC – New chemicals regulation – imposed that new substances, with quantities higher than 10 kg/year since 19th September 1981, needs to go through some type of assessment before being introduced in the market. This regulation is more proactive than the restriction on use which only applies until it is shown that substances already in the market are dangerous; iv) Regulation 793/93 – Evaluation and control of the risks of existing substances – applied to the substances already on the market. This regulation can also be seen as proactive because it aims to look and evaluate chemicals of concern, instead of expecting that some alarm occurs.

The previous legislation has some drawbacks that eventually leaded to the creation of REACH. The main problems were associate with the lack of information available related with toxicity and with the uses that the existing chemicals had. In addition, the regulator had a great difficulty to assess the risks. These drawbacks originated an insufficient protection of the human health and ecosystems (Warhurst, 2006). Moreover, the awareness to toxicity exposure increased amongst activist, the media, and the general population. Therefore, the pressure over governments to act and protect the population from chemicals toxicity increased. Another driver that helped to create the REACH regulation was the gradually development of a legal agenda for risk management which includes the precautionary principle (Petry *et al.*, 2006).

2.2.1 REACH regulation

REACH is a European Union regulation concerning the Registration, Evaluation, and Authorisation of Chemicals. REACH places the responsibility on industry to assess and manage the risks that chemicals can present to human health and the environment. The principal aim of REACH is to enhance the protection of human health and ecosystems as well as improve the competitiveness of the European chemical industry (European Commission, 2006; Askham *et al.*, 2012). Another important objective of REACH regulation is to encourage, and in some circumstances to guarantee, that substances reported as harmful are eventually replaced by available and viable (economically and technically) alternatives with lower toxicity (European Commission, 2006).

The three main processes of REACH regulation – Registration, Evaluation and Authorisation of chemicals – are now detailed. Registration is intended to register all chemicals manufactured or imported at more than 1 ton/year in Europe. On contrast with previous regulation no distinction is made between new substances or substances already in the market (Hansen *et al.*, 2007). The information required is registered at European Chemical Agency (ECHA) and is related with its uses and with physicochemical properties. As the tonnage produced or imported per year increases the information required also increases, in which is also needed data about other toxicity and ecotoxicity properties (Cohen, 2011). Evaluation is the step in which the government evaluates the information provided in the registration. The information is checked to ensure compliance with REACH, evaluating the danger a substance can pose to human health or environment (Cohen, 2011). The evaluation can lead to additional testing, recommendations, or restrictions (Hansen *et al.*, 2007).

In Authorisation, the substances of very high concern (SVHC) – PBT; vPvB, and CMRs (carcinogens, mutagens and substances toxic to reproduction) –, are identified accordingly with criteria outlined in Annex XIII. The substances which exceeds the limits imposed are nominated to a candidate list and prioritized to be restricted or banned (Cohen, 2011). For these substances an authorisation for their use is required, which can be obtained if one of two requirements is meet: demonstrate that the use of the chemical is controlled and safer; or that there is a socioeconomic need for its use (Hansen *et al.*, 2007).

Part of this PhD thesis is focused on improving the authorisation process that deals with the classification of SVHC. As mentioned before, substances of very high concern (SVHC) are classified accordingly with criteria outlined in Annex XIII of REACH, in which limits are established for the physicochemical properties of the substances that are assumed to characterize its hazard to human health and ecosystems. The properties considered in Annex XIII are related to persistence (water, soil, and sediment), bioaccumulation and toxicity, in which two levels of regulatory limits are established: one level with lower demanding limits which classify the substance as persistent, bioaccumulative or toxic (PBT); and other with higher requiring limits that classify the substances as very persistent or very bioaccumulative (vPvB). The violation of only one of the regulatory limits is sufficient to classify a chemical as SVHC.

Underlying the employment of this classification system are the following ideas: i) the potential consequences to human health and ecosystems associated with the emission of a certain substance are essentially dependent on a restricted number of the substance´s properties, ii) the regulatory limits are equivalent from the perspective of the potential consequences to human health and ecosystems, iii) the consequences to human health and ecosystems arising from the emissions associated with the unrestricted production and use of substances exceeding those limits are unacceptable, so they need to be replaced by suitable alternatives.

These aforesaid ideas raise several issues that need to be clarified. It is necessary to understand if, individually, the properties associated with persistence, bioaccumulation, and toxicity are representative of the behavior of substances in the environment, and if the limits established by REACH for each one of that properties are equivalent from the point of view of the potential toxicological impact. It is also necessary to ascertain if other physicochemical properties, not considered in the SVHC classification, as well as if the combinatorial effect of different properties, pose a significant contribution to the impact. In fact, Petry *et al.* (2006) show some apprehension on prioritizing substances based solely on some inherent psychochemical properties, which can bias the classification. As stated by Blainey *et al.* (2010), even if the imposition of limits is an applicable manner to compromise regulatory criteria, the SVHC identification procedure cannot be perceived as absolute scientific criteria for the assessment of the consequences to ecosystems and human health, due to the potential importance of the combinatorial effect of different properties to the impact. Therefore, this PhD thesis intends to contribute to the clarification of the issues pointed before, focusing on comprehending the importance of the combinatory effect of different physicochemical properties to the toxicological consequences on human health. Furthermore, it is also proposed a classification system based on toxicological impacts that includes the influence of combining the physicochemical properties and environment characteristics, as an alternative to analyzing only the limits for physicochemical properties.

2.3 USEtox method

Assessment of toxicity impacts on human health and ecosystems are of central importance even for Life-Cycle Assessment studies. However, different Life-Cycle Impact Assessment methods usually fail to arrive at the same toxicity impact for a certain substance (Caneghem *et al.*, 2010; Mattila *et al.*, 2011), thus toxicity issues are not typically addressed in LCIA. The high uncertainty related with the toxicity characterisation factors (approximately twelve orders of magnitude) also contributed to neglect the toxicity issues (Rosenbaum *et al.*, 2008).

Recently, the USEtox method was developed with the aim to improve the toxicological assessment in Life-Cycle Assessment studies. In 2008, the USEtox method was recommended by UNEP/SETAC, reaching for the first time consensus on how to calculate chemical characterization factors in LCA. The consensus was obtained essentially due to i) the largest substance coverage presently available; ii) the transparent calculation of characterisation factors; and the lower estimated uncertainty (100 – 1000 for human health, and 10 – 100 for freshwater ecotoxicity) in comparison with previous LCIA methods (Rosenbaum *et al.*, 2008). The USEtox impact categories were also recommended by the European Commission's Joint Research Centre to assess toxicity impacts (EC-JRC, 2011).

The USEtox method calculates the characterisation factors (CF) to human toxicity (cancer and non-cancer) and ecotoxicity based on fate, exposure and effect factors (Rosenbaum *et al.*, 2008). The three factors mentioned before are calculated based on the physicochemical properties and the environmental characteristics that influences the fraction of chemical substance that exchange between the different compartments (air, water and soil) – fate; the real fraction taken (bioaccumulated) by the organisms – exposure; and the toxicity for humans and different trophic organisms (e.g. plants, microorganisms, algae, fish) – effect (Rosenbaum *et al.*, 2008). Therefore, the USEtox method converts the physicochemical properties and the environment characteristics into potential impacts for ecosystems and human health. Figure 2.1 shows the framework of USEtox to calculate the toxicity characterisation factors that are used to assess the potential toxicity impacts.

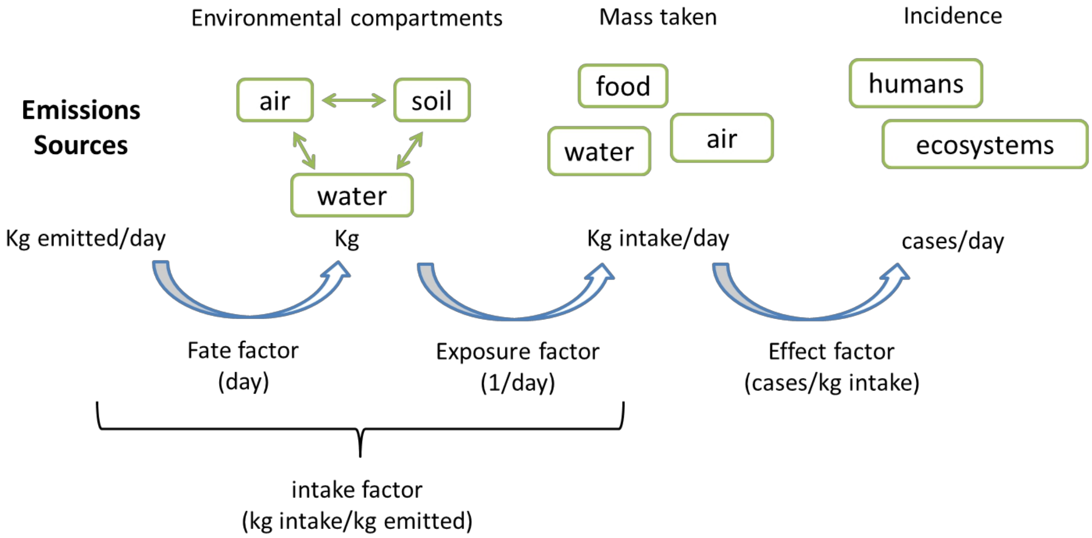

Figure 2.1. USEtox framework for calculating the toxicity impacts on human health and ecosystems (adapted from Fantke *et al.*, 2015).

USEtox provides the possibility to select where the emission will occur. Among the different options, USEtox considers six environmental compartments: urban air, continental air, freshwater, sea water, natural soil, agricultural soil. The selection of an emission compartment is necessary to determine the partition of a substance to different media (e.g. air, soil). Each one of these media has its own environmental characteristics that will determine the behaviour of a substance on the environment (the fate and exposure). USEtox method also allows choosing between a global or continental scale.

The toxicological impacts are expressed in comparative toxicity units for human health (CTUh) and ecosystems (CTUe). Rosenbaum *et al.* (2008) described in detail the units for characterization factors, defining Human Toxicity as “provides the estimated increase in morbidity cases in the total human population per unit mass of a chemical emitted” and Ecotoxicity “provides an estimate of the potentially affected fraction of species (PAF) integrated over time and volume per unit mass of a chemical emitted”.

Despite the consensus that USEtox reached, the method still contain some concerns related with uncertainty. In order to display a robust toxicity assessment, USEtox method has provided two sets of characterisation factors (recommended and interim) based on the level of reliability of the toxicity assessment. The recommended characterisation factors are the ones that have reached a scientific consensus, whilst the interim characterisation factors are classified as provisional due to the relatively high uncertainty (Rosenbaum *et al.*, 2008). Metals, amphiphilic, and dissociating substance are classified as interim in USEtox, so the use of characterisation factors for these substances should be used with great caution due to inherent uncertainty (Rosenbaum *et al.*, 2008). These substances show a high uncertainty due to deficiencies in the model to consider the substances complex behaviour on the environment or the lack of available substance data (Fantke *et al.*, 2015).

Chapter 3 - Life-Cycle Assessment of production and use of ammunition

Summary: This section includes the assessment of the main environmental hotspots associated with the life-cycle of ammunition. Due to absence of life-cycle databases, the creation of "gate-to-gate" life-cycle inventories associated with energetic material production is the base to assess the life-cycle environmental impacts of ammunition. Section 3.1 provides the novel "gate-to-gate" life-cycle inventories of energetic material. The procedures to create the inventories to any energetic material are also provided. A comprehensive analysis is also carried out which compare the production impacts of energetic materials with the impacts associated with the production of common chemicals. The main environmental and toxicological impacts related to the production and use phase of ammunition are also highlighted in this section. For that purpose, LCA is employed to calculate the environmental and toxicological impacts of two applications: the production and use of generic large calibre ammunition (section 3.2); and the comparison of the production and use of four types of small calibre ammunition (section 3.3). Section 3.4 provides an evaluation of the magnitude and significance of the impacts of ammunition based on normalisation factors from the domestic emissions for Europe.

3.1 Energetic material production

This section describes the life-cycle model developed for the energetic material production. The difficulty to obtain data is significantly noticeable for the production of energetic materials, principally due to information confidentiality. Companies are not comfortable to provide data that can be covered by intellectual property or industrial secret which leads to scarcity of information regarding raw material, energy consumption, and emissions. The most common life-cycle databases do not cover this type of products, so data regarding the production and use of explosives is not available, as well as the chemicals used in their production, hindering the environmental impact assessment of explosives. In fact, in the Ecoinvent database the only information available refers to a civil explosive for which the data about its production was obtained based on estimations as almost no real data was available (Kellenberger *et al.*, 2007).

The life-cycle inventories created were principally based on literature which covers information regarding the materials and energy used for the energetic material production. When the information from literature was scarce, or even for situations where the information was absent, the life-cycle inventories were created based on the procedure developed by Hischier *et al.* (2005), as was implemented in other LCA studies (Zackrisson *et al.*, 2010; Schlanbusch *et al.*, 2014; Wang and Yuan, 2014). This approach suggests: using an efficiency level of 95 % for the stoichiometric chemical equation to account for raw materials consumption; basing consumption of electricity and heat on average values (0.33 kWh and 2 MJ per kg of product) that are typical of the chemical industry (Gendorf, 2000); and estimating that 0.2 % of the input materials will be emitted into the air.

The life-cycle inventories of the production of twenty energetic materials was implemented: TNT, RDX, HMX, PETN, nitroglycerine, nitrocellulose, nitroguanidine, black powder; picric acid, mercury fulminate, lead aside, DDNP, tetrazene, lead picrate, lead styphnate, barium nitrate, antimony sulphide, lead dioxide, zinc peroxide, and calcium silicide. Life-cycle inventories to intermediary substances used to produce the energetic materials and primers that are not presented in the Ecoinvent database were also created, such as hexamine, pentaerythritol, and guanidine nitrate. Moreover, the inventory for gun powders (single, double and triple base powders) and two explosive mixtures (composition B and C4) were also developed. The inventories of the twenty energetic materials created are detailed in Appendix III.

Based on the life-cycle inventories of the energetic materials, and using the CML and USEtox life-cycle impact assessment methods, were calculated the environmental and toxicological impacts for the following most common explosives: black powder, TNT, RDX, HMX, PETN, nitroglycerine, nitrocellulose, nitroguanidine. Table 3.1 shows the life-cycle impacts associated with the common used energetic materials with a legend describing the type of data used: I – material and energy consumption from literature (emissions calculated based on Hischier *et al.* (2005)); II – only material consumption from literature (energy consumed and emissions calculated based on Hischier *et al.* (2005)); III – only stoichiometric calculations (materials, energy consumed, and emissions calculated based on Hischier *et al.* (2005)).

Table 3.1. Impacts per kg of type of energetic material produced.

Impact category	Black Powder (II)[*]	HMX (II)[#]	Nitrocellulose (I)[*]	Nitroglycerine (II)[*]	Nitroguanidine (II)[*]	PETN (II)[*]	RDX (II)[*]	TNT (I)[*]
Abiotic depletion (kg Sb eq.)	3.53E-02	**3.43E-01**	1.97E-02	2.75E-02	1.48E-01	7.07E-02	4.72E-02	2.71E-02
Acidification (kg SO_2 eq.)	3.45E-02	1.35E-01	9.03E-02	3.44E-02	**1.49E-01**	2.39E-02	2.45E-02	6.19E-02
Eutrophication (kg PO_4^{-3} eq.)	9.06E-03	**5.38E-02**	2.00E-02	8.92E-03	3.84E-02	3.41E-03	1.03E-02	5.46E-03
Global warming (kg CO_2 eq.)	1.29E+01	**4.24E+01**	6.53E+00	5.85E+00	3.21E+01	5.37E+00	8.59E+00	5.06E+00
Ozone layer depletion (kg CFC-11 eq.)	5.15E-07	**3.92E-06**	3.74E-07	1.96E-06	1.62E-06	1.34E-07	5.34E-07	1.88E-07
Photochemical oxidation (kg C_2H_4 eq.)	2.29E-03	**2.58E-02**	2.72E-03	1.22E-03	**2.53E-02**	1.04E-02	7.73E-04	2.09E-03
Primary energy (MJ prim.)	8.95E+01	**7.82E+02**	5.72E+01	6.56E+01	3.23E+02	1.54E+02	1.02E+02	6.10E+01
Human toxicity, cancer (cases)	3.31E-10	2.17E-09	3.20E-10	2.58E-10	1.00E-09	**1.12E-08**	9.37E-10	1.24E-10
Human toxicity, non-cancer (cases)	1.31E-09	6.41E-09	**5.07E-08**	9.20E-10	3.76E-09	8.47E-10	8.25E-10	5.90E-10
Ecotoxicity (PAF.m^3.day)	3.22E-03	6.62E-01	**1.34E+01**	2.47E-03	1.11E-02	2.26E-01	5.06E-02	1.78E-03

[*] source of information based on Urbansky (1968, vol. 1-4); [#] source of information based on Fedoroff *et al.* (1960).

It is observed that HMX is the substance with higher impacts for six out of the ten impact categories, mainly due to the complex syntheses which requires more raw materials than the other energetic materials. Nitrocellulose shows significant impacts for non-cancer Human Toxicity and Ecotoxicity principally associated with the emissions of insecticides into the soil (Profenofos, Cyfluthrin, Chlorpyrifos, and Aldicarb) for the cultivation of cotton (main raw material used for the production of nitrocellulose). Nitroguanidine and PETN presents higher impact for Acidification and cancer Human Toxicity, respectively, both due to the main raw material production. As for the Acidification category, guanidine contributes to 65 % of the total impact for the production of nitroguainidine; whilst the emission of formaldehyde associated with the manufacture of pentaerythritol dominates (higher than 95 %) the impact associated with PETN production for cancer Human toxicity.

The data used to create the life-cycle inventories for the energetic materials, as mentioned before, were mainly from literature sources or assumptions carried out in the absence of those sources. Therefore, the impact associated with the energetic material production and some common chemicals are compared in order to evaluate the burdens of energetic materials with the burdens of well-known substances. Four chemicals from four different arbitrarily selected chemical groups were selected: an alcohol (ethanol), an aldehyde (formaldehyde), an aromatic (benzene), and a CFC (trifluoromethane). The impacts related to the production of the selected chemicals were calculated based on inventory data from Ecoinvent (Althaus *et al.*, 2007), and using the life cycle impact assessment methods CML and USEtox.

Figure 3.1 presents the life-cycle impact for eight energetic materials and the four aforesaid chemicals. Is it possible to see that the energetic materials present higher impact than the chemical substance selected as reference for all the categories, with exception of trifluoromethane which shows the higher impact for three impact categories (Photochemical oxidation, cancer, and non-cancer Human Toxicity). The reason for the higher impacts associated with energetic material production is possibly related to the nitrification process which implied the use of high quantities of strong acids such as nitric acid or sulphuric acid. Nevertheless, not considering the outliers (HMX and nitroguanidine), the impacts related with energetic materials are similar or only one order of magnitude higher with the ones obtained for the selected chemicals.

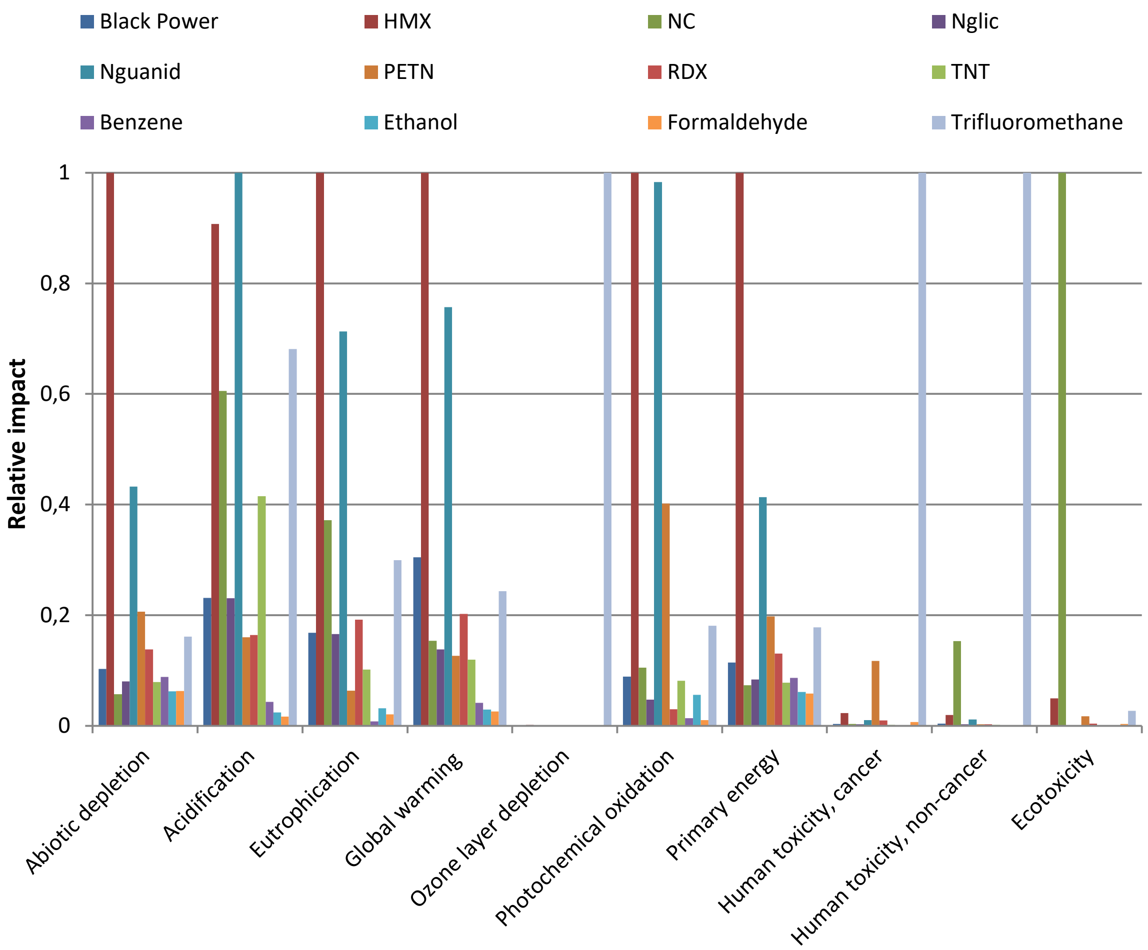

Figure 3.1. Impact comparison for the production of eight energetic materials and four common chemical substances.

The employment of the recommendations presented before to create life-cycle inventories of energetic materials will facilitate the Life-Cycle Assessment studies of ammunition. In fact, the assessment carried out for the energetic materials is ground-breaking, and provides the information necessary to overcome the obstacle of data scarcity. This procedure, even if rather crude, is an alternative to neglecting explosives (and chemicals) in LCA. The impact assessment done to energetic materials can contribute to minimize the information scarcity associated with the environmental impact assessment of ammunition, as for the other materials (metals, plastics) the data are well-known and thoroughly studied. The life-cycle inventories created can be used as a baseline by ammunition producers, designers, or researchers interested in this topic, to extrapolate the recommendations to other types of energetic materials not covered in this study in order to evaluate and provide appropriate alternatives in an environmental perspective.

3.2 Generic 155 mm ammunition[1]

This section describes the work carried out as part of a contribution to the report developed for the NATO task group RTO-TR-AVT-179 - Design for Disposal of Present and Future Munitions and Application of Greener Munition Technology (RTO, 2014). The main objective of this task group was to present tools that can be used in an environmental assessment in order to minimize the impact of all processes governing military activities. The Portuguese contribution for that report was to demonstrate the feasibility and the type of information obtained when the LCA methodology is employed to quantitatively assess the environmental impacts associated with production, use and disposal of ammunitions. For that purpose a generic 155 mm ammunition was selected, since it was representative of many similar ammunition of this calibre, as agreed by the researchers who participated in the aforementioned AVT-179 task group.

3.2.1 Life-Cycle Inventory for production and use of a generic 155 mm ammunition

Figure 3.2 shows the Life-cycle model that includes the production and use of the generic 155 mm ammunition. The data associated with the production phase are essentially the raw materials production; whilst for the use phase the emissions from the combustion of the propellant and the detonation of the warhead were considered. Assembling is the only process not accounted in the model due to lack of data (e.g. energy consumption). The functional unit was defined as a generic large calibre 155 mm ammunition.

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[1] *Significant portions of this section appear in: Ferreira C, Ribeiro J, Almada S, Freire F (2017) Environmental Assessment of Ammunition: the Importance of a Life-Cycle Approach, Propellants, Explosives, Pyrotechnics 42: 44-53. DOI: 10.1002/prep.201600158*

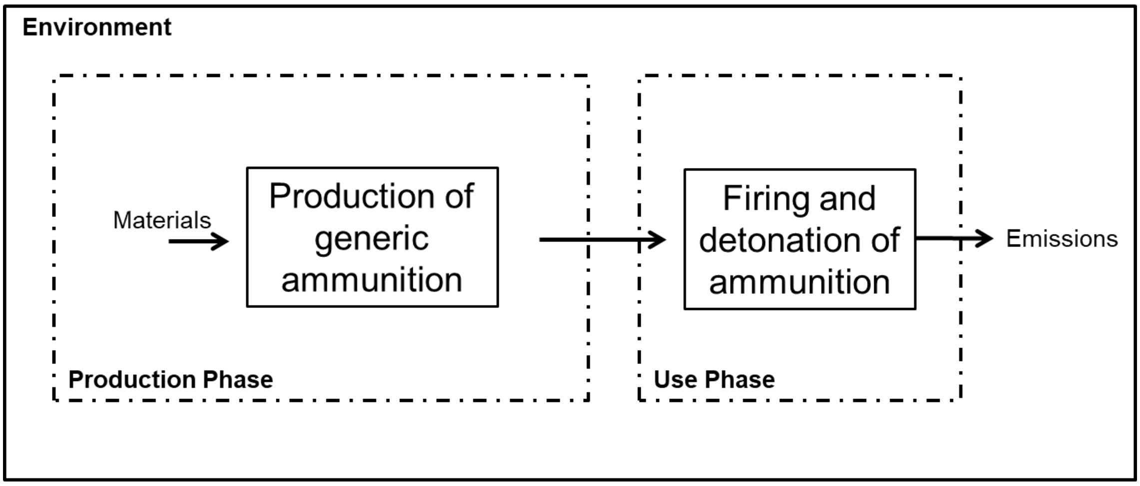

Figure 3.2. Life-Cycle model associated with the generic ammunition.

Table 3.2 shows the constituents of the generic 155 mm ammunition. The total weight of the ammunition is 77.192 kg (22 kg container + 55.192 kg projectile). It was assumed that the container is reused by 10 ammunition. Figure 3.3 shows a representation of the main components of the generic 155 mm ammunition: projectile, fuze, propellant charge and container.

Table 3.2. Components of the generic 155 mm ammunition.

Ammunition components		Amount (kg)
Warhead	Steel casing	35.5
	Copper (driving band)	0.5
	Composition B	8.5
	PETN (booster)	0.02
Propellant Charge	Triple base powder	9.5
	Black powder (primer)	0.055
	Boron-potassium nitrate (igniter)	0.03
	Lead (decoppering agent)	0.085
Fuze	Aluminium	0.45
	Brass	0.45
	Electronic parts	0.1
	RDX (detonator)	0.002
Container	Steel	22.0

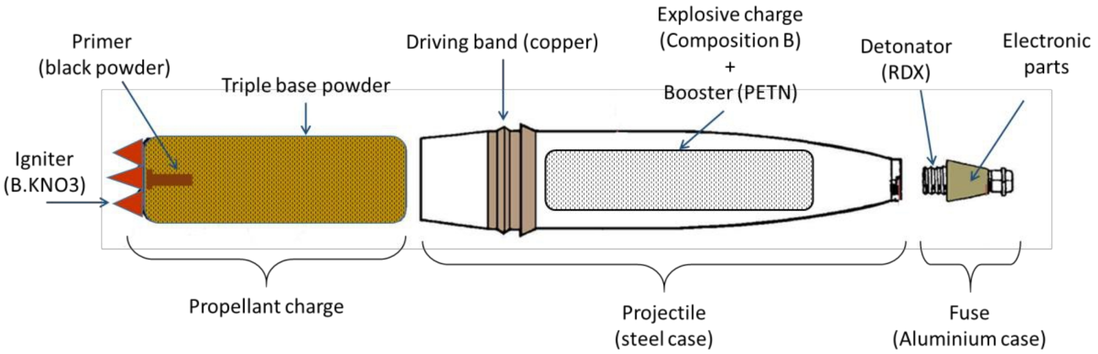

Figure 3.3. Representation of the components that build-up the generic 155 mm ammunition (without the container).

For the use phase it was considered the emissions associated to the ammunition firing (point of fire) and detonation. The point of fire emissions were measured from a range of weapons fired in an enclosed facility operated by the Aberdeen Test Center, and the details about the tests carried out are described in Onasch *et al.* (2008). The capture of gaseous products and particulates was performed with a sampling probe located either fixed on a tripod or handheld during firing to obtain measurements at the desired locations (muzzle, breech, breathing zone). Then, the emissions were measured in a mobile laboratory stationed within 30 meters of the weapons systems. Muzzle plume emissions were sampled downwind for the 155 mm ammunitions using the sampling tripod mentioned above, in which twenty individual shots were fired. The emissions were provided in g/g propellant and can be associated to any type of similar 155 mm ammunition. The point of fire emissions associated with the combustion of the propellant for the generic 155 mm ammunition are shown in Table 3.3, in which the gaseous and fine particulate matter in the air was measured, but the energetic material that can be originated from the incomplete burning of the propellant was not sampled.

Table 3.3. Point of firing emissions associated with the generic 155 mm ammunition.

Emissions (kg/155 mm ammunition)			
Carbon dioxide	2.74E+00	Hydrogen cyanide	3.78E-02
Carbon monoxide	4.64E+00	Acrylonitrile	2.29E-05
Nitrogen monoxide	3.90E-04	Acetic acid	1.44E-04
Nitrogen dioxide	3.14E-04	Ethyl acetate	8.98E-05
Formaldehyde	8.63E-05	Furan (total)	8.98E-05
Acetonitrile	2.80E-04	Black carbon	1.55E-03
Acetaldehyde	3.20E-05	Sulphate	3.04E-04
Benzene	9.03E-04	Nitrate	1.22E-04
Ethylbenzene	2.19E-04	Ammonium	9.69E-05
Toluene	2.79E-04	PAH	2.85E-06
Styrene	4.87E-05	Lead (particulate)	4.30E-07

The U.S. Army Environmental Command (USAEC) established a program to measure emissions from the detonation of ordnance due to the lack of trustworthy data concerning emissions from training. The detonation emissions were published in the report from U.S. Army Environmental Command (2009) that comprehends air emission factors for three types of calibre munitions (81 mm; 105 mm and 120 mm) based on data obtained during training exercises at U.S. Army installations. The report mentioned above was selected because it has the major representation of substances measured and the sampling procedures carried out are reliable and consistent in accordance with EPA (Environmental Protection Agency) test methods or sound methodology which were reviewed by that agency Emission Measurement Center (US) (U.S. Army Environmental Command, 2009).

The emission factors were developed on a “per item” basis and are related to the detonation of a 120 mm projectile; however the report stated that the data significantly correlates with 155 mm ammunition detonation emissions. Table 3.4 shows the detonation emissions for the generic ammunition. Regarding the energetic materials sampled only nitroglycerine was detected; the concentrations for other energetic materials (e.g. TNT, RDX) were under the detection limits.

Table 3.4. Detonation emissions associated to the generic 155 mm ammunition.

Emissions (kg/155 mm ammunition)					
Carbon dioxide	1,91E-01	Phenol	4,09E-07	Antimony	1,50E-05
Carbon monoxide	4,54E-03	Phosphorus	3,86E-05	Arsenic	3,45E-07
Oxides of nitrogen	1,32E-02	Propinaldehyde	1,50E-05	Barium	1,32E-05
Sulphur dioxide	3,54E-04	Propylene	1,95E-05	Cadmium	2,32E-04
Acetaldehyde	3,04E-05	Toluene	1,04E-05	Magnesium	1,14E-01
Acetonitrile	2,68E-06	Xylene	9,08E-07	Manganese	6,36E-05
Acetophenone	1,09E-06	Acetylene	2,95E-03	Lead	3,31E-06
Ammonia	1,50E-05	Benzaldehyde	8,17E-06	Chromium	7,72E-06
Benzene	3,54E-05	2-butenal	2,41E-06	Cobalt	2,86E-06
Beryllium	9,53E-08	1-butene	3,81E-06	Copper	6,36E-06
Carbon disulphide	3,68E-06	Cis-2-butene	1,09E-06	Zinc	1,18E-04
Chloromethane	2,18E-06	Trans-2-butene	1,23E-06	Dioxin (total)	6,81E-12
Ethylbenzene	2,45E-06	Diethylphthalate	9,53E-07	Furan (total)	7,26E-06
Ethene	9,99E-05	Dodecane	1,95E-06	$PM_{2.5}$	7,26E-02
Formaldehyde	1,45E-05	Ethane	3,18E-05	PM_{10}	1,63E-01
Methylene chloride	1,68E-05	Hexaldehyde	5,90E-06		
2-methylnaphthalene	3,09E-07	Methyl ethyl ketone	4,99E-06		
Naphathalene	2,72E-06	1-propyne	1,54E-06		
Nitroglycerin	5,45E-06	Valeraldehyde	8,17E-06		

3.2.2 Life-Cycle Impact Assessment of a generic 155 mm ammunition

Firstly, the Life-Cycle Impact Assessment results associated with the main components of the ammunition (production phase) and associated with the firing or detonation emissions (use phase) are presented. A detailed analysis of the specific contributors to the total impact associated with the ammunition components and emissions (detonation and firing) are also presented.

Figure 3.4 presents the environmental and toxicological impacts calculated to the two life-cycle phases considered in this study (production and use) and the main contributors to that impact. It is observed that the impact associated with the production of the ammunition components is dominant to the environmental categories and the ecotoxicity category. For these categories, the impacts associated with the production of the ammunition components represent more than 80% to the total life-cycle impact (production and use phase), with exception of the photochemical oxidation category

(60%). The higher contributors to that impact share are related with production of the heavier parts of the ammunition: the propellant charge and the warhead. Eutrophication is the only exception in which the main contributor is associated with the fuze production (44%), mainly due to the production of the integrated circuit used on the electric components.

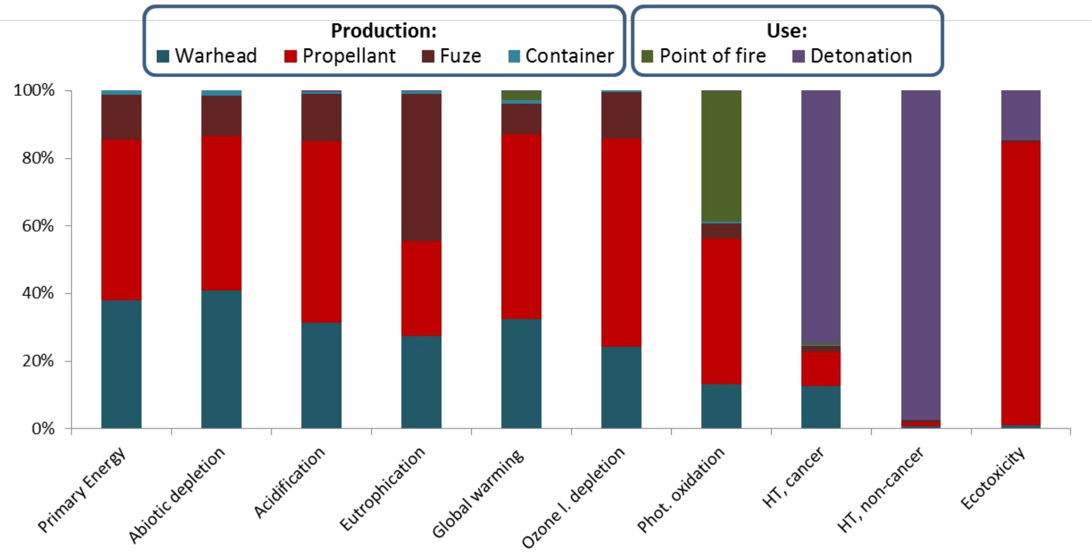

Figure 3.4. Life-Cycle impact contribution to the total impact of the generic 155 mm ammunition.

Figure 3.5 details the specific contributors to the total impact associated with the production of the ammunition components. The impacts associated with the warhead production are essentially due to production of the composition B and the steel confinement. Brass from the warhead also significantly contributes to the non-cancer Human Toxicity impact category. It is also shown that the impact associated with the propellant production, which completely dominates the ecotoxicity category (higher than 80%) and has a significant contribution to the ozone layer depletion and global warming impact categories (with a contribution higher than 50% in both cases), are mainly due to the triple base powder production. A detailed analysis allows us to observe that the impact related with the triple base powder production for ecotoxicity are essentially associated with the emissions of insecticides into the soil (Profenofos, Cyfluthrin, Chlorpyrifos, and Aldicarb) for the cultivation of cotton (used for the production of nitrocellulose that is one of the triple base powder major ingredient) that contributes proximally to 62% of the total impact for this impact category.

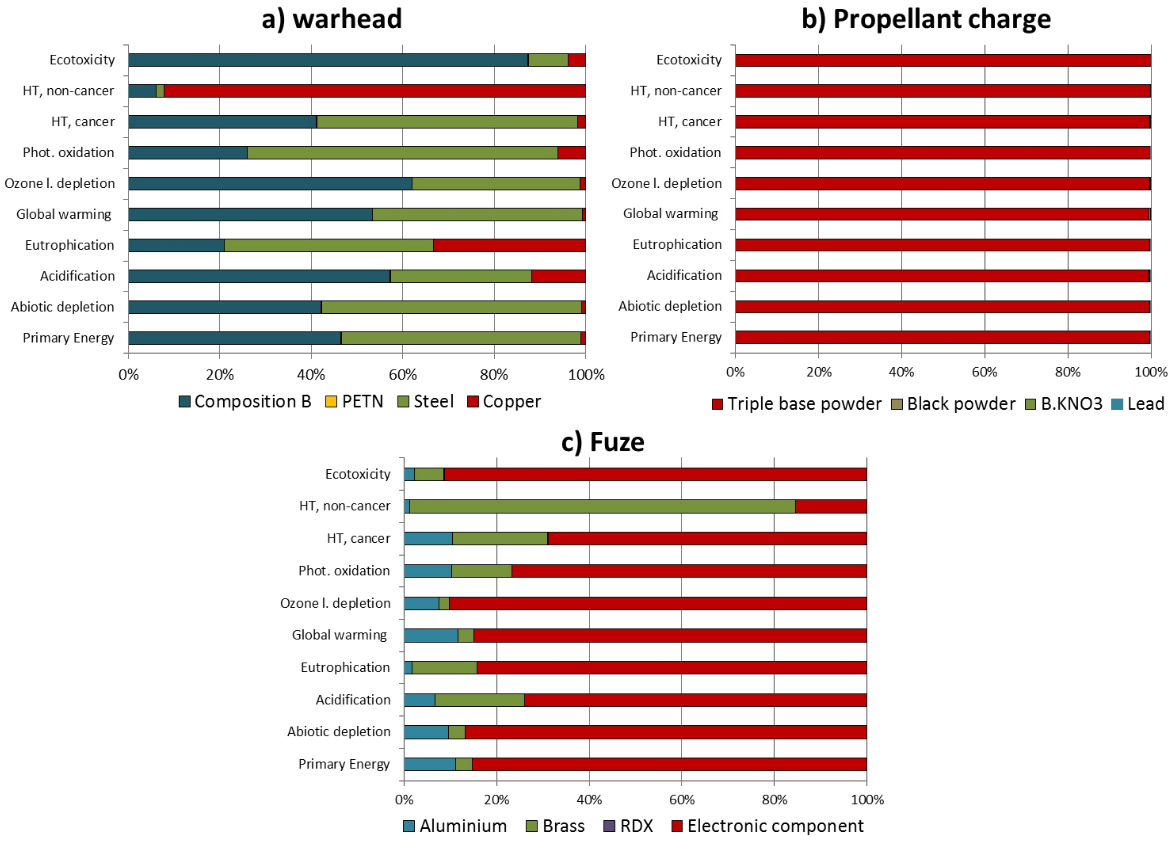

Figure 3.5. Main contributors to the impacts associated with the production of the main components of the generic 155 mm ammunition.

Figures 3.6 and 3.7 shows the contributors to the impact associated with ammunition firing and detonation during the use phase, respectively. The impacts for human toxicity (cancer and non-cancer effects) are completely dominated by the emissions of the detonation products associated with the use phase of the ammunition life-cycle. It is important to mention that the impacts associated with the emission from the detonation of the explosive are higher than the impacts associated with the emissions from the combustion of the propellant charge even if the mass of propellant is slightly higher than the mass of the explosive. The reason for this is related to the higher quantity of heavy metals contained in the detonation products as compared to the combustion products (see Table 3.3 and 3.4). The highest contributors to the impacts associated with the detonation emissions are cadmium, chromium VI, zinc, and lead. The only exception in which the point-of-fire emissions considerably exhibit higher impacts than the detonation emissions is to Photochemical Oxidation and Global Warming categories. The ammunition firing originates substantial higher emissions of carbon monoxide (1022 times higher) and carbon dioxide (14 times higher) than these emissions originating from ammunition detonation, producing the higher impacts mentioned above. Both emissions from firing and detonation do not have any type of impact for the categories Abiotic depletion and Ozone Layer Depletion.

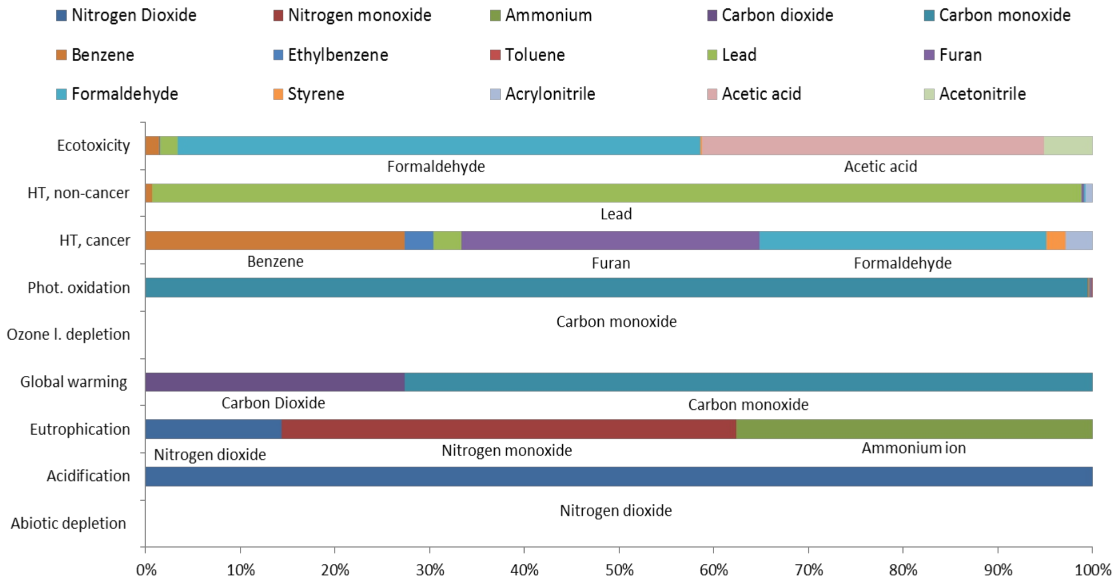

Figure 3.6. Main contributors to the environmental and toxicological impact categories associated with the firing emissions. Note: Abiotic depletion (kg Sb eq.); Acidification (kg SO_2 eq.); Eutrophication (kg PO_4^{-3} eq.); Global Warming (kg CO_2 eq.); Ozone L. Depletion (kg CFC-11 eq.); Phot. Oxidation (kg C_2H_4 eq.); cancer and non-cancer HT (cases); Ecotoxicity (potentially affected fraction of species (PAF).m^3.day).

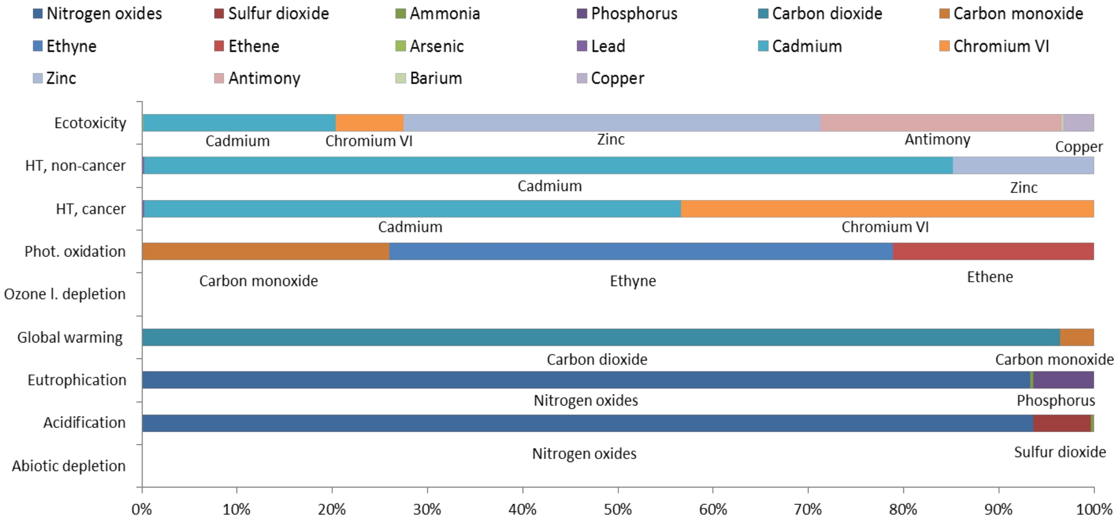

Figure 3.7. Main contributors to the environmental and toxicological impact categories associated with the detonation emissions. Note: Abiotic depletion (kg Sb eq.); Acidification (kg SO2 eq.); Eutrophication (kg PO4-3 eq.); Global Warming (kg CO2 eq.); Ozone L. Depletion (kg CFC-11 eq.); Phot. Oxidation (kg C2H4 eq.); cancer and non-cancer HT (cases); Ecotoxicity (potentially affected fraction of species (PAF).m3.day).

3.3 Small calibre ammunition[2]

The previous section offered an illustrated example of the assessment of life-cycle impacts and identified hotspots for the most relevant ammunition components. In addition, LCA can also be used to compare products with the same function from an environmental and toxicological perspective. The application of LCA to such objectives in the field of ammunitions was described in Ferreira *et al.* (2016) and the main findings of that study are presented in this section. In that paper an ecodesign study for small calibre ammunition whose objective was to identify the potential benefits from lead removal for small calibre ammunitions was presented. However, the consequences of using alternative materials in ammunition manufacturing also needs to be evaluated to ascertain the impact for all life-cycle phases and prevent potential trade-offs. Therefore, the main goal of this section is to assess and compare the environmental and toxicological impacts associated with the life-cycle of four types of 9 mm ammunitions. The four types are combinations of two different projectiles (steel jacket and lead core; copper and nylon composite) and two types of primers (lead primer; non-lead primer). It is also intended to identify opportunities to improve the environmental performance of the ammunition.

3.3.1 System description and Life-Cycle Inventory

A life-cycle model was developed for the production and use phase of four types of 9 mm ammunition based on primary data from the Romanian company U.M. Sadu – Gorj S.A. (production phase) and from Rotariu *et al.* (2015) (use phase). The data is representative for similar small calibre ammunition production in developed countries. Figure 3.8 shows the life-cycle model of the production and use of small calibre ammunition, including the recovery of the ammunition cartridge after firing. Direct emissions associated with the production phase, transport between different life-cycle phases and metal leaching associated with the projectile after firing is not included in the model. A 9 mm small calibre ammunition is defined as the functional unit.

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[2] *Significant portions of this section appear in: Ferreira C, Ribeiro J, Almada S, Rotariu T, Freire F (2016) Reducing impacts from ammunitions: a comparative life-cycle assessment of four types of 9 mm ammunitions, Science of the Total Environment 34-40: 566-567. DOI: 10.1016/j.scitotenv.2016.05.005*

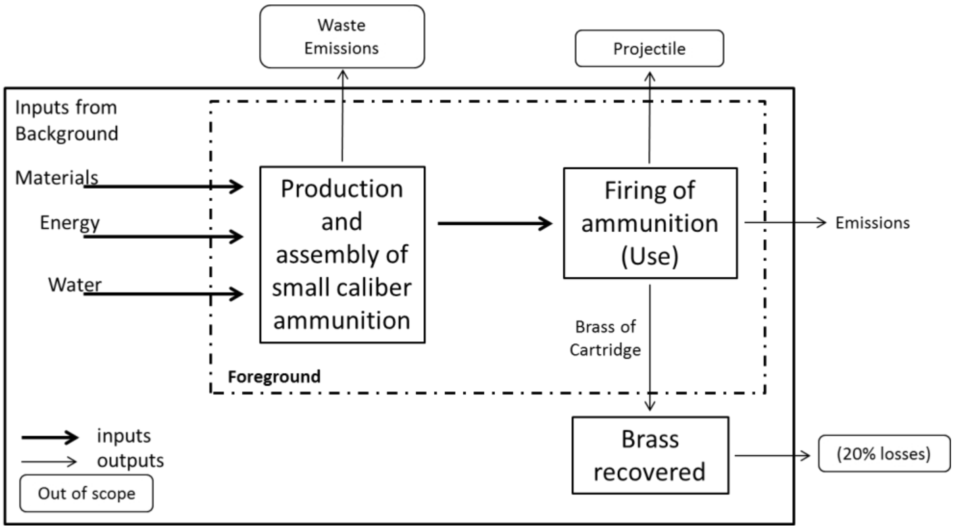

Figure 3.8. Life-Cycle model associated with small calibre ammunition.

A detailed Life-Cycle Inventory (LCI) for the production phase is implemented based on primary data collected from the Romanian company U.M. Sadu – Gorj S.A.. Figure 3.9 shows the combination between the different projectiles and primers for the four different small calibre ammunition, which are described as:

#1) FMJ-TRNPb - ammunition with a steel jacket and lead core bullet (projectile) and a lead primer (TNR-Pb - Lead trinitroresorcinate);
#2) FMJ-DDNP - ammunition with a steel jacket and lead core bullet (projectile) and a non-lead primer (DDNP – Diazodinitrophenol);
#3) Frang-TNRPb - ammunition with copper and nylon composite bullet (projectile) and a lead primer (TNR-Pb - Lead trinitroresorcinate);
#4) Frang-DDNP - ammunition with copper and nylon composite bullet (projectile) and a non-lead primer (DDNP – Diazodinitrophenol).

Figure 3.9. The four 9 mm small calibre ammunition, with combination of two different projectiles and primers (Rotariu *et al.*, 2015).

Table 3.5 shows the materials and components used in the production of the mentioned 9 mm ammunition. Table 3.6 presents the energy and water requirement for the manufacture and assembling of the ammunition, which is similar for the four types.

Table 3.5. Materials used for the production of four types of 9 mm ammunition.

	#1		#2		#3		#4	
	Constitution	Amount (kg)	Constitution	Amount (kg)	Constitution	Amount (kg)	Constitution	Amount (kg)
Cartridge	Brass	4.9E-03	Brass	4.9E-03	Brass	4.9E-03	Brass	4.9E-03
Projectile	Steel	3.9E-03	Steel	3.9E-03	Nylon	4.1E-03	Nylon	4.1E-03
	Lead	6.1E-03	Lead	6.1E-03	Copper	1.0E-03	Copper	1.0E-03
	Antimony powder	9.5E-05	Antimony powder	9.5E-05				
Primer	Brass	2.4E-04	Brass	2.4E-04	Brass	2.4E-04	Brass	2.4E-04
	TNR-Pb	1.0E-05	DDNP	6.3E-06	TNR-Pb	1.0E-05	DDNP	6.3E-06
	Tetrazene	1.3E-06	Tetrazene	1.3E-06	Tetrazene	1.3E-06	Tetrazene	1.3E-06
	Barium nitrate	4.9E-06			Barium nitrate	4.9E-06		
	Antimony sulphide	1.3E-06	Zinc peroxide	1.4E-05	Antimony sulphide	1.3E-06	Zinc peroxide	1.4E-05
	Lead dioxide	1.3E-06	Titanium powder	3.7E-06	Lead dioxide	1.3E-06	Titanium powder	3.7E-06
	Calcium silicide	1.3E-06			Calcium silicide	1.3E-06		
Propellant	Single base powder	4.1E-04	Single base powder	4.1E-04	Single base powder	4.1E-04	Single base powder	4.1E-04
	Cardboard	3.2E-04	Cardboard	3.2E-04	Cardboard	3.2E-04	Cardboard	3.2E-04
Total weight		**1.6E-02**		**1.6E-02**		**1.1E-02**		**1.1E-02**

Table 3.6. Energy and water requirement for manufacturing and assembling of a 9 mm ammunition.

Electricity	0.046 kWh/bullet
Natural gas	0.240 MJ/bullet
Water	2.042 kg/bullet

Assessment of the emissions associated with ammunition firing is performed following Rotariu *et al.* (2015), in which is provided information in more detail regarding the emission collection and analysis. A 9 mm lab weapon having the barrel tightly inserted in polyethylene recipients (HDPE 60L drums for the collection of solid residues and LDPE bags sheeted on wood frames – 250 to 500 L – for the collection of gaseous products and metallic fumes) is fired ten times for each type of ammunition. The metal content (Pb, Cu, Zn and Sb) in the residues and fumes are analysed using Atomic Absorption Spectrometry (AAS) and Scanning Electron Microscopy - Energy-dispersive X-ray spectroscopy (SEM-EDX). The gaseous emissions (CO_2, CO, HCN, NO, NO_2, NH_3, CH_4) are detected using freshly calibrated electrochemical sensors inserted in the recipients and two MiniWarn data acquisition systems (Draeger, Germany). The data is processed using the *Gas Vision 5.8.2* software.

Table 3.7 shows the emissions associated with the firing of the ammunition, in which the higher values are highlighted in bold for each emitted gas or metal. CO, NO and NO_2 emissions are similar for all the four ammunitions, while ammunition #1 and #2 have higher emissions for NH_3, HCN, CH_4, Pb and Sb. The ammunition with a composite projectile (#3 and #4) shows significantly higher emissions for Cu. The lead free ammunition (copper and nylon composite and non-lead primer) is the one presenting lower emissions of Zn and Pb, in comparison to the other three types of ammunition.

Table 3.7. Emissions associated with firing of four types of 9 mm ammunition.

Substance	**Emissions (mg/bullet)**			
	#1	**#2**	**#3**	**#4**
CO	**198.65**	**184.75**	119.21	118.76
CO_2	**101.79**	**96.79**	58.56	57.93
NO	3.80	3.22	3.85	**4.41**
NO_2	**0.64**	**0.62**	0.49	0.52
NH_3	**3.10**	**2.46**	1.67	1.84
HCN	**1.77**	**1.22**	0.18	0.13
CH_4	**1.10**	**0.96**	0.61	0.59
Pb	**3.14**	**1.04**	0.81	0.04
Cu	0.55	0.41	**4.85**	**5.21**
Zn	**0.12**	**0.11**	**0.19**	0.03
Sb	**0.37**	**0.20**	0.15	ND

ND – emission of antimony (Sb) for ammunition #4 was not detected.

3.3.1.1 Assumptions and Limitations

Some assumptions are made due to method limitation or lack of data. With regards to the projectile that after firing remains in the soil, it was not possible to obtain information concerning the quantity and nature of metals which are eroded and leached. Those impacts are influenced by soil and weather characteristics and the LCA methodology does not address site-specific impacts, which can bias the assessment. As a consequence of the two facts mentioned before, it is assumed that the projectile after firing is out of the study scope. The transport is also not included due to uncertain provenance of the materials and the local of ammunition use. With regard to the cartridge, it is assumed that half is collected in the shooting ranges (50%) and the brass recovered displaces an equal quantity of virgin brass with losses of 20%.

The ammunition producer provided primary data related to production of lead styphnate (TNR-Pb) and diazodinitrophenol (DDNP). For tetrazene the data is taken from literature (Urbanski, 1968), whilst for the other five substances (barium nitrate, antimony sulphide, lead dioxide, zinc peroxide and calcium silicide) the life-cycle inventories were created based on the recommended approach as mentioned in Section 3.1.

3.3.2 Life-Cycle Impact Assessment of small calibre ammunition

Firstly, the Life-Cycle Impact Assessment results are presented for the full life-cycle of the four 9 mm ammunition. Then, the main impact contributors for each one of the life-cycle phases and impact categories are detailed. Figure 3.10 presents the environmental and toxicological impacts calculated to the three life-cycle phases considered in this study: production, use and brass recovery (cartridge). The results are converted to values between 0 and 1 (being 1 the highest impact value for each category), in order to simplify the representation and comparison of the impact categories with different units in the same graph. It is observed that the production phase has a higher contribution to the environmental impact categories, whilst use phase shows a higher contribution to the toxicity categories. The recovery of the cartridge presents a positive impact for all the categories, but with low significance for the overall impact.

Figure 3.11 shows the impact contributors associated with production phase. The analysis is carried out to show the contribution to the total impact of the energy consumption and material used for each one of the ammunition main components (projectile, cartridge, primer and propellant). The results are shown as a percentage of the total impact for each one of the categories. It is important to mention that the cartridge, the propellant and the energy requirement are equal for all ammunition, so the overall contribution to the impact of these components and energy is maintained. As a result, the impact variation observed from ammunition to ammunition arises from the alternative projectiles and primers. However, variation in relative contribution of these components might be observed from ammunition to ammunition, once the relative impact of the projectile and primer in the total impact may also change. Figure 3.12 shows the contributors to the impact associated with ammunition firing during the use phase. The analysis is similar as the one described above for the production phase (Figure 3.11), in which the results are shown as a percentage of the total impact for each one of the categories.

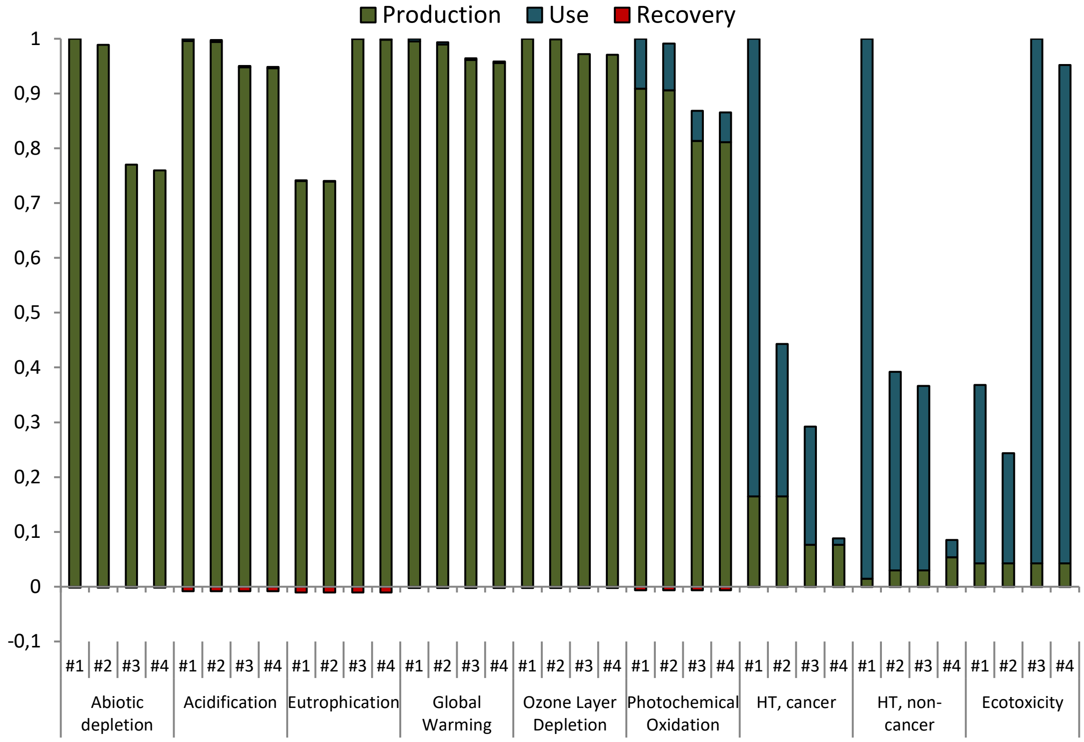

Figure 3.10. Life-Cycle impact comparison between the four 9 mm ammunition (#1 – steel-lead projectile with lead primer; #2 – steel-lead projectile with non-lead primer; #3 – composite projectile with lead primer; #4 – composite projectile with non-lead primer).

3.3.2.1 Contribution to the Production phase impact

For the six environmental categories, which impact values are essentially determined by the effects associated with the production phase due to the use of similar amount of resources (raw materials and energy), the ammunition with same type of projectile present similar impacts. Note that as a result of the small amount of primer presented in all ammunition (less than 2% of the ammunition total mass) the impact contribution is minor to the overall impact. In fact, it is observed that the main contributors to the production phase impacts are the energy consumption (for the ammunition production) and the cumulative embodied impacts associated with the materials used in the production of the projectile and the cartridge (Figure 3.11). As mentioned above, the cartridge and the energy requirement are the same for all ammunition, so the impact variation observed can only be associated to differences in the projectile.

It is not clear which ammunition presents an improved environmental performance based on the six environmental categories. For three out of six categories (Acidification, Global Warming and Ozone Layer Depletion) the results for ammunition #3 and #4 presents only slightly lower impact (-5%) than the ones obtained for ammunition #1 and #2.

Nevertheless, ammunition #1 and #2 presents significantly higher impacts for Abiotic Depletion (23%) and Photochemical Oxidation (13%); while the ammunition with nylon-copper projectile #3 and #4 present a higher impact for Eutrophication (26%). Based on the results, the improvement of the environmental performance of small calibre ammunition can arise from i) a reduction in energy requirement; ii) the substitution of traditional brass cartridge, for plastic or cardboard or, eventually, the use of caseless ammunition; and iii) a composite projectile with equivalent mass and size but with other materials instead of copper-nylon, such as steel-nylon (or other potential combinations) to decrease the impacts in Eutrophication (or other potential trade-offs).

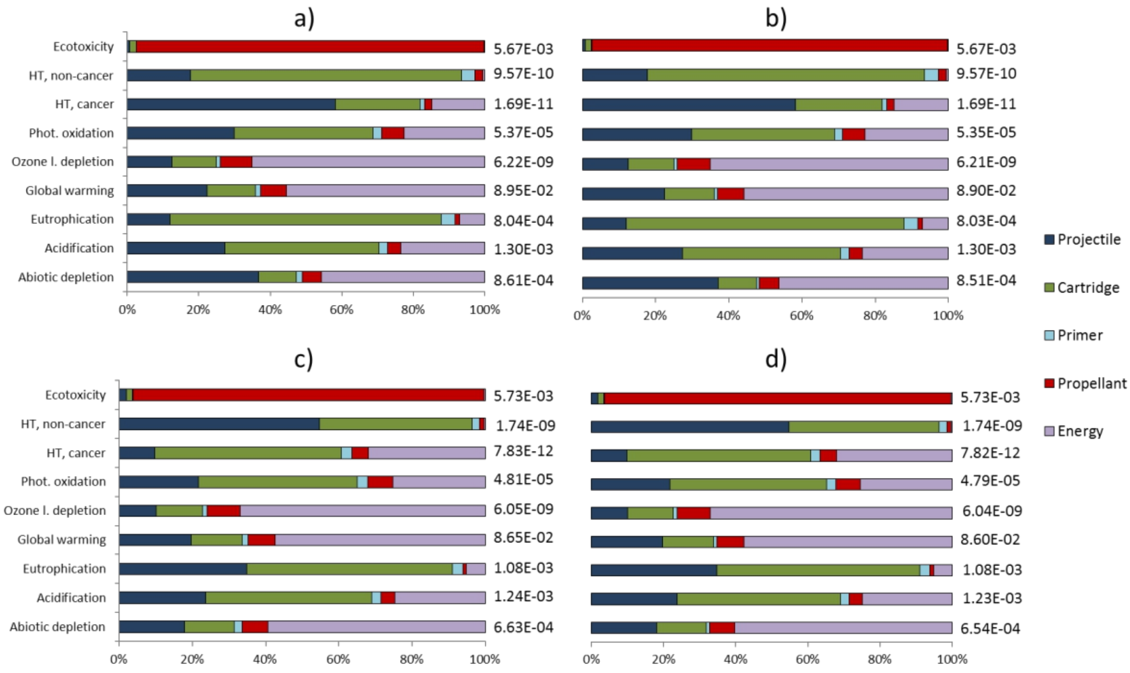

Figure 3.11. Contribution to the impacts associated with the production of four different 9 mm ammunition: a) #1 - steel and lead projectile with lead primer; b) #2 - steel and lead projectile with non-lead primer; c) #3 - composite projectile with lead primer; d) #4 - composite projectile with non-lead primer. Note: Abiotic depletion (kg Sb eq.); Acidification (kg SO_2 eq.); Eutrophication (kg PO_4^{-3} eq.); Global Warming (kg CO_2 eq.); Ozone L. Depletion (kg CFC-11 eq.); Phot. Oxidation (kg C_2H_4 eq.); cancer and non-cancer HT (cases); Ecotoxicity (potentially affected fraction of species (PAF).m^3.day).

3.3.2.2 Contribution to the use phase impact

For the Human Toxicity categories, the impacts are essentially associated with the emissions from firing (use phase). Figure 3.10 shows that substitution of lead from the primer allowed a reduction of 56% – cancer effects – and 61% – non-cancer effects – of the total impact (ammunition #1 vs ammunition #2); while the use of the composite projectile allowed an impact reduction of 71% – cancer effects – and 63% – non-cancer effects – (ammunition #1 vs ammunition #3). Substitution of lead in the primer and projectile (ammunition #4) almost completely avoided the impacts associated with the use phase. It should be mentioned that the lead emitted from the ammunition with lead free primer and projectile (ammunition #4) might be associated to the propellant. The composition of the additives and binders used in the propellant of these ammunitions is unknown; however lead stearate is a common lubricant used in ammunitions which can be the origin of the lead emissions (Zajtchuk and Bellamy, 1993).

Figure 3.12 shows that lead dominates the impact contribution for the Human Toxicity categories, so the reduction of lead emitted (Table 3.7) have a direct effect on the decrease of the impact. Nevertheless, for non-cancer Human toxicity, zinc also has a considerable influence and its relative contribution to this category increase as the amount of lead emissions decreases. The impact of copper in human health is also of high relevance, since this metal can potentially cause metal fume fever and it was reported that this acute effect caused military people to remain out of action for several hours (Moxnes *et al.*, 2013). For Ecotoxicity, it is observed that ammunition with non-lead projectiles present around 65% higher impacts comparatively with ammunition with lead projectiles. The reason for this impact is consequence of a tremendous increase of copper emissions for ammunition #3 and #4 (Table 3.7), which presents a higher effect for ecosystems than antimony (which is the main contributor to Ecotoxicity impact for ammunition #1 and #2).

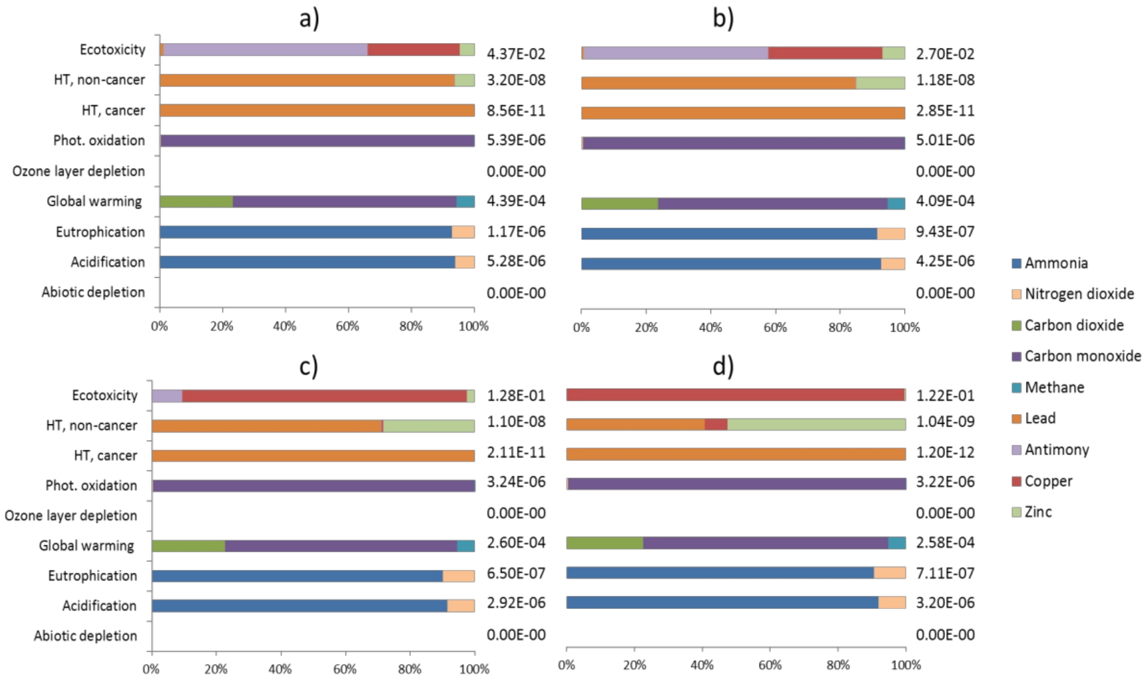

Figure 3.12. Contribution to the impacts associated with the use of four different 9 mm ammunition: a) #1 - steel and lead projectile with lead primer; b) #2 - steel and lead projectile with non-lead primer; c) #3 - composite projectile with lead primer; d) #4 - composite projectile with non-lead primer. Note: Abiotic depletion (kg Sb eq.); Acidification (kg SO_2 eq.); Eutrophication (kg PO_4^{-3} eq.); Global Warming (kg CO_2 eq.); Ozone L. Depletion (kg CFC-11 eq.); Phot. Oxidation (kg C_2H_4 eq.); cancer and non-cancer HT (cases); Ecotoxicity (potentially affected fraction of species (PAF).m^3.day).

These results emphasise the importance of removing lead from the ammunition components due to high chronic effects for human health. It is observed a decrease of the potential impact on human health when free lead materials are used in the primer and in the projectile, which can be an appropriate solution to apply in shooting ranges during training. Nevertheless, this approach should be carried out with precaution in order to prevent the shifting of the toxicity impacts origin to other metal emissions (such as copper, zinc and antimony). Therefore, to support such decisions the application of a life-cycle approach (and ecodesign studies), such as the one presented, is required.

3.4 Evaluation of the significance of the impacts associated with ammunition

In the introduction of this thesis the main motivation, the significance of the problem and the reasons to assess the environmental impacts associated with ammunition were presented. However, as some can argue that the life-cycle impacts of ammunition are not significant in comparison with the impacts from other products or systems, it is important to evaluate their relevance. In LCA the relevance of the impacts can be evaluated through

Normalisation (ISO 14040, 2006), an optional step in LCA that relates the LCIA results associated with a certain product or service by dividing it with the impacts associated to a reference activity or situation (Kim *et al.*, 2013). The activity whose impacts have been selected by policy makers as a reference – normalisation factors – is usually the regional economic system (Sleeswijk *et al.*, 2008). That means the normalisation factors for each impact category are the yearly impacts associated with the emissions and extraction data of a certain regional or global economic activity.

Recently, Benini *et al.* (2014) published normalisation factors for impact categories based on the available statistic of the emissions occurring within (domestic inventory) the EU-27 countries. This inventory underlays an extensive collection of emissions into air, water, and soil as well as resources extracted for the year 2010, which expresses the total impact of the EU-27. The domestic values for 2010 are more complete in terms of substance coverage than previous datasets, so these normalisation factors have been identified as the most robust for the normalisation step. Normalisation factors per person based on the Eurostat data on the EU-27 population in 2010 (499 million inhabitants) were also developed. Table 3.8 presents the normalisation factors and their inherent robustness – uncertainty – for the impact categories. The impact categories were selected accordingly with the units of the normalisation factors that are the same of those used to calculate the impacts for the small calibre ammunition.

Table 3.8. Normalisation factors for domestic emissions for Europe and per person (Benini *et al.*, 2014).

Impact categories	Domestic Normalisation factors	Domestic Normalisation factors (per person)	Overall robustness
Resource depletion (kg Sb eq.)	5.03E+07	1.01E-01	Medium
Climate change (kg CO_2 eq.)	4.60E+12	9.22E+03	Very high
Ozone depletion (kg CFC-11 eq.)	1.08E+07	2.16E-02	Medium
Human toxicity, cancer (CTU_h)	1.84E+04	3.69E-05	Low
Human toxicity, non-cancer (CTU_h)	2.66E+05	5.33E-04	Low
Ecotoxicity (CTU_e)	4.36E+12	8.74E+03	Low

For this study the normalisation was carried out for the ammunition #1 presented in Section 3.3 – the most common ammunition used –, considering a world production of 13×10^9 small calibre ammunitions per year (Anders and Weidacher, 2006). Table 3.9 shows the impacts of the production and use of small calibre ammunition normalised using as reference the domestic emissions for Europe. For each impact category, the values were calculated by dividing the life-cycle impacts, shown in the second column of that table, by the normalisation factors. The normalisation impacts can be understood as an impact fraction of the total impact for the domestic activity in Europe. This means the fraction of the European domestic emissions that produce an impact equivalent to that associated with the production and use of the yearly amount of ammunition. A higher normalised impact means a major relevance of that impact. Figure 3.13 shows the normalisation of the life-cycle impact of ammunition considering the total population of Europe (499 million), allowing to comprehend the share of the population whose impacts associated with their domestic emissions would be equivalent to those of the small calibre ammunition.

The analysis of the results shown on Table 3.9 and on Figure 3.13 highlight the relevance of the impacts associated with the ammunition production life-cycle for the abiotic depletion impact category. For this impact category, the normalised impacts are as high as those associated with the domestic activities of 110 million European inhabitants – approximately 22% of the total EU-27 population. The higher relevance to this impact category in comparison to the other impact categories is probably related to the underestimation of the impacts associated with the domestic inventory in EU-27 for resource depletion. In fact, only 37% of the metals are covered in the domestic inventory, which can imply to an overestimation of the relevance of this impact category over others (Benini *et al.*, 2014). The second most relevant impact category is the human toxicity with non-cancer effects. For this category, the impacts associated with ammunition production and use are about the same as those produced by the domestic emissions of a city of 800 000 inhabitants, approximately the same as Marseille or larger than Athens, Stockholm or Amsterdam.

Table 3.9. Normalised impacts for the world production and use per year of small calibre ammunition.

Impact categories	Ammunition production and use (per bullet)	Ammunition production and use (13×10^9 bullets)	Normalised impact
Resource Depletion (kg Sb eq.)	8.61E-04	1.12E+07	2.22E-01
Climate Change (kg CO_2 eq.)	9.00E-02	1.17E+09	2.54E-04
Ozone depletion (kg CFC-11 eq.)	6.22E-09	8.09E+01	7.49E-06
Human toxicity, cancer (CTU_h)	1.03E-10	1.33E+00	7.25E-05
Human toxicity, non-cancer (CTU_h)	3.30E-08	4.29E+02	1.61E-03
Ecotoxicity (CTU_e)	4.93E-02	6.41E+08	1.47E-04

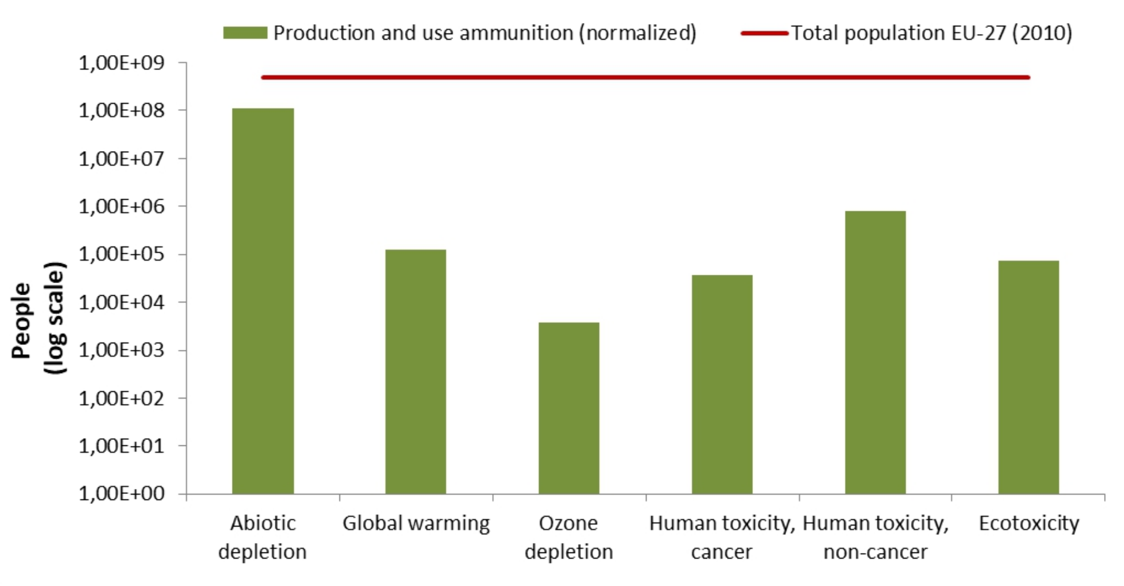

Figure 3.13. Representation of the impact of small calibre ammunition that is equivalent to the average impact per person in EU-27 (2010), calculated using the normalised factors per person (Benini *et al.*, 2014).

3.5 Concluding remarks

This section described the creation of life-cycle inventories for energetic materials and the approach used to overcome the difficulties referent to acquisition of data, principally for the production phase. The environmental and toxicological impacts of two case studies associated with the production and use phase of ammunition were also calculated. Those case studies were: i) generic 155 mm ammunition, and ii) comparison between four types of small calibre ammunition. Moreover, the relevance of the impacts associated with ammunition production and use by employing normalisation factors for Europe (and per person) was assessed.

The calculation of the impacts associated with the production of energetic materials was difficulty and time consuming to accomplish due to lack of data; however with the employment of a simplified approach recommended for the Life-Cycle Assessment studies it was possible to overcome this obstacle and create the life-cycle inventories associated with the production of energetic materials. The life-cycle impact related with the most common energetic material was compared with selected chemicals used by the industry in order to understand the similarity (or not) between them. It was observed, with some exceptions, that the impacts for the production of energetic material are similar or one order of magnitude higher than those of the chemicals selected. The assessment carried out for the energetic materials is ground-breaking because it was not published any study about this issue until now. Moreover, the impact assessment for energetic materials contributed to fill the gap that was preventing the assessment of the environmental impacts associated with ammunition, as for the other materials (metals, plastics) the impacts are well-known and studied. The results obtained can be used as a baseline by ammunition producers, or researchers interested in this topic, to determine the environmental impacts of ammunition in order to enhance the environmental profile of ammunition. In addition, producers and designers of ammunition can also calculate the impacts for alternatives energetic materials, such as those used in insensitive ammunitions, using the recommendations presented in this section to understand if the alternatives offer appropriate solutions.

The analysis carried out, and the results presented to the generic ammunition, will allow decision makers, be they shooting range managers, ammunition procurement officers, ammunition producers or others, to become more aware of the main environmental and toxicological problems associated with ammunition production and use. It is expected that shooting ranges managers will be essentially interested in the impacts associated with the use phase, whilst procurement officers and producers will be concerned with the entire life-cycle. As a result, it becomes possible to define strategies to manage or mitigate those problems (e.g. where to focus the efforts to reduce a certain specific risk associated with ammunition life-cycle) and carry out tailored modifications to decrease the impacts associated with the hotspots.

For the small calibre ammunition assessment, it is important to mention that the identification of undesired consequences associated with the lead replacement, which was expected to be a logical path for “greener” small calibre ammunitions, was only possible via the employment of the LCA methodology. These negative consequences are observed for the ecosystem impact (ecotoxicology category) and are essentially related to the emission of copper particles due to the projectile erosion during firing. The identification of this trade-off, which could only be made with the application of a life-cycle approach, is relevant for shooting range managers so that they may be aware of the potential consequences of using these ammunitions on ecosystems around the area they manage. Moreover, these conclusions are also significant for ammunition producers in order to persuade them to search for alternatives that mitigate those adverse consequences.

Chapter 4 - Life-Cycle Assessment of ammunition disposal

Summary: This section presents the life-cycle models developed to assess the environmental impacts of ammunition disposal. The main objective is to ascertain which ammunition disposal technique shows lower environmental and toxicological impacts. Section 4.1 presents the life-cycle assessment of ammunition disposal by incineration in static kiln with flue gas treatment; whilst section 4.2 shows the life-cycle impact of ammunition disposal by open detonation. Section 4.3 presents a novel technique to ammunition decommission, in which it is intended to assess the potential benefits associated with the valorisation of energetic material incorporated in civil explosives with the employment of the system expansion method. A life-cycle assessment of a civil explosive production is also carried out in order to calculate the potential benefits from the energetic material valorisation. In section 4.4 is presented the environmental comparison of the three techniques to disposal ammunitions.

Armed Forces possess significant quantities of military munitions which have to be dispose of when they reached their end-of-life or become obsolete. The main demilitarization contractors are established in United States, which is the largest market representing approximately a sixth of the total stockpile (around 450 000 tonnes), and Western Europe (Small Arms Survey, 2013). It is difficult to ascertain the exact number of munitions decommissioned but it is estimated more than half a million tons just in western countries (Wilkinson and Watt, 2006). Beyond the western countries, other parts of the world also have significant amounts of munitions to decommission where they are a safety hazard and present a potential risk for terrorist activities (Wilkinson and Watt, 2006). Decommission is also an onerous process in which costs are estimated at approximately 1600 USD per tonne of item (RTO, 2010).

Disposal of ammunitions needs to be carried out under secure conditions and with minimum impact on environment. Currently, the majority of ammunitions are disposed of in incinerators which usually have associated sophisticated gas treatment systems. However, such sophisticated elimination installations also present restrictive limitations associated to the capacity, energy requirement and operation/maintenance costs. Open detonation is considered the technique with higher environmental impacts due to release of emissions without control and the contamination associated with unexploded (or low order) ordnance; however, there are still some debate which technique should be employed.

The energetic material from ammunitions (e.g. powder and TNT) is a product with high energy content. Therefore, instead of consuming energy to dispose this product it can be used for other purposes. Valorisation of energetic material from ammunition by incorporation into civil explosives can be a solution to overcome the problems related with incineration. The valorisation of the energetic material intends to avoid the incineration of military ammunitions and the inherent environmental impacts associated with that process. Consequently, the incorporation of the energetic material also avoids the impacts associated with the displacement of the emulsion matrix components.

Previous experimental work has shown the feasibility of blending energetic material (powders and TNT) in ammonium nitrate (AN) emulsions explosives (a common type of civil explosive used for mining and road construction). Ribeiro *et al.* (2014) studied the behaviour properties related to emulsion explosives with energetic material incorporated concluding that adding up to 20% w/w of single and double base powders was not observed formation of any new chemical specimens. However, a slight change in the performance of the emulsion was verified in which the detonation velocity and shock sensitivity presented higher values than conventional emulsion explosives. Ribeiro *et al.* (2014) also demonstrated that simple processing techniques (grinding) is sufficient to incorporate the energetic materials in the emulsion explosive matrix.

The main objective of this section is to present the appropriate manner to dispose of military ordnances with the minimum impact on the environment. Consequently, it is assessed the environmental and toxicological impacts associated with three demilitarisation techniques: Open detonation, incineration in a static kiln with gas treatment, and valorisation of energetic materials by incorporation into civil explosives.

4.1 Demilitarisation by incineration in a static kiln[3]

The main goal is to present a comprehensive life-cycle assessment of the ammunition disposal performed by the Portuguese company idD. A life-cycle model was developed for the entire demilitarisation process, which includes dismantling ammunition, discharging the energetic material, incineration, and the subsequent treatment of gases. The main process is the incineration of the energetic material (explosives and propellants)

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[3] *Significant portions of this section appear in: Ferreira C, Ribeiro J, Mendes R, Freire F (2013) Life-Cycle Assessment of Ammunition Demilitarization in a Static Kiln, Propellants, Explosive, Pyrotechnics. 38: 296-302. DOI: 10.1002/prep.201200088*

in a static kiln with a gas treatment system. A detailed inventory was implemented, based on primary data collected from idD, in which this process is representative of similar processes that occur in developed countries.

4.1.1 Life-Cycle model for ammunition demilitarisation

The model focuses on ammunition at the end of its life-cycle, omitting the previous LC phases. According to Clift *et al.* (2000), LCA studies of waste management usually cover the waste management activities themselves, from the site where the waste occurs to the emissions released into the environment. The activities which produce the waste are omitted from the analysis. Therefore, the system under study starts with waste collection, which is sometimes described as waste entering the system with "zero burdens" (Clift *et al.*, 2000). Following this approach, the model covers the following processes: dismantling of ammunition, discharge of energetic material, incineration and subsequent gas treatment. Figure 4.1 presents the flowchart for ammunition demilitarisation. The incineration and gas treatment processes are distinct but sequential and are modelled as a single process. The same procedure was adopted for the dismantling and discharging processes (also modelled as a single process). A simplified model was also developed for the manufacture and transport of equipment.

Incineration (or thermal treatment) takes place in a static kiln (electrically heated), at a typical rate of 20 kg of TNT equivalent (kg TNT eq) per hour at temperatures ranging from 400ºC to 600ºC. After particulate cleaning in a cyclone, the resulting gas is directed to the gas treatment installation. Gas treatment is a complex process comprising four phases: post-combustion, selective catalytic reduction (SCR), gas scrubbers, and adsorption. In the post-combustion phase, the gases resulting from the thermal treatment of the energetic material are co-fired with an air-propane gas mixture to ensure complete combustion, leading to the oxidization of VOC (volatile organic compounds), hydrocarbons, CO, dioxins, and furans. On exit, these gases are cooled rapidly before entering the unit for NO_x removal. The SCR system removes NO_x by adding a solution of urea. The gas absorption process involves three steps: an acid scrubber for the precipitation of heavy metals and particulates, an alkaline scrubber for pH neutralization, and a spray precipitator to filter gases (SO_2, SO_3, HCl, HF) and thin particulates. The acid scrubber uses hydrochloric acid, whilst the alkaline scrubber consumes sodium hydroxide and hydrogen peroxide. Finally, adsorption is performed using zeolite for accurate separation of H_2O, CO_2, and SO_2. This unit is the last filter (control) before the gases are released into the atmosphere.

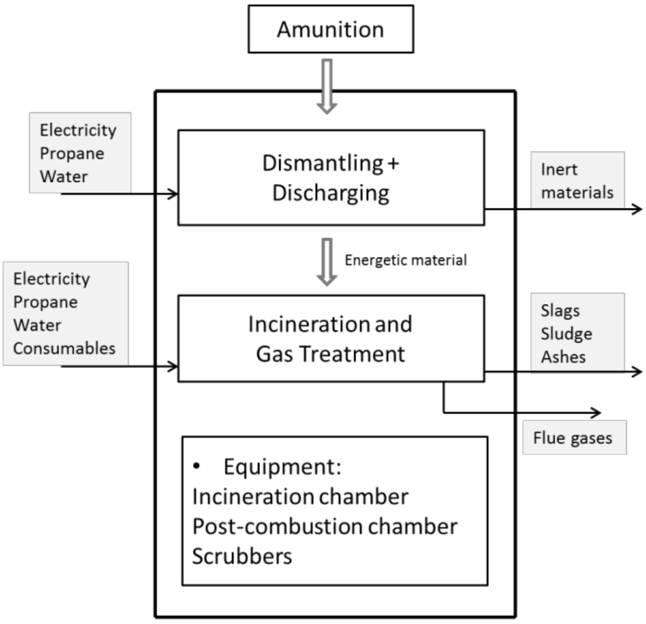

Figure 4.1. Flowchart representing ammunition demilitarisation.

4.1.2 Life-Cycle Inventory for ammunition disposal in a static kiln

A detailed life-cycle inventory (LCI) was implemented, based on the idD operations. Data was collected for one entire month (November 2011), in which the unit functioned for 312 h. The energetic material incinerated during this month was mainly composition B (85%), single base powder (11%), lead azide (3.2%), and double base powder (0.8 %). This is representative of the typical energetic materials incinerated by idD during the last three years. The functional unit was defined as 1 kg of TNT equivalent (kg TNT eq), which corresponds to 4.5 MJ of energy content (Keshavarz, 2005). Table 4.1 provides the inventory of the dismantling and discharging process. Table 4.2 lists the operation data for the incineration and gas treatment process. The LC model includes the indirect impacts associated with the production and transport of materials and energy inputs. In terms of electricity generation, the Portuguese 2004 electricity mix was assumed, including losses during medium voltage transmission and transformation from high voltage. The production of propane includes all “cradle-to-gate” processes (such as refinery process emissions and wastewater treatment) and transport to idD. Propane combustion emissions are included in the flue gas emissions (incineration emissions), simultaneously with the emissions from the incineration of energetic material.

Table 4.1. Inventory for dismantling and discharging (per kg TNT eq).

	Dismantling and Discharging		
	Energy		
Inputs	Electricity	1.369	kWh
	Propane	0.479	kg
	Materials		
	Water	6.161	kg

Table 4.2. Inventory for incineration and gas treatment (per kg TNT eq).

	Incineration and Gas Treatment			
	Energy			
Inputs	Electricity			7.860 kWh
	Propane			1.320 kg
	Materials			
	Water			15.31 kg
	Urea			0.280 kg
	Nitric acid			0.078 kg
	Sodium Hydroxide			0.060 kg
	Hydrogen Peroxide			0.004 kg
	Zeolite			0.050 kg
	Materials			
Outputs	Sludge			0.008 kg
	Fly ashes			0.032 kg
	Ash and Slag			0.040 kg
	Emissions to air			
	2,3,7,8 TCDD*	8.65E-13 kg	NO_x	4.06E-03 kg
	1,2,3,4,7,8 HxCDD*	1.73E-12 kg	SO_2	3.98E-04 kg
	1,2,3,7,8,9 HxCDD*	8.65E-13 kg	Hg	1.71E-06 kg
	1,2,3,4,6,7,8 HpCDD*	8.65E-13 kg	Cd	1.54E-06 kg
	OCDD	8.65E-15 kg	As	3.33E-06 kg
	Furan	9.52E-12 kg	Ni	2.47E-06 kg
	HF	8.36E-05 kg	Pb	2.05E-06 kg
	HCl	8.36E-05 kg	Cu	2.05E-06 kg
	VOC	6.55E-04 kg	Cr	2.05E-06 kg
	CO	1.28E-03 kg	CO_2	6.24E+00 kg
	H_2S	2.81E-04 kg	PM	4.20E-04 kg

*Dioxins.

The inventory for the manufacture of the equipment and transport to Portugal is shown in Table 4.3. The lifetime of the equipment is assumed to be 10 years, during which 16 tons of energetic material is incinerated. The inventory for the equipment manufacture is simplified due to lack of information, in which is only presented the most important material constituents (material type and weight).

Table 4.3. Inventory for equipment manufacturing and transportation.

Equipment				
	Main material Composition	Amount (kg)	Transport, distance (km)	Type of transport
Incineration chamber	Metal	17000	3984	Lorry
Post combustion chamber	Metal	5150	2521	Lorry
Acid Scrubber	Polypropylene	43.3	2521	Lorry
Alkaline Scrubber	Glass fibre	21.7	2521	Lorry
Spray Precipitator	Polypropylene	14.4	2521	Lorry

4.1.3 Life-Cycle Impact Assessment of ammunition disposal in a static kiln

Life-cycle impact assessment (LCIA) results are presented for the primary energy requirement (CED method) and the environmental categories (CML and USEtox methods). Firstly, the results show the contribution of each type of process, by operation (dismantling and discharging, incineration and gas treatment) and equipment. Secondly, a comprehensive analysis of processes with high impacts is presented. Table 4.4 presents the LCIA results associated with the disposal of 1 kg TNT eq. of energetic material.

The incineration and gas treatment operations have the highest impact in all ten categories. The impacts of incineration and gas treatment range from 76% (Ecotoxicity) to 90% (Global Warming) of the total impacts in the ten categories. With regard to the other processes, equipment manufacture shows a low impact contribution (1% to 6%); while dismantling ranges from 4% (non-cancer Human Toxicity) to 21.5% (Ecotoxicity).

Table 4.4. Life-cycle impact assessment results for ammunition demilitarisation.

Category	Unit	Process		Equipment	Total
		Dismantling	Incineration/ Gas treatment		
Primary Energy	MJ prim	(18.2%) 40.7	**(79.9%)** 179.1	(1.9%) 4.3	(100%) 224.1
Abiotic Depletion	kg Sb eq	(18.0%) 1.8E-02	**(79.8%)** 8.1E-02	(2.20%) 2.0E-03	(100%) 1.0E-01
Acidification	kg SO_2 eq	(15.0%) 1.1E-02	**(83.5%)** 6.1E-02	(1.54%) 1.0E-03	(100%) 7.3E-02
Eutrophication	kg PO_4 eq	(12.6%) 6.6E-04	**(83.0%)** 4.0E-03	(4.40%) 2.3E-04	(100%) 4.9E-03
Global Warming	kg CO_2 eq	(7.70%) 1.15	**(90.5%)** 13.4	(1.80%) 0.27	(100%) 14.8
Ozone Layer Depletion	kg CFC-11 eq	(20.2%) 2.8E-07	**(78.5%)** 1.1E-06	(1.24%) 1.7E-08	(100%) 1.4E-06
Photochemical Oxidation	kg C_2H_4	(15.6%) 4.7E-04	**(80.3%)** 2.0E-03	(4.19%) 1.3E-04	(100%) 2.0E-03
Human Toxicity, cancer	CTUh	(10.9%) 4.9E-11	**(85.8%)** 3.8E-10	(3.30%) 1.5E-11	(100%) 4.5E-10
Human Toxicity, non-cancer	CTUh	(7.4%) 3.9E-11	**(86.7%)** 4.6E-10	(5.9%) 3.2E-11	(100%) 5.3E-10
Ecotoxicity	CTUe	(21.5%) 2.7E-03	**(76.1%)** 1.0E-02	(2.40%) 3.1E-04	(100%) 1.3E-02

Figure 4.2 details the contribution of the incineration and gas treatment operations to the LCIA results. The energy requirement (electricity generation and propane production) is the main contributor in eight out of ten of the impact categories. However, this contribution varies across the different categories. Propane production is the main factor responsible for Ozone Layer Depletion (58%) and Ecotoxicity (66%), whereas electricity is the main factor responsible for Acidification (72%), Eutrophication (49%), Photochemical Oxidation (68%), and cancer Human Toxicity (66%). In terms of the Primary Energy and Abiotic Depletion, the propane and electricity impact contributions are similar.

Urea is the most important contributor to Human Toxicity with non-cancer effects (41% of the total impact), due the carbon sulphide emissions (CS_2) in urea production. Flue gas represents the direct emissions from the combustion of energetic material and propane, and contributes significantly to Global Warming (46%), mainly due to CO_2 emissions from propane combustion. Flue gas emissions also contribute significantly to cancer

Human Toxicity (6%, due to the emissions of dioxins) and Eutrophication (12%, mainly due to NO_x emissions).

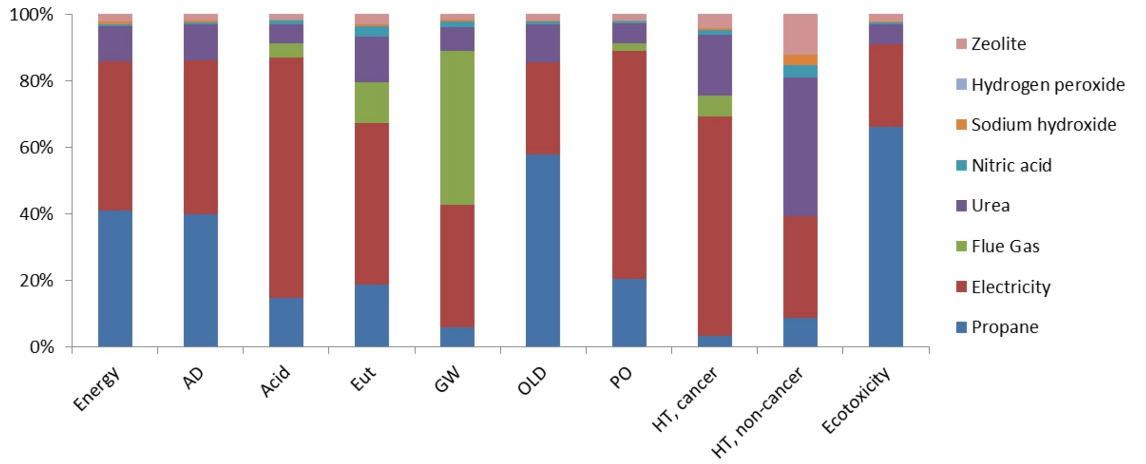

Figure 4.2. Main contributors to the incineration and gas treatment impacts.

4.1.4 Sensitivity Analysis of the influence of the electricity mix

The previous assessment demonstrated that the demilitarisation process in Portugal is significantly dependent of high energy requirements associated with the incineration and gas treatment procedures. Therefore, a comparative assessment considering three electricity mixes (US, China and Sweden), beyond the Portuguese mix, is carried out to analyses the influence of the energy requirement to the potential environmental impacts for other countries. These three electricity mixes were selected in order to obtain a wide spectrum of the contribution from different energy sources. The electricity mixes are based on data from the year 2004 (Dones *et al.*, 2007).

Figure 4.3 shows the impact comparison for the incineration of ammunition in a static kiln process using different electricity mixes. The electricity mixes with high share of carbon sources presents high impacts as expected. The US mix is mainly based in coal and nuclear sources and presents the high primary energy requirement; however ammunition disposal in China presents the highest impact for Global Warming as the electricity mix is predominantly based on coal which leads to high carbon emissions. In fact, for a disposal process in China, instead in Portugal, the total impact could increase for Abiotic Depletion, Acidification, Global Warming and Photochemical Oxidation. The electricity mix from Sweden is based on hydro and nuclear and that is reflected with lower impact to all environmental categories.

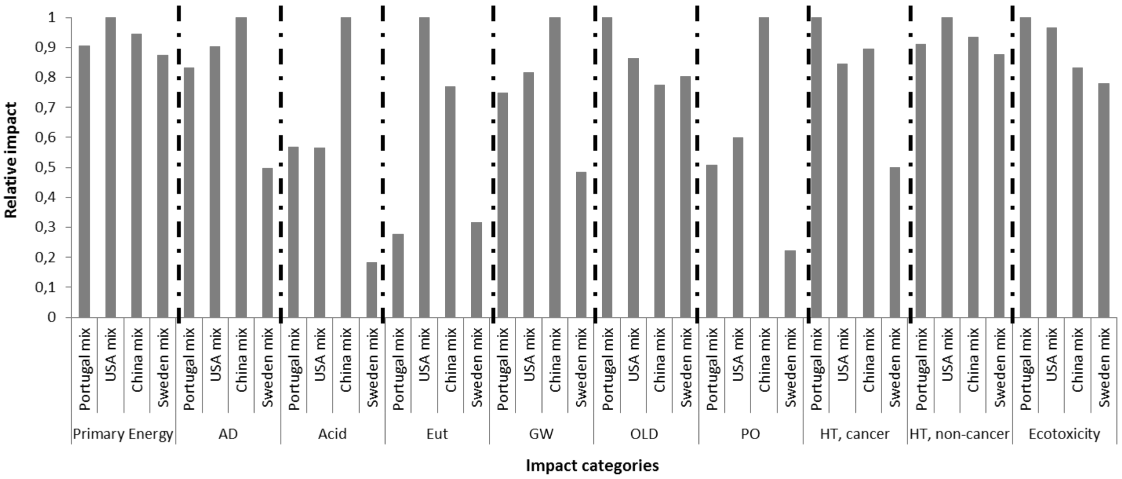

Figure 4.3. Impact comparison associated with the incineration of ammunition in a static kiln considering four different electricity mixes.

4.2 Demilitarisation by open detonation

The main goal is to present a comprehensive life-cycle assessment of the ammunition disposal by Open Detonation. A life-cycle model was developed for the open detonation process, which includes preparation of the detonation charge and the detonation emissions. The inventory was implemented based on data from reports that contains information regarding open detonation.

4.2.1 Life-Cycle model and inventory for open detonation

The life-cycle model covers the preparation of the charges to set up the detonation and the emissions associated with the detonation. The functional unit selected is the disposal of the generic 155 mm generic ammunition with a charge of 8.5 kg of composition B in the projectile, which corresponds approximately to 10.2 kg TNT.

The life-cycle inventory regarding the materials used for setting up the detonation of the ammunition pile was compiled from Bellow *et al.* (2008). Those materials are listed on Table 4.5 which includes the C4 PBX explosive initiator and the gravel used per ammunition detonated. The data for the detonation emissions was considered identical to the emissions used for the ammunition use in section 3.2.1 (see Table 3.4).

Table 4.5. Donor and gravel used for the detonation of the generic 155 mm ammunition.

Materials	Amount (kg/ 155 mm ammunition)
C4 initiator	0.6
Gravel	1138.5

4.2.2 Life-Cycle Impact Assessment of ammunition disposal by open detonation

Life-cycle impact assessment (LCIA) results are presented for the primary energy requirement, six environmental categories and three toxicological categories. Figure 4.4 shows the contribution of the materials and detonation emissions to the total impact associated with the Open Detonation of the generic 155 mm ammunition. The impact associated with production of C4 and gravel is the higher contributor to eight out of the ten impact categories, in which this contribution varies across the different categories. Production of C4 is the higher contributor to the categories Abiotic depletion and Global warming; whilst gravel production is the higher contributor to Primary energy, Acidification, Eutrophication, Ozone layer depletion, Photochemical oxidation, cancer Human toxicity and Ecotoxicity.

The contribution of the impact associated with gravel to the categories cancer Human Toxicity and Ecotoxicity (74% and 46% respectively) was unexpected, since the assessment related with the use of the generic 155 mm ammunition showed that emissions significantly contributes to the toxicity categories. The reason for this high contribution is related with heavy metal emissions (mainly chromium VI) associated with the use of industrial machine and the conveyor belt to round and crush the gravel. The higher impact contribution for non-cancer Human Toxicity (92% respectively) is associated with, as it would be expected, the emission of the detonation products. This impact is mainly associated with the emission of heavy metals: cadmium (85%) and zinc (15%).

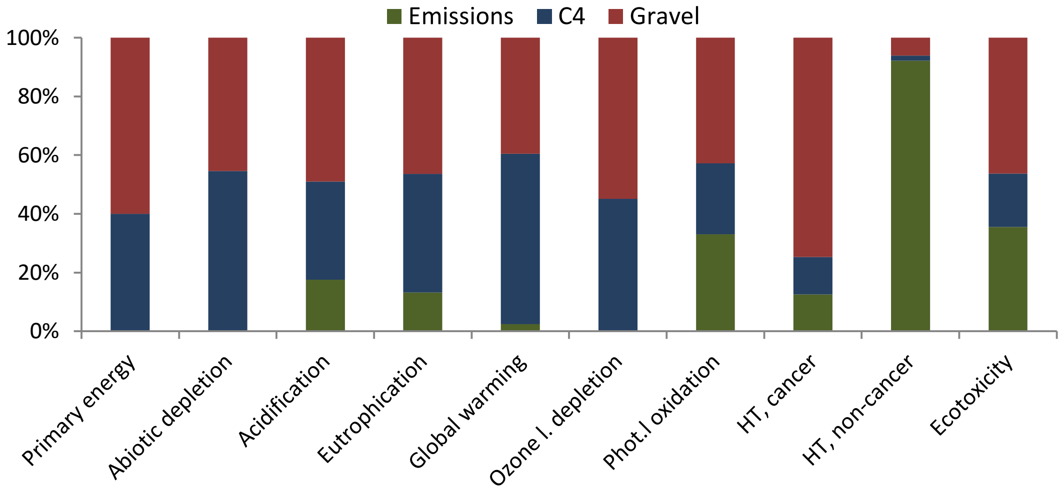

Figure 4.4. Life-Cycle Impact contributions to the open detonation of the generic 155 mm ammunition.

4.3 Valorisation of energetic material from ammunition via incorporation into civil explosives

This section describes the valorisation of energetic material from ammunition by incorporation into civil explosives, as an alternative to conventional decommissioning. Therefore, the main goal is to assess the potential energy and environmental benefits arising from the incorporation of energetic material from disposed of military ammunition into ammonium nitrate based emulsion explosives, allowing for the displacement of the incineration of the energetic materials and of the production of an equivalent quantity of emulsion explosives. The energy and environmental benefits resulting from this valorisation are assessed, as an alternative to conventional ammunition disposal, with the employment of the system expansion method to overcome the multifunctional problem due to the additional function associated with the production of civil explosive. System expansion allows accounting the potential benefits from the energetic material valorisation by assigning the environmental burdens avoided to the main conventional services.

4.3.1. Life-Cycle Model and Inventory for energetic material valorisation

The industrial ecology approach associated with the energetic material valorisation and the employment of the system expansion method to overcome the inherent multifunctional problem of this process is showed in this section.

Figure 4.5 shows the flowchart representing the process of the energetic material valorisation by incorporation into emulsion explosives. This process includes the dismantling procedure (carried out as was described for the conventional disposal process in section 4.1) to separate the different ammunition components and unload the energetic material. The dismantling originates a different batch of energetic materials, in different forms (e.g. prills, sticks, particles and flakes), so it was needed to grind each one of these energetic material to achieve a consistent final product batch in order to incorporate it in the emulsion explosive. An energy consumption of 0.9 kWh per kg TNT equivalent for the grinding process was estimated (based on the power of the grinder and the grinding time). The energetic material grinded was incorporated in the emulsion matrix, displacing an equal amount of its components (ammonium nitrate, mineral oil and emulsifier), and the resulting mixture was then sensitized by adding hollow polymer or glass microspheres (sensitizing agent). The new operation of incorporation combined with mixing the energetic material and the matrix can result in a supplementary consumption of energy; nevertheless, due to lack of data related to that specific operation, the value of energy consumption in the production of this type of emulsion was considered equal to the one of the conventional process.

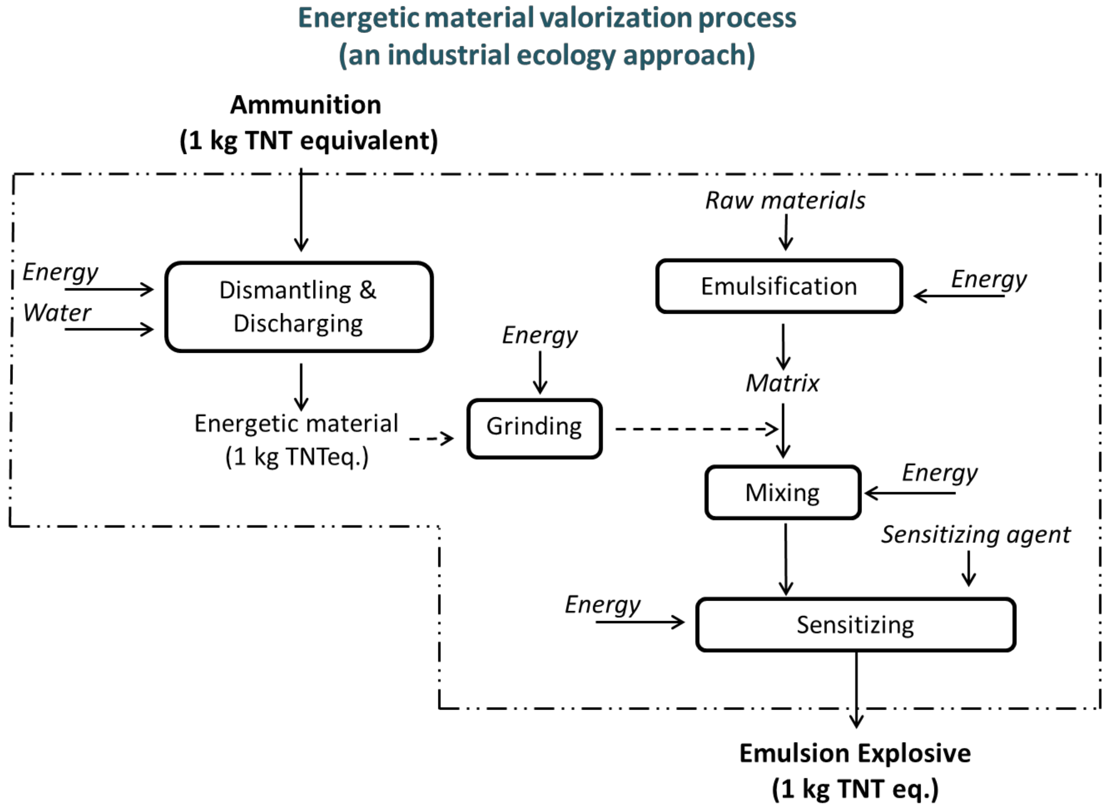

Figure 4.5. Simplified flowchart representing the valorisation of 1 kg TNTeq of energetic material via incorporation into civil explosive.

The incorporation of the energetic material from military ammunition into civil explosives is a way to valorise a waste that otherwise would be burned with significant energy and environmental impacts. This incorporation originates a multifunctional process. The primary function of this new approach is still to disposal 1 kg of TNT equivalent of energetic material from military ammunition, however, at the same time, this process also ensure the function to produce 1 kg of TNT equivalent of emulsion explosive. The multifunctional problem is overcome following the ISO 14040 recommendations (ISO 14040 2006), in which, to avoid allocation associated to the waste stream, is employed the system expansion method. The system expansion method is selected in order to appropriately address the consequences of changing the conventional process, as it is usually applied, for recycling activities (Zamani *et al.*, 2015; Shen *et al.*, 2012; Bohne *et al.*, 2008; Nuss e*t al.*, 2013).

Based on the system expansion method, the extra elements from the production of emulsion explosives with energetic material incorporated are also accounted for in order to address the potential consequences associated with the energetic material valorisation. Therefore, the system boundaries of the conventional energetic material disposal process are enlarged to include the extra function, production of 1 kg of TNT equivalent of civil explosive, to the new functional unit (Clift *et al.*, 2000). The functional unit for this industrial ecology approach is defined as the disposal of 1 kg of TNT equivalent of energetic material from ammunition via incorporation in the production of emulsion explosive. The consequent reference flow includes materials and energy associated with the valorisation of 1 kg of energetic material, which corresponds to the disposal of 1 kg of TNT equivalent of energetic material as well as the production of 1 kg TNT equivalent of emulsion explosive.

With the employment of the system expansion method is possible to answer the following question: what are the consequences of the energetic material valorisation due to the inclusion of the additional process? The energetic material valorised originates a double modification to the conventional ammunition disposal process by i) avoiding the incineration and flue gas treatment process associated with the ammunition disposal and ii) displacing the emulsion explosive matrix production. Hence, the aforementioned consequences, which are the environmental burdens avoided to the main service, are accounted by subtracting them from the total burdens in the conventional disposal process (Azapagic and Clift, 1999). Figure 4.6 shows a representation of the system expansion and the burdens that are avoided due to the valorisation of the energetic material. The calculation of the potential benefits can be represented in the following formula: Total impacts from energetic material valorisation = Dismantling of military ammunition + Grinding energetic material from military ammunition - Displaced production of emulsion explosive.

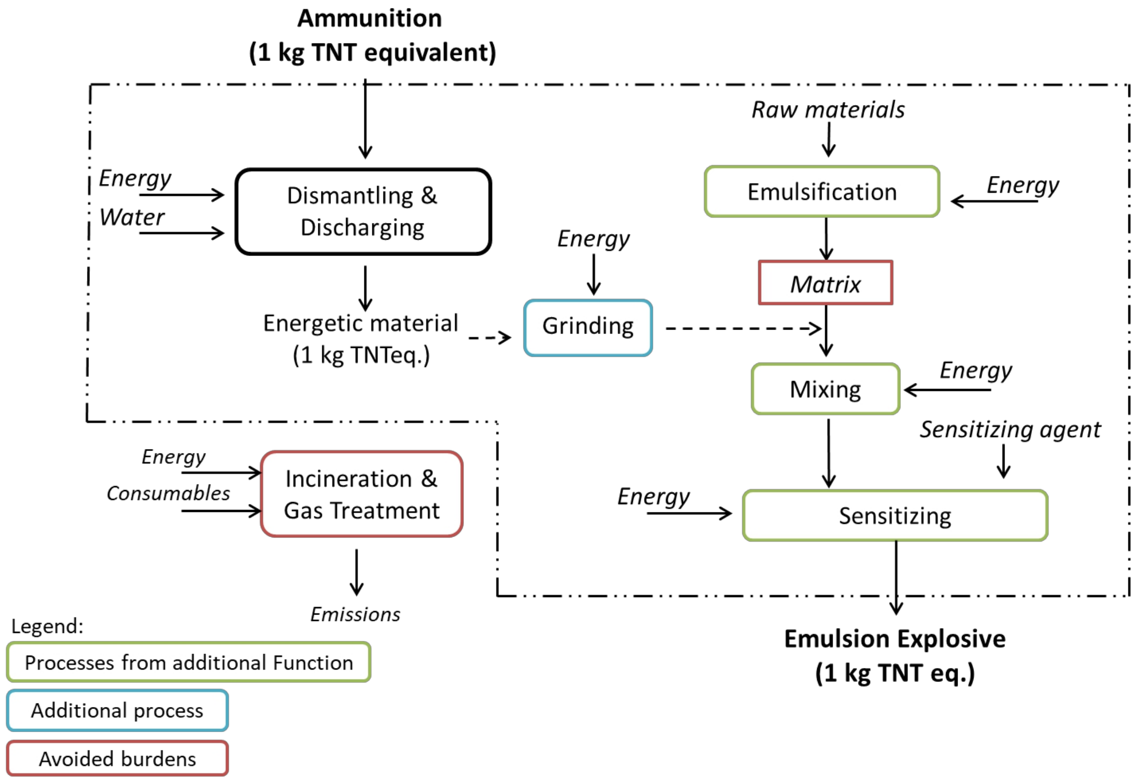

Figure 4.6. Simplified flowchart highlighting the processes of the additional function, and the avoided burdens associated with the valorisation of 1 kg TNTeq of energetic material via incorporation into civil explosive.

The life-cycle impacts associated with the conventional civil explosive production need to be assessed in order to calculate the potential benefits originated from the energetic material valorisation. The life-cycle assessment for the production of an emulsion explosive is described in detail in section 4.3.2.

4.3.2 Life-Cycle Assessment of a civil explosive production[4]

The main goal of this section is to present a comprehensive LCA of the production of a civil explosive in order to be possible to calculate the potential benefits associated with energetic material valorisation. The civil explosive considered is an emulsion explosive, which is prepared with a matrix (ammonium nitrate and water with a mixture of oils and emulsifiers) and a sensitizing agent. An LC model ("cradle-to-gate") was developed for the entire emulsion explosive production process, including explosive components, emulsification, sensitization, packaging and transportation. A detailed inventory was implemented, based on primary data collected from a specific European company producing emulsion explosives, which is representative of similar industrial processes

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[4] *Significant portions of this section appear in: Ferreira C, Freire F, Ribeiro J (2015) Life-cycle assessment of a civil explosive, Journal of Cleaner Production 89: 159-164. DOI: 10.1016/j.jclepro.2014.11.027*

taking place in developed countries. The name of the company was kept anonymous due to a confidentiality agreement to obtain industry process data.

A second goal of this study is to assess the environmental impacts of five alternative explosive compositions in order to identify the compositions with lower impacts and opportunities for improvement. Three complementary Life-Cycle Impact Assessment (LCIA) methods were used to assess ten impact categories: primary energy, six environmental impacts (CML method) and three toxicity impacts (USEtox method).

4.3.2.1 Life-Cycle Model and Inventory for emulsion explosive production

The Life-Cycle model and Inventory developed to assess the emulsion explosive production carried out was based on a specific European company, which is representative of similar processes that occur in developed countries. This company produces exclusively emulsion explosives with an annual production (2013) of 10 000 tonnes, 70% of which incorporating aluminum. The model follows a cradle-to-gate LCA and covers the following processes: transport of raw material, emulsification, sensitization and packaging. Figure 4.7 presents the Life-Cycle model flowchart for the emulsion explosive production. The emulsification, sensitization and packaging are distinct processes, but sequential, and were modelled as a single process.

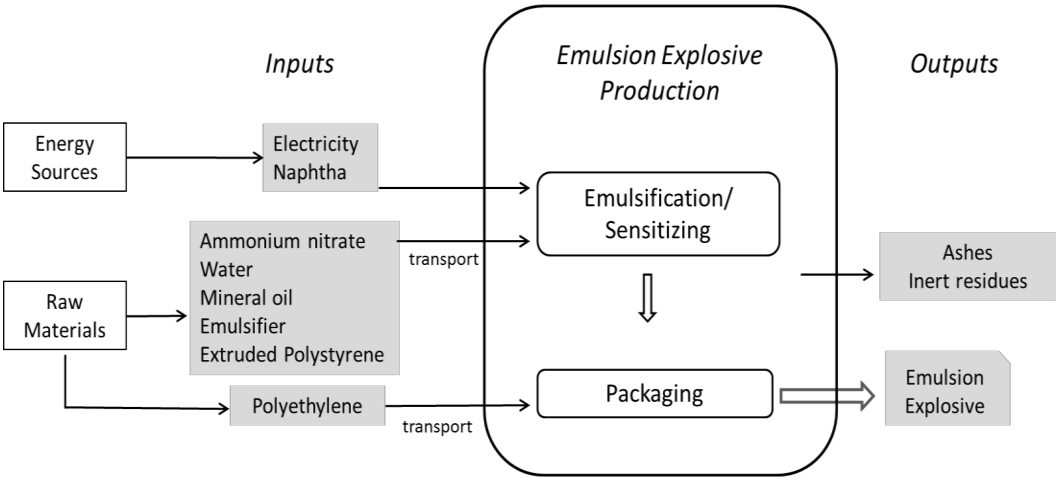

Figure 4.7. Flowchart representing the emulsion explosive production.

The functional unit was defined as 1 kg of TNT equivalent, corresponding to 4.5 MJ of energy content (Keshavarz, 2005). The corresponding reference flow includes materials and energy associated with the production of 1.45 kg of emulsion explosive, for the reason that it was considered that 1 kg of emulsion explosive has 3.14 MJ of energy content.

A detailed LCI was implemented based on process data (from the year 2010) provided by a European company; whilst secondary data was obtain using the Ecoinvent v2.2 database (http://www.ecoinvent.ch/). The components used in the preparation of the emulsion explosive were i) ammonium nitrate added in the form of prills (granules) with a diameter of 1 - 2 mm, ii) water, iii) mineral oil (liquid), iv) an emulsifier (liquid) and v) a sensitizing agent (hollow microspheres with 70 microns of diameter, considered as extruded polystyrene, XPS). Data for the emulsifiers were not provided due to confidentiality, and two alternative emulsifiers were considered: Polycarboxylate (base composition) and Carboxymethyl (alternative composition).

Tables 4.6 and 4.7 provide the mass and energy inventory of the emulsion explosive production. Table 4.8 details the transportation data for the emulsion explosive constituents. The LC model includes the indirect impacts associated with the production and transport of materials and energy inputs, assuming the electricity mix for Portugal and naphtha as fuel used in the industrial boiler. The waste treatment of minor process outputs, such us inert material (plastics, metals, paper) and ashes were left out of the system boundary due to lack of information.

Table 4.6. Mass balance Inventory for the emulsion explosive production (per kg TNTeq).

Inputs	
Constituents	**Amount**
Ammonium Nitrate	1.06 kg
Water	0.16 kg
XPS	0.03 kg
Mineral oil	0.13 kg
Polycarboxylate	0.07 kg
Packing	
Polyethylene	0.05 kg
Outputs	
Emulsion explosive (includes packing)	1.50 kg
Ashes	0.002 kg
Inert material	0.003 kg

Table 4.7. Energy requirement of the emulsion explosive production (per kg TNTeq).

Energy Requirement	**Amount**
Electricity	0.11 kWh
Naphtha	0.01 kg

Table 4.8. Transportation of the constituents for the emulsion explosive production.

Type of Transport	Distance (km)
Tank trunk (AN)	394
Trailer (XPS)	3624
Trailer (oil)	77
Trailer (Polyc.)	1155
Ship (Polyc.)	5217

Table 4.9 presents five alternative emulsions explosive compositions, which are based in alternative oils, sensitizing agents, emulsifier agents and addition of materials in the matrix to assess potential environmental improvements in production of the emulsion explosive. The base composition represents the baseline emulsion composition described before. In the composition #1 and #2, aluminum and sodium nitrate are added to the base composition, respectively, assuming that aluminum displaces an equal mass quantity of the matrix and sodium nitrate displaces an equal mass quantity of ammonium nitrate. Composition #3 includes an alternative vegetable oil (rapeseed oil), which replaces mineral oil. Composition #4 includes an alternative emulsifier (Carboxymethyl), which replaces Polycarboxylate. In composition #5, an alternative sensitizing agent (glass microspheres) replaces XPS.

Table 4.9. The five alternative explosive compositions considered (alternatives presented in bold).

Alternative compositions	Constituents (kg/kgTNTeq)								
	Ammonium Nitrate	Oils		Sensitizing agent		Emulsifier agent		Other constituents	
		Mineral	Vegetal	XPS	Glass micros.	Polycarboxylate	Carboxymethyl	Aluminum	Sodium Nitrate
Base composition	1.06	0.13	(-)	0.03	(-)	0.07	(-)	-	-
#1	0.94	0.12	(-)	0.02	(-)	0.06	(-)	**0.08**	-
#2	0.96	0.13	(-)	0.03	(-)	0.07	(-)	-	**0.10**
#3	1.06	(-)	**0.13**	0.03	(-)	0.07	(-)	-	-
#4	1.06	0.13	(-)	0.03	(-)	(-)	**0.07**	-	-
#5	1.06	0.13	(-)	(-)	**0.03**	0.07	(-)	-	-

Table 4.10 presents the process data for production of the emulsion explosive composition #1. There was addition of aluminum, which increases the energy content of the emulsion explosive to 3.35 MJ/kg, corresponding to 1.36 kg of emulsion explosive (1 kg TNTeq, the functional unit). The aluminum is added to the emulsion explosive in the form of flakes with sizes between 0.15 and 1.4 mm. For composition #2 (addition of 7% of sodium nitrate), the energy content remains the same of the base composition because, according to Lu and Liu (2008), the energy content of emulsion explosives starts decreasing for sodium nitrate percentages higher than 9%.

Table 4.10. Inventory associated with the production of composition #1 (per kg TNTeq).

Inputs	
Constituents	**Amount**
Ammonium Nitrate	0.94 kg
Water	0.14 kg
XPS	0.02 kg
Mineral oil	0.12 kg
Polycarboxylates	0.06 kg
Aluminum	0.08 kg
Packing	
Polyethylene	0.05 kg
Outputs	
Emulsion explosive (includes packing)	1.41 kg
Ashes	0.002 kg
Inert material	0.003 kg

4.3.2.2 Results and discussion

Firstly, the energy demand and environmental impacts associated with the base composition of the emulsion explosive production is showed. Secondly, the comparative analysis of the energy and environmental impacts associated with the five different emulsion explosive compositions is presented.

4.3.2.2.1 Energy and environmental impacts associated with the base composition

Table 4.11 presents the LCIA of the production of 1 kg TNTeq of the base composition. The components of the emulsion explosive are responsible for the highest impact in all ten categories, ranging from 81% (Ecotoxicity) to 99% (Human Toxicity, cancer). Transport of constituents contributes to the impacts from 0.8% (Human Toxicity, non-cancer) to 17% (Ecotoxicity), mainly due to ammonium nitrate transportation. Figure 4.8 details the contribution of the raw materials of the emulsion explosive to the LCIA.

Ammonium nitrate is the main contributor for the ten impact categories, ranging from 58% (Ecotoxiciy) to 95% (Human Toxicity, non-cancer). The contribution of ammonium nitrate is mainly associated with the use of ammonia and nitric acid in their production. The impact associated with the mineral oil ranges from 1.5% (Global Warming and cancer Human Toxicity) to 19% (Ecotoxicity).

Table 4.11 Energy and environmental impacts associated with the base composition. The highest impact is presented in bold.

Impact Categories	Emulsion composition	Transport of constituents	Energy	Total
Primary Energy (MJ prim.)	72.4 **(87.6%)**	8.7 (10.5%)	1.6 (1.9%)	82.7 (100%)
Abiotic depletion (g Sb eq)	32.5 **(87.8%)**	3.8 (10.3%)	0.7 (1.9%)	37.0 (100%)
Acidification (g SO_2 eq)	24.0 **(92.7%)**	1.2 (4.8%)	0.6 (2.5%)	25.8 (100%)
Eutrophication (g PO_4^{3-} eq)	6.6 **(95.7%)**	0.2 (2.7%)	0.1 (1.6%)	6.9 (100%)
Global warming (kg CO_2 eq)	8.1 **(92.9%)**	0.6 (6.3%)	0.1 (0.8%)	8.8 (100%)
Ozone layer depletion (mg CFC-11eq)	0.46 **(83.9%)**	0.07 (14.6%)	0.001 (1.5%)	0.55 (100%)
Photochemical oxidation (mg C_2H_4 eq)	550 **(82.2%)**	94 (14.0%)	25 (3.8%)	669 (100%)
Human toxicity, cancer (CTU_h)	2.6E-10 **(96.7%)**	5.4E-12 (2.0%)	3.7E-12 (1.4%)	2.7E-10 (100%)
Human toxicity, non-cancer (CTU_h)	1.0E-09 **(99.0%)**	8.1E-12 (0.8%)	2.4E-12 (0.2%)	1.1E-09 (100%)
Ecotoxicity (CTU_e)	0.004 **(81.3%)**	7.0E-04 (17.0%)	7.5E-05 (1.7%)	0.004 (100%)

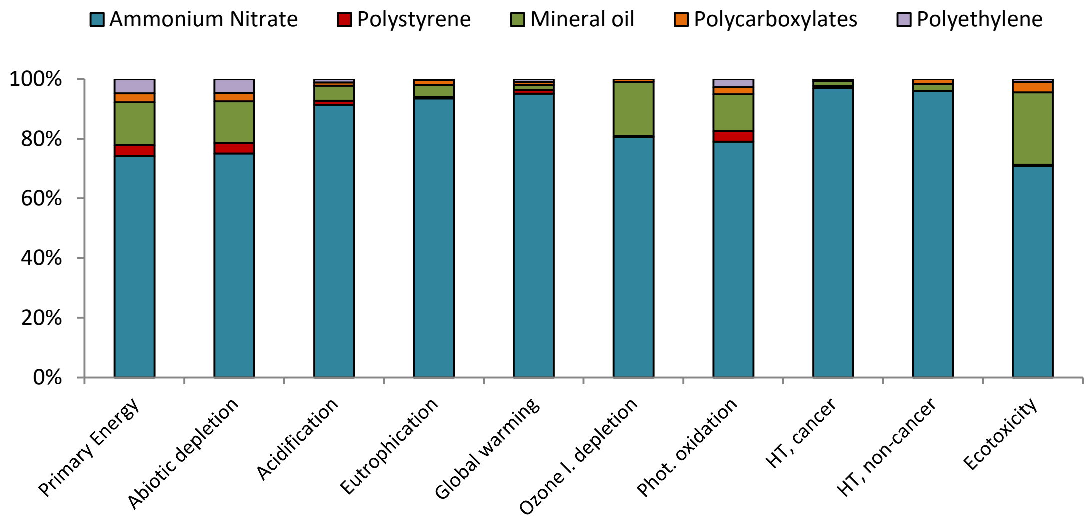

Figure 4.8. Contribution of the constituents of the emulsion explosive (base composition).

4.3.2.2.2 Comparative analysis of five different emulsion explosive compositions

Table 4.12 presents a comparison of the energy demand and environmental impacts (the highest is shown in bold while the lowest is underlined) associated with the five different emulsion explosive compositions. The impacts relatively to the base composition were also calculated (% inside brackets) to identify the compositions with more potential to reduce impacts, as discussed in detail below.

The displacement of the matrix by sodium nitrate (composition #2) leads to a reduction in all impacts, comparatively with the base composition. Moreover, composition #2 presents lower environmental impacts for eight out of ten impact categories compared to the other five emulsion explosive compositions (Primary energy – 7%; Acidification – 8%; Eutrophication – 14%; Global Warming – 9%; Photochemical Oxidation – 8%; cancer Human Toxicity – 7,4%; non-cancer Human Toxicity – 12%; Ecotoxicity – 7%).

Compositions #3 and #4 present the highest increase in impacts, comparatively to the base composition. Composition #3 shows an increase in four impact categories (Acidification; Eutrophication; non-cancer Human Toxicity; and Ecotoxicity. The highest increase is associated with the emissions referent to the use of fertilizers (main contributor is ammonium nitrate) and pesticides (main contributor is cypermetrin) in the cultivation phase of vegetable oil, due to which composition #3 dominates the Ecotoxicity impacts. Composition #4 presents an increase in five impacts (Primary Energy; Abiotic depletion; Global Warming; Ozone Layer Depletion; and cancer Human Toxicity). The emulsifier Carboxymethyl presents higher impacts for all the impact categories compared with the Polycarboxylate (base composition).

Table 4.12 Energy and environmental analysis (per kg TNTeq) of five emulsion explosive compositions (variation relatively to the base composition inside brackets). The highest energy demand and environmental impact is shown in bold while the lowest is underlined.

Impact category	Base composition	#1	#2	#3	#4	#5
Primary energy (MJ prim.)	82.6	84.5 (2.3%)	76.8 (-7.0%)	80.6 (-2.4%)	**87.9** **(6.4%)**	80.4 (-2.7%)
Abiotic depletion (g Sb eq)	37.0	37.0 (0.0%)	34.0 (-8.1%)	33.0 (-11.0%)	**39.0** **(5.4%)**	36.0 (-2.7%)
Acidification (g SO_2 eq)	26.0	26.0 (0.0%)	24.0 (-7.7%)	**28.0** **(7.7%)**	27.0 (3.8%)	26.0 (0.0%)
Eutrophication(g PO_4^{3-} eq)	7.0	7.0 (0.0%)	6.0 (-14.0%)	**9.0** **(29.0%)**	7.0 (0.0%)	7.0 (0.0%)
Global warming (kg CO_2 eq)	8.8	8.4 (-4.5%)	7.9 (-9.0%)	8.9 (1.3%)	**9.0** **(2.5%)**	8.7 (-0.3%)
Ozone layer depletion (mg CFC-11 eq)	0.55	0.52 (-5.5%)	0.51 (-7.3%)	0.50 (-9.1%)	**0.62** **(12.7%)**	0.55 (0.0%)
Photochemical oxidation (mg C_2H_4 eq)	669.0	**859.0** **(28%)**	616.0 (-7.9%)	623.0 (-7.0%)	730.0 (9.1%)	658.0 (-1.6%)
Human toxicity, cancer (CTU_h)	2.7E-10	2.7E-10 (0.0%)	2.5E-10 (-7.4%)	2.9E-10 (7.4%)	**3.0E-10** **(11.0%)**	2.7E-10 (0.0%)
Human toxicity, non-cancer (CTU_h)	1.0E-09	1.0E-09 (0.0%)	9.7E-10 (-12.0%)	**1.1E-09** **(10.0%)**	1.0E-09 (0.0%)	1.0E-09 (0.0%)
Ecotoxicity (CTU_e)	0.0044	0.0044 (0.0%)	0.0041 (-6.8%)	**0,158** **(3850.0%)**	0.005 (25.0%)	0.0044 (0.0%)

Composition #1 presents an increase in Photochemical Oxidation (28%) and Primary energy (2.3%), comparatively to the base composition. However, for the other nine impact categories, composition #1 shows similar impacts (Abiotic Depletion; Acidification; Eutrophication; Human Toxicity; and Ecotoxicity) or lower impacts (Ozone layer Depletion; and Global Warming). Composition #5 shows similar impacts to the base composition for six impacts (Acidification; Eutrophication; Ozone Layer Depletion; Human Toxicity; and Ecotoxicity), whilst for the other four impacts there is a reduction, ranging from -0.3% (Global Warming) to -2.7% (Primary Energy and Abiotic Depletion).

4.3.3 Life-Cycle Impact Assessment of energetic material valorisation

Life-Cycle Impact Assessment results associated with the energetic material valorisation are presented in this section. Figure 4.9 shows the impact comparison between the conventional ammunition disposal process by incineration and the energetic material valorisation process. An analysis solely to the comparison of the two approaches to dispose of military ammunition shows that the valorisation of energetic material allows a significant decrease of the total impact. The reduction of the impacts resulting from the valorisation of 1 kg TNT equivalent of energetic material ranges between 102% (Photochemical Oxidation) to 290% (non-cancer Human Toxicity). The grinding process, an operation specific for the new approach, presents an almost irrelevant contribution to the life-cycle impacts in all categories.

The preeminent benefit of this approach to eight out of the ten impact categories considered arises from the complete avoidance of the energetic material incineration and flue gas treatment. Just the avoidance of the incineration and gas treatment procedure contributes to decrease in average approximately 80% of the environmental impacts. These findings might be explained due to high energy requirement of the incineration and flue gas treatment referent to the conventional disposal process. Those high energy requirements are needed to heat-up and maintain the kiln at the required temperature (400 ºC to 600 ºC) as well as to operate the equipment used in the flue gas treatment (post-combustion chamber, selective catalytic reduction systems, and scrubbers), which is the price to pay in order to obtain cleaner emissions. Moreover, due to safety reasons, the static kiln only operates with small batches of energetic material (up to 20 kg TNT equivalent per hour), which increases its time of operation and the specific energy consumption.

A minor influence of the incineration procedure is observed for the categories non-cancer Human Toxicity and Eutrophication. The life-cycle impact averted for these impact categories are associated with the displacement of the emulsion explosive matrix components, principally ammonium nitrate, which significantly contributes to the decrease of impact. In fact, the major benefits are observed for these two impact categories due to the higher contribution of the ammonium nitrate production for these categories (indicating that the inherent impacts avoided for its displacement are also greater) than the impacts associated with the incineration procedure.

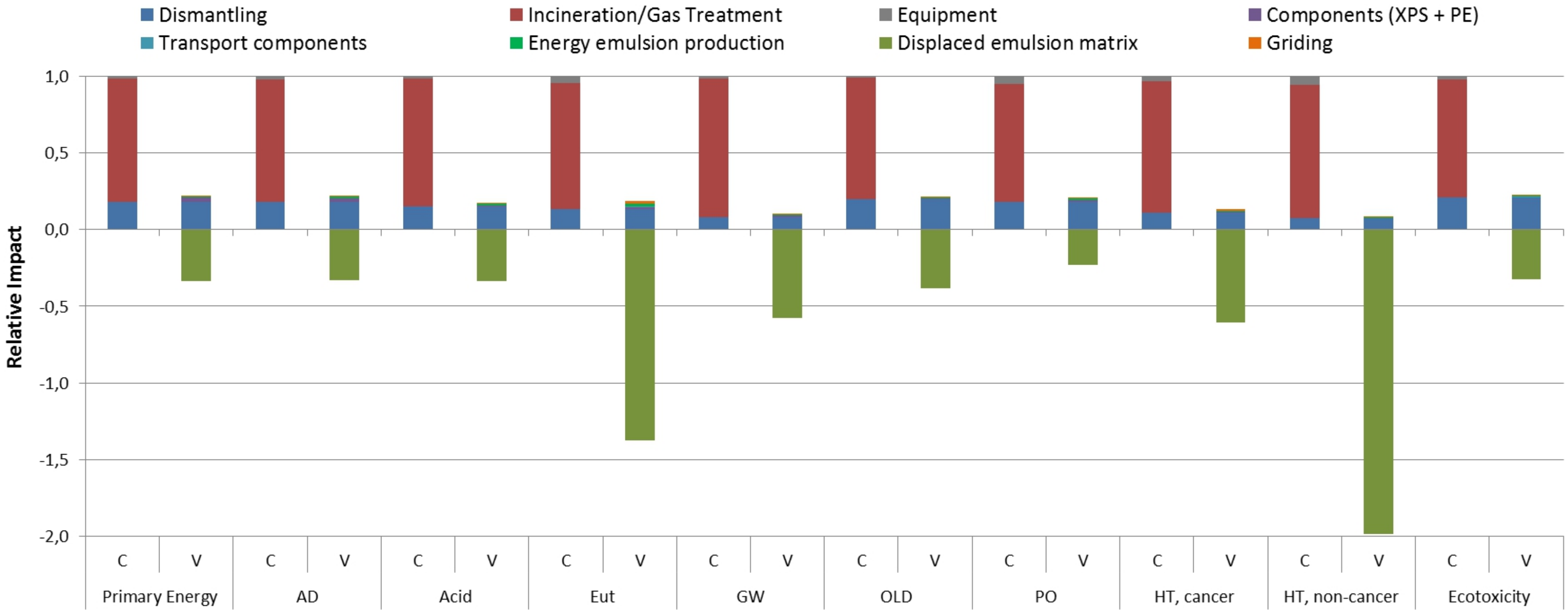

Figure 4.9. Comparison between the impacts associated with the conventional ammunition disposal by incineration process (C), and the process associated with the valorisation of energetic material from ammunition (V) (per kg TNTeq.).

4.4 Comparison between ammunition disposal techniques

In this section, a comparison between the environmental and toxicological impacts associated with three disposal processes (open detonation [OD], incineration in a static kiln with gas treatment [IGT], and valorisation of energetic material [V]) was carried out. For the three demilitarisation processes, the functional unit considered is the disposal of the 155 mm generic large calibre ammunition with a charge of 8.5 kg of composition B in the projectile, which corresponds approximately to 10.2 kg TNT.

Figure 4.10 shows the comparison of the environmental and toxicological impacts between the three disposal techniques: open detonation, incineration with flue gas treatment, and valorisation of energetic material. For the six environmental categories, the IGT process presents higher impacts due to the high energy requirements in the static kiln and in the gas treatment system (electricity for the kiln and propane gas for the post-combustion chamber). However, Open Detonation shows higher impacts than IGT and energetic material valorisation (V) for the toxicological impact categories. Valorisation of energetic material from ammunition presents negative environmental impacts (benefits) for all the impacts categories.

The analysis of environmental and toxicological impacts associated with three alternative ammunition disposal techniques have shown that the direct impacts (e.g. emissions from OD/OB) significantly contributes to the toxicological impact categories; whilst the indirect burdens (energy and material consumption) have a significant influence on the environmental categories. This outcome represents a trade-off between the open detonation process and the incineration process to dispose of military ammunition, so the selection of the appropriate technique of ammunition disposal will depend on the purpose and the relative importance of each impact category for the decision makers or stakeholders. Nevertheless, the valorisation of energetic material is the technique with better results to decommission military ammunition.

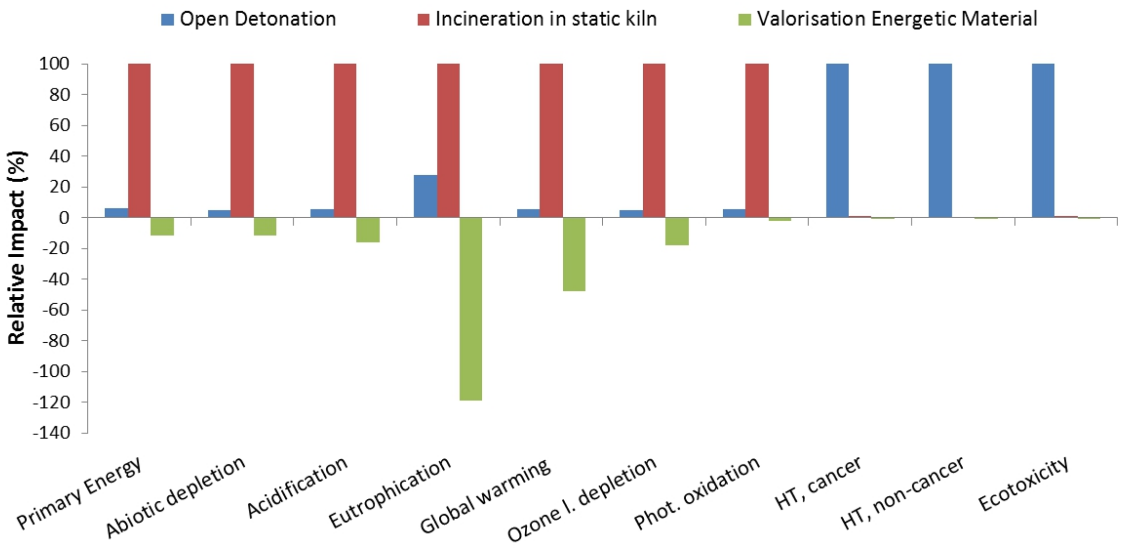

Figure 4.10. Comparison of the impacts between Open Detonation, Incineration in static kiln with Gas Treatment, and Valorisation of energetic material.

4.5 Concluding remarks

Demilitarisation of ammunition that has reached the end of its life-cycle or become obsolete has to be carried out with minimum energy and environmental impacts. This chapter presented the environmental and toxicological impacts associated with three demilitarisation techniques (Open detonation, incineration in a static kiln with gas treatment, and valorisation of energetic material from ammunition incorporated into civil explosives) in order to determine which technique to dispose of military ordnances shows the minimum impact on the environment. The main findings, that enhance our understanding of the demilitarisation process, are summarised following.

The results obtained to demilitarisation by incineration in a static kiln shows that the main factor responsible to the life-cycle impact are the energy requirements (electricity and propane). The elimination of ammunition using incineration requires considerable amounts of energy, which does not make much sense as the energetic material itself frequently is still in good conditions owning a worthwhile value that can be exploited. Therefore, other approaches to dispose of military ammunition should be investigated to minimise this dependency of energy requirement.

The energetic material valorisation is an industrial ecology approach, and an alternative to conventional decommissioning. Energetic material valorisation avoids the conventional decommission of military explosives by incineration in static kiln with flue gas treatment, as well as displaces part of the components of the matrix of the emulsion explosive. The main benefits arising from the energetic material valorisation are associated with the avoidance of the incineration of military ammunition; nonetheless, the displacement of the components of the emulsion explosive also presents a noteworthy influence to the impact avoided for this industrial ecology approach.

The comparison between the three disposal techniques shows that open detonation has higher toxicological impacts than the other two processes: incineration in static kiln, and energetic material valorisation. The higher impact contribution of open detonation for non-cancer Human Toxicity (92% of the total impact) is, as would be expected, associated with the emission of the detonation products. Unexpectedly, for the cancer Human Toxicity and Ecotoxicity categories the highest impact contribution (74% and 4% of the total impacts, respectively) is related to the production of the gravel used to cover the charges – prior to the detonation and to fill the crater after the detonation. It is important to emphasise that this last surprising and important result could only be assessed because a holistic life-cycle approach was used in this study.

This assessment also shown that the benefits obtained from the energetic material valorisation were considerably significant. However, there are still some hindrances to incorporate energetic material from military ammunitions into civil explosive, mainly due to commercial and technical issues. The companies that actually produce civil explosives will be compelled to inform their clients that they are buying explosives with recycled material incorporated, with some variations in their performance and safety characteristics compared to the standard explosives, which might not be well accepted by the producers. Furthermore, different types of ammunition are the source of energetic material that will be incorporated in the civil explosives, leading to diverse batches of energetic material (significantly different from one to another) that will demand for supplementary quality control methods.

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Chapter 5 - A hazard classification system based on incorporation of REACH regulation limits in the USEtox method

Summary: This section presents the development of a new framework to improve the classification of hazard substances based on the life-cycle impact assessment method USEtox to calculate characterisation factors (CFs) of virtual substances, hypothetical substances whose properties are based on the regulatory limits established by REACH regulation. As a result, the CFs of the virtual substances calculated can represent a reference to understand the significance of the toxicological impacts on human health. Section 5.1 presents the limitations of the hazard classification system from REACH regulation, describes the concept of virtual substance (VS), and the new conceptual framework proposed to calculate the toxicological CFs for virtual substances is presented in detail. The toxicological CFs calculated for each virtual substance permits to comprehend the potential effects of combining different physicochemical properties into toxicological impacts. Moreover, a new hazard classification system based on the toxicological CFs calculated with USEtox for virtual substances that integrate the REACH limits is proposed to assist in the evaluation of safer toxicological alternatives. Section 5.2 shows a practical example in which is assessed alternatives to dibutyl phthalate (substance restricted by REACH) with the employment of the classification system proposed.

5.1 Background and objectives

REACH is a European Union regulation concerning the registration, evaluation, and authorization of chemicals that aims to enhance the protection of human health and ecosystems as well as improve the competitiveness of the European chemical industry (European Commission, 2006; Askham *et al.*, 2012). With REACH, European authorities intend to encourage, and in some circumstances to guarantee, that substances reported as harmful are replaced by available, economically and technically viable alternatives with lower toxicity (European Commission, 2006). Harmful substances, named as substances of very high concern (SVHC), are classified according to the criteria outlined in Annex XIII of REACH, in which limits are established for the physicochemical properties of the substances that are assumed to represent a hazard to both human health and ecosystems (European Commission, 2006).

The properties considered in Annex XIII of REACH are associated with persistence (water, soil, and sediment), bioaccumulation, and toxicity, in which two levels of regulatory limits are established: one level with limits which classify the substance as persistent, bioaccumulative or toxic (PBT); and other level with higher limits that classify the substances as very persistent or very bioaccumulative (vPvB). The violation of only one of the regulatory limits is sufficient to classify a substance as SVHC (European Commission, 2006). Underlying the employment of this classification system are the following ideas: i) the potential consequences to human health and ecosystems associated with the emission of a certain substance are essentially dependent on a restricted number of the substance's properties, ii) the regulatory limits are equivalent from the perspective of the potential consequences to human health and ecosystems, iii) the consequences to human health and ecosystems arising from the emissions associated with the unrestricted production and use of substances exceeding those limits are unacceptable, so they need to be replaced by suitable alternatives.

The aforesaid ideas not only require deeper investigation, but they also raise several additional issues that need to be clarified. It is necessary to understand if, individually, as proposed by REACH the properties associated with persistence, bioaccumulation, and toxicity are representative of the behavior of substances in the environment, and if the limits established by REACH for each one of these properties are equivalent from the perspective of the potential toxicological impact. It is also necessary to ascertain whether other physicochemical properties, not considered in the SVHC classification as well as the combinatorial effect of different properties, pose a significant contribution to the impact. In fact, Petry *et al.* (2006) show some apprehension in prioritizing substances based solely on certain inherent psychochemical properties, which can bias the classification. As stated by Blainey *et al.* (2010), even if the imposition of limits is an applicable manner to compromise regulatory criteria, the SVHC identification procedure cannot be perceived as absolute scientific criteria for the assessment of the consequences to ecosystems and human health, due to the potential importance of the combinatorial effect of different properties on the impact.

USEtox method can be employed to calculate toxicological characterization factors (CFs) of substances via converting the physicochemical properties and environment characteristics into potential impacts for ecosystems and human health (Rosenbaum *et al.*, 2008). Therefore, USEtox not only takes into account the parameters employed for the SVHC classification, but also considers other relevant parameters, such as inter media partition coefficients, and combines them with the environment characteristic (e.g. precipitation rate, wind speed, soil erosion) to determine fate and exposure behaviors of substances.

By way of example, dibutyl phthalate, a substance widely used in a variety of products, was identified as a SVHC and thus included in Annex XIV of REACH (substances that need authorization to be used) due to its toxicity; however, this substance has lower toxicological characterization factors than benzene (which was not identified as an SVHC), accordingly to the USEtox method. The fact that USEtox considers others parameters and the influence of its combination, leads to the divergence observed between the REACH classification system and USEtox toxicological CFs. In the specific case of the abovementioned example, the higher value of water solubility and vapor pressure for benzene results in higher toxicological CFs when compared to dibutyl phthalate.

The objective of this section is to contribute to the discussion of the previously mentioned issues, focusing on comprehending the importance of the combinatory effect of different physicochemical properties on the toxicological consequences on human health. To achieve this goal, a conceptual framework is proposed to calculate toxicological CFs associated with virtual substances, defined as based on the regulatory limits imposed by REACH regulation. Toxicological CFs are calculated for eight virtual substances considering the physicochemical properties half-life in air ($t_{1/2}$ air), half-life in water ($t_{1/2}$ water), half-life in soil ($t_{1/2}$ soil); half-life in sediment ($t_{1/2}$ sediment); octanol-water partition coefficient (k_{ow}); water solubility (Sol_{25}); Effect Dose for human toxicity (ED_{50}); and an extreme scenario. Based on the toxicological CFs calculated it is possible to i) assess the equivalence between the limits established for the different physicochemical properties; ii) evaluate the significance of the combinatorial effect from different physicochemical properties into potential impacts; and iii) present recommendations to improve, support, and facilitate the classification of SVHC in REACH regulation. Furthermore, a new tool is proposed to assist in the evaluation of safer toxicological alternatives for substances banned or restricted by REACH.

5.1.1 Definition of the virtual substance

The concept of virtual substance (VS) is proposed to enable a clear evaluation of the importance of the combinatory effect of the physicochemical properties to the toxicological impacts, which would not be feasible with a set of real substances. A virtual substance is a hypothetical substance which the physicochemical properties half-life in water ($t_{1/2}$ water), half-life in soil ($t_{1/2}$ soil); half-life in sediment ($t_{1/2}$ sediment); octanol-water partition coefficient (k_{ow}); and Effect Dose for human toxicity (ED_{50}) are determined by the limits established by Annex XIII of REACH regulation; while for the half-life in air ($t_{1/2}$ air), and the water solubility (Sol_{25}) the limits are obtained from the literature. A list of the properties that characterize the virtual substances, and the respective limits, are presented in Table 5.1. The vPvB limits are not included in the analysis as the first threshold (PBT limits) is considered sufficient to compare the virtual substances and understand the influence of the combination of all physicochemical properties into impacts.

Table 5.1. Limits considered for the physicochemical properties that characterises the virtual substances.

Parameters	**PBT**	**source**
$t_{1/2}$ air	> 2 days	Scheringer *et al.*, 2006
$t_{1/2}$ water	> 40 days	European Commission, 2006
$t_{1/2}$ soil	> 120 days	European Commission, 2006
$t_{1/2}$ sediment	> 120 days	European Commission, 2006
Log k_{ow}	> 4.5	European Commission, 2006
Sol_{25}	> 1 mg/L	Vighi and Calmari, 1993
LD_{50}	[25 - 200] mg/kg	European Commission, 2008

The calculation of the toxicological CFs are made for eight different sets of VS. Seven VS are identified as having the value of one of the mentioned properties that coincide with the limit which determines it PBT (see table 1), while the values of all the other properties are one order of magnitude below the limit. Each one of these virtual substances is referred by the property whose value is equal to the limit (e.g. VS Sol25 is the virtual substance which value coincides with the limit for water solubility). Also considered was an extreme scenario associated with a virtual substance with the values of all its physicochemical properties coinciding with the limits in order to comprehend the influence of the combinatory effect (this scenario was entitled as extreme virtual substance). Table 5.2 presents the eight virtual substances created, including the values assumed for each physicochemical property.

Table 5.2. Baseline limits for the physicochemical properties used to create the eight virtual substances.

Parameters	Units	Virtual Substances							
		VS $t_{1/2}$ air	VS $t_{1/2}$ water	VS $t_{1/2}$ soil	VS $t_{1/2}$ sediment	VS k_{ow}	VS Sol_{25}	VS ED_{50}	Extreme VS
$t_{1/2}$ air	days	**2**	0.2	0.2	0.2	0.2	0.2	0.2	2
$t_{1/2}$ water	days	4	**40**	4	4	4	4	4	40
$t_{1/2}$ soil	days	12	12	**120**	12	12	12	12	120
$t_{1/2}$ sediment	days	12	12	12	**120**	12	12	12	120
k_{ow}	(-)	3162	3162	3162	3162	**31623**	3162	3162	31623
Sol_{25}	mg/L	0.1	0.1	0.1	0.1	0.1	**1**	0.1	1
ED_{50}	mg/kg	2000	2000	2000	2000	2000	2000	**200**	200

5.1.2 Framework and scenarios developed to calculate the characterization factors of the virtual substance

Figure 5.1 show the concept framework developed to calculate toxicological characterization factors for virtual substances using the USEtox method. Some assumptions were carried out to implement the framework, which is explained below. The properties of the virtual substances, selected based on the legal limits as described before, were incorporated in the USEtox; however, for some properties a unit conversion is required. The regulatory limits for half-lives are defined in days, but conversion to biodegradation rates (second^{-1}) is needed in accordance with the approach described in Huijbregts *et al.* (2010). The same approach is carried out for the toxicity limit property (LD_{50}) based on the extrapolation acute-to-chronic effects from Rosenbaum *et al.* (2011).

Beyond the physicochemical properties whose values are established based on legal or literature limits (presented in table 1), other properties are required to calculate the toxicological characterization factors of the VS with USEtox. The properties k_{doc}, k_{oc} and BAF_{fish} are calculated based on the legal values of k_{ow}, using the recommended equations described in Huijbregts *et al.* (2010). The remaining physicochemical properties of the virtual substances necessary for the calculation of the CF, which are independent of any regulatory limit, are: molecular weight (MW), vapour pressure (P_{vap}) and Henry's Law coefficient (k_H). For these properties the subsequent approach is followed: the k_H was calculated from the MW, the P_{vap}, and the value of water solubility according to the equation recommended in Huijbregts *et al.* (2010) – $k_H = (P_{vap} \times MW) \div Sol_{25}$ –; while the values for molecular mass and for vapour pressure vary in a range that covers the majority of organic substances: $MW \in [10 – 1000$ g/mol$]$ and $P_{vap} \in [1.0E-07 – 1.0E+05$ Pa$]$. More information about the calculation of Henry's law coefficient is detailed in the Appendix IV-1.

Table 5.3 lists the values of the physicochemical properties of each one of eight virtual substances, with the units converted to be included in the USEtox method. The calculation of the characterization factors are carried out for six different emission compartments: continental air, urban air, freshwater, sea water, natural soil and agricultural soil. Overall, forty-eight toxicological CFs are calculated considering the combination of the eight virtual substances for six different emission compartments.

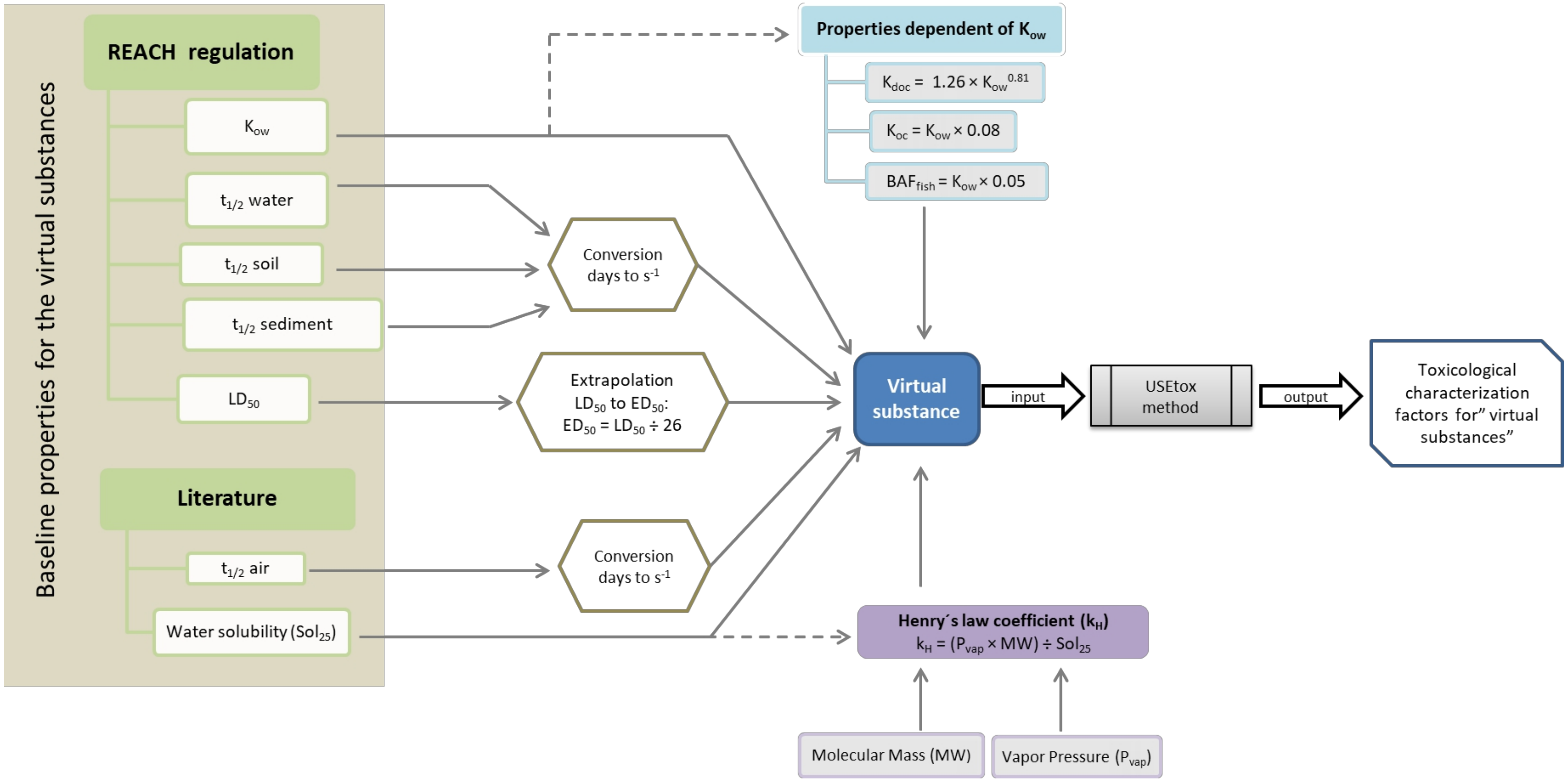

Figure 5.1. Framework developed to calculate the toxicological characterization factors of the virtual substances.

Table 5.3. Scenarios associated with the eight virtual substances characterised by the PBT limits.

Parameters	Units	Scenarios for PBT virtual substances							
		VS $t_{1/2}$ air	VS $t_{1/2}$ water	VS $t_{1/2}$ soil	Vs $t_{1/2}$ sediment	VS k_{ow}	VS Sol_{25}	VS ED_{50}	Extreme VS
k_{ow}	(-)	3162	3162	3162	3162	**31623**	3162	3162	31623
k_{oc}	L/kg	862	862	862	862	5564	862	862	5564
Sol_{25}	mg/L	0.1	0.1	0.1	0.1	0.1	**1**	0.1	1
k_{deg} air	s^{-1}	**7.80E-06**	5.50E-05	5.50E-05	5.50E-05	5.50E-05	5.50E-05	5.50E-05	7.80E-06
k_{deg} water	s^{-1}	3.40E-06	**2.10E-07**	3.40E-06	3.40E-06	3.40E-06	3.40E-06	3.40E-06	2.10E-07
k_{deg} soil	s^{-1}	4.82E-07	4.82E-07	**6.50E-08**	4.82E-07	4.82E-07	4.82E-07	4.82E-07	6.50E-08
k_{deg} sediment	s^{-1}	1.03E-07	1.03E-07	103E-07	**1.40E-08**	1.03E-07	1.03E-07	1.03E-07	1.40E-08
k_{doc}	L/kg	253	253	253	253	2530	253	253	2530
BAF_{fish}	L/kg	158	158	158	158	1581	158	158	1581
ED_{50}	kg/lifetime	76.9	76.9	76.9	76.9	76.9	76.9	**7.69**	7.69
MW	g/mol	[10 - 1000]	[10 - 1000]	[10 - 1000]	[10 - 1000]	[10 - 1000]	[10 - 1000]	[10 - 1000]	[10 - 1000]
P_{vap}	Pa	[1.0E-07 – 1.0E+05]	[1.0E-07 – 1.0E+05]	[1.0E-07 – 1.0E+05]	[1.0E-07 – 1.0E+05]	[1.0E-07 – 1.0E+05]	[1.0E-07 – 1.0E+05]	[1.0E-07 – 1.0E+05]	[1.0E-07 – 1.0E+05]
k_H	$Pa.m^3/mol$	[1.0E-05 – 1.0E+09]	[1.0E-05 – 1.0E+09]	[1.0E-05 – 1.0E+09]	[1.0E-05 – 1.0E+09]	[1.0E-05 – 1.0E+09]	[1.0E-06 – 1.0E+08]	[1.0E-05 – 1.0E+09]	[1.1E-06 – 1.1E+08]

5.1.3 Results and discussion

In this subsection the CFs calculated for the virtual substances considering six emission compartments are presented and discussed. Firstly, the toxicological equivalence of the limits established for the different physicochemical properties is evaluated. The relevance of the combinatory effect of the substance's properties on a substance hazard classification system such as REACH is also analyzed. The influence of the k_H parameter on the CFs and the importance of its inclusion in the hazardous classification system are discussed. Secondly, the toxicological CFs calculated for the VS are used as references in a hypothetical classification system tested with real substances, as an alternative to analyzing only the limits for physicochemical properties.

5.1.3.1 Comparison between the toxicological characterization factors of the eight virtual substances

Characterization factors obtained for the different VS are compared taking into account the emission compartment in order to facilitate the analysis of the toxicological equivalence of the different regulatory or literature limits. Given as representative examples, Figures 5.2 to 5.4 present the CFs obtained for the emission compartments urban air, freshwater, and natural soil, respectively. The CFs associated with the other three emission compartments are shown in the Appendix III-2 (figures A1 to A3). In all the aforementioned figures, for each virtual substance, instead of a single value, a range of values of the CFs due to the k_H variation is presented in a logarithmic scale. The toxicological CFs are shown for the extreme values (minimum and maximum k_H), and for the interval of k_H that comprises the majority of organic substances in USEtox [1.0E-06 Pa.m^3.mol^{-1}; 1.0E+02 Pa.m^3.mol^{-1}] represented by a dark line in Figures 5.2 to 5.4.

The analysis of the results shows that, with the exception of the extreme virtual substance, within each emission compartment the toxicological CFs are similar or do not vary more than one order of magnitude. This variation is under the magnitude of the USEtox uncertainty (evaluated in two to three orders of magnitude for recommended CFs), so it can be reasoned that the regulatory limits associated with the different virtual substances are equivalent from the point of view of their effectiveness on imposing limits to the toxicological consequences of substances. This observation is in accordance with SVHC classification, indicating that the existence of only one physicochemical property with a value above the regulatory limits is sufficient to identify a hazardous substance.

Another important result that deserves to be highlighted is related to the marginal difference observed between the CFs obtained for the seven VS (in which only one parameter is coincident with the regulatory and literature limits) and the extreme VS (in which all physicochemical properties are near the regulatory and literature limits). The differences of approximately two orders of magnitude observed are on the limit to be considered a significant variation. Therefore, a substance with physicochemical properties marginally coincident with the limits considered in this study can still pose higher toxicological impacts than a substance that has just one of its physicochemical properties marginally above the regulatory limits (consequently classified as potentially hazardous). The influence of the combinatory effect of different physicochemical properties on their toxicological impact is not negligible, so the application of a hazardous classification system based on the values of individual properties can be insufficient and can bias the classification.

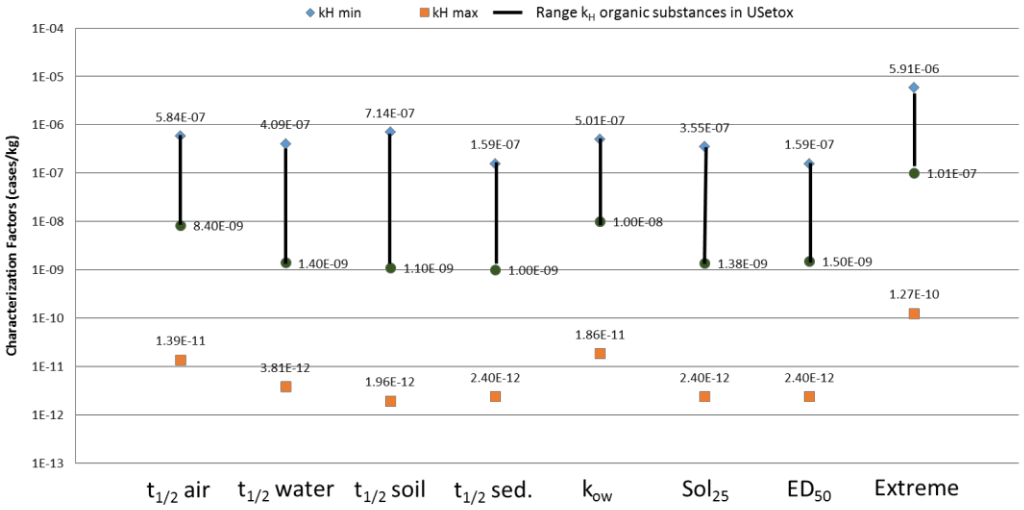

Figure 5.2. Toxicological characterization factors associated with the eight virtual substances in urban air emission compartment.

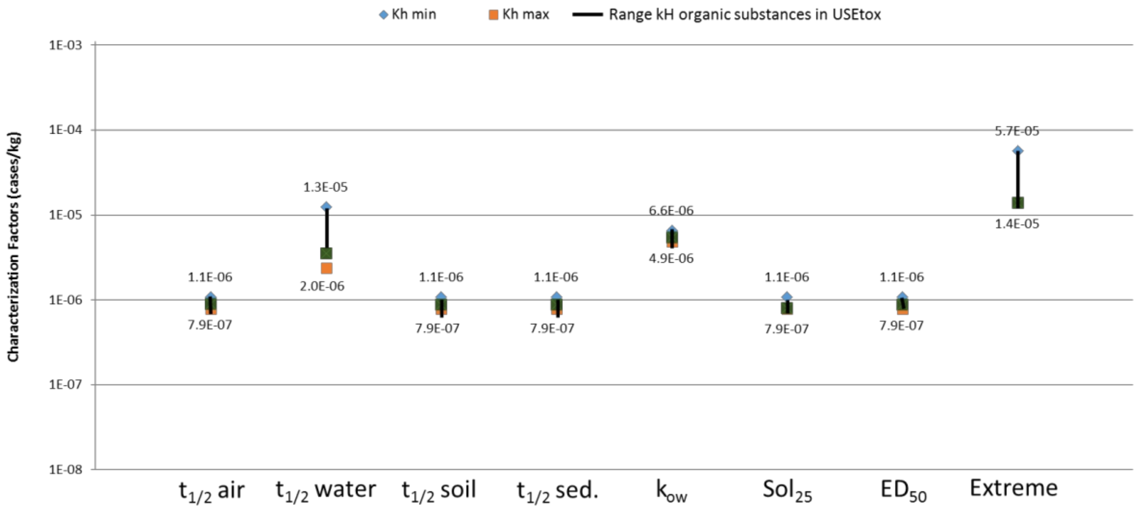

Figure 5.3. Toxicological characterization factors associated with the eight virtual substances in freshwater emission compartment.

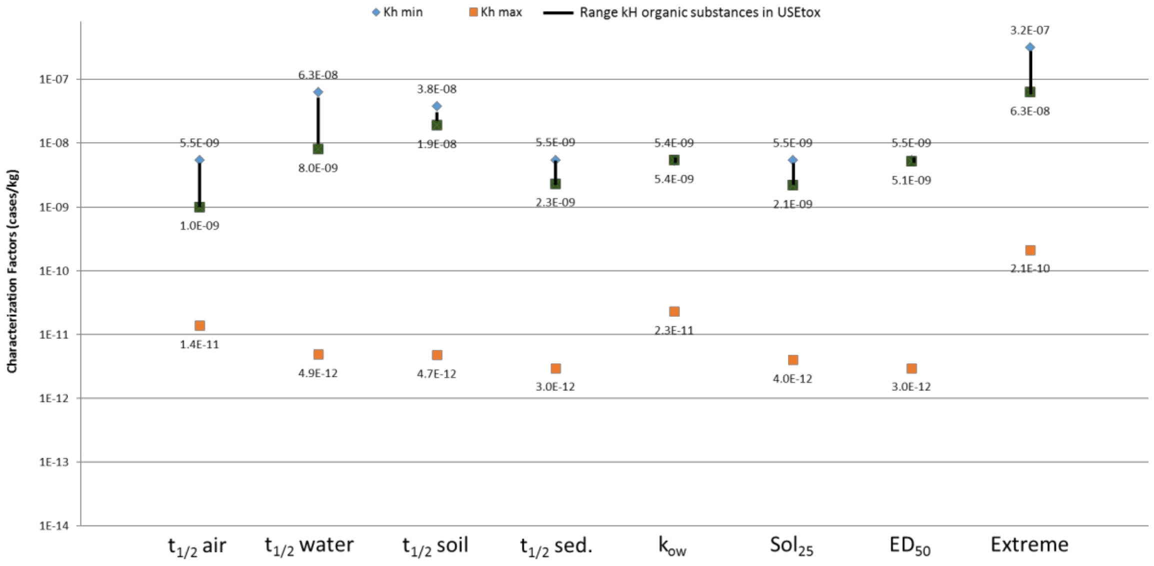

Figure 5.4. Toxicological characterization factors associated with the eight virtual substances in natural soil emission compartment.

Another interesting behavior drawn from this assessment is related to the influence of Henry's law coefficient (k_H) on the calculated toxicological CFs, principally for the air and soil emission compartments. That influence, in the specific case of the virtual substance ED_{50}, is presented in Figure 5.5 considering three emission compartments (urban air, freshwater and natural soil) with the results for the other emission compartments being similar. The pattern observed for the virtual substance ED_{50} (and the conclusions drawn) is also obtained for the other six virtual substances, which can be seen in Figures B4 to B9 (Appendix IV-3).

The results presented in Figure 5.5 show that the toxicological CFs for an emission into air is highly dependent on k_H. This behavior reflects the intrinsic nature of this parameter and the specific characteristics of the different emission compartments. In fact, k_H is essentially an air-water partition coefficient inferring the direction and rate of transfer of a substance between air and water compartments (Mackay *et al.*, 2006). A high value of k_H (which implies a high value of vapor pressure) indicates a substance with a tendency to evaporate and remain in the air compartment. However, the probability of a person being exposed to a certain substance existing in air is lower than the same equal amount of a substance in the water compartment. This outcome is associated with the high number of bioavailability vectors of the later emission compartment in comparison with air compartment, which results in a lower intake factor and a lower toxicological CF.

A similar explanation can be formulated for the characterization factors variation on the emission compartment natural soil due to the k_H parameter. High values of k_H (1.0E+01 $Pa.m^3.mol^{-1}$ or 1.0E+03 $Pa.m^3.mol^{-1}$) increase the tendency for the movement of a substance from soil to air, which reduces its bioavailability and the value of the CFs; while low values of k_H increase the tendency of the substance to maintain on the soil (and/or moves toward the water compartment) which increases its bioavailability and, consequently, its toxicological CFs. In contrast, the toxicological CFs for an emission into water are not significantly affected by the k_H parameter (Figure 5.3). The explanation to this behavior is possibly related to the predominant influence of the gas or liquid mass transfer coefficient (Trapp and Matthies, 1996), instead of the k_H and vapor pressure parameters, to the water-air diffusion mechanisms that determine the mass exchange between the water and air compartments.

Henry's law coefficient significantly influences the calculation of the toxicological characterization factors with a high variation for an emission into air and soil. This parameter, which is highly influenced by the vapor pressure and water solubility, should be included in the identification of a substance of very high concern (SVHC) to improve the ascertainment of the potential toxicological impact of chemical substances. In fact, these physicochemical parameters are required in the registration step of a chemical in REACH regulation; however, the authorization step (SVHC classification) does not consider them which can bias the toxicological evaluation.

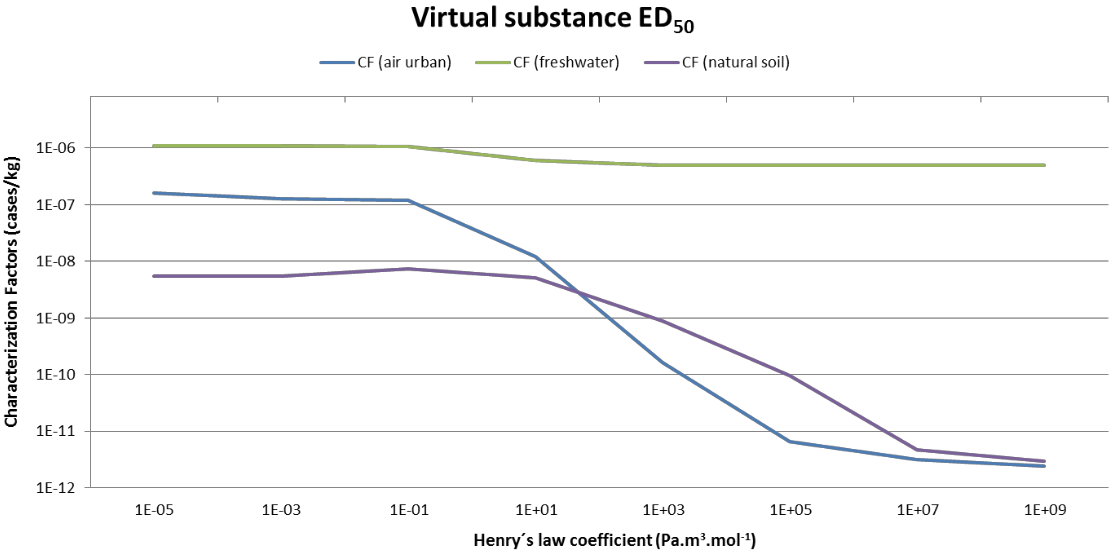

Figure 5.5. Variation of the toxicological characterization factor for the virtual substance ED_{50} relatively to the Henry's law coefficient (for the emission compartments urban air, freshwater, and natural soil).

5.1.3.2 Toxicological thresholds applied to real substances banned or restricted by REACH regulation

One of the problems associated with the inclusion of a life-cycle approach in a hazard classification system for substances is the absence of a reference that reflects an unacceptable level of toxicological impact. The current hazard classification system defines limit values for some physicochemical properties above which the substances are considered dangerous, so the problem mentioned above centers on finding the toxicological impact level corresponding to those limits. The incorporation of those limits relative to the physicochemical properties in a virtual substance is a valid approach to address that problem. It is possible to consider that if a virtual substance for the REACH classification system is an allowable – in the limit – substance, so the respective toxicological impacts can be seen as reference, or threshold, corresponding to the limit of the acceptable level of toxicological impact.

A hazard classification system based on toxicological impact is proposed by means of the set of virtual substances previously defined that are compared with a set of nine real substances. The majority of the real substances selected are included in Annex XIV of REACH, which lists the substances subject to authorization for placement on the market, and its selection is made to cover a wide range of reasons for restriction (e.g. high persistence, high toxicity), but also to ensure that all of them are included in the USEtox database. Beyond those substances, the organic substances RDX (1,3,5-

Trinitroperhydro-1,3,5-triazine), benzene, toluene, and ethanol are also considered in the comparative analysis to cover substances not included in Annex XIV, but included in the USEtox database. The list of all substances selected, and the motive, if any, for their inclusion in Annex XIV, is shown in Table 5.4. All the substances considered in Table 5.4, even if not posing a toxicity level high enough to be included in Annex XIV, have some type of consequences for human health, thus a non-zero toxicological characterization factor.

Table 5.4. Substances selected to the comparative analysis with the toxicological characterization factors, and the information (if any) regarding some type of restriction in REACH regulation.

Substance	Restriction in REACH Regulation
Dibutyl phthalate (CAS 84-74-2)	Annex XIV: T-R (1B)
2,4-dinitrotoluene (CAS 121-14-2)	Annex XIV: T-C (1B)
Musk xylene (CAS 81-15-2)	Annex XIV: vPvB
Trichloroethylene (CAS 79-01-6)	Annex XIV: T-C (1B)
1,2-dichloroethane (CAS 107-06-2)	Annex XIV: T-C (1B)
RDX (CAS 121-82-4)	n/a
Benzene (CAS 71-43-2)	Annex XVII: C; M
Toluene (CAS 108-88-3)	CoRAP; Annex XVII
Ethanol (CAS 64-17-5)	n/a

Legend: T-R (1B) – toxic to reproduction category 1B; T-C (1B) – toxicity carcinogenic category 1B; vPvB – very persistence or very bioaccumulative; M – Mutagenic; CoRAP - Community rolling action plan.

The values of the CFs obtained for the real substances and for the virtual substance ED_{50} are shown in Figure 5.6 for the emission compartments urban air, freshwater and natural soil (the results for any of the other VS, or the other congener emission compartments, would be similar). For both the VS and for each emission compartment, the CFs shown, which can be seen as a reference, correspond to the limits of the typical variation of the k_H for the organic substances listed in USEtox (1.0E-06 $Pa.m^3.mol^{-1}$ corresponding in the Figure 5.6 by ED_{50} min; and 1.0E+02 $Pa.m^3.mol^{-1}$ corresponding in the Figure 5.6 by ED_{50} max).

A first analysis of the characterization factors associated with real substances shows that RDX (one of the substance not included in Annex XIV of REACH) presents the highest toxicological CFs; while ethanol and toluene show the lowest values among all substances. Benzene has an intermediate toxicological impact in comparison with the other real organic substances. The reasons for the result obtained for the RDX can be justified by a combination of factors that includes elevated values of persistency (the values for half-lives that are near the regulatory limits), and water solubility (59.7 mg/L) – parameter not considered in the SVHC classification –, that contributes to a low Henry's law coefficient (2.0E-06 $Pa.m^3.mol^{-1}$), thus a tendency to result in high intake factors and high CFs. As for benzene, the combination of high water solubility (1790 mg/L), a significant persistence in water, and a significant toxicity are probably the justification for the observed impacts. These results are evidence of the importance of the combinatory effect to the toxicological impacts as well of the significance of neglecting a physicochemical property such as water solubility, neither of which are addressed in the REACH classification system.

Comparison of the toxicological CFs obtained for the real organic substances with the CFs obtained for the VS (considered as references or thresholds) can be used as a basis for a hazardous classification system. The classification proposed, itself open for discussion, is based on the definition of three situations corresponding to different hazard levels. The substances with CFs above the upper threshold of the VS for all the emission compartments are considered as the most concerning substances. The substances that present this pattern are: RDX, 2,4-dinitrotoluene, and musk xylene. The second level associated with an intermediate hazard concern includes the substances which CFs overcome the upper thresholds of the VS for only one of the emission compartments. Two of the substances selected for this analysis are found at this intermediate level: benzene and 1,2-dichloroethane. Finally, the less worrying situation occurs when, for all the emission compartments, the CFs of a substance are below the upper thresholds of the VS. Ethanol, toluene, dibutyl phthalate, and trichloroethylene are the substances included in this level.

Dibutyl phthalate and trichloroethylene are included in Annex XIV due to their effect over reproduction or carcinogenicity, respectively, with either of these reasons being enough to classify them as SVHC. Nevertheless, even when taking those characteristics into consideration – USEtox accounts for those effects in the calculation of the impacts – the small values of chronic toxicity, the low bioavailability, and low persistence indicate their CFs as being lower than those of the VS considered as a threshold. Musk xylene, despite presenting a very low toxicity (high values of ED_{50}), the combination of a very high persistence in water and in sediment, and a high bioaccumulation (k_{ow}) leads to a toxicological impact similar to that of 2,4-dinitrotoluene with higher toxicity (with low value of ED_{50}).

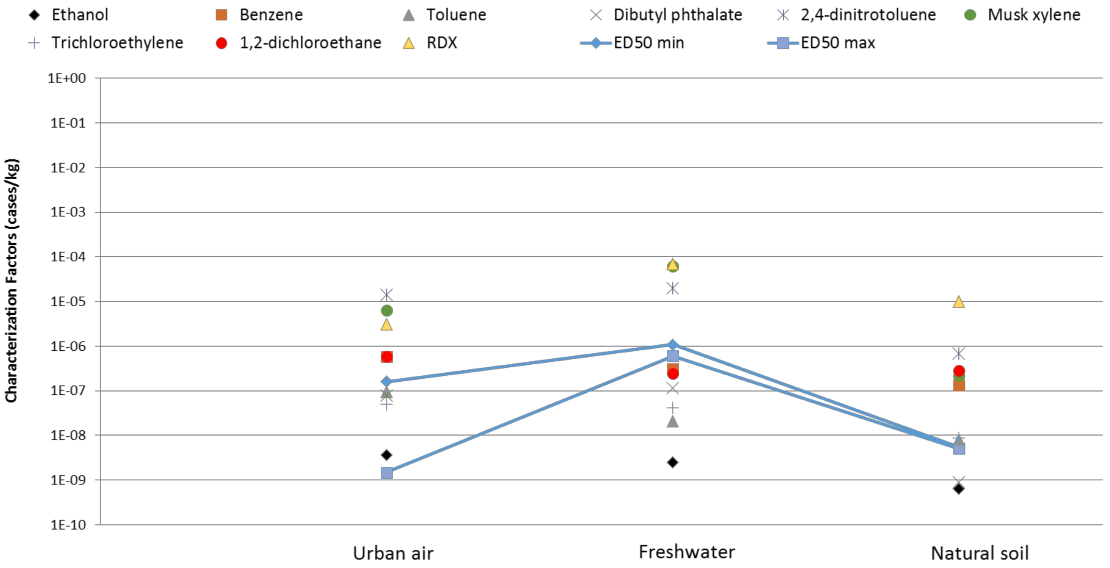

Figure 5.6. Comparison between the toxicological characterization factors of the virtual substance ED_{50} with real organic substances.

5.2 Assessment of alternatives for substance restricted by REACH

In the previous subsection a hazard classification system, alternative to the classification of SVHC as it is proposed by the REACH regulation, was tested with real substances. In this subsection the proposed classification system is employed in the selection of the alternatives to dibutyl phthalate which production is restricted as its properties exceed the regulatory limits imposed by REACH regulation. For that reason, the potential toxicological hazard of four possible alternatives is assessed based on the comparison of their toxicological CFs with the toxicological thresholds determined for the virtual substances in order to select the alternative(s) with lower toxicity hazard.

5.2.1 Calculation of toxicological characterisation factors to dibutyl phthalate and its alternatives

Dibutyl phthalate (DBT) is a substance used, among other applications, as a plasticizer in gun propellant production that, due to its toxicity properties, is included in Annex XIV of REACH that refers substances which need authorization to be used. Dibutyl phthalate is considered toxic to reproduction (R61 – may cause harm to the unborn child; R62 – possible risk of impaired fertility); and dangerous for the environment (R50 – very toxic to aquatic organisms), so it need to be replaced by alternatives with lower toxicity. A vast amount of substitutes to dibutyl phthalate can be found in the literature (Böhnlein-Mauß and Kröber, 2017), so the potential alternative plasticizes explored to substitute dibuyl phthalate are:

1) Diisononylphthalate (CAS 28553-12-0)
2) Dioctylsebacate (CAS 122-62-3)
3) Dioctyl terephthalate (CAS 6422-86-2)
4) Oxydiethane-2,1-diyl dibenzoate (CAS 120-55-8)

These four alternatives are not included in the USEtox database, so the respective toxicological characterisation factors (CFs) were calculated inputting the physicochemical properties of these substances in the USEtox method. The values required to carry out the assessment were taken from the ECHA (European Chemical Agency) database, which is provided on the ECHA website (http://echa.europa.eu/pt/home). The only exception is for the half-live parameters that are determined with the EPI Suite^{TM}, as recommended in Huijbregts *et al.* (2010).

Table 5.5 presents the physicochemical properties used to calculate the toxicological CF, including the regulatory limits for comparison purposes. It is observed that the limits for octanol-water partition coefficient (k_{ow}) are largely exceeded by diisononylphthalate, dioactyl sebacate, and dioctyl terephthalate. Dibutyl phthalate also exceeds the limit for k_{ow} and water solubility, but the values are close to the limits. Oxydiethane-2,1-diyl dibenzoate only exceed the limit for water solubility.

With regard to the toxicity parameters, a high ecotoxicity value (low values of EC_{50}) for dibutyl phthalate and dioctyl terephthalate is observed. In fact, this high ecotoxicity was expected since these two substances shows values lower than the REACH limit (0.01 mg/L). The highest values for human toxicity (low values of ED_{50}) are detected to dioctyl terephthalate and oxydiethane-2,1-diyl dibenzoate, but either do not exceed the limits imposed by REACH. Moreover, it was not found evidences of cancer effects for any of the substance mentioned.

The selection of the alternative with lower toxicological impact based solely on the analysis of the parameters shown in Table 5.5 is challenging. Even when a comparison with the limits imposed by REACH is considered, is difficult to affirm with certainty which is the substance that shows a lower toxicological consequence on human health. In fact, all the alternatives presented can be identified as hazard on human health when considering the SVHC classification, and as a consequence their production and use can be restricted in the future. The hazard classification of the alternatives to dibutyl phthalate can be simplified through the comparison of their toxicological CFs with the toxicological CFs for virtual substances. The advantage of carry out the hazard classification based on the CFs for virtual substances is principally due to using only one value that incorporates the influence of all physiochemical properties, instead of evaluating each property independently.

Table 5.5. Data used to calculate the toxicological characterisation factors associated with dibutyl phthalate and its alternatives with the employment of the USEtox method.

Properties	Hazard limits	Dibutyl phthalate	Diisononylphthalate	Dioctyl sebacate	Dioctyl terephthalate	Oxydiethane-2,1-diyl dibenzoate
MW	(-)	2.78E+02	4.19E+02	4.27E+02	3.91E+02	3.14E+02
k_{OW}	(3.16E+4)	3.16E+04	2.34E+09	1.20E+10	6.46E+07	1.58E+03
k_{oc}	(5.56E+3)	1.38E+03	3.31E+05	1.84E+08	1.17E+05	1.50E+03
k_H	(-)	1.83E-01	1.50E-01	1.24E+00	9.76E+01	1.48E-04
P_{vap}	(-)	2.68E-03	7.20E-05	1.45E-04	1.00E-04	1.80E-05
Sol_{25}	(1)	1.12E+01	2.00E-01	5.00E-02	4.00E-04	3.83E+01
k_{deg} air	(7.80E-06)	6.96E-06	1.75E-05	4.65E-05	1.65E-05	2.84E-05
k_{deg} water	(2.10E-07)	9.25E-07	2.14E-07	5.30E-07	5.30E-07	5.30E-07
k_{deg} sediment	(6.50E-08)	1.03E-07	2.38E-08	5.89E-08	5.89E-08	5.89E-08
k_{deg} soil	(1.40E-08)	4.63E-07	1.07E-07	2.65E-07	2.65E-07	2.65E-07
$av_{logEC50}$	(-)	-7.45E-02	8.58E-02	5.86E-01	-1.26E+00	5.85E-01
$ED_{50\ noncanc}$	(7.69)	2.46E+02	1.90E+02	7.48E+02	1.69E+01	1.20E+01
$ED_{50\ canc}$	(-)	n/a	n/a	n/a	n/a	n/a
BAF_{fish}	(1.58E+02)	1.67E+02	2.31E+02	1.36E+02	8.40E+02	7.92E+01

Units: MW (g.mol^{-1}); k_{ow} (dimensionless); k_{oc} (L.kg^{-1}); k_H (Pa.m^3.mol^{-1}); P_{vap} (Pa); Sol_{25} (mg.L^{-1}); k_{deg} air (s^{-1}); k_{deg} water (s^{-1}); k_{deg} sediment (s^{-1}); k_{deg} soil (s^{-1}); $av_{logEC50}$ (mg.L^{-1}); ED_{50} (kg/lifetime); BAF_{fish} (L.kg^{-1}).

5.2.2 Toxicological thresholds applied to dibutyl phthalate and the alternatives

Figures 5.7, 5.8, and 5.9 present the CFs obtained for dibutyl phthalate, the four alternatives, and for the virtual substance ED_{50} for the emission compartments urban air, freshwater, and natural soil, respectively. The CFs for the VS ED_{50} corresponds to the values obtained for the minimum limit of the typical variation of the k_H for the organic substances listed in USEtox (1.0E-06 $Pa.m^3.mol^{-1}$). It was selected this virtual substances as an example, but the results for any of the other VS would be similar.

The classification proposed is based on the definition of three situations corresponding to different hazard levels. The substance oxydiethane-2,1-diyl dibenzoate are included in the first level as the substances with the most concerning hazard as they present toxicological CFs above the threshold of the VS ED_{50} for all the emission compartments. The second level associated with an intermediate hazard concern includes the substances which CFs overcome the thresholds of the VS for, at least, one of the emission compartments. Diisononylphthalate and dioctyl terephthalate are the substances that present this pattern, presenting a toxicological CF higher than the threshold – diisononylphthalate for an emission into air; dioctyl terephthalate for an emission into air and natural soil).

Finally, dibutyl phthalate and dioctyl sebacate are included in the less worrying situation as their toxicological CFs are below the thresholds of the VS ED_{50} for all the emission compartments. The justification for dibutyl phthalate appear under the CFs threshold is probably because this substance is considered a SVHC due to its toxicity properties to reproduction, which has no regulatory limit value. Therefore, the combination of the toxicity values with the other physicochemical properties leads to a lower toxicological CF than the CFs of the virtual substance.

From the results, it is observed that the alternative to dibutyl phthalate with lower toxicity hazard is dioctyl sebacate. It is important to note that this evidence could not be made from the analysis of the values of the physicochemical properties shown in Table 5.5. In fact, dioctyl sebacate shows the highest value of k_{ow}, and hardly could be include in the list of potential alternatives. However, the combination of this high bioaccumulation tendency with the other physicochemical properties originates a lower toxicological CFs than all the alternatives. This result demonstrates the influence of considering the combination of all the physicochemical parameters and the importance of calculating the toxicological impact instead of only evaluate the hazard on human health based on some parameters independently.

The hazard classification system with the employment of the toxicological CFs from the virtual substances, which act as a threshold that reflects the maximum limit allowed for a toxicological impact, helps to identify and select the alternatives with lower potential consequence on human health. The identification of appropriate substitutes is extremely difficult by analysing only the physicochemical parameters, and unforeseen consequences can arise from the combination of these parameters. In fact, when is performed a comparison of the parameters for all alternatives, oxydiethane-2,1-diyl dibenzoate appears to be the alternative with lower potential hazard; however, the combination of both high human toxicity (low ED_{50} value) and water solubility, as well a low Henry's law coefficient originates higher toxicological CFs in comparison with the other alternatives.

In this case the identification of the appropriate alternative was easier as only one substance presents toxicological CFs under the toxicological thresholds. Nevertheless, the additional information obtained from the employment of the toxicological CFs from the VS helps to identify not only the substance with lower toxicological impacts, but also what are the appropriate substitutes for restricted substances – all the substances under the toxicological thresholds). The identification of more than one substance based on a reference is of great importance as other environmental or technical characteristics can influence the selection of safer alternatives, principally when a shift of impacts is observed (e.g. selection of a substance that presents lower toxicological impacts, but either has a higher impact in the production phase or is required a higher quantity to perform the same function of the conventional products). The preliminary analysis of the toxicological characterisation factors with the inclusion of the toxicological thresholds also supports decision makers to present motives and advantages associated with the selection of certain alternatives, or present justifications for the absence of appropriate alternatives to substances in the Annex XIV of REACH regulation.

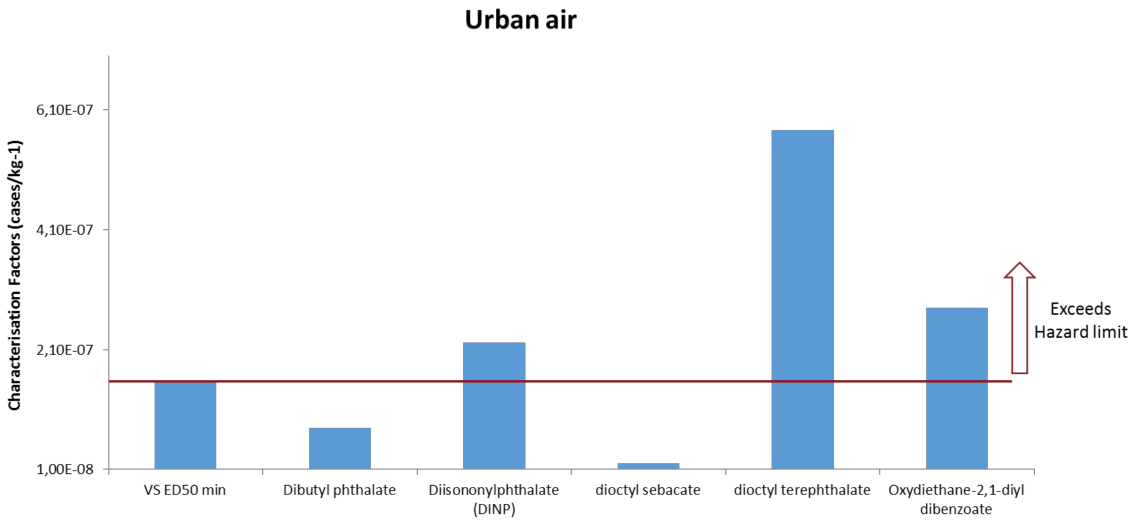

Figure 5.7. Comparison between the toxicological characterization factors of the virtual substance ED_{50} with dibutyl phthalate and four alternatives for the emission compartment urban air.

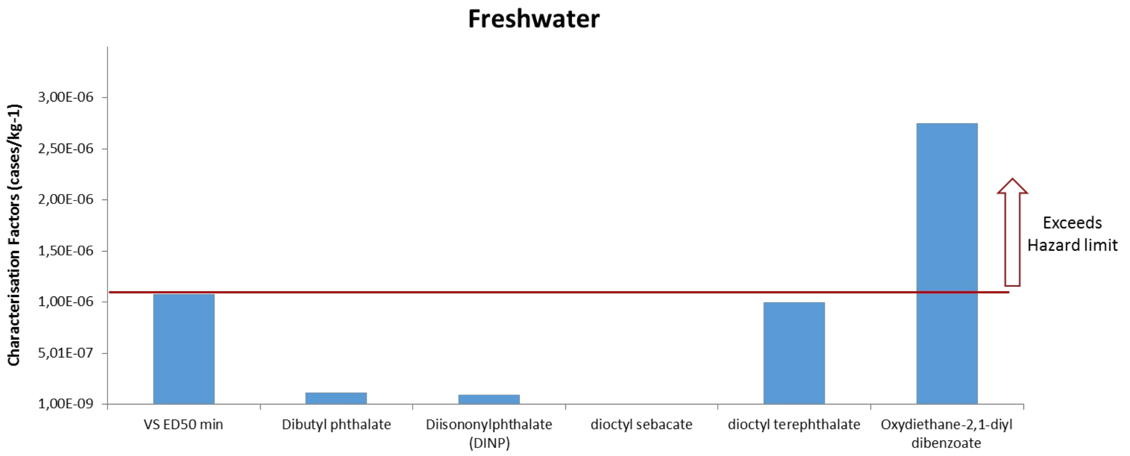

Figure 5.8. Comparison between the toxicological characterization factors of the virtual substance ED_{50} with dibutyl phthalate and four alternatives for the emission compartment freshwater.

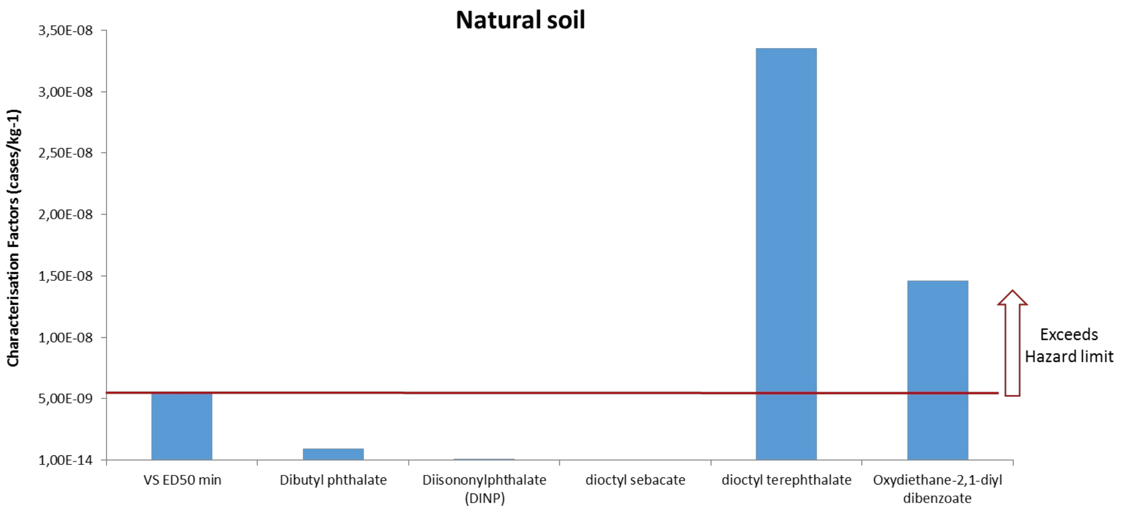

Figure 5.9. Comparison between the toxicological characterization factors of the virtual substance ED_{50} with dibutyl phthalate and four alternatives for the emission compartment natural soil.

5.3 Concluding remarks

The conceptual framework presented aims to improve the SVHC classification of chemical substances through the calculation of CFs for virtual substances and by this way incorporating the regulatory limits from REACH regulation into the life-cycle impact assessment method USEtox. A detailed analysis to the CFs for the virtual substances allowed to conclude that: i) the limits established by REACH for different physicochemical properties of a substance are equivalent from the point of view of their ability to evaluate the impact on human health; ii) the combinatorial effect of the different physicochemical properties is not negligible when evaluating the hazard potential of a substance; iii) parameters such as water solubility or Henry's law coefficient, not included in the REACH regulation classification system, are as relevant as others presently included on that classification system to evaluate hazard to human health.

The toxicological CFs for virtual substances may be seen as a reference of what is an acceptable toxicological impact, and can be employed in a hazard classification of chemical substances to provide additional information to screen or rank the substances according to their chemical toxicity, enhancing the ability to comprehend and predict potential unintended consequences or trade-offs. The proposed hazard classification system not only incorporates more parameters than the ones considered in REACH regulation, but also takes in consideration the combinatory effect to calculate toxicological impacts on humans. In addition, the classification of safer alternatives is facilitated by using a quantitative classification based on a single parameter – the toxicological CFs – that integrates the different physicochemical properties of the substances, instead of identifying SVHC solely based on the comparison of at least five physicochemical properties. The hazard classification system was tested evaluating i) the hazard potential of a set of real substances restricted by REACH regulation, and ii) the hazard potential of a set of alternative substances to dibutyl phthalate (substance restricted by REACH).

Chapter 6 - Conclusions

6.1 Key finding and contributions

In this PhD thesis insights about two main objectives, which are independent but complementary, associated with the life-cycle environmental impacts of ammunition were provided. Those insights were: i) implementation of life-cycle assessment methodology to military munitions in order to assess the environmental and toxicological burdens associated with the production, use, and disposal of ammunition; and ii) creation of a conceptual framework to calculate the toxicological characterisation factors of virtual substances, defined based on the regulatory limits from REACH regulation, to comprehend the importance of the combinatory effect of different physicochemical properties to the toxicological consequences on human health. Ultimately, this new framework intends to improve the toxicological assessment of substances, and help the industry (beyond the military industry) to classify substance of very high concern and understand the significance of the toxicological impacts related to conventional or new products.

The analysis carried out to address the two aforementioned topics included the following steps:

- Implementation of life-cycle inventories to energetic materials that are the baseline to assess the life-cycle environmental impacts of ammunition (section 3.1). A standard to create inventories to any energetic material was also provided. A comprehensive analysis was carried out to compare the impacts of energetic materials with common chemicals.

- An attributional life-cycle assessment was employed to the production and use phase of ammunition in order to identify the main environmental and toxicological hotspots (Chapter 3). For that purpose, two case studies related to production and use of ammunition were addressed: i) the production and use of generic large calibre ammunition (section 3.2); and ii) the comparison of the production and use of four types of small calibre ammunition (section 3.3).

- Normalisation factors based on the domestic emissions for Europe were employed to the impacts associated with the production and use of the small calibre ammunition with the aim to deliver a reference that can be used to estimate their magnitude and significance (section 3.4).

- A life-cycle model was developed to ascertain which ammunition disposal technique shows lower environmental and toxicological impacts (chapter 4). The disposal techniques considered were: i) incineration in static kiln with flue gas treatment, ii) open detonation, and iii) valorisation of energetic material via its incorporation in civil explosives. To quantify the potential benefits associated with the valorisation of energetic material of ammunition a system expansion method was employed.

- Development and implementation of a novel conceptual framework to assess the toxicological characterisation factors associated with virtual substances (hypothetical substance) defined based on the regulatory limits imposed by REACH to classify substance of very high concern (chapter 5). The assessment of those CFs permitted to evaluate if the limit values established for the physicochemical properties are equivalent in terms of the potential toxicological consequence on human health, and comprehend the effects arising from the combination of different physicochemical properties into toxicological impacts.

- Insights on the REACH regulation were provided, namely the identification of physicochemical properties not considered on the SVHC classification (water solubility, half-life in air) that presents similar significance and relevance to those already included on the classification system (section 5.1).

- Application of CFs associated with the virtual substances as toxicological thresholds, seen as a reference for toxicological impacts, to help classify and screen the toxicological impact of real substances with the aim to facilitate the selection of safer alternatives for substance banned (or restricted) by REACH. For that purpose, a practical example was addressed focused on the assessment of alternatives to dibutyl phthalate (substance restricted by REACH) (section 5.2).

An important contribution from this thesis is the ground-breaking creation of life-cycle inventories for energetic materials, and the proposal of an approach, based on Hischier *et al.* (2005), to overcome the difficulties referent to acquisition of data, mostly for the production phase of this type of materials. Environmental assessment for the energetic materials was difficult and time consuming to accomplish due of lack of data; however, the employment of simplifications for the creation of life-cycle inventories, performed accordingly with common accepted recommendations, contributed to overcome the obstacle of data scarcity to energetic materials. The impact assessment carried out for energetic materials contributed to close the gap that was preventing the studies associated with environmental impact of ammunition, as the other materials (metals, plastics) are well-known and studied.

Comprehensive life-cycle assessment studies referent to production, use, and disposal of ammunition helped to assess and highlight the main hotspots for this product. In particular, the LCA performed demonstrated the importance of applying a life-cycle approach to military systems by illustrating that the information obtained from these studies outweigh the effort needed to overcome the difficulties stemming from data collection. Moreover, the employment of a life-cycle perspective shed some light in unexpected consequences or trade-offs related to “green” paths for ammunition. The major example about this issue was the assessment done for small calibre ammunition, in which was identified an undesired consequence associated with lead replacement in ammunition. The alternative projectile studied (without lead) showed higher impact for ecosystems due to higher emission of copper particles.

Another important aspect regarding the application of a life-cycle perspective was observed for ammunition disposal, enhancing our understanding of the demilitarisation burdens. Disposal techniques in which the most significant impact contribution are associated with indirect impacts (e.g. energy requirement) presents a high burden to the environmental categories; whilst direct emissions are associated with higher impact contribution to the toxicological categories. As a result, demilitarisation by incineration show higher impacts for the environmental impact categories, and open detonation higher impacts for the toxicological impact categories. This trade-off shows that a new solution can be proposed to minimize the environmental burdens associated with ammunition disposal. Consequently, the valorisation of the energetic material from ammunition through its incorporation in civil explosives, as an alternative to conventional decommissioning, is a novel industrial ecology approach that shows lower environmental and toxicological impacts, principally due to the avoidance of the indirect impacts associated with energy consumption during the incineration of military ammunition.

One main scientific outcome from this research is the proposal of a conceptual framework that aims to improve the toxicological hazard assessment of chemical substances, and facilitating its classification as substances of very high concern (SVHC). Inclusion of regulation limits from REACH in the life-cycle toxicological impact assessment method USEtox provided the ability to present a reference to understand the significance of the potential toxicological impacts. The regulatory limits from REACH for some physicochemical properties were converted on toxicological impacts via the creation of virtual substances that embed those limits, allowing the evaluation of the influence of the combination of different physicochemical properties in toxicological impacts.

The comprehensive analysis to the toxicological characterisation factors of the different virtual substances permitted to verify that for each emission compartment the toxicological CFs are similar and do not vary more than one order of magnitude. Therefore, it can be deduced that the regulatory limits associated with the different virtual substances are equivalent from the point of view of their ability on imposing limits to the toxicity hazard of the chemical substances. It is also important to highlight that the toxicological CFs of a substance is not determined by the values of each one of its physicochemical substance individually; the different physicochemical properties of the substances tend to act together (combine) and influence its hazard toxicity.

The framework developed and the assessment carried out also permitted to conclude that some parameters not included in the SVHC classification according with the REACH regulation (water solubility and half-life in air) can significantly influence the behaviour of substances on the environment, and as a consequence its toxicological hazard. The impacts related to the virtual substances associated to those properties are similar (hence with the same relevance) to those of the virtual substances properties associated with the physicochemical properties included in the SVHC classification. Furthermore, the influence of the Henry´s law coefficient (directly proportional to the vapour pressure and inversely proportional to the water solubility) on the toxicological CF calculated, principally for the air and soil emission compartments, is of utter relevance. These physicochemical properties need to be included in the SVHC classification to improve the ascertainment of the potential toxicological burdens to human health.

Another important achievement of this PhD thesis is the use of the toxicological CFs from the virtual substances as a reference (threshold) to the toxicological CFs of real substances. The comparison of the toxicological CFs of a real substance with those thresholds improves the hazard classification system as it takes into account the contribution of all physicochemical properties as well as the combinatory effect in that assessment. Therefore, the use of toxicological CFs in the hazard assessment – instead of the individual value of the physicochemical properties – can change the classification of hazard substances as was observed for the particular case dibutyl phthlate, in which the most promisor alternative presented higher toxicological CFs.

Another important aspect is that the screening for alternatives to substance banned by REACH by the use of the toxicological thresholds is facilitated and more objective. In fact, the substances presented as alternatives for restricted substances can also be SVHC – for the reason that shows values of some of the physicochemical properties above the limits established by REACH – and it is difficult to devise, based only in the analysis of the physicochemical properties, the less harmful from a toxicological point of view. Therefore, the comparison of the toxicological CFs with the thresholds can also help identify the substances that expectably have more probability of being restricted in the future. The features described above of this new approach was tested with the practical case of dibutyl phthalate, in which the hazard ranking and classification was assessed for four potential alternatives to that substance.

The key findings from this thesis are displayed in the following paragraphs referent to the three research questions formulated in Chapter 1 (Table 1.1).

1. *What are the life-cycle environmental impacts (and hotspots) associated with the production and use phase of ammunition? Are those impacts significant?*

   The analysis for the production and use phase of the generic ammunition and small calibre ammunition allowed to conclude that the production phase has a higher contribution to the environmental impact categories, whilst use phase shows a higher contribution to the toxicity categories.

   The assessment carried out to the generic 155 mm ammunition presented significant impacts in the production phase due to indirect impacts associated with the production of the main components: warhead, propellant charge and the fuze. As for the small calibre ammunition, in addition to the energy requirement, the main contributors to the impact of the production phase is also related to the ammunition components (projectile and cartridge).

For the use phase, the impacts are associated with the direct emissions: from firing and detonation in the large calibre ammunition, and from firing and barrel/projectile erosion in the case of the small calibre ammunition. Impacts of the generic large calibre ammunition for human toxicity (cancer and non-cancer effects) are completely dominated by the emissions of the detonation products. The highest contributors to the impacts associated with the detonation emissions are metals: cadmium, chromium VI, zinc, and lead. The point-of-fire emissions also presented a significant impact for the impact categories Photochemical Oxidation and Global Warming categories due to emissions of carbon monoxide and carbon dioxide. Toxicological impacts on humans and ecosystems for the small calibre ammunition were also due to heavy metal emissions.

Two important results associated with the environmental assessment of ammunition production and use phase were observed due to the employment of a life-cycle approach. Firstly, a detailed analysis to the impact contribution related to the triple base powder production (generic 155 mm ammunition) showed that emissions of insecticides into the soil for the cultivation of cotton (used for the production of nitrocellulose that is one of the triple base powder major ingredient) are the main contributor to Ecotoxicity. This impact is so significant that is the only impact contribution of the production phase that presents a higher impact that the use phase to the total life-cycle for the toxicity categories. Secondly, the analysis for the small calibre ammunition demonstrated the toxicological benefits of removing lead from the ammunition components are very relevant; nevertheless, the lead free ammunition presented other toxicological burdens due to higher emissions of copper that contributes considerably to a significant increase of the total impact on ecosystems.

The significance of the environmental impact related to the production and use of small calibre ammunition was evaluated to understand the relevance of that impacts. The annually production and use of small calibre ammunition contributes to approximately 20% of the total EU-27 population for the abiotic depletion category. The second most relevant impact category is the human toxicity with non-cancer effects, in which the impacts associated with ammunition

production and use are approximately similar to the domestic emissions of a city of 800 000 inhabitants.

The analysis of the significance of the ammunition environmental impact was carried out with the employment of normalisation factors considering the domestic inventory for EU-27 countries that underlay an extensive collection of emissions into air, water, and soil as well as resources extracted for the year 2010, which expresses the total impact of the EU-27.

2. *What is the appropriate technology, in a life-cycle perspective, to disposal ammunition?*

Energetic material valorisation via incorporation into civil explosives, an industrial ecology approach alternative to conventional decommissioning, shows the most satisfactory results to disposal ammunition from an environmental perspective.

Employment of the system expansion model allowed accounting the potential benefits associated with the energetic material valorisation: avoid the conventional elimination of military explosives (incineration in static kiln with flue gas treatment), and the displacement of part of the matrix components of the emulsion explosive. In average, more than 147% of the total impact for all impact categories is avoided due to the valorisation of the energetic material. The preeminent benefit is associated with the complete avoidance of the energetic material incineration and flue gas treatment. Solely the avoidance of this procedure contributes to reduce approximately 80% of the environmental impacts.

The comparison between the demilitarisation techniques incineration in static kiln with flue gas treatment and open detonation shows a trade-off between the environmental and the toxicological burdens.

The analysis of the results associated with these two alternative ammunition disposal routes have shown that the direct impacts (e.g. emissions from OD) significantly contribute to the toxicological categories; whilst the indirect burdens (energy and material consumption) have a significant influence on the environmental categories. This tendency represents a trade-off, in which lower emissions are obtained (representing lower direct impacts), while increasing the indirect impact associated with the consumption of materials and energy.

3. *How to improve the toxicological hazard classification system of chemical substances and strengthen the reliability of the identification of substances of very high concern*

A new conceptual framework based on USEtox method to calculate the toxicological characterisation factors (CFs) for virtual substances, hypothetical substances embedding regulatory limits from REACH to classify SVHC allowed to i) assess the equivalence between the limits established for the different physicochemical properties; ii) evaluate the significance of the combinatorial effect from different physicochemical properties into potential impacts; and iii) present recommendations to improve, support, and facilitate the classification of SVHC in REACH regulation.

A conceptual framework to assess the toxicological CFs associated with virtual substances permitted clarifies some concerns regarding the REACH classification system, principally comprehending the importance of the combinatory effect of different physicochemical properties on human health impacts. Shed light on the scientific gaps of the current SVHC classification system can help the enhancement of the classification of hazard substances. In addition, the CFs of the virtual substances can provide the industry with a new tool to assess supplementary information to evaluate safer toxicological alternatives for substances banned or restricted by REACH.

The analysis of the toxicological CFs for each virtual substance allowed to conclude that the different physicochemical properties of the substances tend to combine and influence its hazard toxicity; the toxicological CFs of a substance are not determined by the values of each one of its physicochemical substance individually, thus classify substances of very high concern based on some parameters cannot be enough to ascertain the potential toxicological impact (hazard) to human health

The assessment also allowed to show that some parameters such us water solubility or half-life in air not included in the REACH regulation classification system are as relevant as others presently included in REACH to evaluate hazard on human health. The major example is the parameter Henry´s law coefficient (calculated from the parameters molecular mass, water solubility and vapour pressure) that induced a variation of many orders of magnitude to the toxicological CFs, mostly for an emission into air and soil. These physicochemical parameters are required to the registration step of a chemical in REACH regulation; however, the authorisation step (SVHC classification) does not consider them which can bias the toxicological evaluation. These conclusion can be extrapolate to aware that a substance that presents values of the physicochemical properties under the toxicological limits, and is not considered a substance of very high concern, can still pose a significant toxicological impact.

The proposed hazard classification system, based on the toxicological CFs of the virtual substances calculated with USEtox method, can be used to evaluate the significance of potential toxicological impacts and to provide additional information to screen or rank the substances according to their chemical toxicity, enhancing the ability to comprehend and predict potential unintended consequences or trade-offs.

The current hazard classification system defines limit values for some physicochemical properties above which the substances are considered dangerous. The incorporation of those limits referent to the physicochemical properties in a virtual substance is a valid approach to define the acceptable level of toxicological consequences on human health. Therefore, the CFs of the virtual substances may be seen as a reference, or a threshold, of what is an acceptable toxicological impact, and can be employed in risk assessment or in a hazard classification of chemical substances. This hazard classification system not only incorporates more parameters than the ones considered in REACH regulation, but also takes in consideration the combinatory effect to calculate toxicological impacts on humans. In addition, the classification of safer alternatives is facilitated by using a quantitative classification based on toxicological impacts – single parameter –, instead of using a multi-parameter assessment based on the values of the different physicochemical properties of the substances.

The feasibility of this approach was evaluated via the employment of the toxicological thresholds to a real practical case of dibutyl phthalate. Dibutyl phthalate is a plasticizer used in ammunition propellant that, due to its toxicity properties to reproduction and aquatic organisms, is included in Annex XIV of REACH related to substances that need authorisation to be putted in the market. Based on this assessment it was concluded that dioctyl sebecate is the only alternative with lower toxicological CFs and under the toxicological thresholds.

The findings from this thesis will allow decision makers be they shooting range managers, ammunition procurement officers, ammunition producers or others, to become more aware of the main environmental and toxicological problems associated with the production, use, and disposal of ammunition. The analysis presented helps defining strategies to manage or mitigate ammunition burdens and carry out tailored modifications to decrease the impacts associated with ammunition hotspots. The toxicological framework can help to persuade stakeholders or ammunition developers/producers to mitigate the adverse consequences and put in the market safer toxicological alternatives. Furthermore, the improvement of the SVHC classification presented in this thesis can be included in the authorisation step of REACH regulation in order to provide an enhanced toxicological assessment of organic substances.

6.2 Limitations and topics for future research

Creation of life-cycle inventories to energetic materials as well as the recommendations provided to facilitate the implementation of inventories to energetic materials are a significant improvement to enhance the environmental assessment associated with ammunition production. Nevertheless, even with the participation in the EDA project ERM (Environmentally Responsible Munitions) in which the industry partaken, in overall was not possible to compile primary data regarding the production of energetic materials used in ammunition. As mentioned in the introduction of this thesis the industry is not confident to make available data for energetic material production, and is challenging to demonstrate to the military industry the potential benefits from this type of collaboration. In fact, the only example in which the industry collaborated with real data was for the small calibre ammunition assessment, demonstrating the advantages of a life-cycle perspective to ammunition. The lack of data can lead to less reliable studies as the conclusions drawn are based on assumptions or outdated information.

One possible solution to obtain the data required is to follow the approach made for the plastic industry in which the data is a “black-box” in Ecoinvent in order to maintain the confidentiality. This approach can be adapted for energetic materials and munitions to increase the will of the military industry to collaborate and provide the information needed to strengthen the databases. Therefore, for situations in which the industry want to maintain the information secret, would be provided non-disclosure agreements to ensure the confidentially of the information; and the main conclusions and results would be available to general public, but maintaining the critical information in a “black box”. The forthcoming knowledge acquired could also help improving the guidelines in how to implement the inventory for any type of ammunition not covered yet; facilitating future environmental impact assessment studies associated with ammunition, and also enhancing the reliability of those studies.

The necessary increase of primary data availability for ammunition needs also to address insensitive ammunition. This type of ammunition may include different energetic material formulations, production processes, and the less sensitiveness can also pose different burdens on the environment. For instance, the demilitarisation of insensitive ammonium has shown some problems associated with the difficulty to detonate this type of ammunition. It is relevant to address this issue in future assessments to understand if insensitive ammunition, despite being safer, shows environmental trade-offs. The case of insensitive ammunition can be extrapolated to other types of new ammunition that are placed in the market.

To improve the life-cycle studies about ammunition contamination, it is important to address in the future two important issues. Firstly, the environmental impact assessment of ammunition use need to include the dud rates associated with life-firing training. By this way the assessment accounts the percentage of unexploded ordnances that can contaminate the environment with energetic materials; consequently the life-cycle studies are more consistence and representative of what take place in real training situations. Secondly, the degradation products of energetic materials need to be accounted. The energetic material when reach the water or soil are not immutable and new substances arises from biotic or abiotic degradation, resulting in different organic or inorganic substances. These substances can have a different behaviour and as a consequence different potential toxicological impacts from the original energetic materials emitted, so the assessment of the toxicological impact associated with the degradation products is of great importance. The difficulty is to know which are the degradation products and the percentage rate of that degradation; nevertheless, some work has been evaluating these issues that can be used in the future to complete the life-cycle studies of ammunition contamination.

Regarding the hazard classification system proposed in this PhD thesis it is intended to address in the future some subjects that are discussed in detailed as following. The toxicological thresholds calculated for each virtual substance did not include cancer effects, even that the toxicological characterisation factors calculated from USEtox method includes cancer effects, because no regulatory limit exists for this toxicity effect. REACH regulation classifies the substance of very high concern which presents cancer effects based on a weight of evidence – a substance is or is not carcinogenetic. Therefore, it would be important in the future, if possible, to include that effect in the hazard classification system by using a conservative limit for carcinogenic effects to calculate the toxicological thresholds in order to enhance the robustness of the proposed classification system.

The conceptual framework develop to evaluate the toxicity hazard on human health was not possible to carried out for ecosystems, as no sufficient limits from REACH, other regulation or literature was found in order to calculate the toxicological characterisation factors for ecosystems. Classification of SVHC to ecosystems in REACH regulation is only done based on the regulatory threshold to the long-term no-observed effect concentration (NOEC) or EC_{10} for marine or freshwater organisms (Annex XIII of REACH regulation). However, to calculate the ecotoxicological impacts in USEtox with reliable confidence are required at least three different trophic levels, constraining the possibility to create toxicological thresholds for this impact category.

Assessment of the uncertainty related to the assumptions performed and the limits selected for the physicochemical parameters (with the employment of Monte Carlo simulation techniques) would benefit the analysis proposed by ascertaining the robustness of this approach. Furthermore, the new approach can be extended to other types of impact categories (e.g. water footprint, climate change), integrating various types of legal limits on other life-cycle impact assessment methods. A life-cycle approach is important to determine potential trade-offs between different types of potential impacts, so only assessing toxicological impacts can be insufficient to provide safer alternatives.

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APPENDIX I: CORE PUBLICATIONS (ABSTRACTS)

Life-Cycle Assessment of Ammunition Demilitarization in a Static Kiln

Carlos Ferreira[a], José Ribeiro[*a], Ricardo Mendes[a] and Fausto Freire[a]
[a]ADAI-LAETA, Department of Mechanical Engineering, University of Coimbra, Coimbra, Portugal.
[*]Corresponding author: jose.baranda@dem.uc.pt

Abstract:

The demilitarization of ammunition that has reached the end of life (or become obsolete) has to be carried out with minimum energy and environmental impacts. The Portuguese Armed Forces have significant amounts of ammunition that need to be eliminated. In order to assess and improve ammunition demilitarization, a life-cycle approach must be adopted. The main goal of this article is to present a comprehensive life-cycle assessment (LCA) of the ammunition demilitarization performed by the Portuguese company IDD (Industria de Desmilitarização e Defesa). A life-cycle model was developed for the entire demilitarization process, which involves ammunition dismantling, discharging, the incineration of energetic material, and the subsequent flue gas treatment. A detailed inventory was based on data collected from the IDD. A life-cycle impact assessment was carried out, based on three complementary methods used to assess a total of ten impact categories: cumulative energy demand (primary energy); CML 2001 (six environmental impact categories) and USEtox (three toxicological categories). The results show that the main contributor in nine out of the ten impact categories is the incineration and gas treatment process, due to the high energy requirements (electricity and propane). Nevertheless, equipment manufacture also has a significant impact in the Human Toxicity (non-cancer) category, mainly related to the manufacture of the static kiln. These findings enhance our understanding of demilitarization using a static kiln, showing that the associated impacts are significant and should be reduced.

Keywords: Demilitarization · Life-cycle assessment · Energy · Environment

Life-cycle assessment of a civil explosive

Carlos Ferreira[a], Fausto Freire*[a], José Ribeiro[a]
[a]ADAI-LAETA, Department of Mechanical Engineering, University of Coimbra, Portugal
*Corresponding author: fausto.freire@dem.uc.pt

Abstract:

To reduce the environmental impacts of civil explosive production, it is essential to adopt a life-cycle perspective. The main goal of this article is to present a comprehensive Life-Cycle Assessment of civil explosive production and assess the environmental impacts of five alternative explosive compositions in order to identify the compositions with lower impacts and opportunities for improvement. A detailed inventory was implemented, based on data collected from a specific European company. Three complementary Life-Cycle Impact Assessment (LCIA) methods were used to assess primary energy, six environmental impacts (CML method) and three toxicity impacts (USEtox method). The results obtained with the CML and USEtox were compared with a recent LCIA method (ReCiPe), aiming at improving the robustness of our conclusions and understanding the differences between LCIA methods. The results showed that the main contributor for the ten impact categories is the emulsion explosive composition, mainly due to ammonium nitrate production. The comparison of five alternative emulsion explosive compositions showed that the inclusion of sodium nitrate leads to a reduction in impacts. A contribution analysis carried out with ReCiPe provided similar conclusions with those calculated with CML; however ReCiPe and USEtox calculated different toxicology impacts, due to different substances coverage and characterization factors.

Keywords: Environmental impacts; Emulsion explosive compositions; Life-Cycle Impact Assessment (LCIA); Primary energy

Reducing impacts from ammunitions: A comparative life-cycle assessment of four types of 9 mm ammunitions

Carlos Ferreira[a], José Ribeiro[a*], Sara Almada[b], Traian Rotariu[c], Fausto Freire[a]
[a]ADAI-LAETA, Department of Mechanical Engineering, University of Coimbra, Portugal
[b]CINAV - Laboratório Explosivos Marinha, Base Naval de Lisboa – Alfeite, Portugal
[c]Military Technical Academy, Romanian Ministry of National Defence, Romania
[*]Corresponding author: jose.baranda@dem.uc.pt

Abstract:

Increase of environmental awareness of the population has pressured research activities in the defence area to cover environment and toxicity issues, where have been considered appropriate manners to reduce the environmental and toxicological impacts of ammunition. One of the adopted approaches to achieve such goal involves the replacement of lead and other heavy metals by alternative materials. However, the consequences of using alternative materials in ammunitions manufacturing are uncertain for the other life-cycle phases and trade-offs can occur. The present paper describes the potential benefits from the replacement of lead in the primer and in the projectile of a 9 mm calibre ammunition. For that purpose, it is assessed and compared the environmental and toxicological impacts associated with the life-cycle of four ammunitions: combination of two types of projectiles (steel jacket and lead core; copper and nylon composite) with two types of primers (lead primer; non-lead primer). In addition, some potential improvements for the environmental performance of small calibre ammunition are also presented. To assess the impacts two Life-Cycle Impact Assessment methods are applied: CML for six environmental categories and USEtox to three toxicity categories. Results showed that the conclusion drawn for environmental and toxicological impact categories are distinct. In fact, ammunition production phase presents higher impacts for the environmental categories, whilst the operation phase has a higher impact to the toxicity categories. The substitution of lead in the primer and in the projectile provides a suitable alternative from a toxicology perspective; however, the composite projectile still presents some environmental concerns. The conclusions drawn are important for the procurement (and design) of environmental responsible ammunitions, in order to avoid (or decrease) the impacts for their manufacture and the effects on human health (e.g. shooters) and ecosystems near shooting ranges or hunting areas.

Keywords: Environmental impact; Human health; Life-cycle approach; Small calibre ammunitions

Environmental Assessment of Ammunition: the Importance of a Life-Cycle Approach

Carlos Ferreira[a], José Ribeiro[a*], Sara Almada[b], Fausto Freire[a]
[a]ADAI-LAETA, Department of Mechanical Engineering, University of Coimbra, Portugal
[b]CINAV - Laboratório Explosivos Marinha, Base Naval de Lisboa – Alfeite, Portugal
[*]Corresponding author: jose.baranda@dem.uc.pt

Abstract:

Environmental research related with military actions has been focused on the monitoring of contaminants from live-fire training and munitions disposal. It is important to take a further step and use this information to assess the environmental impacts of this contamination. In addition, it is relevant to assess the consequences of using different alternatives in a life-cycle perspective to avoid unexpected problems, and assess the hotspots of ammunition manufacturing in order to decrease the impacts in terms of other types of environmental burdens. The Life-Cycle Assessment (LCA) methodology can be employed to quantitatively assess the environmental impacts associated with munitions. LCA can assist the decision makers in answering some questions: are "green" ammunitions presenting lower environmental impacts than standard ones? What should be done to improve the performance of ammunitions from an environmental point of view? The aim of this paper is to demonstrate the importance of assessing the impacts of ammunitions in a life-cycle perspective and highlight the main environmental concerns. Three applications of LCA are presented: the production and use of generic large calibre ammunition; the comparison of the production and use of four types of small calibre ammunitions; the assessment of two technologies for ammunition disposal. The conclusions drawn can aid in providing tailored and supported decisions in order to decrease the impacts of ammunitions in a life-cycle perspective

Keywords: Environmental impacts; Life-Cycle Assessment (LCA); Military activities; Toxicological impacts

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APPENDIX II: FULL LIST OF PUBLICATIONS

Articles in international journals with scientific refereeing

Published

Ferreira C, Ribeiro J, Mendes R, Freire F (2013) Life-Cycle Assessment of Ammunition Demilitarization in a Static Kiln, *Propellants, Explosives, Pyrotechnics* 38, 2: 296 - 302.
doi: 10.1002/prep.201200088.

JCR Impact Factor® (2014): 1.604

Ferreira C, Freire F, Ribeiro J (2015) Life-cycle assessment of a civil explosive, *Journal of Cleaner Production* 89, 1: 159 - 164.
doi: 10.1016/j.jclepro.2014.11.027.

JCR Impact Factor® (2016): 4.959

Ferreira C, Ribeiro J, Almada S, Rotariu T, Freire F (2016) Reducing impacts from ammunitions: A comparative life-cycle assessment of four types of 9 mm ammunitions, *Science of The Total Environment* 566-567, 1: 34 - 40.
doi: 10.1016/j.scitotenv.2016.05.005.

JCR Impact Factor® (2016): 3.976

Ferreira C, José R, Almada S, Freire F (2017) Environmental Assessment of Ammunition: the importance of a life-cycle approach, *Propellants, Explosives, Pyrotechnics* 42, 1: 44 - 53.
doi: 10.1002/prep.201600158

JCR Impact Factor® (2016): 1.604

Submitted or in final preparation for submission to ISI-indexed journals

Ferreira C, José R, Freire F (2017) A hazard classification system based on incorporation of REACH regulation limits in the USEtox method (submitted)

Ferreira C, Ribeiro J, Freire F, Clift R (2017) Valorization of energetic material from ammunition disposal through incorporation in civil explosives (in final preparation)

Papers and oral communications in proceedings of national and international conferences with scientific refereeing

1. Ferreira C, Ribeiro J, Freire F, Clift R (2016) Valorization of energetic material from ammunition in civil explosives, ECI, Life Cycle Assessment and other Assessment Tools for Waste Management and Resource Optimization, Calabria, Italy.

2. Ferreira C, Freire F, Almada S, Ribeiro J (2016) Toxicity hazard assessment of sea dumped ammunitions with USEtox, AVT-269 Research Workshop (RSW): Sea dumped munitions and environmental risk, Varna, Bulgaria.

3. Ferreira C, Freire F, Ribeiro J (2015) Environmental impact of an emulsion explosive in a life-cycle perspective, 18th International seminar NTREM – New trends in research of energetic materials, Pardubice, Czech Republic.

4. Ferreira C, Ribeiro J, Freire F (2015) Life-Cycle Assessment methodology: a tool for the evaluation of environmental and toxicological impacts of ammunitions, 2nd European Conference of Defence and the Environment, Developing Technical and Practical Solutions for Environmental Protection of Heavy Weapon Ranges, Helsinki, Finland.

5. Ferreira C, Ribeiro J, Freire F (2015) Improvement of the toxicological assessment based on limits imposed by REACH regulation, 2nd Discussion Forum on industrial ecology and life-cycle management, Coimbra, Portugal.

6. Ferreira C, Ribeiro J, Freire F (2015) Do the substances banned by REACH actually have a significant toxicological impact?, GSEBS – Greener and safer energetic and ballistic systems, Bucharest, Romania.

7. Ferreira C, Freire F, Ribeiro J (2014) Extended life-cycle assessment applied to military systems, Discussion Forum on industrial ecology and life-cycle management, Coimbra, Portugal.

8. Ferreira C, Freire F, Rotarium T, Almada S, Ribeiro J (2014) Life-Cycle Assessment applied to small calibre ammunition, AVT-243-RSM-035 – Next Generation Greener Energetics and their Management, Brussels, Belgium.

9. Ferreira C, Ribeiro J, Almada S, Freire F (2014) Evaluation of alternatives substances to those banned by REACH supported with Life-Cycle Assessment, AVT-243-RSM-035 – Next Generation Greener Energetics and their Management, Brussels, Belgium.

10. Ferreira C, Ribeiro J, Freire F (2013) Determination of toxicological characterisation factors based on parameters defined by REACH, Energy for Sustainability 2013 – Sustainable Cities: Designing for People and the Planet, Coimbra, Portugal.

11. Ferreira C, Ribeiro J, Freire F (2013) Life-Cycle Assessment of ecotoxicity characterisation factors for substances presented in UXO based on REACH parameters, The Seventh International Disposal Conference and Exhibition, Eksjö, Sweden.

12. Ferreira C, Esteves E, Silva P, Tomé G, Freire F (2013) Comparative life-cycle assessment of two car armrests produced at CIE-Plasfil, Energy for Sustainability 2013: Sustainable Cities: Designing for People and the Planet, Coimbra, Portugal.

Posters

Ferreira C, Ribeiro J, Freire F, (2017) Assessment of toxicological thresholds based on legal limits from REACH regulation, SETAC conference, May 7–11, Brussels. Belgium

Ferreira C, Freire F, Ribeiro J (2016) Impact of REACH over energetic materials: toxicological assessment of alternatives substances to dibuthyl phathalate, 19th International seminar NTREM – New trends in research of energetic materials, Pardubice, Czech Republic.

Ferreira C, Ribeiro J, Freire F (2013) Avaliação de Ciclo de Vida de munições: Relevância e aplicação a munições de baixo calibre, 10ª Conferencia Nacional do Ambiente, Aveiro, Portugal.

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APPENDIX III: Life-cycle inventory of energetic materials – Supplementary information

Table A1 to A20 shows the data to create the life-cycle inventories for the energetic material. The first column of each table presents the data regarding the production of the main energetic materials; in the next columns are shown the life-cycle inventories created to intermediary substances that are also not presented in the Ecoinvent database. The life-cycle inventories created were principally based on literature information, covering data regarding the components and energy used for the energetic material production. When the information from literature was scarce, or even for situations where the information was absent, the procedure developed by Hischier *et al.* (2005) was followed to create the life-cycle inventories (as described in section 3.1). These inventories not contemplate residues or waste emissions into water or soil, due to lack of data, being that the reason for the incongruent mass balance (total mass of the used components might be higher than the total mass of the products). The tables A1 to A20 also presents a legend describing the type of data used: I – material and energy consumption from literature (emissions calculated based on Hischier et al. (2005)); II – only material consumption from literature (energy consumed and emissions calculated based on Hischier et al. (2005)); III – only stoichiometric calculations (materials, energy consumed, and emissions calculated based on Hischier et al. (2005)).

Table A1. Life-cycle inventory for the production of RDX, and the intermediary product hexamine.

Level 1	Level 2
RDX production (1 kg) (II)	
*Components**:	
Hexamine (0.8 kg)	**Hexamine production (1 kg) (I)** *Components*+*:* Ammonia (0.51 kg); Formaldehyde (1.3 kg) *Emissions air*#*:* Ammonia (0.001 kg); Formaldehyde (0.002 kg) *Energy*+*:* Electricity (0.35 kWh); Steam (0.65 MJ)
Nitric acid (1.89 kg)	
Emissions air#*:*	
Nitric acid (0.0036 kg)	
Energy#*:*	
Electricity (0.333 kWh)	
Steam (2 MJ)	

*Urbansky (1968); #recommendations from Hischier *et al.* (2005); +Aldehydes India Company

Table A2. Life-cycle inventory for the production of HMX, and the intermediary product hexamine.

Level 1	Level 2
HMX production (1 kg) (II)	
Components[$]:	
Hexamine (0.5 kg)	**Hexamine production (1 kg) (I)** See RDX production
Acetic anhydride (4.06 kg)	
Acetic acid (4.75 kg)	
Formaldehyde (0.085 kg)	
Ammonium nitrate (2.3 kg)	
Emissions air[#]*:*	
Acetic acid (0.0095 kg)	
Formaldehyde (0.0002 kg)	
Ammonium nitrate (0.005 kg)	
Acetic anhydride (0.008 kg)	
Energy[#]*:*	
Electricity (0.333 kWh)	
Steam (2 MJ)	

[$] Fedoroff *et al.* (1960); [#] recommendations from Hischier *et al.* (2005)

Table A3. Life-cycle inventory for the production of TNT, and the intermediary products Oleum, Sodium bisulphite, and Sodium sulphite.

Level 1	Level 2
TNT production (1 kg) (I)	
Components[*]:	
Oleum (2.25 kg)	**Oleum production (1 kg) (III)** *Components*[#]*:* Sulphuric acid (0.8 kg); Sulphur trioxide (0.2 kg); *Energy*[#]*:* Electricity (0.333 kWh); Steam (2 MJ)
Sodium bisulphite (0.065 kg)	**Sodium bisulphite production (1 kg) (III)** *Components*[#]*:* Sodium carbonate (1.02 kg); sulphur dioxide (0.615 kg); *Emissions air*[#]: sulphur dioxide (0.001 kg) *Energy*[#]*:* Electricity (0,333 kWh); Steam (2 MJ)
Sodium sulphite (0.01 kg)	**Sodium sulphite production (1 kg) (III)** *Components*[#]*:* Sodium hydroxide (0.64 kg); sulphur dioxide (0.51 kg); *Emissions air*[#]: Sodium hydroxide (0.001 kg); sulphur dioxide (0.001 kg) *Energy*[#]*:* Electricity (0.333 kWh); Steam (2 MJ)
Sulphur dioxide (0.001 kg)	
Toluene (0.49 kg)	
Nitric acid (1.1 kg)	
Emissions air[α]*:*	
PM_{10} (0.00013 kg)	
Sulphur dioxide (0.00012 kg)	
N_{ox} (0.009 kg)	
Nitric acid (0.0005 kg)	
Energy[*]*:*	
Electricity (0.135 kWh)	
Steam (3.7 MJ)	

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005); [α]Environment Australia (1999)

Table A4. Life-cycle inventory for the production of PETN, and the intermediary product Pentaerythritol.

Level 1	Level 2
PETN production (1 kg) (II)	
Components[*]:	
Pentaerythritol (0.44 kg)	**Pentaerythritol production (1 kg) (III)** *Components*[#]*:* Acetaldehyde (0.323 kg); Formaldehyde (0.882 kg); Lime (0.272 kg) *Emissions air*[#]*:* Acetaldehyde (0.0006 kg); Formaldehyde (0.002 kg); *Energy*[#]*:* Electricity (0.333 kWh); Steam (2 MJ)
Nitric acid (0.08 kg)	
Acetone (1.76 kg)	
Sodium carbonate (0.007 kg)	
Emissions air[*]*:*	
Nitric acid (0.0002 kg)	
Acetone (0.0035 kg)	
Energy[*]*:*	
Electricity (0.333 kWh)	
Steam (2 MJ)	

[*] Urbansky (1968); [#] recommendations from Hischier *et al.* (2005)

Table A5. Life-cycle inventory for the production of Nitroglycerine.

Nitroglycerine production (1 kg) (II)
Components[*]:
Glycerine (0.42 kg)
Sulfuric acid (1.01 kg)
Nitric acid (1.04 kg)
Sodium carbonate (0.006 kg)
Emissions air[#]*:*
Nitric acid (0.002 kg)
Sulfuric acid (0.002 kg)
Energy[#]:
Electricity (0.333 kWh)
Steam (2 MJ)

[*] Urbansky (1968); [#] recommendations from Hischier *et al.* (2005)

Table A6. Life-cycle inventory for the production of Nitrocellulose

Nitrocellulose production (1 kg) (I)
Components[*]:
Cellulose (0.6 kg)
Nitric acid (1.4 kg)
Sulfuric acid (0.81 kg)
Emissions air$^{\alpha}$*:*
Sulphur dioxide (0.035 kg)
N_{ox} (0.015 kg)
Nitric acid (0.0095 kg)
Sulfuric acid (0.0003 kg)
Energy [*]:
Electricity (0.065 kWh)

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005); $^{\alpha}$Environment Australia (1999)

Table A7. Life-cycle inventory for the production of Black powder.

Black powder production (1 kg) (II)
Components[*]*:*
Potassium Nitrate (0.78 kg)
Charcoal (0.19 kg)
Sulphur (0.03 kg)
Energy[#]:
Electricity (0.333 kWh)
Steam (2 MJ)

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005)

Table A8. Life-cycle inventory for the production of Picric acid, and the intermediary product Oleum.

Level 1	Level 2
Picric acid production (1 kg) (II)	
Components[*]*:*	
Oleum (2.6 kg)	**Oleum production (1 kg) (III)**
	See TNT production
Nitric acid (1.32 kg)	
Benzene (0.61 kg)	
Sodium carbonate (0.31 kg)	
Sodium hydroxide (0.68 kg)	
Chlorine (0.54 kg)	
Emissions air[#]*:*	
Nitric acid (0.003 kg)	
Benzene (0.0012 kg)	
Sodium hydroxide (0.0014 kg)	
Energy[#]*:*	
Electricity (0.333 kWh)	
Steam (2 MJ)	

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005)

Table A9. Life-cycle inventory for the production of Mercury fulminate.

Mercury fulminate production (1 kg) (II)
Components[*]*:*
Mercury (0.8 kg)
Nitric acid (8.0 kg)
Ethanol (6.64 kg)
Emissions air[#]*:*
Nitric acid (0.016 kg)
Ethanol (0.013 kg)
Sodium hydroxide (0.0014 kg)
Energy[#]*:*
Electricity (0.333 kWh)
Steam (2 MJ)

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005)

Table A10. Life-cycle inventory for the production of Lead dioxide.

Lead dioxide production (1 kg) (III)
Components[#]*:*
Lead oxide (1.05 kg)
Sodium chloride (0.84 kg)
Hydrochloric acid (0.02 kg)
Energy[#]*:*
Electricity (0.333 kWh)
Steam (2 MJ)

[#] recommendations from Hischier *et al.* (2005)

Table A11. Life-cycle inventory for the production of Zinc peroxide.

Zinc peroxide production (1 kg) (III)
Components[#]*:*
Zinc oxide (0.88 kg)
Hydrogen peroxide (0.37 kg)
Emissions air[#]*:*
Zinc oxide (0.0017 kg)
Hydrogen peroxide (0.0007 kg)
Energy[#]*:*
Electricity (0.333 kWh)
Steam (2 MJ)

[#] recommendations from Hischier *et al.* (2005)

Table A12. Life-cycle inventory for the production of Calcium silicide.

Calcium silicide production (1 kg) (III)
Components[#]*:*
Quicklime (0.61 kg)
Silica sand (1.31 kg)
Charcoal (0.66 kg)
Energy[#]*:*
Electricity (0.333 kWh)
Steam (2 MJ)

[#] recommendations from Hischier *et al.* (2005)

Table A13. Life-cycle inventory for the production of Lead aside, and the intermediary products Lead nitrate; and Sodium aside.

Level 1	Level 2
Lead aside production (1 kg) (II)	
Components[*]:	
Lead Nitrate (1.18 kg)	**Lead Nitrate production (1 kg) (III)** *Components*[#]: Lead (0.747 kg); Nitric acid (1.05 kg); *Emission air*[#]: Nitric acid (0.0021 kg); Nitric oxide (0.068 kg); *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)
Sodium aside (0.4 kg)	**Sodium aside production (1 kg) (III)** *Components*[#]: Sodium (1.73 kg); Ammonia (0.028 kg); Iron sulphate (0.012 kg); *Emissions air*[#]: Ammonia (0.00005 kg); *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)
Starch (0.04 kg)	
Emissions air[#]:	
Sodium aside (0.0008 kg)	
Energy[#]:	
Electricity (0.333 kWh)	
Steam (2 MJ)	

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005)

Table A14. Life-cycle inventory for the production of Lead picrate, and the intermediary products Lead nitrate; and Picric acid.

Level 1	Level 2
Lead picrate production (1 kg) (II))	
Components[*]:	
Lead Nitrate (1.68 kg)	**Lead nitrate production (1 kg) (III)** (see lead aside)
Picric acid (0.68 kg)	**Picric acid production (1 kg) (II)** (see picric acid)
Ethanol (3.59 kg)	
Emissions air[#]:	
Picric acid (0.001 kg)	
Ethanol (0.007 kg)	
Energy[#]:	
Electricity (0.333 kWh)	
Steam (2 MJ)	

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005).

Table A15. Life-cycle inventory for the production of Nitroguanidine, and the intermediary products Guanidine nitrate, and Calcium cyanimide.

Level 1	Level 2	Level 3
Nitroguanidine production (1kg) (II)		
Components[*]*:*		
Guanidine nitrate (1.36 kg)	**Guanidine nitrate production (1 kg) (II)** *Components*[*]*:* Ammonium nitrate (2.0 kg); Ammonia (0.13 kg); Calcium cyanimide (1.6 kg) *Emissions air*[#]*:* Ammonia (0.0003); Ammonium nitrate (0.004); *Energy*[#]*:* Electricity (0.333 kWh); Steam (2 MJ)	**Calcium cyanimide production (1 kg) (III)** *Components*[#]*:* Calcium carbide (0.8 kg); Nitrogen (0.18 kg) *Emissions air*[#]*:* Nitrogen (0,0004) *Energy*[#]*:* Electricity (0.333 kWh); Steam (2 MJ)
Sulfuric acid (3.0 kg)		
Emissions air[#]*:*		
Sulfuric acid (0.006 kg)		
Energy[#]*:*		
Electricity (0.333 kWh)		
Steam (2 MJ)		

[*] Urbansky (1968); [#] recommendations from Hischier *et al.* (2005)

Table A16. Life-cycle inventory for the production of DDNP, and the intermediary products Sodium nitrite, Sodium picramate, Sulfamic acid, and Sodium sulphide.

Level 1	Level 2	Level 3
DDNP production (1 kg) (II)		
Components[β]*:*		
Sodium nitrite (0.38 kg)	**Sodium nitrite production (1 kg) (III)** *Components*[#]: Quicklime (0.8 kg); sodium nitrate (1.82 kg); Sulfamic acid (1.382 kg); *Emission air*[#]: sulfamic acid (0.003 kg); *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)	**Sulfamic acid production(1kg) (III)** *Components*[#]: Urea (0.33 kg); Sulphur trioxide (0.43 kg); Sulphuric acid (0.53 kg); *Emission air*: Urea (0.0007 kg); Sulphur trioxide (0,0009 kg); Sulphuric acid (0.001 kg); *Energy*: Electricity (0.333 kWh); Steam (2 MJ)
Sodium Picramate (1.14 kg)	**Sodium Picramate production (1 kg) (III)** *Components*[#]: picric acid (1.375); sodium hydroxide (0.1); Sodium sulfide (2.2); *Emission air*[#]: sodium hydroxide (0.0002); *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)	**Sodium sulphide production (1 kg) (III)** *Components*[#]: Sodium sulphate (1.82); Charcoal (0.61); *Emissions air*[#]: Sodium sulphate (0.0036); *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)
Hydrochloric acid (0.6 kg)		
Emissions air[#]*:*		
Sodium nitrite (0.0008 kg)		
Energy[#]*:*		
Electricity (0.333 kWh)		
Steam (2 MJ)		

[β] SADU; [#] recommendations from Hischier *et al.* (2005)

Table A17. Life-cycle inventory for the production of tetrazene, and the intermediary products Sodium nitrite, Aminoguanidine sulphate, Aminoguanidine, Cyanimide, and Hydrazine.

Level 1	Level 2	Level 3	Level 4
Tetrazene production (1 kg) (II)			
Components[*]:			
Acetic acid (1.2 kg)			
Sodium Nitrite (1.48 kg)	**Sodium nitrite production (1 kg) (III)** (see DDNP)		
Aminoguanidine sulphate (1.85 kg)	**Aminoguanidine sulphate production (1 kg)** *Components*[#]: Aminoguanidine (0.48 kg); Sulphuric acid (0.63 kg) *Emission air*[#]: sulfuric acid (0.0012 kg) *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)	**Aminoguanidine production (1kg) (III)** *Components*[#]: Cyanimide (0.60 kg); Hydrazine (0.46 kg); *Emission air*[#]: Cyanimide (0.0012 kg); Hydrazine (0.0009 kg); *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)	**Cyanimide production (1 kg) (III)** *Components*[#]: Calcium carbide (1.6 kg); carbon dioxide (1.10 kg); *Emission air*[#]*:* carbon dioxide (0.0022 kg) *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ) **Hydrazine production (1kg) (III)** *Components*[#]: Ammonia (1.12 kg); Hydrogen peroxide (1.12 kg) *Emission air*[#]: Ammonia (0.0022 kg); Hydrogen peroxide (0.0022 kg) *Energy*[#]*:* Electricity (0.333 kWh); Steam (2 MJ)
Emissions air[#]*:*			
Acetic acid (0.0024 kg)			
Sodium Nitrite (0,003 kg)			
Energy[#]*:*			
Electricity (0.333 kWh)			
Steam (2 MJ)			

[*]Urbansky (1968); [#]recommendations from Hischier *et al.* (2005)

Table A18. Life-cycle inventory for the production of Lead styphnate, and the intermediary products Trinitroresorcinate, 1,3 Dinitrobenzene, Dinitrobenzene, and Lead nitrate.

Level 1	Level 2	Level 3	Level 4
Lead styphnate production (1 kg) (II)			
Components$^{\beta}$*:*			
Trinitroresorcinate (1.25 kg)	**Trinitroresorcinate production (1 kg) (III)** *Components*$^{\#}$: 1,3 diaminobenzene (0.98 kg); Hydrochloric acid (0.33 kg); *Energy*$^{\#}$: Electricity (0.333 kWh); Steam (2 MJ)	**1,3 Dinitrobenzene production (1 kg) (III)** *Components*$^{\#}$: Dinitrobenzene (1.08 kg); Hydrogen (0.167 kg); Ethanol (3.14 kg); Zinc (0.11 kg); *Emission air*$^{\#}$: Ethanol (0.006); *Energy*$^{\#}$*:* Electricity (0.333 kWh); Steam (2 MJ)	**Dinitrobenzene production (1 kg) (III)** *Components*$^{\#}$: Nitrobenzene (0.89 kg); sulphuric acid (1.06 kg); Nitric acid (0.48 kg); *Emission air*$^{\#}$: Nitrobenzene (0.0018 kg); sulphuric acid (0.002 kg); Nitric acid (0.001 kg); *Energy*$^{\#}$*:* Electricity (0.333 kWh); Steam (2 MJ)
Lead nitrate (2.12 kg)	**Lead nitrate production (1 kg) (III)** (see lead azide)		
Sodium bicarbonate (0.8 kg)			
Emissions air$^{\#}$:			
Trinitroresorcinate (0.0025 kg)			
Energy$^{\#}$:			
Electricity (0.333 kWh)			
Steam (2 MJ)			

$^{\beta}$SADU; $^{\#}$recommendations from Hischier *et al.* (2005)

Table A19. Life-cycle inventory for the production of Barium nitrate, and the intermediary products Barium carbonate, and Barium sulphide.

Level 1	Level 2	level 3
Barium nitrate production (1 kg) (III)		
Components[#]*:*		
Barium carbonate (0.75 kg)	**Barium carbonate production (1 kg) (III)** *Components*[#]*:* Barium sulphide (0.86 kg); Sodium sulphate (0.72 kg); *Emissions air*[#]*:* Sodium sulphate (0.0014 kg) *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)	**Barium sulphide production (1 kg) (III)** *Components*[#]*:* Barite (1.4 kg); Charcoal (0.07 kg) *Energy*[#]: Electricity (0.333 kWh); Steam (2 MJ)
Nitric acid (0.75 kg)		
Emissions air[#]:		
Nitric acid (0.0015 kg)		
Energy[#]:		
Electricity (0.333 kWh)		
Steam (2 MJ)		

[#] recommendations from Hischier *et al.* (2005)

Table A20. Life-cycle inventory for the production of Antimony sulphide, and the intermediary products Antimony thrichloride, Sodium thiosulfate, and Sodium sulphite.

Level 1	Level 2	level 3
Antimony sulphide production (1 kg) (III) *Components*[#]*:*		
Antimony trichloride (0.67 kg)	**Antimony trichloride production (1 kg) (III)** *Components*[#]*:* Antimony (0.59 kg); chlorine (0.49 kg); *Emissions air*: chlorine (0.001 kg) *Energy*: Electricity (0.333 kWh); Steam (2 MJ)	
Sodium thiosulfate (0.46 kg)	**Sodium thiosulfate production (1 kg) (III)** *Components*[#]*:* Sodium sulphite (0.82 kg); Sulphur (0.21 kg); *Emissions air*[#]: Sulphur (0.0004 kg) *Energy*[#]*:* Electricity (0.333 kWh); Steam (2 MJ)	**Sodium sulphite production (1 kg) (III)** *Components*[#]*:* Sodium hydroxide (0.64 kg); Sulphur dioxide (0.51 kg) *Emissions air*[#]*:* Sodium hydroxide (0.001 kg); Sulphur dioxide (0.001 kg) *Energy*[#]*:* Electricity (0,333 kWh); Steam (2 MJ)
Energy[#]*:* Electricity (0.333 kWh) Steam (2 MJ)		

[#] recommendations from Hischier *et al.* (2005)

APPENDIX IV: A hazard classification system based on incorporation of REACH regulation limits in the USEtox method – Supplementary information

1. Calculation of Henry´s law coefficient

The Henry´s law coefficient is calculated taking into account the ranges of values for vapor pressure and molecular mass as well as using the legal value for water solubility (that is fixed based on the regulatory limit provided in Table 5.1). Calculation of Henry´s law coefficient is based on a range of values, so the iteration to obtain the values for this parameter is described following. The calculation started with a fixed value for vapor pressure (1.0-7 Pa) and the molecular weight is varied for the extreme values (10 and 1000 g/mol). Then, a new value for vapor pressure is fixed and the molecular weight is varied again. This iteration is carried out until the extreme value of vapor pressure is reached (1.0+5 Pa).

Table B1 shows the calculation of the Henry´s law coefficient that is based on the variation of the parameters molecular mass and vapor pressure, for seven virtual substances (in which the value for water solubility is one order of magnitude lower than the legal limit). Table B2 shows the calculation of the Henry´s law coefficient to the particular cases of the virtual substance water solubility and extreme virtual substance considering the PBT limits.

Table B1. Calculation of the Henry´s law coefficient based on the variation of the parameters molecular mass and vapor pressure for seven virtual substances – exception of VS water solubility and extreme VS.

Parameters	(Sol_{25} = 0.1 mg/L)						
P_{vap} MW	1.0E-07	1.0E-05	1.0E-03	1.0E-01	1.0E+01	1.0E+03	1.0E+05
10	1.0E-05	1.0E-03	1.0E-01	1.0E+01	1.0E+03	1.0E+05	1.0E+07
1000	1.0E-03	1.0E-01	1.0E+01	1.0E+03	1.0E+05	1.0E+07	1.0E+09

P_{vap} – vapour pressure; MW – molecular mass; Sol_{25} – water solubility

Table B2. Calculation of the Henry´s law coefficient based on the variation of the parameters molecular mass and vapor pressure for the virtual substance water solubility and extreme virtual substance.

Parameters	(Sol_{25} = 1 mg/L) - PBT						
P_{vap} MW	1.0E-07	1.0E-05	1.0E-03	1.0E-01	1.0E+01	1.0E+03	1.0E+05
10	1.0E-06	10E-04	1.0E-02	1.0E00	1.0E+02	1.0E+04	1.0E+06
1000	1.0E-04	1.0E-02	1.0E00	1.0E+02	1.0E+04	1.0E+06	1.0E+08

P_{vap} – vapour pressure; MW – molecular mass; Sol_{25} – water solubility

2. Comparison between the toxicological characterisation factors

Figures B1 to B3 presents the toxicological CFs of the virtual substance obtained for the emission compartments continental air, sea water, and agricultural soil, respectively. In all the aforementioned figures, for each virtual substance, instead of a single value, is presented in a logarithmic scale a range of values of the CF due to the k_H variation. The toxicological CFs are shown for the extreme values (minimum and maximum k_H), and for the interval of k_H that comprises the majority of organic substances in USEtox [1.0E-06 Pa.m^3.mol^{-1}; 1.0E+02 Pa.m^3.mol^{-1}] represented by a dark line. The analysis drawn for these emissions compartments are similar than the ones presented for the toxicological CFs associated with the virtual substances considering the emission compartments urban air, freshwater, and natural soil.

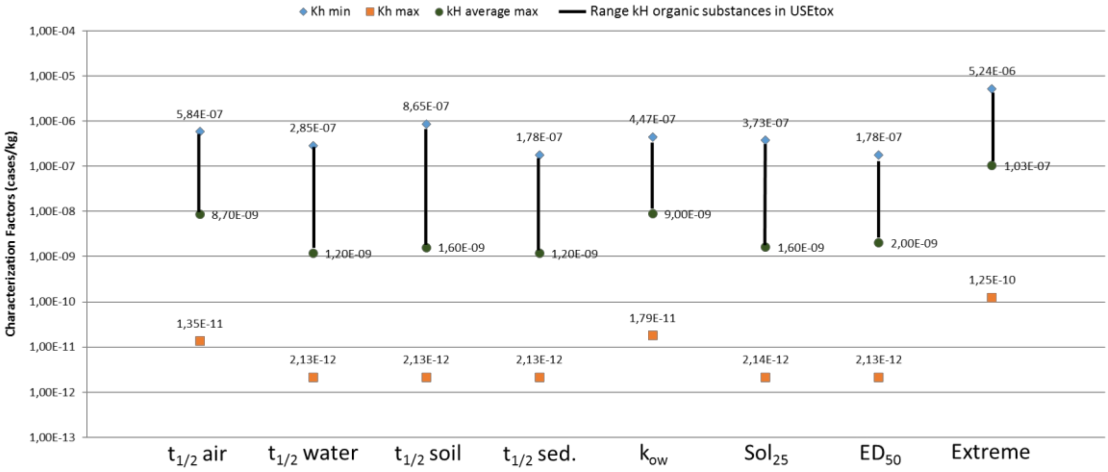

Figure B1. Toxicological characterization factors associated with the eight virtual substances in continental air compartment.

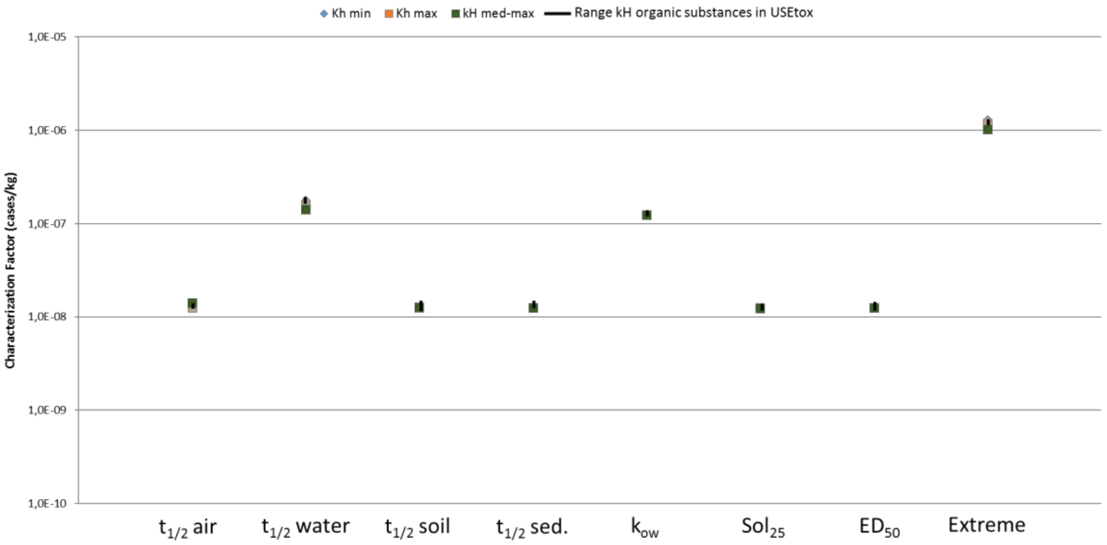

Figure B2. Toxicological characterization factors associated with the eight virtual substances in sea water compartment.

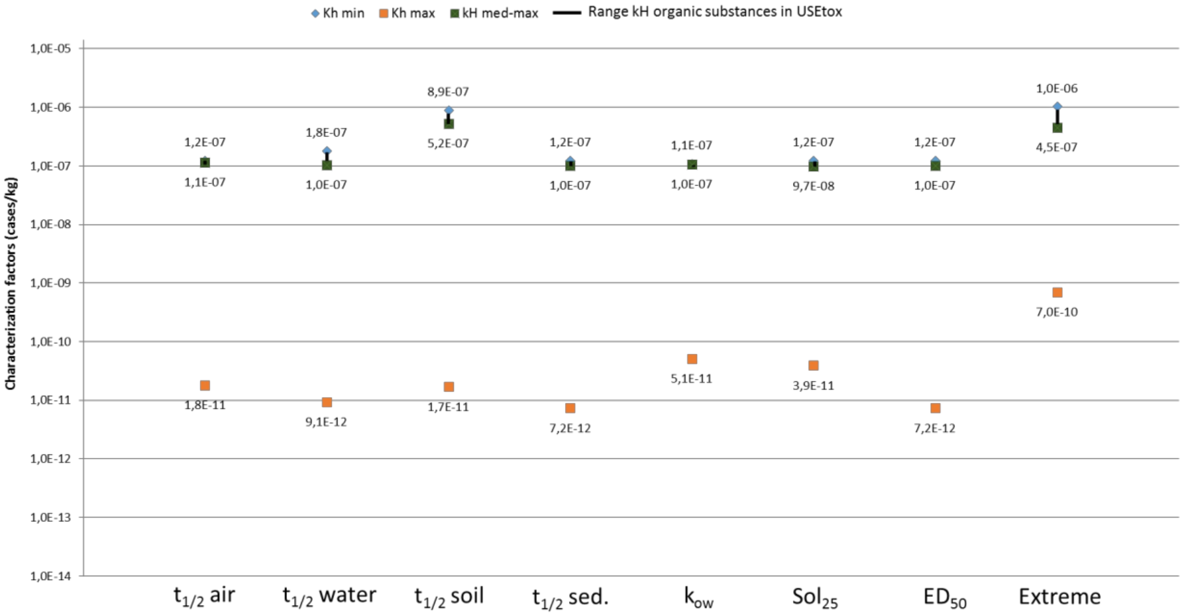

Figure B3. Toxicological characterization factors associated with the eight virtual substances in agricultural soil compartment.

3. Influence of the Henry´s law coefficient (k_H) to the toxicological characterization factors

Figures B4 to B9 presents the influence of the Henry´s law coefficient (k_H) on the calculated toxicological CFs, considering the emission compartments urban air, freshwater and natural soil (the results for the other emission compartments are similar). The results show a similar pattern as the one observed for the virtual substance ED_{50}, as the toxicological CF for an emission into air and soil are highly dependent of k_H. The reasons for this behaviour are presented in detail in section 5.1.3.1.

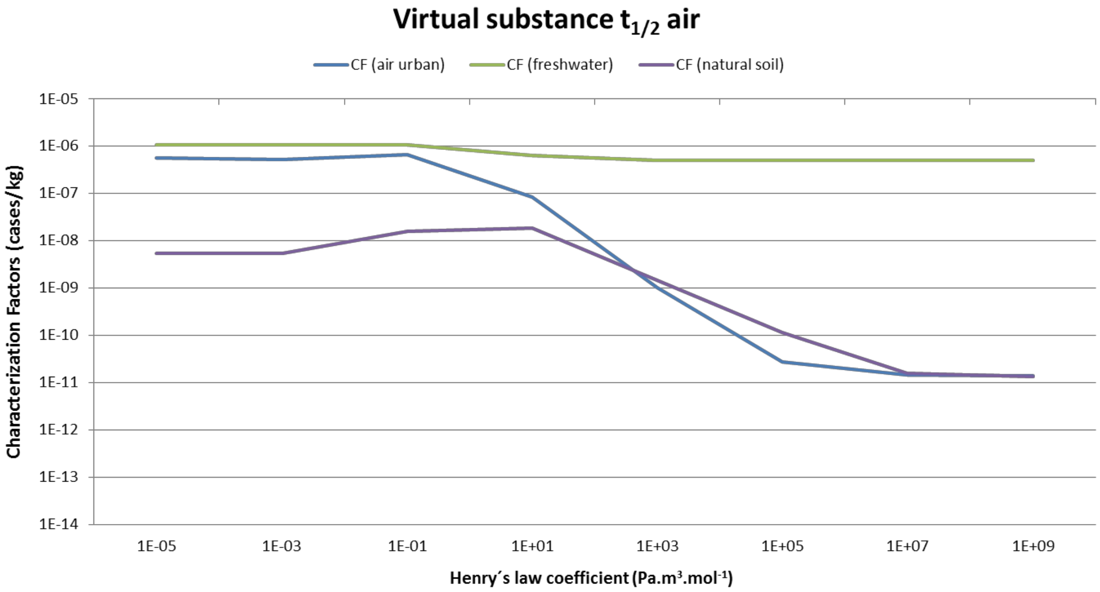

Figure B4. Variation of the toxicological characterization factor for the virtual substance $t_{1/2}$ air relatively to the Henry´s law coefficient (for the emission compartments urban air, freshwater, and natural soil).

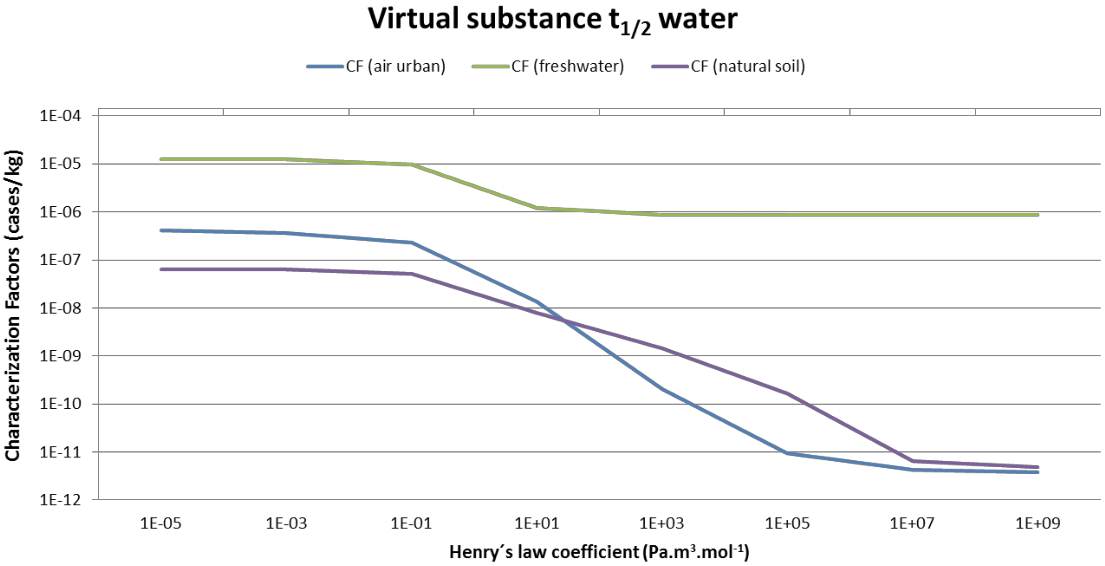

Figure B5. Variation of the toxicological characterization factor for the virtual substance $t_{1/2}$ water relatively to the Henry´s law coefficient (for the emission compartments urban air, freshwater, and natural soil).

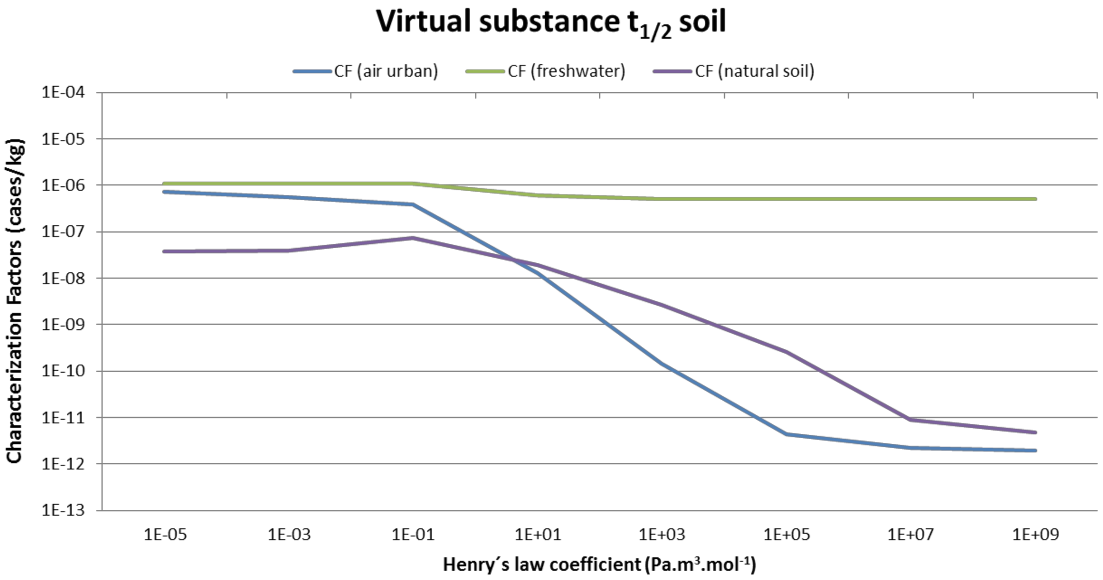

Figure B6. Variation of the toxicological characterization factor for the virtual substance $t_{1/2}$ soil relatively to the Henry´s law coefficient (for the emission compartments urban air, freshwater, and natural soil).

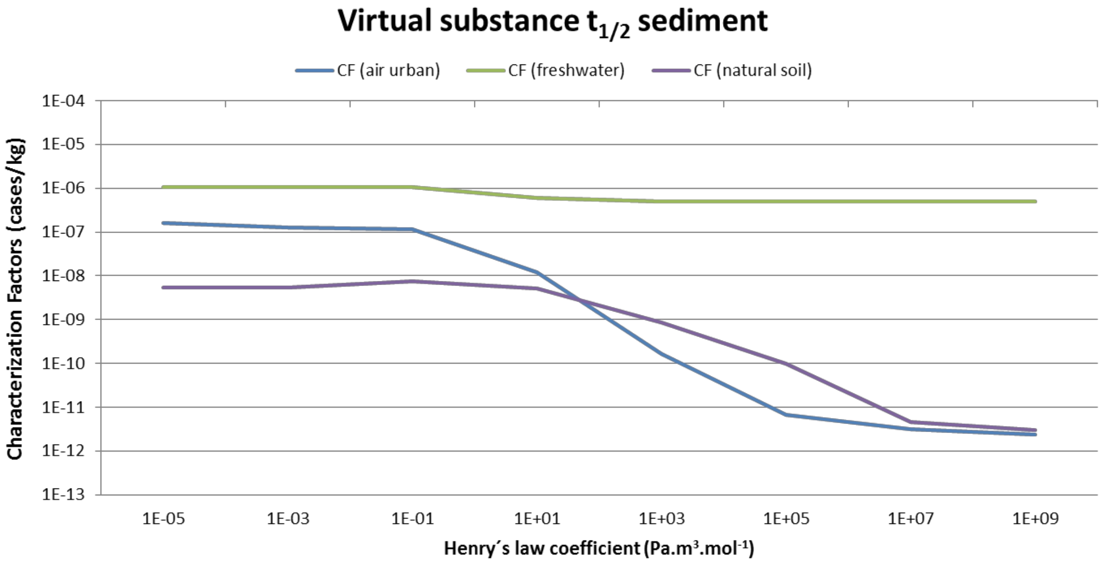

Figure B7. Variation of the toxicological characterization factor for the virtual substance $t_{1/2}$ sediment relatively to the Henry´s law coefficient (for the emission compartments urban air, freshwater, and natural soil).

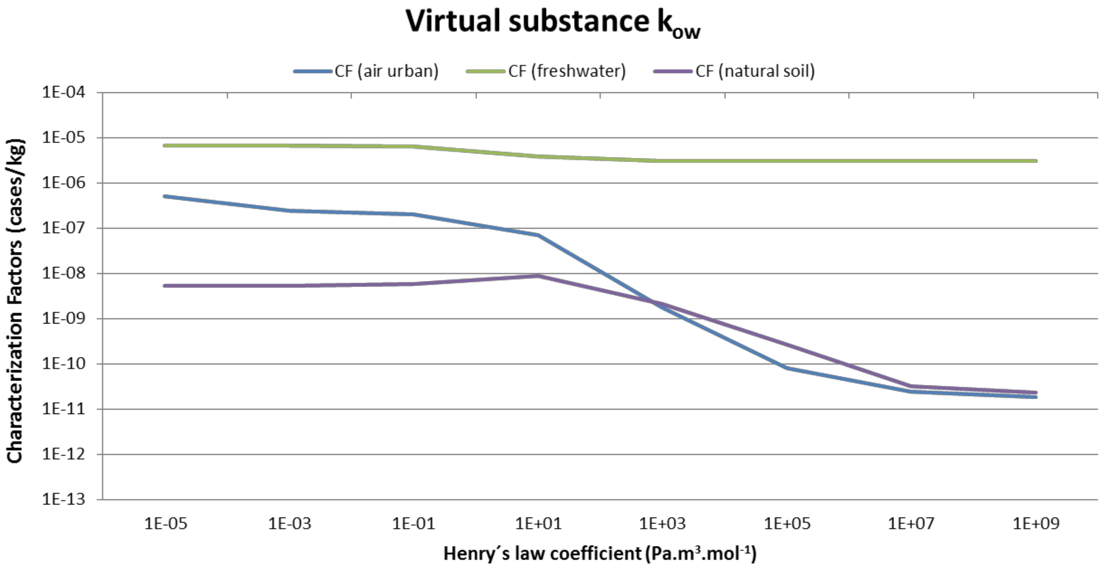

Figure B8. Variation of the toxicological characterization factor for the virtual substance k_{ow} relatively to the Henry´s law coefficient (for the emission compartments urban air, freshwater, and natural soil).

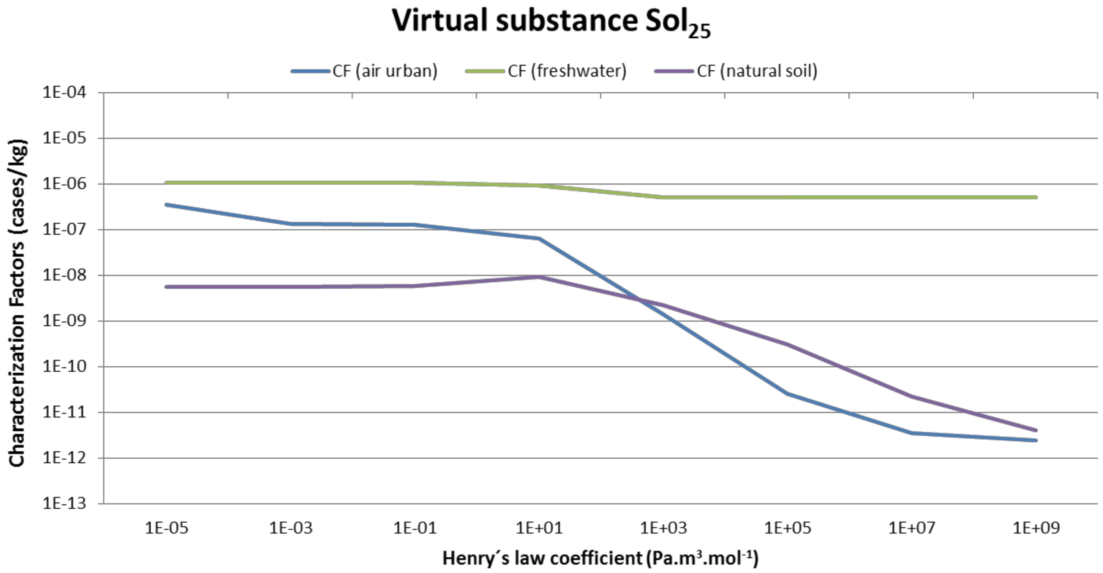

Figure B9. Variation of the toxicological characterization factor for the virtual substance Sol_{25} relatively to the Henry´s law coefficient (for the emission compartments urban air, freshwater, and natural soil).

Source of images in the cover of the thesis: Rotariu T, Petre R (2014) Final Report CR-1128, Environmentally Responsible Munitions, MTA, CBRN, Bucharest; TNO (2014), Netherlands Final report, EDA-ERM, Netherlands; MSIAC (2011), Munition and Propellant Disposal and its Impact on the Environment, NATO AVT-177 Symposium on Munition and Propellant Disposal and its Impact on the Environment, 17 October, Edinburgh, Scotland.