CRANFIELD UNIVERSITY

ENCINA GUTIERREZ CARAZO

INVESTIGATION INTO THE FATE AND TRANSPORT OF INSENSITIVE HIGH EXPLOSIVES IN SANDY SOILS TO INFORM THE DEVELOPMENT OF A COMPUTATIONAL SIMULATION

Cranfield Defence and Security
Centre for Defence Chemistry

PhD
Academic Year: 2018 - 2022

Supervisor: Dr. Melissa Ladyman
Associate Supervisor: Prof. Frederic Coulon
August 2022

CRANFIELD UNIVERSITY

Cranfield Defence and Security
PhD

Academic Year 2018 – 2022

Encina Gutierrez Carazo

Investigation into the fate and transport of Insensitive High Explosives in sandy soils to inform the development of a computational simulation

Supervisor: Dr. Melissa Ladyman
Associate Supervisor: Prof. Frederic Coulon
August 2022

© Cranfield University 2022. All rights reserved. No part of this publication may be reproduced without the written permission of the copyright owner.

ABSTRACT

The use of less-sensitive energetic formulations for military training activities has driven the replacement of traditional explosive fills by a new generation known as Insensitive High Explosives (IHE). Due to their novelty, little is understood about their behaviour in the environment when deposited as part of a formulation, specifically how long they may persist and the likelihood of transport of significant concentrations to groundwater. However, it is impractical to empirically investigate the behaviour of IHE in all possible environmental conditions and scenarios, and as of yet, there is no single computational model that enables simulation of persistence of IHE in soil. Therefore, the aim of this thesis was to provide insight into the chemical behaviour of IHE to simulate their fate and transport in sandy soils. To achieve this, the key parameters governing IHE dissolution, transport through soil and degradation were identified, highlighting that the partitioning coefficient regulated IHE mobility through soil; rainwater pH modified IHE dissolution and soil temperature had a significant influence on IHE degradation. These parameters were used to develop a stochastic model able to simulate breakthrough times and concentrations in sandy soil environments. Comparison of simulated breakthrough concentrations of IHE to empirical soil columns proved that the model was able to representatively predict how IHE behaved in soil specifically concentration in leachate over time, which would be invaluable in evaluation of the environmental risks posed by IHE residues and to support soil remediation strategies in contaminated areas.

Keywords: NTO, DNAN, stochastic modelling, transport, dissolution, degradation

ACKNOWLEDGEMENTS

I would like to thank the following people who have helped me undertake this research:

My supervisors Dr. Melissa Ladyman, Prof. Frederic Coulon and Dr Tracey Temple for their enthusiasm for the project, their support, encouragement, and patience and for being an example for me throughout this PhD.

BAE Systems and EPSRC for funding this research and Cranfield University for offering me the opportunity to pursue my doctorate.

The staff members of CDC and especially Sue Hardy for their friendship and support.

The other PhD students on campus, and a special mention to Dr. Chris McGee, who has helped me since the first week and with whom I share a strong and eternal friendship.

My partner Kostas – I simply couldn't have done this without you. No matter how little you understood about my project and situation, you were a continuous source of support.

And to my parents, who I know have been very proud of me since the start of this journey.

TABLE OF CONTENTS

ABSTRACT i
ACKNOWLEDGEMENTS iii
TABLE OF CONTENTS iv
LIST OF FIGURES vii
LIST OF TABLES x
LIST OF EQUATIONS xii
LIST OF ABBREVIATIONS xiii

CHAPTER 1. Introduction 1
1.1 Aim and objectives 5

CHAPTER 2. Literature review. Computational modelling of fate and transport processes of Insensitive High Explosive in soil: principles and challenges. 8
2.1 Introduction 9
2.1.1 Environmental problems posed by explosive residues 9
2.1.2 Explosives and explosive formulations 9
2.1.3 The need for computational modelling 11
2.2 Behaviour of explosives in the environment 13
2.2.1 Transport 13
2.2.2 Fate 17
2.2.3 Physico-chemical features and model dimension 18
2.3. Simulating the fate and behaviour of explosives in the environment: the need from a computational perspective 21
2.3.1 Number of dimensions considered for computational models 21
2.3.2 Deterministic approach 23
2.3.3 Stochastic approach and Monte Carlo method 38
2.4 Towards an integrated approach for modelling explosives 41
2.5 Conclusion 42

CHAPTER 3. Simulation of the transport of Insensitive High Explosive residues in sandy soil columns 44
3.1 Introduction 45
3.2 Materials and methods 47
3.2.1 Soil Preparation and Characterisation 47
3.2.2 Preparation of IHE compound stock solutions 48
3.2.3 Determination of K_d 48
3.2.4 Soil column experiments 49
3.2.5 High Performance Liquid Chromatography coupled with Diode array Detector (HPLC-DAD) 49

3.2.6 The construction of the model in GoldSim 50
3.2.7 Sensitivity analysis 54
3.3 Results and Discussion 55
3.3.1 Simulating NTO and DNAN transport in quartz sand 55
3.3.2 Simulating NTO and DNAN transport in sandy soils 57
3.3.3 Sensitivity analysis 60
3.3.4 Simulating NTO and DNAN transport in soil using Kd and Monte Carlo method 601
3.4 Conclusion 65

CHAPTER 4. Simulation of the dissolution process of Insensitive High Explosive residues in rainwater. 68
4.1 Introduction 69
4.2 Material and methods 71
4.2.1 IHE formulation particles and solvents 71
4.2.2 Soils 71
4.2.3 Dissolution drip tests of the IHE formulation 72
4.2.4 Soil column experiments 73
4.2.5 High Performance Liquid Chromatography with Diode Array Detector (HPLC-DAD) 74
4.2.6 Dissolution process in the stochastic simulation 75
4.2.7 Sensitivity analysis 77
4.3 Results and discussion 78
4.3.1 Effect of water pH on the dissolution curves for DNAN, NTO and RDX in an IHE formulation 78
4.3.2 Determination of dissolution rates 81
4.3.3 Comparison of simulated and experimental dissolution and transport of IHE particles in soils 82
4.3.4 Sensitivity analysis using water at different pH and temperature 86
4.4 Conclusions and recommendations 88

CHAPTER 5. Determination of the influence of temperature on the degradation of Insensitive High Explosive residues 90
5.1 Introduction 91
5.2 Materials and methods 93
5.2.1 Soil characteristics, IHE solution and solvents 93
5.2.2 Evaluation of the contribution of the abiotic and biotic processes on the degradation of the IHE formulation 94
5.2.3 Influence of temperature on the degradation of the IHE formulation in soil 95
5.2.4 Extraction method for IHE constituents in soil 95

5.2.5 High Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD) 96
5.3 Results and discussion 96
5.3.1 Influence of the abiotic and biotic processes on the degradation of the IHE formulation 96
5.3.2 Influence of temperature on the degradation of the IHE constituents in soil 100
5.3.3 Calculation of kinetic parameters for each IHE constituents in soil 103
5.3.4 Discussion of the degradation kinetics and activation energy 107
5.4 Conclusions and recommendations 108

CHAPTER 6. Assessment of the performance of a stochastic model for the simulation of Insensitive High Explosive fate and transport 110
6.1 Introduction 111
6.2 Experimental design for comparison to simulation 113
6.2.1 Experimental design for indoor soil columns 114
6.2.2 Experimental design for outdoor soil columns 114
6.3 Development of the model in GoldSim 114
6.2.1 Model dimensions, timescale, and water inflow 115
6.2.2 Simulating transport (advection and sorption) 116
6.2.3 Simulating dissolution rate of the IHE formulation 117
6.2.4 Simulating degradation rates 118
6.2.5 Run settings and stochastic simulation 118
6.4 Results and discussion 119
6.4.1 Assessing the performance of the model for simulating IHE fate and transport in indoor sandy soil columns 119
6.4.2 Assessing the performance of the model for simulating the fate and transport of IHE in outdoor sandy soil columns. 125
6.4.3 Applicability of the model developed in GoldSim 132
6.5. Conclusions and recommendations 133

CHAPTER 7. Conclusions and recommendations for future work 135
7.1 Overview of the key findings and contribution to knowledge 135
7.2 Recommendations for future work 143

REFERENCES 144

LIST OF FIGURES

Figure 1.1 Thesis structure aligned to chapter titles 7

Figure 2.1 Molecular structure of common traditional (top) and new (bottom) explosive constituents 11

Figure 2.2 Schematic of the main processes involved in the fate and transport of explosives in soil. 14

Figure 2.3 Comparison of some the molecular structure of some explosive constituents (top) and other organic compounds such as herbicides, pesticides and insecticides (bottom)..... 26

Figure 2.4 Mechanisms for the reduction of nitro groups of nitroaromatic compounds.. 26

Figure 2.5 Molecular structure of NTO and carbendazim that shares a nitrogenated heterocycle with nitro, amide and carboxylic groups 34

Figure 2.6 Processes in water and sediment described by TOXSWA software. 35

Figure 3.1 Calibration curve for NTO (blue) and DNAN (orange) obtained in the HPLC-DAD 50

Figure 3.2 Picture of the model developed in GoldSim to study NTO and DNAN transport in sandy soil columns. 52

Figure 3.3 Comparison between the GoldSim simulation and laboratory experiment breakthrough curves in quartz sand for a) NTO and b) DNAN 55

Figure 3.4 Comparison between the GoldSim simulation and laboratory experiment breakthrough curves for a) NTO in sand b) DNAN in sand c) NTO in sandy loam and d) DNAN in sandy loam..... 58

Figure 3.5 Sensitivity analysis. Variation of NTO breakthrough curve (C/Co over time) in sandy soil when modifying the value of a) soil density, b) soil porosity, c) tortuosity and d) Kd of NTO in sand 60

Figure 3.6 Comparison between the GoldSim simulation, including Kd as a distribution element and 101 realizations using Monte Carlo, and laboratory experiment breakthrough curves for a) NTO in sand b) DNAN in sand c) NTO in sandy loam and d) DNAN in sandy loam..... 62

Figure 4.1 Dissolution curve of NTO, DNAN and RDX in an explosive formulation using a) rainwater pH 6.5 at 12 ^{o}C and b) acid rainwater pH 5.0 at 12 ^{o}C 73

Figure 4.2 Experimental and simulated breakthrough of a) NTO in sand b) DNAN in sand c) NTO in sandy loam and d) DNAN in sandy loam. 74

Figure 4.3 Sensitivity analysis of NTO breakthrough in a) sand and b) sandy loam; and DNAN breakthrough in c) sand and d) sandy loam using rainwater at pH 5.0 and pH 6.5. 79

Figure 4.4 Sensitivity analysis of NTO breakthrough in a) sand and b) sandy loam; and DNAN breakthrough in c) sand and d) sandy loam using rainwater at 12 ^{o}C and 20 ^{o}C..... 84

Figure 4.5 Sensitivity analysis of NTO breakthrough in a) sand and b) sandy loam; and DNAN breakthrough in c) sand and d) sandy loam using rainwater at pH 5.0 (brown dotted line) and pH 6.5 (black dotted line). 86

Figure 4.6 Sensitivity analysis of NTO breakthrough in a) sand and c) sandy loam; and DNAN breakthrough in b) sand and d) sandy loam using rainwater at 12°C (brown dotted line) and 20 ^{o}C (black dotted line)..... 87

Figure 5.1 Calibration curve of the IHE constituents in the HPLC: NTO (blue circles), DNAN (orange triangles) and RDX (grey squares). 96

Figure 5.2 Residual mass $(\%)_{w}$ over time of NTO, DNAN and RDX in sterilised sand (SS), natural sand (NS), sterilised sandy loam (SL) and natural sandy loam (NL)..... 97

Figure 5.3 Comparison of NTO, DNAN and RDX mass degradation over 56 days in sand and sandy loam at different temperature: 4°C (triangles), 12°C (squares) and 20°C (dots). 102

Figure 5.4 Comparison of the NTO degradation in sand at 20°C by adjustment to zero, first and second degradation order equations 105

Figure 5.5 Rate constant against temperature for ach IHE compound in sand (orange circles) and sandy loam (blue squares)..... 107

Figure 6. 1 Comparison between the simulated and measured breakthrough concentrations found in leachate in indoor soil columns of a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam. 121

Figure 6. 2. Breakthrough curves for a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam in accelerated indoor experiments. 123

Figure 6. 3 Comparison between the simulated and measured plume concentrations found in leachate in outdoor soil columns of a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam. 127

Figure 6. 4 Breakthrough curves for a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam in outdoor experiments..... 129

LIST OF TABLES

Table 1.1 Environmental impact caused by traditional explosive fills and the IHE constituents replacing them. 2

Table 2.1 Main processes that explosives undergo in the environment and key parameters used for explosive fate and transport. 20

Table 2.2 Comparison of potential deterministic models for predicting fate and transport of explosives in the environment. 37

Table 3.1 Characterisation of quartz sand, sand and sandy loam soil 47

Table 3.2 Experimental K_d values and standard deviation for DNAN and NTO in sand and sandy loam performed in triplicates 49

Table 3.3 Table with inputs for GoldSim. All of them were inputted as single value elements (not stochastic). 51

Table 3.4 Pipe Pathway properties used in GoldSim to model the dimensions of the soil column. 53

Table 3.5 Parameters used for the sensitivity analysis and their values 54

Table 4.1 Chemical characterisation of sandy and sandy loam soils. Total Organic Content (TOC), Total Carbon and Nitrogen (TCN). 71

Table 4. 2 Soil bulk density, soil porosity and soil water partition coefficient for NTO and DNAN in each soil 72

Table 4.3 Model parameters used in GoldSim to simulate the transport of NTO and DNAN in sand and sandy loam soils. All the inputted data was experimentally measured to replicate experimental conditions…. 71

Table 4.4 Experimental dissolution rates for DNAN and NTO measured at different rainwater pH and temperature and used in the sensitivity analysis .. 728

Table 5.1 Characterisation of the sand and sandy loamy soil. 944

Table 5.2 Mass recovery (%) of IHE compounds at day 0 in each soil and treatment using acetonitrile: water (1:1) 95

Table 5.3 IHE formulation half-life and degradation rates calculated in each soil at different temperature. 105

Table 5.4 Arrhenius activation energy (kJ mol-1) for each IHE compound in each soil 107

Table 6. 1 Month number and rainfall values used to simulate seasonal rainfall in outdoor conditions 105

Table 6. 2 Parameters inputted in GoldSim to simulate advection and sorption processes of DNAN and NTO in soil. 106

Table 6. 3 Dissolution rates of DNAN and NTO for indoor and outdoor conditions. 107

Table 6. 4 Degradation rates of NTO and DNAN determined at 12 ^{o}C (outdoor) and 20 ^{o}C (indoor) in sandy soils. 107

LIST OF EQUATIONS

Equation 2.1 Advection Dispersion Equation 15

Equation 2.2 Fick's law..... 15

Equation 2.3 Soil-water partition coefficient 156

Equation 2.4 Langmuir isotherm 156

Equation 2.5 Freudlich isotherm..... 156

Equation 2.6 Octanol-carbon partition coefficient..... 158

Equation 2.7 Octanol-water partition coefficient..... 159

Equation 3.1 Experimental soil water partition coefficient 48

Equation 3.2 Advection equation in GoldSim 53

Equation 3.3 Partitioning governing equation in GoldSim 53

Equation 3.4 Retardation factor in GoldSim 53

Equation 4. 1 Zero order dissolution equation..... 75

Equation 4. 2 Noyes-Whitney equation 81

Equation 5.1 Zero order reaction equation..... 104

Equation 5.2 First order reaction equation 104

Equation 5.3 Third order reaction equation 104

Equation 5.4 First order half lifetime..... 105

Equation 5.5 Equation of Arrhenious..... 106

Equation 5.6 Equation of Arrhenious for first order degradation..... 107

Equation 5.7 Activation energy from first order degradation equation..... 107

Equation 6.1 Root Mean Square Error 121

LIST OF ABBREVIATIONS

2-ANAN	2-Amino-4-nitroanisole
4-ANAN	4-Amino-2-nitroanisole
ACN	Acetonitrile
ATO	3- Amino-1,2,4-triazol-5-one
cm	Centimetres
day	Days
DAD	Diode Array Detector
DNAN	2,4-dinitroanisole
DNP	Dinitro pyrazole
dS	Decisiemens
g	Grams
h	Hour
HMX	Octahydro- 1,3,5,7-tetranitro- 1,3,5,7-tetrazocine
HPLC	High Performance Liquid Cromatography
HTO	3- hydroxylamino-1,2,4-triazol-5-one
IHE	Insensitive High Explosives
IMX	Insensitive Munition Explosive
K_d	Soil-water partition coefficient
Kg	Kilograms
K_{OC}	Organic carbon partition coefficient
K_{OW}	Octanol- water partition coefficient
L	Litres
m	Metres
mg	milligrams
mL	Millilitres
mm	Milimetres
nm	Nanometres
min	Minutes
mon	Month
NTO	5-nitro-1,2,4-triazol-3-one
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
ppm	Parts per million
s	Seconds
TNT	2,4,6-Tri-nitrotoluene
USEPA	United States Environmental Protection Agency
UK	United Kongdom
µg	Microgram

CHAPTER 1. Introduction

Insensitive High Explosives (IHE) are a new generation of explosive formulations that are less likely to be accidentally detonated (Francois et al., 2018). This type of formulation enables IHE to be safer to handle, store and transport compared to traditional explosive fills, and thus, their use is constantly increasing for military activities and in particular during military training (Walsh et al., 2017). The novelty of the IHE fills relies on the combination of chemical constituents to achieve optimum performance, yet their detonations can be inefficient due to low order detonations or non-functioning munitions. Consequently, the continuous use of IHE in the same locations can deposit high quantities of IHE residues onto the soil (Persico et al., 2022; Walsh et al., 2018). The insensitivity of these energetic formulations has led to issues when being disposed of by traditional methods, such as blow-in-place detonations and open burning, which increase IHE residues remaining on soil surfaces (Pichtel, 2012; Walsh et al., 2013). Therefore, these activities can lead to contamination, which poses the question of how to assess the environmental impact caused by IHE residues.

These new IHE formulations have replaced traditional explosive fills containing 2,4,6-trinitrotoluene (TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). Some examples of IHE constituents include 3-nitro-1,2,4-triazol-5-one (NTO) to replace RDX and HMX; and 2,4-dianisole (DNAN) to replace TNT. In the past, legacy explosives have been reported to leave residues that cause environmental problems (**Table 1.1**). Though the environmental behaviour of traditional explosive constituents has been fully investigated, (Beck et al., 2018; Johnson and Reddy, 2015; Pennington and Brannon, 2002) knowledge on the environmental impact of novel IHE constituents such as DNAN and NTO remains scarce, particularly when they are deposited as a formulation. These chemicals have different physicochemical properties compared to traditional explosive fills such as higher water solubility, lower density and more mobile in soil (Arthur et al., 2018; Mark et al., 2016; Temple et al., 2018). This warrants a dedicated study of their behaviour in the environment.

Environmental impact of traditional explosives	Traditional explosive	IHE constituent replacement
- Pink water coloration (Showalter et al., 1994) - Toxicity to fish (Eum et al., 2016) - Toxicity to rodents (Johnson and Reddy, 2015)	TNT	DNAN
- Toxicity to invertebrates in soil (Robidoux et al., 2001) - Bioaccumulation in agricultural crops (Groom et al., 2002)	HMX	NTO
- Contamination in drinking water (Etnier, 1989) - Toxicity in humans (Kaplan et al., 1965) - Bioaccumulation and toxicity in plants (Harvey et al., 1991) - Toxicity and hypotrigliceremia in rats (Levine et al., 1990)	RDX	NTO

Table 1. 1 Environmental impact caused by traditional explosive fills and the IHE constituents replacing them.

Usually, the study of the behaviour of explosive residues starts in soil systems, as this is mainly where their residues are deposited after military activities. Once the explosive traces are in contact with the soil, they interact with the different particles of the system, initiating their movement and degradation. For this reason, the work carried out in this thesis has been focused on soil environments, considering their complex matrix and the environmental conditions at which they are exposed. Consequently, to assess the impact of IHE in soil, it was necessary to understand the processes that their residues undergo once deposited. **Chapter 2** outlines these processes, which are hereby defined as their *fate* and *transport,* along with the formulas that most representatively describe their behaviour and the main key parameters to study that behaviour.

The first process after IHE residual deposition in the environment is usually dissolution and transmission into soil. This process is usually caused by the contact of IHE residues with water (such as rainfall) that facilitates IHE dissolution and infiltration into the soil matrix. The rate of this transmission depends on environmental conditions (e.g., rainfall temperature and pH) and the solubility of the chemical (Byrn, Zografi and Chen, 2017). Although the water solubility of DNAN and

NTO has been already reported (Pennington and Brannon, 2002; Taylor et al., 2013), it is still unknown how DNAN and NTO dissolve in a formulation and what parameters influence the overall IHE dissolution rates. To that end, the dissolution rates of IHE residues under different types of rainwater (pH 5.0 and 6.5) are illustrated in **Chapter 4**.

Once dissolved in the soil matrix, IHE constituents break through the soil and it is critical to determine whether they accumulate in the topsoil or whether they could reach groundwater. The former could lead to toxicity to organisms residing in the surrounding areas and the latter could lead to the contamination of drinking water when it reaches an environmental receptor. Because of this, it is necessary to study the breakthrough of IHE residues in soil, which is mainly described by advection and dispersion (Braida et al., 2012). Conversely, IHE residues can undergo adsorption to soil particles, accumulating in the soil and leading to toxicity issues (Lotufo et al., 2015). The interactions between IHE constituents and the soil are complex and depend on factors such as soil bulk density, porosity, organic matter content and the soil water partition coefficient (Mark et al., 2017). Thus, the breakthrough of IHE residues varies depending on the soil type, as, for instance, DNAN has been reported to breakthrough twice as fast in sandy soil than in loamy soil (Arthur et al., 2018). The influence of these interactions and different soil types has not been fully investigated and is therefore explored in **Chapter 3**.

In addition, IHE residues have been reported to undergo chemical and biological degradation in soil (Krzmarzick et al., 2015; Olivares et al., 2016). However, most of the research performed to study biological degradation has used specific bacterial strains that are able to rapidly metabolise IHE constituents for soil remediation strategies (Indest et al., 2017; McGivern et al., 2021; Richard and Weidhaas, 2014). Thus, the base degradation that IHE undergo in natural soils with native microbial colonies is still unknown. Furthermore, most of the studies have been performed at temperatures over 20°C, which provided information of the degradation of the constituents in temperate climates. However, there are no studies discussing how IHE residues degrade in soils located in cold regions such as Raufoss in Norway (explosive manufacture site) or British Army Training Unit Suffield in Canada (military range). Therefore, there is a lack of information on how low soil temperatures

influence the degradation rate and their persistence in soil. These two factors outlined above are thus assessed in **Chapter 5**.

Traditionally, the toxicity and persistence of explosive residues has been studied by performing laboratory (e.g., soil column, bottle point flask tests) and field (e.g., lysimeters) experiments (Brannon et al., 2002; Molina et al., 2006; Temple et al., 2018). Although the use of experimental methods offers a genuine overview of a determined system, they are often limited for environments in which complex processes are simultaneously appearing (Pistocchi, Sarigiannis and Vizcaino, 2010). In addition, the fact that all IHE compounds behave quite differently due to their physico-chemical properties complicates the study of their fate and transport. Furthermore, the use of experimental methods can be time consuming and expensive due to the material and labour required and can be difficult to reproduce over time due to the changes in soil and environmental conditions. The use of contaminants to perform these studies also increases the risk of further contamination of the environment and complicates the disposal and treatment of their residues. Lastly, experimental work is commonly specific for specific systems (e.g., sandy soils) and typically reduced to 'small-scale' due to the size limitation of facilities, hampering understanding of 'the big picture'.

To overcome these issues, the use of computational modelling for assessing contaminant fate and transport in the environment is growing as it allows the investigation and the understanding of the system under a different approach. Computational models enable the study of the interactions between the contaminants and the media (e.g., soil, water, vadose zones…) which, due to their complex nature, are usually poorly understood. Models have been shown to representatively simulate the behaviour of organic contaminant compounds in soil, such as pesticides and hydrocarbons from petroleum (Adriaanse, Boesten and Crum, 2013; Brown et al., 2017; Jarvis et al., 1994). Furthermore, public organisations have recognised their effectiveness and so have integrated them in their protocols. For instance, the United States Environmental Protection Agency has compiled a list of models to use for contaminant risk assessment in water, soil, atmospheric and human health (https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment). However, they require

the estimation of reliable input parameters and the realisation of certain assumptions to achieve representative simulations. It is here where the problem lies in, as so far, the experimental scenarios are difficult to reproduce in simulations due to the number of variables involved in the environment.

Owing to the success of computational models in assessing the behaviour of contaminants (Su et al., 2019), the question arises whether there exist models suitable for studying the environmental fate and transport of explosive residues and whether any could representatively simulate explosive behaviour in different soil types. This knowledge gap is examined in **Chapter 2**, in which several computational models were evaluated, by considering their main features, advantages and limitations. Following an intensive literature search, the computational software GoldSim was selected to conduct the work in this thesis. This is mainly due to its incorporation of stochastic simulations, which enables the addition of input values as probability distributions to representatively simulate environmental variables such as rainfall.

Further to this, the simulation of the fate and transport of IHE in soil is especially challenging as a) experimental input parameters required for use in the simulations are scarce and usually region specific, b) there is not sufficient data in the literature to compare the simulations performed or to validate the computational model developed and c) there is no standardised computational software that has proven to representatively simulate the fate and transport of IHE residues when they are disposed of as a formulation. To overcome this, **Chapter 6** provides the first stochastic model developed in GoldSim that can representatively simulate the fate and transport of IHE constituents in sandy soils under different environmental conditions.

1.1 Aim and objectives

The overall aim of the work presented in this thesis was to provide insight into the chemical behaviour of IHE in soil in order to simulate fate and transport in soil under different environmental settings (e.g., soil type, and temperature profile). This was achieved by focusing on the following objectives:

1. To critically review the literature covering the key parameters used to study environmental fate and transport of IHE residues in the environment and to select and discuss the main computational models that could be used to predict IHE behaviour in soil (**Chapter 2**).

2. To evaluate the capabilities of the GoldSim software for simulating the mobility of IHE constituents in sandy soils and to determine the key parameters necessary for achieving representative simulations (**Chapter 3**).

3. To determine dissolution rates of IHE compounds in a formulation and to representatively simulate how the dissolution process influences the breakthrough curve of an IHE solid residue in sandy soils (**Chapter 4**).

4. To investigate the chemical and biological degradation of IHE chemicals in sandy soils and determine the effect of soil temperature and organic matter content on the total IHE degradation. (**Chapter 5**).

5. To assess the performance of the model developed in GoldSim and to determine to what extent it can representatively simulate the overall fate and transport of IHE residues in sandy soils (**Chapter 6**).

The structure of this thesis is illustrated in **Figure 1.1** to facilitate a better comprehension of the different chapters and how they are connected.

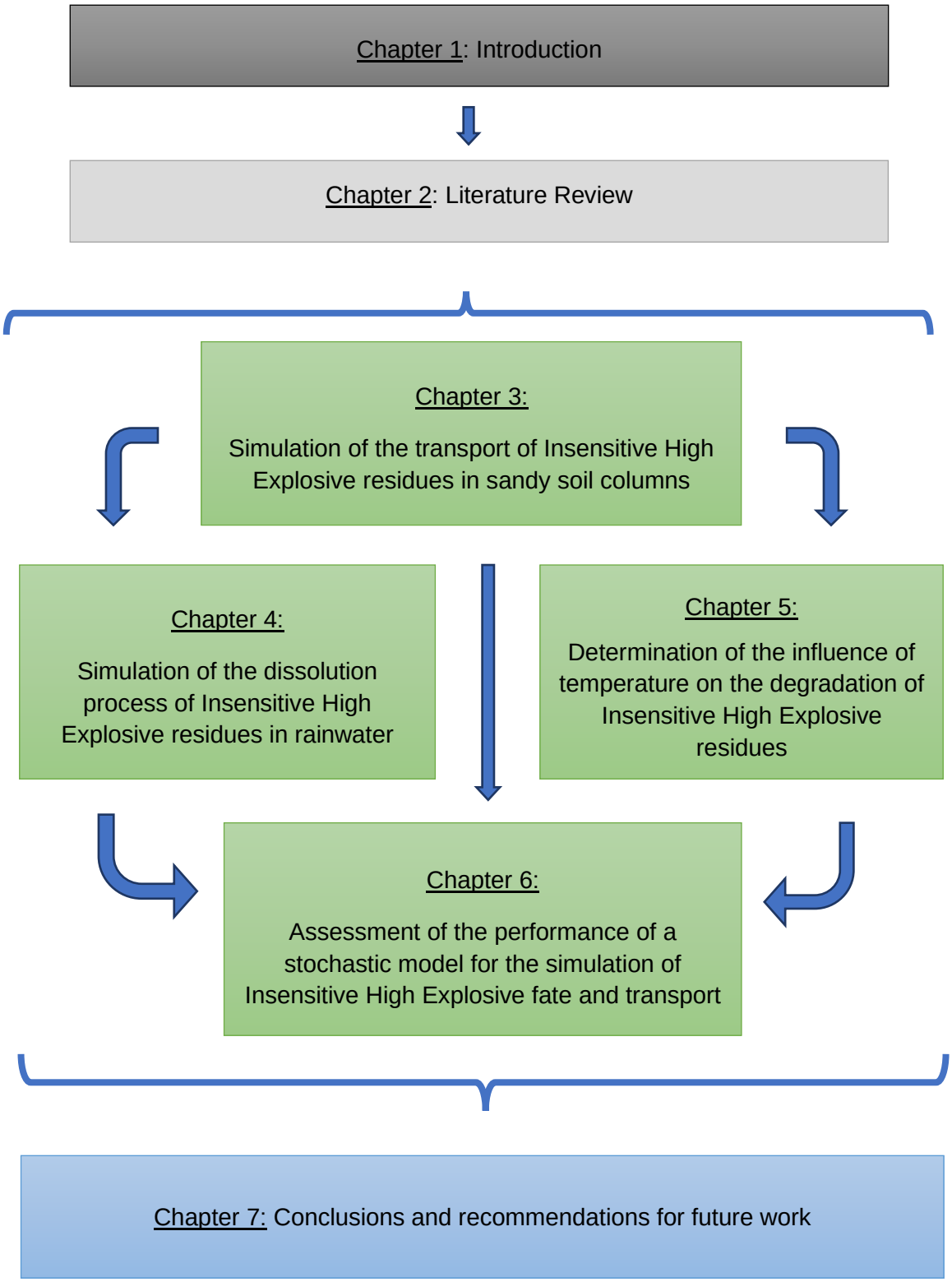


Figure 1. 1 Thesis structure aligned to chapter thesis

CHAPTER 2. Literature review. Computational modelling of fate and transport processes of Insensitive High Explosive in soil: principles and challenges.

ABSTRACT

The use of insensitive munitions for military, mining and demolition activities can lead to contamination of the environment. Commonly, their environmental impact has been assessed by conducting experimental and field work, although this approach is often impractical and time consuming due to the large number of environmental and chemical properties combinations. To overcome this issue, the use of computational modelling is growing as large-scale simulations can be performed in shorter periods of time and can provide a better understanding of complex interactions. However, there is still little information about the main processes involved in the fate and transport of explosive residues in the environment and which computational models could be suitable for simulating the environmental behaviour of the constituents contained in formulations. This review provides an overview of the main fate and transport processes that explosive residues undergo once they are deposited including mathematical descriptions of phase partitioning of chemicals, mechanisms of their transfer between and within environmental media, and their degradation in the environment. It then discusses the potential deterministic and stochastic computational models that can be used to model explosives in the environment, highlighting their main advantages, examples, and limitations. On one hand, deterministic models have been already used for other organic compounds, providing representative outcomes that could be similar to those described by explosive formulations due to the similarities in their chemical structure. On the other hand, the stochastic methods, although less used, include variability in the modelling that could be more beneficial for decision-making. Finally, the last section discusses the findings of the study and summarises future research needs and challenges for predicting the fate and transport of explosive constituents using computational tools.

2.1 Introduction

2.1.1 Environmental problems posed by explosive residues

Live-fire training is an essential part of military readiness and one of the main sources of water and soil contamination by explosives (Ferreira et al., 2017). Activities such as manufacturing and disposal by open-burning, second order detonations, blow-in-place detonations and explosive leaching from unexploded ordnance have been demonstrated to deposit up to 50% of the explosive in to soil (Taylor, Bigl and Packer, 2015; Temple et al., 2018). In addition, deposition studies have found that some explosive fills deposit energetic residue after inefficient detonation, which can be considered the main source of environmental contamination due to explosives. To date, it has been estimated that over 1.2 million tonnes of soil are contaminated with explosive residues in the United States of America (USA) (Clark and Boopathy, 2007; Pichtel, 2012). Besides, the impact of explosives has been highlighted in countries such as Spain and England (Lewis, Newcombe and Crawford, 2004) and reported by the European Union (Inglezakis and Zorpas, 2011). Studies have shown than even if 0.0001% of the explosive remains after the first detonation, this can accumulate to kilograms per hectare of explosive residue over time (Temple and Ladyman, 2019). These quantities may, and in some cases already have, exceed the toxicity threshold limits for these chemicals (Clausen et al., 2004; Racine et al., 1992; Taylor, Bigl and Packer, 2015). Thus, the results of these activities and the uncontrolled management and disposal can potentially lead to a negative environmental impact, translated into toxicity towards plants, animals, and humans.

2.1.2 Explosives and explosive formulations

An explosive is a reactive substance containing large amounts of potential energy that rapidly produces a large volume of heat and gas in the form of an explosion when initiated. For this reason, explosives and their residues have been categorized as Class 1 Hazardous Substances by the EU and must be handled in accordance with the relevant legislation (Inglezakis and Zorpas, 2011). Explosives can be divided into classes according to their susceptibility to

initiation where very sensitive materials that can be initiated by relatively small amounts of heat or pressure are categorized as primary explosive; while materials that are relatively insensitive are categorized as secondary or tertiary explosives (Pichtel, 2012). Examples of primary explosives include silver azide, lead styphnate, mercury fulminate, picric acid, lead azide, nitroglycerine and iodine nitride and commonly, small amounts of primary explosives are used to initiate secondary explosives. This type of explosives is very sensitive, and only small quantities are used in munitions. Thus, it is very rare that detectable quantities of these explosives are found in the environment, although contamination by heavy metal constituents of primary explosives has been known to occur at manufacturing facilities [(Wang et al., 2022). Examples of secondary explosives include 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). This group of explosives is the most commonly found on military training ranges due to their large masses used in mortars and artillery shells (González-Forero, 2014). Finally, tertiary explosives or blasting agents are so insensitive to shock that they need to be detonated with secondary explosive constituents instead of primary explosives. An example of a tertiary explosive formulation is fuel oil or ammonium nitrate and associated contamination is often in the form of nitrates, perchlorates and hydrocarbons (Pichtel, 2012).

Traditionally, explosive fills have contained secondary explosives such as HMX, TNT or RDX (Wang et al., 2012). However, the need for less sensitive munitions that are less likely to be accidentally detonated,(e.g. by dropping, or puncture), has driven the development and use of new explosive fills (Sweeney et al., 2015). Often, this is achieved by combining multiple energetic materials into a single formulation, being more complex than traditional explosives as the chemical constituents exhibit much greater diversity of chemical and physical behaviours. For example, 3-nitro-1,2,4-triazol-5-one (NTO), is highly soluble in water (12.6 g L^{-1}, 25^{o}C), acidic (pKa = 3.67) and readily undergoes microbial degradation (Lee and Coburn, 1988; Madeira et al., 2018; Temple et al., 2018), making it more mobile in the soil than most currently used secondary explosives such as TNT. Alternatively, 2,4-dinitroanisole (DNAN), which has a

similar structure and solubility (276 mg L^{-1}) to the currently used TNT, may rapidly undergo biodegradation to toxic intermediates (Davies and Provatas, 2006; Dontsova et al., 2014; Kitcher et al., 2017) (**Figure 2.1**).

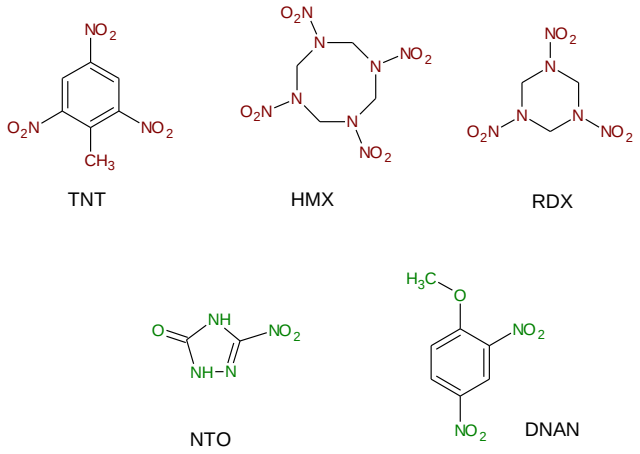


Figure 2. 1 Molecular structure of common traditional (top) and new (bottom) explosive constituents

The increasing use of these new less insensitive explosives has driven the need to understand their persistence and toxicity to the environment. In addition, global defence forces are required to comply with law and minimize environmental impact to prevent wide spread explosive contamination, as has been seen for RDX and HMX (Bordeleau et al., 2008; Clausen et al., 2004). So far, few studies have investigated the behaviour of insensitive munitions once released into the environment, which poses the question of how to assess their environmental impact.

2.1.3 The need for computational modelling

Experimental methodologies have been traditionally used to study explosive interaction with the environment in order to understand potential risks. Soil columns, batch experiments and lysimeters are commonly used experimental approaches to investigate the fate and transport of chemicals in the environment (Alavi et al., 2011; Arthur et al., 2018; Li et al., 2017; Molina et al., 2006). However, these approaches are time consuming, expensive and often cannot be replicated as environmental characteristics change over time (Beck et al., 2018; Mark et al., 2016). In addition, experimental methodologies are

conducted at small scale due to spatial imitations, which reduces representativeness and increases the uncertainty of the outcomes. Furthermore, the study of the persistence of explosive constituents tends to be complicated as the weight percentage of each individual chemical compound can vary significantly between formulation. This phenomenon is particularly notable for explosives formulations in which the combination of constituents is key for optimal target effect. Therefore, it is impractical and highly improbable that the impact of each explosive formulation on the environment can be determined by only conducting laboratory experiments.

To assist experimental methodologies, mathematical and statistical approaches are frequently employed in the form of computational fate and transport models to assess the behaviour and persistence of pollutants in the environment. The use of computational models can significantly reduce experiment duration and cost and makes it possible to investigate various environments without the need to find contaminated samples or artificially contaminate natural soils (Zhang, Zhong and Zhang, 2020). A wide range of models are available, and the choice of which one to use is usually governed by the purpose of the study, the assumptions made, the medium (e.g., soils) and the degree of uncertainty present. This approach allows the user to define and decide what processes are more significant in a selected scenario and representatively simulate their behaviour.

For explosive residues, this raises a challenge as a) little has been reported regarding fate and transport of insensitive explosive formulations in the environment and their governing processes are largely unknown, b) there is a lack of the key parameter data necessary for use as inputs in the simulations, and c) few computational models have been applied to investigating explosive fate and transport. It is clear there is a need to review existing environmental models for their applicability to simulating the behaviour of post detonation explosive residues in the environment. Therefore, the aim of this work was to critically review the performance of existing models by identifying the key factors influencing the behaviour, fate, and persistence of chemicals in the environment and with specific reference to explosive constituents and similar

chemicals. The review comprises three sections: The first section provides a comprehensive overview of the key factors that must be considered when modelling the fate and transport of explosive constituents. It also provides an overview of the most common mathematical descriptions of phase partitioning of chemicals, mechanisms of their transfer between and within environmental media, and their degradation in the environment. The second section provides an overview of the models that have the potential to be used to model explosive behaviour in the environment according to their mathematical approach. Finally, the last section discusses the findings of the study, offers future research needs and poses challenges for predicting the fate and transport of explosive constituents using computational tools.

2.2 Behaviour of explosives in the environment

2.2.1 Transport

Contaminant transport is defined as the movement of a contaminant from one location to another, e.g., the movement of a chemical explosive in a specified soil. Once an explosive is released into the environment, the first mechanism for the transport and dissemination of its constituents throughout the soil is via dissolution into water (**Figure 2.2**) (Fuller et al., 2012). Dissolution of explosive formulations depends on the solubility of their individual components and the fraction of each constituent exposed to water (Dontsova et al., 2006). Physical parameters such as the water inflow to the soil, pH and high temperatures also play an important role as they influence the solubility and dissolution rate of explosive constituents. Dissolution rate is the main parameter used to describe dissolution, which strongly correlates to temperature and particle surface area (Lynch, Brannon and Delfino, 2002). In particular, surface area is a limiting factor for transferring explosives constituents into the environment (Taylor et al., 2013).

Once the contaminant is dissolved and enters the unsaturated zone (soil) it can be transported by a combination of three main mechanisms: advection, dispersion and diffusion (Amaral et al., 2016). Advection is defined as the transfer of a substance by the flow velocity of a fluid by bulk motion and it

follows conservation laws along with divergence theorem. This describes, for example, the movement of a contaminant in a continuous current such as a river. The contaminant travels and spreads with the water bulk at the same speed (Zhang and Bennet., 1996). This process can also occur in unsaturated zones, as usually water and dissolved substances travel down preferential flow pathways.

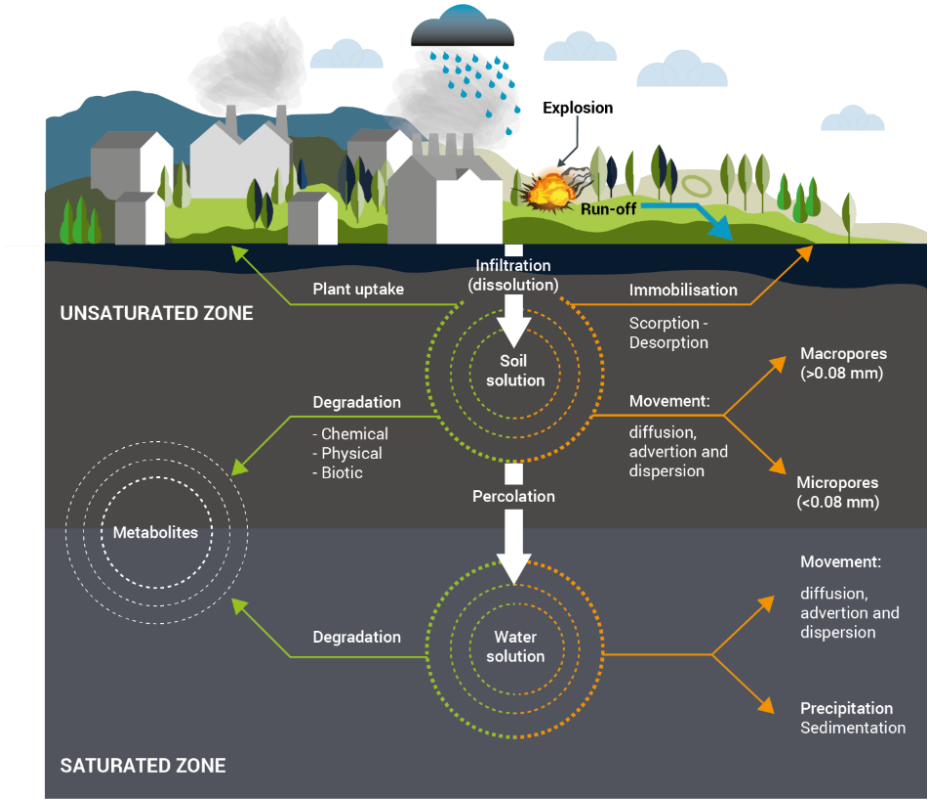


Figure 2. 2 Schematic of the main processes involved in the fate and transport of explosives in soil. Green arrows represent process associated with 'fate' and orange arrows processes associated with 'transport'

Secondly, dispersion explains how contaminants are distributed macroscopically in a continuous phase of another material (Pachepsky, Benson and Rawls, 2000). This process depends on the dispersivity, an empirical property of a porous medium that relates the pore velocity to the dispersion coefficient. Dispersivity has been found to be scale dependent and a natural physical characteristic of porous material that determines the degree of the contaminant spreading. The pathway of a contaminant through macropores in soil is an example of this type of transport. For one-dimensional solute transport

in a homogeneous soil, the advection and dispersion can be described in combination by the advective-dispersive equation (**Equation 2.1**):

$$\frac{\partial c}{\partial t} = D_s \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \qquad \textbf{(Equation 2. 1)}$$

where c is solute concentration (kg L^{-1}), D_s is solute dispersion coefficient (m^2 s^{-1}), v is the average pore-water velocity (L s^{-1}), x is the travelled distance (m), and t is time (s).

Finally, diffusion is the movement of molecules from a region of higher concentration to a region with lower concentrations driven by a gradient in chemical potential and can be described by Fick's law (Steefel et al., 2015). This law states that the diffusive flux of species in solution is proportional to the concentration gradient, as represented in **Equation 2.2**.

$$J = -D \frac{dc}{dx} \qquad \textbf{(Equation 2. 2)}$$

where J is the diffusion flux (kg m^{-2} s^{-1}), D is the diffusion coefficient (m^2 s^{-1}), which is specific to the chemical species considered, c is the concentration (kg m^{-3}) and x the position (m) (Bear and Verruijt, 1987).

Other processes related to transport such as volatilization or root uptake have also been described in the literature (Shahul Hameed and Sadashiva Murthy, 2019; Vila, Lorber-Pascal and Laurent, 2008). Volatilization is the process whereby a dissolved compound passes from the liquid phase to the air without reaching critical temperatures. This process is described by Henry's law, which quantifies the amount of contaminant that can be volatilized. Due to low vapor pressures and Henry's law constants, volatilization of explosive residues from solid or aqueous phases can be assumed to be insignificant (Kalderis et al., 2011).

As dissolved explosive residues travel into and through soil, both reversible and irreversible sorption to soil particles can immobilise the contaminants in the soil

(Arthur et al., 2017). This process is divided into adsorption, in which the particles of the soil matrix become chemically attached to the surface of the soil particles, and absorption, in which the particles are physically immobilised in the soil. Both the physicochemical properties of the solute (e.g. molecular charge, types of bonds between atoms and concentration) and soil properties (e.g. pH and organic matter content) influence sorption processes and therefore explosive retention in the soil (Bronner and Goss, 2011). This process is ruled by sorption kinetics, which explains how a percentage of contaminant is immobilized in the soil. Hence, this mechanism limits the potential migration of the explosive to the groundwater and therefore its transport (Falone, Vieira and Onuska, 2006). Specific types of sorption can be described using the linear isotherm (**Equation 2.3**), Langmuir isotherm (**Equation 2.4**) or Freundlich isotherm (**Equation 2.5**):

$$C_s = K_d * C_e \quad \textbf{(Equation 2. 3)}$$

$$\frac{C_s}{C_e} = \frac{1}{\alpha\beta} + \frac{C_s}{\beta} \quad \textbf{(Equation 2. 4)}$$

$$C_s = K_F * C_e^n \quad \textbf{(Equation 2. 5)}$$

where C_e is the contaminant concentration in solution at equilibrium (kg L^{-1}), C_s is the contaminant mass sorbed per dry unit weight of sorbent (g kg^{-1}), K_d is the equilibrium distribution coefficient (L kg^{-1}), α is the Langmuir adsorption constant (L g^{-1}), β represents the Langmuir maximum amount of absorbed contaminant (g kg^{-1}), n is the unitless Freundlich exponent, and K_F is the Freundlich sorption coefficient (g kg^{-1})(L $mg^{-1})^{1/n}$ (Kasaraneni et al., 2014).

In the Langmuir model, it is assumed that there is only one monolayer on the surface, which means there is no stacking of molecules. Conversely, the Freundlich isotherm does not have this restriction, allowing for particle adsorption to be multi-layered. Though the Langmuir equation has been used previously to describe contaminant absorption in soils (Hao et al., 2018; Xu et al., 2014), the Freundlich equation seems more suitable for modelling explosives in the environment according to the most recent literature (Alavi et

al., 2011; Arthur et al., 2018; Mark et al., 2016). However, the selection of each isotherm will depend on the individual compound (Ayawei, Ebelegi and Wankasi, 2017).

2.2.2 Fate

Contaminant fate is usually a complement to contaminant transport, as it allows determination of the final state of a contaminant which includes its persistence and degradation into other products (Fechner, 2015). In the literature, fate has mainly been studied as biotic and abiotic degradation including photo-degradation (interaction with light), biodegradation (microorganisms) and chemical degradation (interaction with minerals and other chemicals in the soil). Once the chemical undergoes either one, two or even the three of these processes, it transforms into new products (metabolites) that can undergo their own fate and transport processes in the soil. However, due to their complexity and the diminishing concentrations of the transformation products, the behaviour of these products is beyond the scope of this review.

Degradation processes have been described by using certain parameters such as degradation rate constants (Arthur et al., 2017), half-lives (Pennington and Brannon, 2002) and redox potentials (Sagi-Ben Moshe et al., 2012). These parameters describe the velocity at which the contaminants degrade in the environment, thus allowing a better understanding of the persistence of each explosive chemical in the soil. Thus, determining fate of contaminants not only helps to establish the degree of their impact but also enables the evaluation of potential ecotoxicological risk to the environment (Connon, Geist and Werner, 2012).

Additionally, organisms living in the environment can also alter the fate of contaminants as they interact with both the soil and its elements. Often, high concentrations of solid explosive residues are found in the surface layers of soil prior to their dissolution, thus increasing their exposure to plants, animals, fungi and bacteria (Morley et al., 2006). Plants play an important role by up-taking dissolved substances in the soil through their roots, reducing the amount in the soil system. The main parameters used to study this process are the uptake

rate of contaminants, which is highly dependent on the type of plant (Terzaghi et al., 2015). Conversely, bacteria and fungi can decompose explosive residues by transforming them into new chemical compounds that can be released again into the soil (Bernstein et al., 2011; Fida et al., 2014). Although these processes can provide information on the fate of explosive residues, they involve living organisms, which are considered receptors. While these processes affect fate, they were out of the scope of this review.

2.2.3 Physico-chemical features and model dimension

The art of simulating contaminant fate and transport starts with the selection and identification of the main processes involved in the system under study. Once chosen, the models usually need specific inputs such as the contaminant physicochemical properties, which describe how the contaminant behaves physically and chemically in the environment. Physicochemical properties are specific for each chemical compound and influence their physical appearance as well as influence their behaviour in different media (Earl et al., 2003). Some of these properties define the contaminant independent of or partially dependent on the matrix, such as molecular weight, water solubility, vapor pressure, boiling and melting point. In contrast, there are physicochemical properties of the chemical that are highly dependent on the environment, such as partition coefficients. Thus, when modelling fate and transport of explosives, the main physicochemical properties are usually related to soil and water media. The most common is the K_d, which describes the partition of a chemical between the soil and the aqueous dissolution. Organic carbon-water partition coefficient measures the tendency of a contaminant to bind to soils, corrected for soil organic carbon content. The relation between K_d and K_{OC} can be described as follow

$$K_{OC} = \frac{K_d * 100}{\%\ Organic\ carbon} \qquad \textbf{(Equation 2. 6)}$$

The last parameter is the octanol-water partition coefficient (K_{OW}), which measures the partition of a chemical between octanol (non-polar solvent) and water (polar solvent). (Ariyarathna et al., 2016; Detrick, 1991; Earl et al., 2003; Jarvis, 2016).

$$K_{OW} = \frac{Concentration\ in\ octanol}{Concentration\ in\ water}$$ **(Equation 2. 7)**

It is, therefore, important to select the parameters and processes that can suitably describe the fate and transport of explosive formulations in the chosen matrix (e.g., sandy soil), in order to obtain representative simulations.

In addition, the dimensions or size of the model defines the limits or boundaries of the studied area. Computational models can go from small systems, such as the study of small amounts of explosive biodegradation by bacteria, to large ones, such as the transport of explosive residues through an entire ecosystem (UK Government Office for Science, 2018). Depending on the size of the area, some processes or equations can be more representative of contaminant fate and transport processes. As an example, water flow rate through a delimited region can be governed by laminar flow or turbulent flow equations, which depend on the speed of the water bulk, which itself is highly linked to the cross-sectional area of the flow (Skjetne and Auriault, 1999).

In summary, multiple processes are involved in the environmental fate and transport of explosive constituents, which makes the determination of explosive impact a significant challenge. Specifically, it is essential to determine which processes or key parameters are integral to simulate explosive behaviour, and whether they need to be determined empirically (**Table 2.1**). So far, there is no universal answer to that question, as each soil scenario case has different chemicals in variable proportions and the processes controlling the system can vary with minimal changes in the environment. Determination of the chemical properties is key to understanding how they behave and what to expect from them, which can be translated into their persistence and toxicity. Therefore, key parameters must be carefully studied specifically for each scenario.

Table 2. 1 Main processes that explosives undergo in the environment and key parameters used for explosive fate and transport.

Process	Importance	Key parameter	Representation	Reference
Dissolution	Fate and transport	Solubility	s (g L^{-1})	(Monteil-Rivera et al., 2004)
		Dissolution rate	r (g s^{-1})	(Lynch, Brannon and Delfino, 2002)
Advection	Transport	Advection velocity	v (L m^{-2} s^{-1})	(Bear and Verruijt, 1987)
Dispersion	Transport	Solute dispersion coefficient	D_s (m^2 s^{-1})	(Jarvis, Villholth and Ulen, 1999)
Diffusion	Transport	Diffusion coefficient	D (m^2 s^{-1})	(Merdun and Quisenberry, 2004)
Adsorption (and desorption)	Fate and transport	Organic carbon-water coefficient	K_{OC} (L kg^{-1})	(Bronner and Goss, 2011)
		Soil water partition coefficient,	K_d (L kg^{-1})	(Lee, Choi and Kim, 2016)
		n-octanol-water partition coefficient	K_{OW} (dimensionless)	(Monteil-Rivera et al., 2004)
Degradation	Fate	Half life	$t_{1/2}$ (s)	(Scheringer et al., 2004)
		Degradation rate	k (different units depending on the degradation order)	(Alavi et al., 2011; Scheringer et al., 2004)
		Reduction-oxidation potential	Eh (V)	(Regnery et al., 2017)

2.3. Simulating the fate and behaviour of explosives in the environment: the need from a computational perspective

The use of new insensitive munitions constituents has raised the challenge of how to assess the environmental impact of explosive residues when the understanding of their behaviour in different environments is limited. Computational modelling enables the investigation of contaminant fate and transport using representative mathematical approaches to describe how a system evolves under specified conditions. However, to facilitate the study of complex systems and to create efficient computational models, it is necessary to make some assumptions and to include uncertainties within the simulation. Currently, the majority of the models used for the study of contaminants in the environment are multimedia models which include more than one medium (e.g., air, water, soil, vadose zone, slurry, etc.). Multimedia environmental models enable the study of contaminant behaviour in terms of the partitioning characteristics between various environmental phases, providing a comprehensive picture of the transport and potential fate of chemicals contaminants (Su et al., 2019).

Often, computational models that included multimedia scenarios and interactions of complex processes have been linked to more representative simulations. However, a computational model ought to be as simple as possible to allow a better understanding and interpretation of which processes or mechanisms govern the system (Wilson and Collins, 2019). In addition, it needs to be interpretable and accessible, as different people may use it, and it needs to able easily understood. In this section, several potential models for simulating explosive behaviour in the environment have been identified, explaining their mathematical approach and main advantages and providing examples of their application in real studied cases.

2.3.1 Number of dimensions considered for computational models

Computational models can be classified by the number of dimensions studied in the system. Scenarios simulated in one dimension are those in which a model only reflects one direction (e.g., motion in a straight line). As an example, these

approaches can be used to study the breakthrough of contaminants in soil over time, considering only one direction. One dimensional modelling only requires consideration of the variables (such as velocity or depth) that change predominantly in one defined direction along the studied vector, making them simple and quick to create. However, the addition of obstacles is difficult and for example, flow cross sections tend to be interpolated, making the geometry smoother than in models with more dimensions (Gharbi et al., 2016). Therefore, one dimensional models are suitable for low optimization, investigation and review processes in which high accuracy is not required (Nham et al., 2015; Šimůnek et al., 2013).

Two dimensional models allow the simulation of chemical transport in two dimensions, combining horizontal and vertical parameter components (e.g., velocity in *x* and *y* directions). As an example, two dimensional models can simulate the movement of a contaminant in the soil surface over time. No preferential pathways are specified as they are more complex, avoiding some of the assumptions required by one dimensional models, especially for natural environments, where contaminants spread in several spatial directions. However, computational programs used for two-dimensional simulations requires greater technical skill, as often it needs more specific knowledge on the subject to select the most suitable formulas and assumptions. In addition, the lack of a third dimension can limit the representativeness of simulations, being the key determinant in some systems. For these reasons, two dimensional models are suitable for looking at contaminant environmental impacts and reviewing topographical geometry in computational scenarios (Borgesen et al., 2015).

Finally, three dimensional models are those that can study particle movement across height, width, and length. In environmental scenarios, that means the study of complex systems such as flow around structures and contaminant transport in three directions. For instance, it enables the study of the contaminant breakthrough in the soil: vertically and horizontally. Highly detailed construction is necessary for building up the scenarios and they therefore complete one- and two-dimensional simulations. However, as the models are

highly complex, they need more input data and physical parameters for their construction. As a result, they demand longer time periods for running (Beegum et al., 2018). Therefore, these models are suitable for describing complex processes and control structures.

2.3.2 Deterministic approach

Deterministic models are mathematical models in which outcomes are determined using known relationships between states and events. No randomness is included in these types of approaches, so they produce outcomes that are exact solutions, which means that once inputs are established, outcomes are the same no matter the number of times the model is run (Beven, 2002).

Among their advantages, deterministic models can test and explain why something works or behaves the way it does, which makes them suitable for exploratory analysis. As an example, deterministic models are used to study explosive transport in different soils, using soil characteristics (e.g., bulk density), contaminant properties (e.g. molecular weight) and environmental conditions (e.g., water flow) as input data (Arthur et al., 2018; El-Kilani and Belal, 2010). They can also predict the movement and pathways of contaminants from a predetermined source to receptors, and they have been successfully used to study the movement of organic compounds such as pesticides, fertilizers and explosives in air, water and soils (Åkesson et al., 2014; Lammel et al., 2007).

The use of deterministic models is highly valued as it allows one to make absolute assertions. However, many aspects of the physical and real world do not fit in to deterministic approaches as uncertainty is not addressed in the system. There are some cases in which contaminant fate and transport are ruled by processes or parameters that are not completely known or which may vary over space and time. To overcome this limitation, computational models can assess this uncertainty by performing sensitivity analyses. These analyses evaluate the model sensitivity to parameter variability, allocating the sources of uncertainty in its inputs (Saltelli, 2002). This capability is particularly interesting

for assessing which parameters contribute more to a process, for instance, to determine which soil physicochemical parameters regulate transport processes of explosive chemicals in different types of soils (e.g., sand, loam or silt).

Currently, there are several computational programs developed for modelling contaminant fate and transport in the environment. The selection of the most suitable one depends on the purpose and the processes involved in each case. In this review, potential deterministic computational programs suitable for modelling explosive fate and transport have been described and discussed. Moreover, their concept, theory, and advantages, as well as some examples for modelling organic compounds, have been explained below (**Table 2.2**).

2.3.2.1 MACRO

MACRO is a one-dimensional, non-steady state model of non-equilibrium water flow and reactive solute transport in soils. It uses dual porosity modelling, enabling the study of water and solute transport depending on the pore size, distinguishing between macro and micro pores in the soil (Jarvis et al. 1994). For the micropore domain, water flow is governed by Richards equations and solute transport by the advection-dispersion equation. For the macropore domain, the flow is simulated as a power law function of the saturation level in macropores. Further to this, a diffusion path length regulates mass exchange between the domains (Alaoui et al., 2003).

MACRO can simulate contaminant transport where the hydrology is dominated by preferential flow or not or any flow combination between these two extremes, allowing the study of preferential transport pathways (Dubus and Brown, 2002). Water flowing in macropores can be absorbed by unsaturated micropores and the exchange is calculated using a first-order mass expression (Jarvis et al., 1997). Conversely, if micropores become oversaturated in any computational layer, the excess water is routed into the macropores region. Regarding particle movement, particle exchange between the flow regions is included in the model, although it is assumed that particles are not exchanged by diffusive processes in the macropore (Jarvis, Villholth and Ulen, 1999). In micropores, the exchange

is mainly controlled by diffusion and it is calculated using a first order mass transfer expression.

Additional model assumptions include kinetics for solute degradation in both solid and liquid phases, instantaneous or kinetic sorption equilibria and use of Freundlich isotherm to define absorption in each pore domain (Jarvis et al., 1994). In addition, MACRO includes inverse solute modelling, which provides an indirect methodology to estimate the unsaturated hydraulic properties of soils using experimental results as inputs. As a result, it enables the calculation of soil and contaminant parameters (e.g., partition coefficient) as outputs of the model. However, many empirical data are needed to provide sufficient data to determine these unknown parameters (Jarvis et al., 1997).

Among all its uses, MACRO has been utilized to simulate water flow and transport of some organic compounds such as pesticides in a different types of soil (Jarvis, 2016; Larsbo and Jarvis, 2010). It has been also tested to estimate the effect of uncertainties in climate, soil, and chemical properties of pesticides by the addition of extra computational programs such as Multidisciplinary Simulator for Standard Crops (STICS). The addition of subsequent computational programs has allowed the use of MACRO for improving environmental management and decision-making processes as the programme can include several aspects such as climatic conditions, soil-water boundary conditions as well as chemical parameters related to fate and transport processes (Lammoglia et al., 2018). However, its main limitation is that it can only model in one dimension (e.g., depth), and thus, it cannot provide information of processes such as horizontal transport.

MACRO has not been applied to modelling explosives in contaminated environments, yet the interface and the inputs (such as partition coefficients or degradation rates) used for modelling pesticides would also be applicable for modelling explosive residue behaviour in the environment. Pesticides and explosives often share similar molecular structures, and therefore, their fate and transport behaviour in similar environments can be compared **(Figure 2.3)**. As an example, the degradation of nitro groups can follow the same metabolic pathways for both explosives and pesticides rich in these nitrogenated organic

compounds (**Figure 2.4**). This suggests that MACRO could be successfully used to model the fate and transport of explosives in the environment.

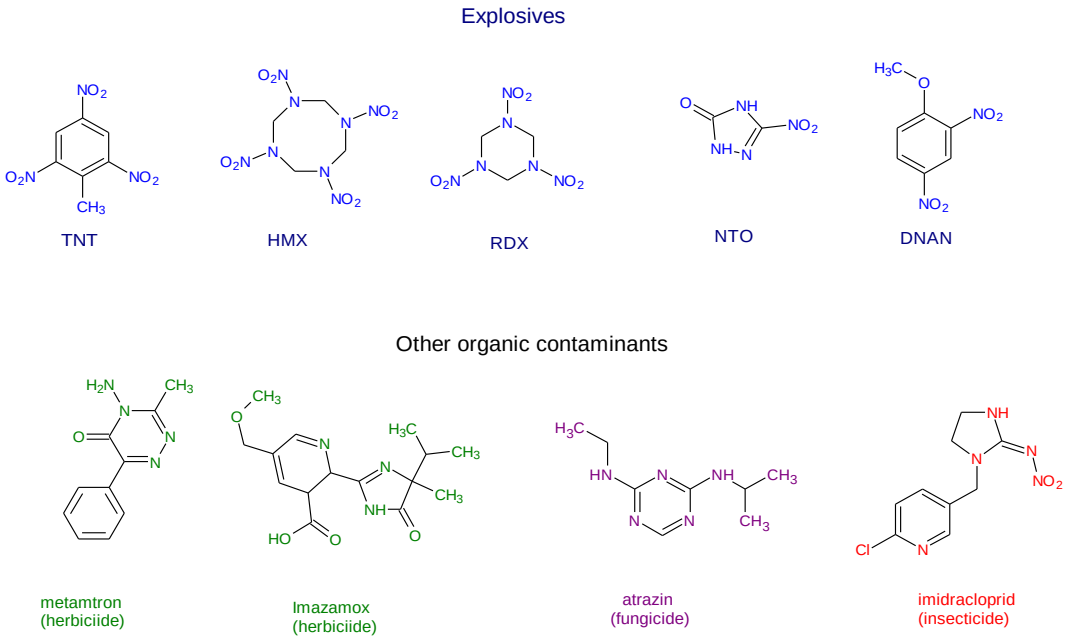


Figure 2. 4 Comparison between some the molecular structure of some explosive constituents (top) and other organic compounds such as herbicides, pesticides and insecticides (bottom).

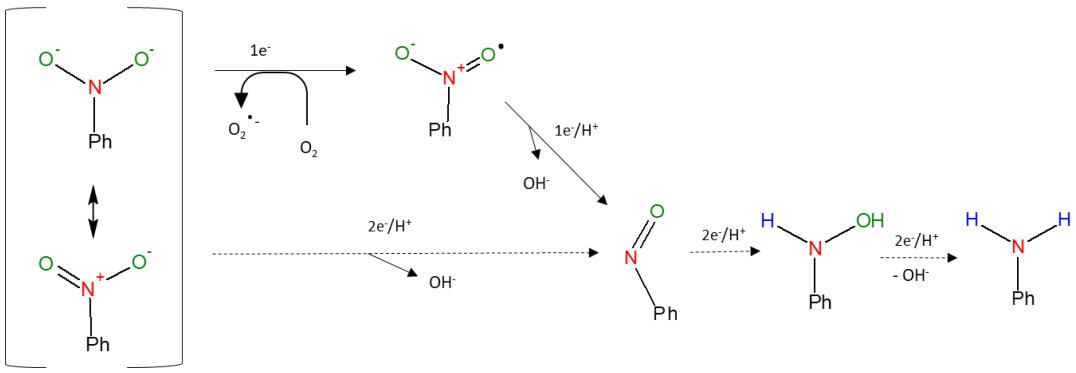


Figure 2. 3 Mechanisms for the reduction of nitro groups of nitroaromatic compounds. The scheme has been adapted from (Esteve-Núñez, Caballero and Ramos, 2001).

3.2.2.2 HYDRUS

HYDRUS was developed to simulate one-dimensional environmental processes such as water flow, heat transport and the movement of solutes in variably saturated porous media (Leju, Ladu and Zhang, 2011; Šimůnek, van Genuchten and Šejna, 2016). This software uses the Richards equation (Ebrahimian and

Noory, 2015) to model different saturated flows of contaminants, and includes Fick's Law based advection-dispersion equations for heat and solute transport (Beegum et al., 2018). HYDRUS describes solute transport such as advective-dispersive transport in the liquid phase as well as diffusion in the gaseous phase, and it considers soil as an inherently open system with air and water exchange, which enables more representative simulations of the real environment (Jacques et al., 2008).

The model is supported by an interactive graphics-based interface for data pre-processing, discretization of the soil profile (different layers with discrete properties can be modelled), and graphic presentation of the results. This allows a more intuitive manipulation of the simulated soil structure data within the model and enables control of which processes are modelled (Kasaraneni et al., 2014). In addition, the program includes "dual-porosity" option, assuming that the liquid phase can be divided into mobile and immobile regions. This option enables the simulation of solute exchange between two liquid regions modelled as a first order process. For explosives, this alternative could be useful as it would describe the sorption of their constituents in the mobile phase and can indicate whether it is an equilibrium or non-equilibrium process (Leju, Ladu and Zhang, 2011).

The main inputs used for contaminant transport are usually the physico-chemical parameters of soil, such as pH, organic carbon content, bulk density, tortuosity and porosity, as well as physical aspects such as depth and soil density (Arthur et al., 2018). In addition, both Langmuir and Freundlich isotherms are commonly simulated and studied to predict the immobilization of the contaminant in the soil, which helps to better understand the rate of transport of contaminants (Mark et al., 2016). Thus, this model can be useful to study equilibrium processes of explosive formulations in soil, allowing the understanding of what chemicals are more likely to undergo soil sorption inside an explosive formulation and which isotherm can representatively describe their behaviour.

On top of that, fate can be can be studied in HYDRUS as a combination of all of degradation processes and in addition, HYDRUS allows development of kinetic

equations such as zero and first order degradation equations (Alavi et al., 2011). Initial contaminant concentration as well as degradation constants (e.g., half-life or reaction rate constant) are commonly the main inputs used for this type of simulation, which suggests that fate can be evaluated using a relatively small dataset as few parameters are required for the simulations (Mallants et al., 2017). Further to this, HYDRUS has the option of inverse solute transport, allowing the addition of experimental data for the prediction of parameters that are controlling the system (Arthur et al., 2018). These features are useful for explosive constituents, as the scarcity of input data for use in computational programs hampers the simulation of the explosive chemicals in a defined system which can be provided by the inverse solute transport function.

HYDRUS has been extensively used for multiple contaminant studies involving different chemical compounds such as pesticides, herbicides and petroleum residues (Kasaraneni et al., 2014; Šimůnek et al., 2013). On top of that, this program has been used to simulate the transport of explosive chemicals with the option using the solute inverse option (Arthur et al., 2018). This function enabled the determination of physicochemical parameters from experimental contaminant behaviour data, which can be useful for predicting how the contaminants behave in different scenarios such as the study of a combination of explosive chemical compounds (Alavi et al., 2011). Therefore, HYDRUS could be a suitable software to simulate and predict the behaviour of explosives especially when their residues come from formulations, where contaminants are often released to soil and water media in combination.

2.3.2.3 Finite Element Subsurface Flow and Transport Simulation System (FEFLOW)

FEFLOW is a three-dimensional multipurpose computational program based on the finite element method, a numerical method that divides a large system into simple parts called finite elements. This computational software was developed for simulating density-dependent, saturated or unsaturated flow, chemical mass transport and solid and fluid heat transport in porous media and processes that include the study of contaminants in the subsurface (Bear and Cheng, 2010). In addition, FEFLOW enables the simulation of contaminants in two dimensions

with the use of Richards equation for describing groundwater flow, and it includes chemical kinetics for one or multiple chemical species and sorption equilibrium (Diersch, 2014).

FEFLOW has previously been used for evaluating and quantifying the behaviour of 37 trace organic compounds at a bank filtration site, allowing their classification depending on their persistence (Sanz-Prat et al., 2020). It has also been used to model fate of pesticides and their metabolites in groundwater, although in this case the programme was part of a coupled sequential system along with Pesticide Emission Assessment at Regional and Local scales (PEARL) (Kupfersberger et al., 2018), which enabled the determination of hydrodynamic transport of the metabolites with lateral groundwater flow, achieving more representative simulations. In addition, FEFLOW has also been used in the two dimensional simulation of fate and transport of several organic contaminants in a variably saturated synthetic aquifer, although discrepancies between measured and simulated trace concentrations were significant, as the model did not incorporate plant uptake and sorption processes (Regnery et al., 2017).

One of the main advantages of FEFLOW is the ability to handle both small and large model dimensions along with the division of the large domains into sub-domains, which allows a high level of organisation and data manipulation and thus, a better understanding of the system. Besides, FEFLOW uses a number of spatially distributed parameters as the basis for the simulation and individually defines the spatial dependence of variables, conditions, and properties. These two features allow the users to create many different simulations depending on the parameters inputted and established starting conditions. This feature makes the program suitable for simulating the persistence and mobility of explosive residues in large areas such as manufacturing sites and training ranges, allowing the assessment of their impact in the surrounding areas and receptors.

2.3.2.5 Pesticide Root Zone Model (PRZM)

The PRZM model is a dynamic and model used to simulate chemical movement in unsaturated soil systems within and below the plant root zone at a daily time step. It has two major components: hydrology and chemical transport, including processes such as erosion, contaminant decay, plant intake, surface runoff, vertical movement and dispersion. (Carsel et al., 1984). It allows the simulation of peak events and the estimation of mass rate, modelling the concentration profiles of the chemicals in a defined section. For that, it employs a finite difference numerical solution using a backwards difference scheme implicit in the software (Carsel et al., 1985). Furthermore, it is one of the models used in environmental risk assessment for pesticide registration (European Union and USEPA).

The PRZM software has been successfully used to predict concentrations of pesticides in surface waters (Teklu et al., 2015), to estimate soil leaching of glyphosate and its main biodegradation product AMPA (Mamy, Gabrielle and Barriuso, 2008) and to simulate mobility and distribution of penconazole and metalaxyl (fungicides) in vineyard soil cores (Marín-Benito et al., 2015). Furthermore, PRZM has been used to simulate the transport of pyrethroids in an agricultural area (Luo, 2019) and the uptake and accumulation of residual compounds in plants (Rodrigo-Ilarri et al., 2020). Some of these organic compounds have chemical structures that are close to explosive constituents, which suggests similar chemical behaviour. Thus, PRZM could be a useful software to assist the understanding of the interactions of explosive residues with root plants and provide insight into the plant uptake process. It could also allow the prediction of concentrations of explosive residues in the soil and plant system, which is highly necessary for assessing the ecological risks posed by explosives in contaminated lands.

The main inputs in the model include daily weather (e.g., precipitation and temperature), soil properties of each layer (bulk density, particle size distribution), contaminant application method (e.g., dissolved or solid particles), chemical interactions of the contaminants with the environment (e.g., K_d, K_{OW} or hydrodynamic dispersion coefficient) and additional information (e.g., dates,

rate). The use of these parameters as inputs for the simulations suggest that the PRZM model could also be utilized to simulate the behaviour of explosive chemicals in similar environments. Further to this, PRMZ has the potential to predict chemical sorption to soil and it has been reported to simulate representatively vertical transport through the soils, an essential process that explosives such as RDX, TNT or DNAN follow due to their low solubility in water and high interaction with the organic particles of the soils.

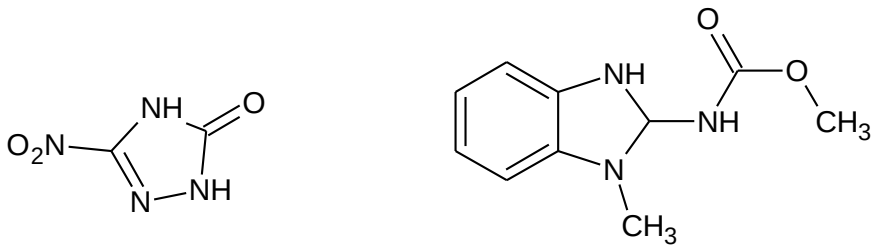
Nevertheless, the PRMZ model comes with some limitations as it has been reported to overestimate the presence of degradation products in complex soils with more than one chemical compound (Marín-Benito et al., 2015). Explosive formulations commonly contain chemicals in combination; thus, the model might not be representative for simulating degradation of explosive formulations. Another study reported the underestimation of the mobility of certain chemicals due to preferential flows that PRZM could not include (Mamy, Gabrielle and Barriuso, 2008). This could present an issue for explosives compounds which are highly soluble in water (such as NTO), but it could be more useful for those which tend to be adsorbed to the soil (such as DNAN).

2.3.2.6 Pesticide Leaching Model (PELMO)

PELMO is a one dimensional simulation model initially created to simulate the vertical movement of pesticides in soil by chromatographic leaching (Klein and Klöppel, 1993). It is based on the PRMZ model, although it has some improvements written by the German Authorities responsible for the registration of pesticides. The software uses the “tipping bucket equations” (Carsel et al., 1984) to simulate water flow across discrete soil layers and the advection–dispersion equation to simulate solute transport. Among its features, PELMO includes consideration of transformation processes of metabolites through to their eventual degradation into carbon dioxide, soil temperatures over 1 m depth and a runoff routine that introduces a new parameter called “fraction of soil water available for runoff”, which includes the fraction of suspended soil in water.

Several processes can be modelled with PELMO and can be found in the European Soil Data Centre (https://esdac.jrc.ec.europa.eu/projects/pelmo), however, the most suitable for simulating explosive behaviour is the contaminant movement described by the advection-dispersion equation, the sorption to soil by using K_d, K_{OC} and Freundlich isotherm with the option of pH dependency. Furthermore, PELMO describes degradation compounds using a first order degradation rate and applying corrections of rate constant with depth, soil temperature and soil moisture. For the by-products, the software can simulate the transport and degradation of up to eight metabolites from the initial compounds. These features could be very useful for modelling degradation of explosive formulations, in which constituents degrade simultaneously but at different velocity.

Traditionally, PELMO has been used to study several common organic contaminants, although it has not been tested with explosives yet. For instance, PELMO has simulated the adsorption mechanisms of an herbicide, 4-chloro-2-methylphenoxy acetic acid (MCPA) to inorganic soil components by assessing the main mechanisms that depend on pH (Paszko, 2014a). The results showed a high retention of the neutral and anionic forms of MCPA to the organic matter, which suggests that the same mechanisms could work for explosive chemicals with ionic forms such as NTO. In addition, PELMO has been used to simulate the sorption of the fungicide carbendazim, to mineral soils by experimentally determining the adsorption coefficients and the degradation rates in each soil (Paszko, 2014b). In this case, a significant fraction of carbendazim was retained by a cation exchange mechanism, being easily available for plants and soil microorganisms. Nevertheless, the carbendazim was barely adsorbed in soils with low contents of organic matter at low soil pH, breaking through the soil and easily reaching groundwater. In this case, the molecular formulation of the carbendazim has some similarities to NTO and some of its organic degradation products, highlighting the potential use of PELMO to simulate degradation and adsorption of explosive constituents in soil (**Figure 2.5**).



NTO Carbendazim

Figure 2. 5 Molecular structure of NTO and carbendazim that shares a nitrogenated heterocycle with nitro, amide and carboxylic groups

The PELMO software has been reported to be suitable for groundwater media but discouraged for surface water in due to the poor simulation performance in comparison to other models (Borgesen et al., 2015). This may raise the question of whether this software can represent the transport and fate of concentrations of explosive chemicals in scenarios such as riverbeds or lakes. It might not be suitable for all the explosive chemicals in a formulation, but it might help to simulate how those chemicals soluble in water such as NTO leach from soils and reach groundwater. Hence, PELMO could be useful to simulate concentrations of leachable explosive residues and to predict their behaviour when, for example, there are spillages at manufacturing sites.

2.3.2.7 Toxic Substances in Surface Water (TOXSWA)

TOXWA is a quasi-two-dimensional model created to simulate pesticide behaviour in a small surface water system such as a ditch or a pond including its sediment. It is also used for regulatory exposure assessment in surface waters in the European Union (FOCUS, 2003). It can calculate contaminant concentrations horizontally in the water layer and both in vertical and horizontal directions in the sediment layer (Beltman and Adriaanse, 1999). The approach used to do that involves four processes: transport, transformation, sorption and volatilization (**Figure 2.6**). The software includes advection and dispersion transport in the water surface while diffusion is added in the sediment layer. The transformation rate covers physical (photolysis), chemical (hydrolysis) and biological (biodegradation) processes as a function of temperature.

Contaminant sorption is divided into two groups: sorption suspended to solids is described by Freundlich isotherm while sorption to macrophytes follows a linear sorption isotherm. Last, contaminants are transported through the water-sediment interface by diffusion and advection. Although volatilization can be considered negligible when environmental fate and transport of explosives are studied, the other three mechanisms can meet the requirements needed to simulate the behaviour of explosive chemicals.

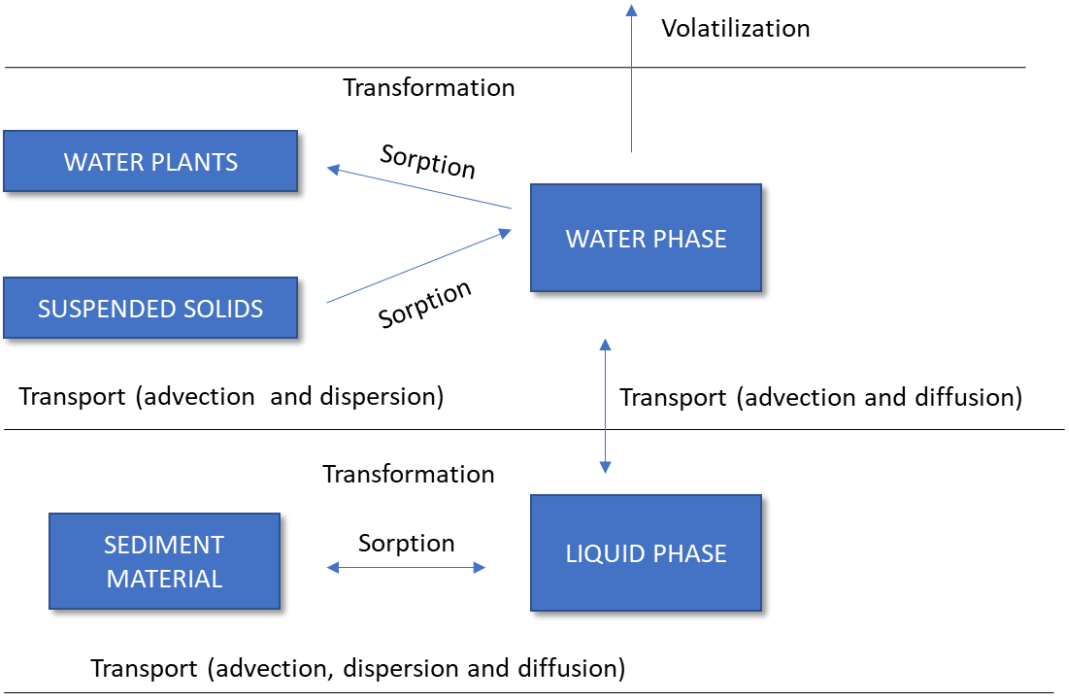


Figure 2. 6 Processes in water and sediment described by TOXSWA software. Picture obtained from the European Soil Data Centre (https://esdac.jrc.ec.europa.eu/projects/toxswa)

TOXSWA has been used to simulate the transport and adsorption to the sediment of three fungicides (fluopyra, N,N-dimethylsulfamide and bixafen) with different sorption coefficients (Dorn et al., 2021) sediment properties (e.g. density, organic matter and porosity) were experimentally measured and diffusion and sorption coefficients were obtained from literature. The results showed representative simulations, highlighting the relevance of diffusion, and adsorption parameters for obtaining representative temporal and spatial concentrations of the chemicals. In addition, TOXSWA was used to examine

degradation and back diffusion processes of some plant protection products (Patterson et al., 2017) and to estimate degradation rates of prosulfocarb (pesticide) in stagnant waters by using inverse modelling (Adriaanse, Boesten and Crum, 2013). The main inputs used for these two studies involved sediment characteristics (organic matter, density, porosity) scenario dimensions and contaminant properties (solubility diffusion constant).

The addition of a sediment layer to the TOXSWA model is a clear advantage to simulate chemical behaviour in a multimedia scenario. Although the model does not include preferential flowrates in sediments, the features described in the model as well as the organic compounds tested share similarities with explosive residues. In addition, the successful application of the model for assessing pesticide exposure in agricultural areas suggests that TOXSWA could be highly useful for simulating explosive behaviour in contaminated sediment and water. Hence, the approach employed by TOXSWA could be suitable to assess the risks posed by explosive constituents in sediment and surface water.

2.3.2.4 Soil and Water Assessment Tool (SWAT)

The SWAT model is a watershed scale, physically-based continuous process model developed by the United Sates Department of Agriculture and Agricultural Research Service (USDA-ARS) to evaluate the impact of land management practices on water, sediment and chemical yields in stagnant scenarios (Neitsch et al., 2011). The main uses of this model have been for exposure prediction, remediation strategies, sensitivity analyses, algorithm improvement and advanced applications such as the model integration with other models and the selection and placement of best management practices (Wang et al., 2019). For that, SWAT describes fate and transport of pesticides using three different mechanisms: field-scale modelling (fate), basin-level modelling (transport) and in-stream process modelling. SWAT users can include input parameters describing land cover, soil, topography and weather, and it simulates terrestrial, ecohydrological and chemical processes, which are routed to surface waters. It is been reported that the most sensitive parameters for simulating contaminant fate and transport are K_{OC}, K_d and half-lives, which control chemical sorption and degradation rates (Luo et al., 2008). These inputs

are the same as those commonly used to describe fate and transport of explosives residues, which suggests that SWAT could be useful to simulate how explosive constituents undergo adsorption organic matter and degradation in soil.

Among its main applications, SWAT has been widely used in assessing and controlling soil erosion and in non-point source pollution systems of pesticides and herbicides. For example, it has been used to characterize annual maximum atrazine concentrations in watersheds (Winchell et al., 2018), chlorpyrifos and diazinon in a river (Chiu, Hunt and Resh, 2016) and organophosphates in surface run off (Wang et al., 2019; Zhang and Zhang, 2011). However, no research has been carried out with explosive chemicals as this group of organic compounds is often neglected in environmental impact assessments. The molecules studied with this model contain numerous groups of nitrogenized and phenyl groups, and some of them share similar structures to explosives such as DNAN or TNT. These similarities suggest similar behaviour in soil and water media, and thus, the possibility to simulate their transport and persistence in soil. Therefore, SWAT could be a suitable programme to simulate explosive fate and transport in river catchments, especially for risk assessment purposes.

Among its limitations, the SWAT model may not be able to representatively simulate chemical fate under very specific field conditions (e.g. rice field module) (Tsuchiya et al., 2018). In addition, it has difficulty simulating root uptake as it applies the same algorithms to describe processes that usually depend on the vegetation types, soil, land use and properties of pollutants (Reichenberger et al., 2007). To address this issue, SWAT allows an algorithm modification and the use of coupled models to increase representativeness (Wang et al., 2019), which could also be useful for studying explosive behaviour in scenarios with vegetation such as military training areas.

Table 2. 2 Comparison of potential deterministic models for predicting fate and transport of explosives in the environment.

Model	Applicable chemicals	Advantages	Limitations	References
MACRO ***(leaching model)***	Pesticides, herbicides and organic contaminants	Different approach to macro and micropore water and solute modelling	Results are not representative of soils with high organic content	(Jarvis, 2016, 1995; Jarvis et al., 1994)
HYDRUS ***(leaching model)***	Explosives, pesticides, petroleum residues, heavy metals	Several approaches depending on the scenario (dual permeability, porosity, hysteresis, etc.) Can simulate transport in soils and vadose zones. It contains a database for different soils	Excessive and highly specific inputs required. Not user-friendly.	(Arthur et al., 2018; Jacques et al., 2008; Leju, Ladu and Zhang, 2011; Seguí et al., 2017)(Alavi et al., 2011)
FEFLOW ***(leaching model)***	Pesticides, inorganic elements	It can simulate advective and dispersive-diffusive transport It representatively simulates water flow at heterogeneous porous media	It does not incorporate bioaccumulation and sorption processes	(Kupfersberger et al., 2018; Ramasamy, Power and Mkandawire, 2018; Regnery et al., 2017)
PRZM ***(leaching model)***	Pesticides, fungicides and herbicides Recommended by	It includes processes involved in the fate of pesticides in the environment Includes key parameters of the soil, chemicals, environmental conditions, and chemical state.	It does not include preferential flow It has been reported to underestimate degradation products	(Carsel et al., 1984, 1985; Chen et al., 2017; Lammoglia et al., 2018; Mamy, Gabrielle and Barriuso, 2008; Marín-Benito et al., 2015)
PELMO ***(leaching model)***	Pesticides, herbicides, fungicides	It can simulate compound degradation into metabolites and contaminant adsorption to soil	Preferential flow and capillary rise are not considered It focuses on surface water and does not include soil media.	(Borgesen et al., 2015; Diamantopoulos et al., 2017; Pereira, Cerejeira and Daam, 2014)
TOXSWA ***(catchment)***	Pesticides, fungicides, plant protection products	It can simulate sorption, transformation, and transport of contaminants in water and sediment. It can calculate degradation constants of contaminants by running inverse modelling	It does not simulate transformation of metabolites It is only valid for surface water and sediment scenarios	(Adriaanse, Boesten and Crum, 2013; Dorn et al., 2021; Oh et al., 2021; Patterson et al., 2017)
SWAT ***(water surface)***	Pesticides and herbicides	It distinguishes between field (fate), basin (transport) and in stream processes	It has difficulty simulating root uptake and very specific environments.	(Janney and Jenkins, 2019; Neitsch et al., 2011; Wang et al., 2019)

2.3.3 Stochastic approach and Monte Carlo method

Currently, it is possible to quantitatively represent uncertainties in simulations using a probabilistic or stochastic approach. This approach incorporates one or more probabilistic elements into the model, which means that the final output of the model will typically be in the form in a probability distribution (Uusitalo et al., 2015). Commonly, the outcomes of a probabilistic simulation are represented as a probability distribution instead of a fixed number, as is the case with deterministic models. These characteristics make probabilistic models suitable for exploring patterns, checking that real patterns conform to theories, completing datasets and studying situations with high uncertainty. A stochastic model is not necessarily more accurate than a deterministic model but can provide additional information and whether this information is of value and helpful to understand and solve the problem depends on the purpose of the model (Blythe, Nisbet and Gurney, 1982; Jackson, Trebitz and Cottingham, 2000). Most probabilistic models use the Monte Carlo method, which relies on repeated random sampling with the aim of obtaining numerical results displayed as a probability distribution (Zhang, Tang and Chen, 2019). The use of this approach is currently growing, developing new techniques, ideas, concepts and algorithms, such as the use of probability to describe the randomness of experiments and processes, (Firestone et al., 1997).

Monte Carlo methods have previously been used to address the uncertainties often presented in the study of environmental problems of contaminant fate and transport (Balakrishnan et al., 2005). Inputs such as environmental conditions (e.g., rainfall rate), physicochemical parameters (e.g., partition coefficients), or other relevant information (e.g., contaminant initial concentration) can be added and studied as probabilistic distributions, thus enabling modelling uncertainty propagation. On top of that, the Monte Carlo method has been used to assess environmental fate and transport of chemical compounds, in which explosive residues can be included, although nothing has been published so far.

GoldSim, is a computational software that can simulate contaminant fate and transport using the Monte Carlo method. GoldSim is designed to carry out dynamic and probabilistic simulations of a system to support management and decision-making processes (Plagnes et al., 2017). It was originally developed to assist the

United States Department of Energy (DOE) in the evaluation of a potential high-level radioactive waste repository located in Nevada, although it is currently being used to help design remediation measures for contaminated sites (Kossik and Miller, 2004). Although it is defined as user friendly and highly graphical, GoldSim also allows use of a high-level programming language for building simulation models.

GoldSim includes a specific add-on extension called GoldSim Contaminant Transport which allows the user to dynamically model mass transport processes in air, water and soil media (Havlová and Vopálka, 2010). It allows the manual addition of chemicals, media, elements and pathways and their connection by coupled sets of differential equations. Further to this, the model provides the freedom to mathematically define the processes occurring and to integrate and link the environmental elements together. Thus, this makes GoldSim a software in which the user can create a scenario from scratch and build this way complex contaminant transport simulations. In addition, GoldSim includes a 'scenario manager' that allows the user to run simulations and directly compare outcomes generated by different sets of input parameters. This capability is extremely useful for running sensitivity analyses, which enable the identification of the degree to which the inputted variables impact the final result. Therefore, the user can determine what variables have the greatest influence on each environmental process and on the total system.

Furthermore, it is highly graphical and object-oriented, and it enables comprehensive visualization of the overall simulation, which promotes a better understanding of the modelled scenario. The results are mainly displayed in a graphical format that aids interpretation as the built-in models are easy to understand and track. The fundamental output generated by GoldSim is simulated mass fluxes (rate of mass flow per unit of area) at specified points and predicted concentrations within environmental media such as air, water and soil (Kossik and Miller, 2004). This specific characteristic is useful for the simulation of the movement and degradation of substances in the environment, as users can follow, understand and modify the model when required (Egeghy et al., 2016).

To run the probabilistic simulations, GoldSim includes, among its features, the Monte Carlo simulation, in which multiple realisations of a system are simulated, being each realisation totally independent of the others. As a consequence, this type of

simulation provides an outcome displayed as probability distribution instead of a single value. The Monte Carlo method included in GoldSim allows, therefore, the representation of uncertainty in processes and parameters when specifying model inputs as probability distribution elements. It also facilitates representation of stochastic processes that vary over time but can only be described statistically (e.g., rainfall and temperature change). In addition, the user can input 'stochastic elements' and select their statistical distribution (e.g., normal, Poisson, or uniform) which enables the explicit representation of variability in the input data for the model. Therefore, it can representatively describe the inputted data and obtain more reliable outputted data displaying its variability range and probability distribution.

The majority of the research described in the literature regarding contaminants in the environment is related to the study of a radioactive particles using GoldSim's Radioactive Transport Module (Lee, Choi and Kim, 2016). GoldSim has been used in waste management to model and calculate long-term transport of radioactive materials near human occupied areas (Panik and Necas, 2013), to model nickel sorption in granite repositories (Lu et al., 2012) and to predict uranium transport from a mill effluent (Plagnes et al., 2017). Although these examples relate to inorganic compounds, the interface elements and structure suggest that GoldSim could be a suitable tool for studying other chemicals.

GoldSim has been also used to model fate and transport of polyaromatic hydrocarbons in chalk. showing the probability distribution of contaminant transport when adding physico-chemical variables as distributions (Cao et al., 2015). In this publication, the fate and distribution of polyaromatic and aliphatic compounds from fuel was studied in a chalk aquifer. K_d was inputted in the model along with the chalk properties (bulk density, and porosity) the dimensions of the aquifer and the flowrate. The model numerically showed how the compounds migrated in chalk and their retardation by the organic carbon content in the chalk. On top of that, the Monte Carlo method provided estimated behaviour of these compounds over 10, 100 and 100 days, which was useful to inform risk assessment posed by these contaminants. These results suggest that GoldSim can be potentially used to assess the transport of explosive residues in soils and their sorption (or retardation) in soils with high organic carbon content.

The main processes described in the studies included dissolution, dispersion, and advection, although GoldSim can simulate chemical partition between to media (e.g. soil and water), degradation and diffusion according to its user guide (GoldSim Technology Group LLC, 2021). The examples showed that GoldSim could representatively and simultaneously simulate the behaviour chemicals in different media, which is useful for studying the environmental mobility and persistence of explosive fills in which chemicals are in combination. Although none of the studies reported to date have modelled the transport of explosives in the environment, GoldSim could be a suitable computational program for modelling and predicting the main processes involved in the environmental fate and transport of explosive residues.

2.4 Towards an integrated approach for modelling explosives

The knowledge and tools for simulating explosive fate and transport in the environment has increased over the last three decades, mainly due to the reduced time, effort and cost compared to laboratory experiments. The majority of the computational methods developed for this purpose have been tested with both organic and inorganic compounds, though few have been used with explosive constituents. As a result, new or combined computational programs are needed to representatively assess explosive behaviour in the environment.

Several potential models to study and predict fate and transport of explosives have been discussed in this review. For each one, the key functions of the software have been detailed as well as several environmental examples in which computational modelling has been used. Most of the discussed models have been used for organic compounds, which share similar chemical structures, such as functional groups or phenyl groups, to those found in explosives. However, few have actually been used with explosive constituents, making it difficult to assess which ones are most suitable for simulating explosive fate and transport.

Several deterministic leaching models have been discussed in this review. FEFLOW can simulate contaminant transport in porous media and groundwater and although it has not been tested with explosives, the features and key parameters needed for the simulation are quite similar to those used to study explosive fate and transport.

Something similar occurs with the PRMZ, PELMO and MACRO models, however, these ones have been described within the framework of the Forum for Coordination of pesticide fate models and their use (FOCUS) for leaching assessment. HYDRUS is the only model that has been used to investigate explosive transport in soil and water media and is therefore able to provide some insight into the key parameters needed to model their behaviour. However all of these models have certain limitations, especially when simulating complex environmental systems (Su et al., 2019).

In addition, two models with different purpose than leaching have been described in this review. TOXWSA have been mainly used to simulate contaminants in surface water and sediment environments, limiting their use when the scenario involves soil systems. SWAT is a catchment-scale hydrological model that has been tested with pesticides, herbicides, and fertilizers, it includes soil environments and most of the processes that explosives undergo once released in the environment. However, it has an air compartment not needed for assessing the environmental impact posed by explosive residues.

Probabilistic computational models using the Monte Carlo method show results as distributions and not a single value. GoldSim is an example of a model which could be used to describe the behaviour of chemicals used in explosive formulations. GoldSim has a specific Contaminant Module that facilitates the addition of inputs and the incorporation of manual mathematical formulas and links between elements in the system. Its interface is easy to use, and it is highly graphical, being more intuitive and facilitating the tracking of simulations by the users. However, GoldSim has not been tested with explosive residues yet, and there is, therefore, still a need to assess whether this model's ability can representatively simulate the fate and transport of simulation of these chemical compounds.

2.5 Conclusion

Computational modelling is, and will continue to be, an integral part of the research and assessment of environmental contaminant impact and help remediation strategies. However, there is still a need to determine the key parameters necessary for each model and purpose. To date, none of the available computational models

allow the assessment of the behaviour and simulation of the fate and transport of multiple explosive constituents in combination, highlighting a challenge and the need to implement novel alternatives. This is key to understand how the explosive material, and especially, the Insensitive High Explosive traces interact and impact the environment.

Currently, there is no single validated methodology or empirical approach for determining the key parameters that allow to describe fully the fate and behaviour of explosive residues in the environment. One alternative could be, for instance, the use of a combined approach where deterministic and probabilistic modelling techniques are used to a) allow the user to create more accurate and representative environments, b) to address and estimate uncertainties in the processes, c) to assess which variables influence the most the fate and transport of the explosive residues and d) to enable the study of the whole picture of contamination in specific environments.

Among all the described computational programmes in this critical review, GoldSim supported all functionalities required to develop a representative model which can be used to understand how traces of explosive material with combination of different chemical compounds would impact the environment. This includes the addition of parameters and their description, the incorporation of complex interactions among water, air and soil media and its ability to perform probabilistic simulations.

CHAPTER 3. Simulation of the transport of Insensitive High Explosive residues in sandy soil columns

ABSTRACT

There is a trend towards the use of Insensitive High Explosives (IHE) for military activities as they are intended to be less prone to accidental detonation compared to traditional explosive fills. This has driven the development of new IHE formulations containing different chemical compounds such as 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO), whose mobility in soil is not fully understood. In this work, the mobility DNAN and NTO, was studied in combination using soil columns filled with sand and sandy loam; two different soils with different organic matter content and particle size distribution. Simultaneously, a stochastic and dynamic model was developed in GoldSim to simulate NTO and DNAN breakthrough curves in each soil. This showed that sorption of the IHE constituents to the soil was the most significant factor in simulating contaminant breakthrough. A sensitivity analysis demonstrated that variation in the soil water partition coefficient (K_d) had the greatest influence when used to simulate the breakthrough curve of IHE constituents in soil. K_d was measured empirically and as expected, K_d was low in the soil with the lower organic content for NTO (0.334 L kg^{-1}) and DNAN (0.401 L kg^{-1}) suggesting high mobility. While K_d for NTO was similar in the sandy loam (0.242 L kg^{-1}) it was significantly higher for DNAN (9.128 L kg^{-1}), which indicated high interactions between DNAN and the organic matter in the soil. The use of stochastic modelling to estimate IHE breakthrough concentrations enabled the uncertainty inherent in environmental systems to be embedded into simulations, thus increasing the simulation accuracy. This study is the first step toward proactive management of IHE in the environment and may support decision making for remediation and mitigation strategies in contaminated lands.

3.1 Introduction

For decades, explosives have been used for defence and industrial purposes (Mark et al., 2016; Walsh et al., 2018). Activities involving the manufacturing of these materials and their disposal by open-burning, as well as second order detonation and blow-in-place detonations have been demonstrated to deposit up to 50% of the explosive on the soil surface leading to potential contamination of nearby water and soil (Temple et al., 2018). Explosive compounds can be toxic to animals (Lotufo et al., 2015) and plants (Vila, Lorber-Pascal and Laurent, 2008) and human health (Kaplan et al., 1965) and therefore, it is essential to mitigate their environmental impact to preserve ecosystems (Beck et al., 2018).

In recent years, the drive for safer explosives has seen the replacement of traditional explosive fills by Insensitive High Explosive (IHE). This new generation of explosive formulations are comprised of constituents such as 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO). However, these new explosive constituents have different physicochemical properties compared to traditional explosives. Specifically, NTO highly soluble in water (12.6 g L^{-1}, 25°C), acidic (pKa = 3.67) and sensitive to biodegradation (Lee and Coburn, 1988; Madeira et al., 2018; Temple et al., 2018). Due to this, NTO is likely to rapidly break through soil and to degrade in soils with high organic matter content (Mark et al., 2016). In contrast, DNAN is less soluble (276 mg L^{-1}, 25°C) though it may undergo biodegradation to more toxic metabolites (Davies and Provatas, 2006; Dontsova et al., 2014; Kitcher et al., 2017). These features promote DNAN and NTO movement through the soil matrix, increasing processes such as adsorption, degradation and plant uptake compared to legacy explosive fills. Nevertheless, the current knowledge of IHE mobility and persistence in the environment is not sufficient, which poses the question of how to determine their transport through soil.

Often, the study of contaminant transport in soil is investigated by performing controlled laboratory experiments attempting to replicate processes that occur in the real environment (Kalderis et al., 2011). These experiments can be classified into static, in which the equilibrium of the system is reached, and dynamic, in which the studied system is in continuous movement and therefore equilibrium is never reached (UK Government Office for Science, 2018). Static experiments, such as

bottle flask tests and microcosms have been performed to study processes affecting persistence such as the degradation rate of explosives and sorption onto soil (Halasz, Hawari and Perreault, 2018; Indest et al., 2017; Krzmarzick et al., 2015; Won and Borden, 2017). In this way, key parameters for defining transport processes such as partition coefficients (soil-water, organic carbon content-water,) of IHE in different media have been quantified. However, some of these parameters are highly dependent on the soil type and the environmental conditions and therefore cannot be extrapolated to other environments.

Dynamic experiments such as soil columns and lysimeters can be used to study IHE mobility in soil (Arthur et al., 2018; Heerspink et al., 2017; Molina et al., 2006; Temple et al., 2018). These studies mainly focus on the advection and sorption process that IHE chemicals undergo in soil. However, these experiments are often conducted on one set of soil type, contaminant and environmental conditions, making it challenging to draw broad conclusions for specific contaminants. In addition, the growing number of IHE formulations makes it impractical to experimentally determine how their residues behave in the soil manly due to the long periods of time required to achieve reliable results and the cost of experimental work (Millar et al., 2004). This issue has motivated the scientific community to search for alternative, non-experimental methods that can assist with assessing the risk posed by IHE in soil.

The development and use of computational methods to study contaminant behaviour in soil has increased during the past two decades (Beck et al., 2018). The principal advantages of using computational methods over laboratory experiments include shorter periods of time for evaluation, lower costs and the ability to obtain results without needing to use potentially harmful contaminants. One such software tool is GoldSim, and its Contaminant Transport Module that employs the Monte Carlo method (GoldSim Technology Group LLC, 2021). This method enables the representation of uncertainty by displaying the outcome as a probability distribution, which provides a more realistic overview of the contaminant behaviour in the soil. GoldSim has representatively simulated the transport of radionuclides (Panik and Necas, 2013), inorganic compounds (Lu et al., 2012) and polycyclic aromatic

hydrocarbons (Cao et al., 2015) in soil. This suggested that GoldSim could be a suitable programme to simulate IHE behaviour in soil.

The aim of this work was to develop a representative model using GoldSim to simulate the transport of NTO and DNAN in two sandy soils with different organic matter content and particle size. To assess the performance of the model, simulated breakthrough times and maximum concentration in leachate were compared to experimental data collected from controlled laboratory soil columns. This also enabled the identification of essential parameters that regulated the transport of explosives in soil, and the creation of a model that could be used to aid environmental risk assessment and remediation strategies in contaminated soil.

3.2 Materials and methods

3.2.1 Soil Preparation and Characterisation

Two soils were purchased from a building merchant in Oxfordshire (UK), classified as ‘sandy loam’ and ‘sand’ soils by their particle size distribution calculated by sieving the soils through seven different mesh size sieves from 2 mm to 63 µm. Quartz sand was purchased from Fisher Scientific UK and used as received. Soils were air-dried for 2 weeks and passed through a 2 mm sieve to remove the largest fractions. Soil moisture content (BS 13772:1990), pH (1:5) and total organic content (BS 13039:2001) were determined according to British Standards. Total Carbon Nitrogen (TCN) content and Total Organic Carbon (TOC) were determined using Elementar Vario ELIII (**Table 3.1**).

Table 3. 1 Characterisation of quartz sand, sand and sandy loam soil.

Soil	Description	TOC (%) [a]	pH [b]	N (%) [c]	C (%) [c]
Quartz sand	Inert material	-	7.1	-	-
Sand	UK sandy	4.9	7.9	0.012	3.22
Sandy loam	UK topsoil	8.0	8.0	0.30	5.11

[a] Determined by incineration at 400 ^{o}C for three days; [b] Determined by griffin pH meter model 80 at room temperature, soil: water (1:5); [c] Determined by Elementar Vario EL III analyser by CHNS analysis

3.2.2 Preparation of IHE compound stock solutions

DNAN was used as purchased from Sigma-Aldrich (98% pure). NTO was synthesised in house (Lee and Coburn, 1988 and Sandyham et al., 2013). A stock solution was made for the column transport studies by dissolving DNAN (40 mg) and NTO (40 mg) in distilled water (1 L) at room temperature for 48 h.

The stock solution containing DNAN and NTO was used to prepare lower concentration solutions (5, 10, 20, 30 and 40 mg L^{-1}) for the determination of the soil water partition coefficient (K_d). These solutions were also used as standards for their analysis by High Performance Liquid Chromatography (HPLC).

3.2.3 Determination of K_d

Samples of quartz sand, sand and sandy loam (5 g) were submerged in several aqueous DNAN and NTO solutions at 5, 10, 20, 30 and 40 mg L^{-1} in 100 mL Erlenmeyer flasks. The flasks were wrapped in foil to avoid UV exposure and shaken for 18 hours at 150 rpm, ambient temperature and pressure (Arthur et al., 2017). Supernatant was removed with a micropipette, filtered through a 2nm nylon filter, and stored at 4°C until analysis by HPLC. A mixture of acetonitrile ACN:water (1:1) (10 mL) was added to the soil samples and shaken for another 24 hours at 150 rpm to extract NTO and DNAN adsorbed to the soil particles. (Temple et al., 2019). The supernatant was then removed and stored at 4°C until analysis by HPLC within 2 days. Experiments were performed in triplicate for DNAN and NTO in each soil.

K_d was determined for NTO and DNAN in sand and sandy loam by dividing the concentrations in the soil fraction by the concentration in the supernatant (**Equation 3.1)**

$$K_d = {[A]_{soil}}/{[A]_{water}} \qquad \text{(Equation 3. 1)}$$

Where $[A]_{soil}$ is the IHE constituent concentration the soil and $[A]_{water}$ is the IHE constituent concentration in the solution, which is the section of the soil that is covered by water (Borgesen et al., 2015).

The results obtained with in this section are displayed in **Table 3.2**

Table 3. 2 Experimental K_d and K_{OC} values and standard deviation for DNAN and NTO in sand and sandy loam performed in triplicates.

IHE constituent	Soil	K_d (L kg^{-1})	K_{OC} (L kg^{-1}) *
NTO	Sand	0.334 ± 0.025	6.81 ± 0.51
	Sandy loam	0.242 ± 0.170	3.025 ± 2.12
DNAN	Sand	0.401 ± 0.082	8.18 ± 1.67
	Sandy loam	9.51 ± 1.51	118.87 ± 18.8

*K_{OC} was calculated from K_d using Equation 2.6 displayed in Chapter 2.

3.2.4 Soil column experiments

Three glass columns (radius 2.5 cm x height 10 cm) were filled with dried and sieved quartz sand, sand or sandy loam soil in triplicate (270.7 ± 0.1 g, 275.6 ± 0.1 g and 195.9 ± 0.1 g respectively) and gently compacted with a flat ended tool until no visible gaps were observed (Dontosova et al., 2006, Temple et al., 2018). The columns were saturated with distilled water (up to 100 mL) and allowed to settle for one hour. DNAN and NTO stock solution (40 mg L^{-1}) was added in 50 mL increments every 5 minutes (Kramoer Dosing Pump, China) for 15 minutes, followed by 40 minutes with distilled water influent. The total time was 55 minutes and leachate coming out of the columns was collected every 5 minutes. Samples were filtered with 0.2 µm polyethylene terephthalate (PET) filters and stored at 4°C, until analysis by HPLC within 2 days.

3.2.5 High Performance Liquid Chromatography coupled with Diode array Detector (HPLC-DAD)

HPLC was performed using a Waters-Alliance 2696 equipped with a Waters 996 photodiode array detector (USA). The analytes were separated on a ZORBAX Eclipse Plus C18 column (4.6 x 150 mm, i.d. 3.5 µm) from Agilent Technologies (Wilmington, DE, USA) maintained at 30°C. Samples were injected with a syringe loading injector fitted with 10 µL loop. Optimum chromatographic conditions were obtained with a linear gradient of 40% ACN and 60% water acidified 0.1% with formic acid. The flow rate was set at 1.5 mL min^{-1} and the analytes were quantified via UV absorbance with optimum sensitivity detected at 296 nm for DNAN and 315

nm for NTO. Retention times were 1.01 minutes for NTO and 4.96 minutes for DNAN. A calibration curve was obtained by plotting the concentration against corresponding peak area for each analyte **(Figure 3.1)** and both peak areas of samples and standards were determined by Empower 2 software (Waters). For this method, limit of detection was 0.5 mg L^{-1} and limit of quantification was 1.4 mg L^{-1} for both DNAN and NTO (Fawcett-Hirst et al., 2020).

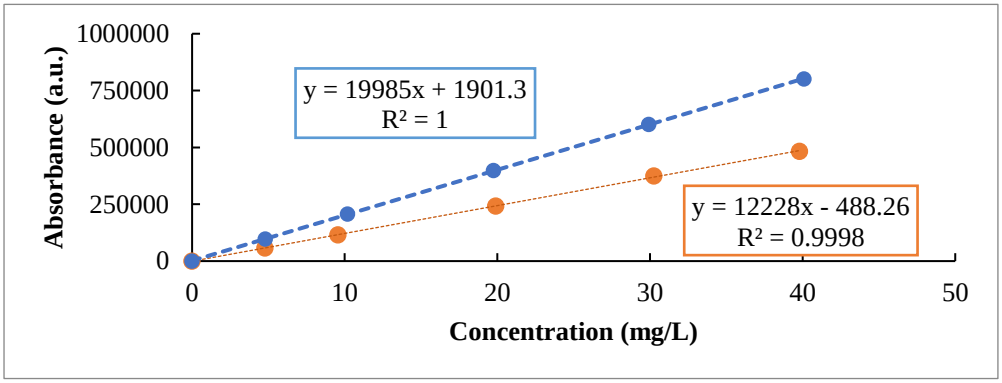


Figure 3. 1 Calibration curve for NTO (blue) and DNAN (orange) obtained in the HPLC-DAD. Both lines show a $R^2 > 0.999$ which indicates optimum fit.

3.2.6 The construction of the model in GoldSim

The simulation of DNAN and NTO transport in sandy soils was performed using the Contaminant Transport Module in GoldSim version 14.0 (GoldSim Technology Group LLC, 2021). This module is an add-on extension to the GoldSim simulation software framework that allows the user to dynamically model mass transport processes in different scenarios. In order to assess the performance of the model, the results of two the experimental setups were compared against the simulation output. Specifically, the setups consisted of two soil columns filled with sand and sandy loam.

The model framework contained the following elements:

- Material: Fluid (water), Soil (sand or sandy loam) and Species (NTO and DNAN)
- Pathway: Cell Pathway (leachate) and Pipe Pathway (soil column)

- Input: Data (e.g. soil parameters, indoor inflow, DNAN and NTO initial mass), Stochastic (e.g degradation rates, dissolution rates, K_d,) and Time Series (outdoor inflow)
- Function: Selector (choosing dissolution rates over time) and Expression (equations describing different fate and transport processes)
- Result: Time History result (NTO and DNAN concentration in leachate).

The properties of the different soils, water and contaminants were defined in the element of Material which includes the species, water and the solids used for modelling. In the Species element the molecular weight of DNAN and NTO (198 and 130 g mol^{-1} respectively) was specified. Quartz sand, sandy soil and sandy loam soil were considered the 'Solid' and therefore actual bulk density and porosity were inputted from experimental measurements in triplicate (**Table 3.3**). The soil density was calculated dividing the mass of wet soil by the volume it occupied. The porosity was calculated dividing the pore volume (water volume absorbed by the dry soil) by the soil. Last, soil tortuosity was estimated from experimental porosity parameters using a table described by Alaoui et al., 2003. (Alaoui et al., 2003). Although the porosity levels might look low compare to the bulk density reported, both parameters were measured directly from the soil and the only explanation of why the look alike could be due to a potential uneven packing method used to compact the increments of the soil when they were added to the column.

Table 3. 3 Table with inputs for GoldSim. All of them were inputted as single deterministic value elements (not stochastic).

Soil Type	Parameter	Value	Justification
Quartz sand	Bulk Density	1.38 g cm^{-3}	Experimentally measured
	Porosity	0.36	Experimentally measured
	Tortuosity	0.6	Estimated
Sand	Bulk Density	1.40 g cm^{-3}	Experimentally measured
	Porosity	0.29	Experimentally measured
	Tortuosity	0.5	Estimated
Sandy loam	Bulk Density	1.09 g cm^{-3}	Experimentally measured
	Porosity	0.44	Experimentally measured
	Tortuosity	0.5	Estimated

The model was constructed using basic initial inputs displayed as Data elements and Functions. The scenario started with an initial contaminant concentration that was spilled from a tank into the soil column, which is represented by a specific type of Pathway element called a Pipe. Influent (40 mg of NTO and 40 mg of DNAN) was simulated as dissolved in 1 L of water before entering the 'Pipe Pathway' to match soil column experiments. Each soil was defined as the Solid inside the 'Pipe Pathway' and its main dimensions and properties were defined according to the parameters used in the laboratory soil column experiments (**Table 3.4)**. The contaminant was added to the column as a continuous concentration of 40 mg L^{-1} for both DNAN and NTO using the option Input Rate. The continuous inflow and outflow passing through the soil column was 10 ml min^{-1} for both containers with contaminated and non-contaminated water **(Figure 3.2)**

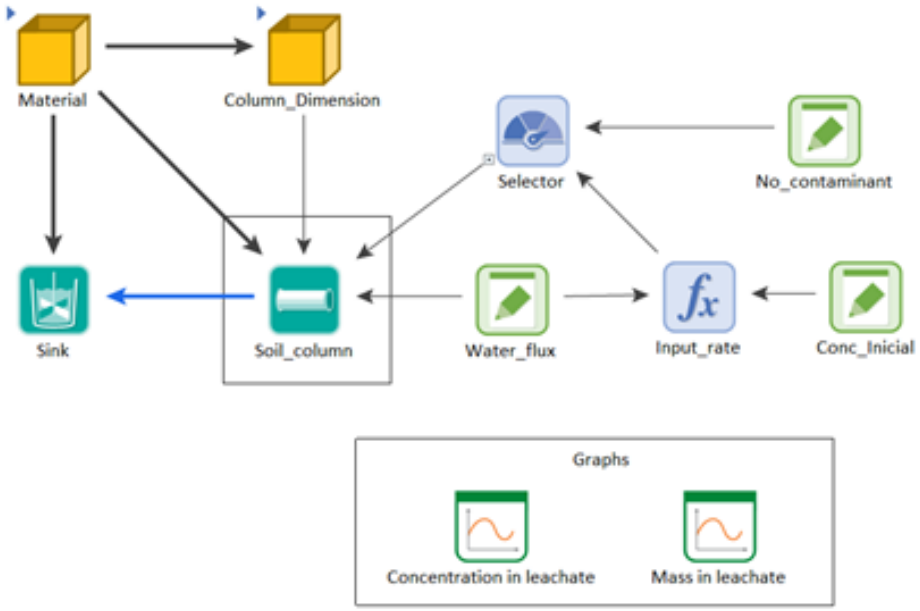


Figure 3. 2 Picture of the model developed in GoldSim to study NTO and DNAN[l] transport in sandy soil columns.

Table 3. 4 Pipe Pathway properties used in GoldSim to model the dimensions of the soil column.

Parameter	Value	Justification
Length (cm)	10	Measured
Radius (cm)	2.5	Measured
Area (cm^2)	19.6	Calculated
Volume (cm^3)	196	Calculated
Perimeter (cm)	16	Calculated
Dispersivity (cm)	1	GoldSim help handbook

GoldSim simulates contaminant transport by using the advection equation (**Equation 3.2**)

$$\frac{dC}{dt} = -v * \frac{dC}{dx} \quad \textbf{(Equation 3. 2)}$$

where *t* is time (min) *v* is the water seepage velocity per area (cm s^{-1}), *C* is the contaminant concentration (mg L^{-1}) and *x* is the length of the column (cm).

It also uses the partitioning governing equation (**Equation 3.3**)

$$\frac{dM}{dt} = Q * \frac{M}{V + K_d G} \quad \textbf{(Equation 3. 3)}$$

Where *M* is the mass of contaminant (mg), *V* is the volume of water in the column (mL), K_d is the contaminant soil-water partition coefficient (mL kg^{-1}) *G* is the soil mass in the column (kg), *t* is time (min) and *Q* is the water flowrate (mL min^{-1}).

Last, to estimate how long contaminants needed to leched out of the column, the model included the retardation factor (R) for each contaminant (**Equation 3.4**).

$$R = 1 + \frac{d * K_d}{n} \quad \textbf{(Equation 3. 4)}$$

where d is the soil bulk density (kg L^{-1}), K_d is the contaminant soil-water partition coefficient (L kg^{-1}) and n is the soil porosity.

In addition, the Monte Carlo method was used to describe uncertainties and to understand what inputted parameters participate the most on the contaminant breakthrough curves. For the second part of the study, NTO and DNAN K_ds obtained in each soil were inputted in the model as a uniform distribution, whereas the rest of inputs used in the model remained invariable, so the variability in outcome was easier to visualize and identify. The model was run as well with 10, 1001 and 10001 iterations showing little differences on the outcome between 101 and 10001 iterations. Therefore, the simulation settings were modified, to allow for 101 realizations, as it was considered representative enough for assessing this model developed in GoldSim.

3.2.7 Sensitivity analysis

Sensitivity analysis was performed by making minor adjustments (slight variations) to the input values for bulk density, porosity, tortuosity and K_d and observing how NTO breakthrough curve varied. DNAN results for this sensitivity analysis were expected to be the same, as the model works with the same parameters for both chemical compounds. Sensitivity analysis was primarily conducted on sandy soil, as quartz sand is inert, and it is not representative of a real matrix. The input values varied in the analysis were chosen randomly, but realistically (i.e., a soil can never have a porosity of 100%) (**Table 3.5**). Small variations that made significant changes to the NTO breakthrough curve (output) of the simulation were consequently considered key parameters and were therefore determined experimentally for the specific soil and contaminant mixtures.

Table 3. 5 Parameters used for the sensitivity analysis and their values

Parameter	Values	Percentage Variation (%)
Bulk density (g/L)	1.20, 1.40, 1.60 1.80	60
Porosity	0.20, 0.25 0.30 0.35	75
Tortuosity	0.5, 0.6, 0.7, 0.8	40
Partition coefficient (l/kg)	0.0, 0.1, 0.2, 0.3, 0.4,	40

3.3 Results and Discussion

A model was built to simulate the transport of DNAN and NTO in quartz sand (inter material) and two sandy soils with different organic matter content and particle size distribution. To assess the performance of the model, simulated NTO and DNAN breakthrough curves in the soils were compared to the ones obtained by conducting, simultaneous soil column transport experiments.

3.3.1 Simulating NTO and DNAN transport in quartz sand

The first iteration of the DNAN and NTO GoldSim transport model only considered bulk density, tortuosity and porosity as soil properties, using an initial K_d =0 (as calculated based on the equivalent laboratory quartz sand column). As quartz sand is an inert material, no interactions between the IHE constituents and the soil were considered, and the only chemical property included in this version of model was the molecular mass of DNAN and NTO. To enable direct comparison between simulated and experimental results, leachate concentration was normalised over the initial concentration (C/C_O) and plotted against time (**Figure 3.3**).

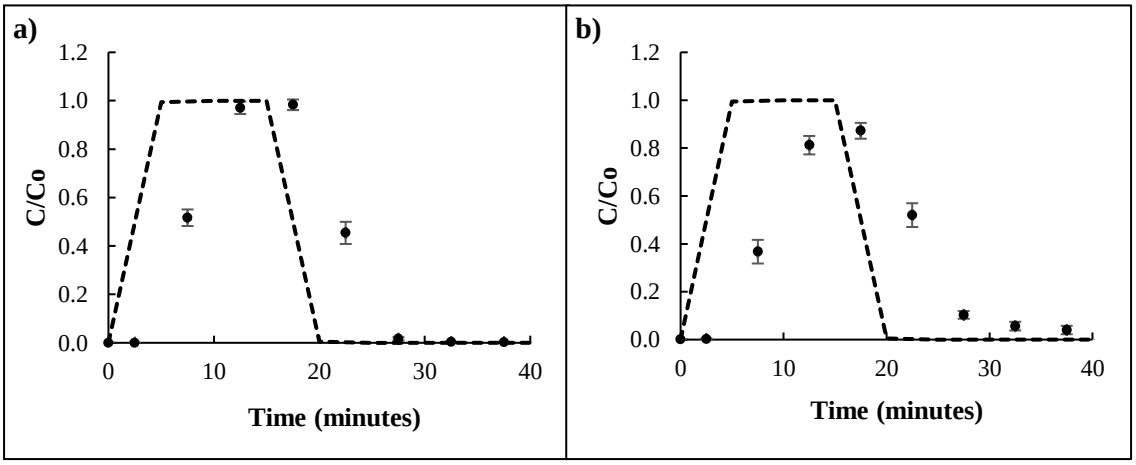


Figure 3. 3 Comparison between the GoldSim simulation and laboratory experiment breakthrough curves in quartz sand for a) NTO and b) DNAN. The dots indicate experimental results and the discontinuous line indicate simulated results

The initial simulation compared well to laboratory column experiments with DNAN and NTO in quartz sand. Experimentally, NTO concentration peaked between 15 and 20 minutes with the outflow concentration matching the inflow concentration and reaching 100%. DNAN concentration peaked between 15 and 20 minutes, although the highest recorded concentration was only 87% of the initial concentration. The

total recovery of DNAN and NTO after passing through the quartz sand column were 105 and 104%, respectively, due to standard errors in the experimental procedure (e.g., peristaltic pump flow volume) in comparison to GoldSim simulation (100%). Over the duration of the experiment, NTO and DNAN did not undergo physical nor chemical degradation nor irreversible adsorption to the matrix, which was expected for the quartz sand control.

The GoldSim simulation modelled similar peak breakthrough concentrations, estimating 100% for both DNAN and NTO. However, simulated contaminant breakthrough curves, particularly the gradients of increasing and decreasing DNAN and NTO concentration were not representative of experimental ones. The experimental breakthrough concentrations increased gradually to a peak, whereas breakthrough concentrations in GoldSim simulations plateaued at the influent concentration for ten minutes. Experimentally, increasing gradients (0.81 min^{-1} for NTO and 0.60 min^{-1} and DNAN) were not as steep as those simulated by GoldSim (1.37 min^{-1} for both IHE constituents). Experimental decreasing gradients (-0.67 min^{-1} for NTO and -0.46 min^{-1} for DNAN) differed to those simulated (-1.37 for both IHE constituents) more significantly. Therefore, GoldSim was not able to simulate the slight retardation of DNAN and NTO in quartz sand, simulating maximum concentration at only 5 minutes after the initial influent entered the column for both DNAN and NTO compared to 20 minutes experimentally. This implies that, without diffusion process and K_d values, GoldSim assumes immediate contaminant transport to the bottom of the Pipe Pathway and thus instantaneous appearance in the leachate.

A possible explanation for the differences between the gradients may be due to the experimental set up, as the flow rate was slightly variable when adding the NTO and DNAN (stock) solution to the column. In addition, the model did not account for hydrodynamic dispersion. Hydrodynamic dispersion describes the mixing processes of solute in porous media (Shi et al., 2016), and it is dependent on the flow rate and the dispersity factor, which at the same time, is related to the structure and texture of the soil. The addition of the hydrodynamic dispersibility could have potentially delayed the simulated contaminant breakthrough, through quartz sand was assumed

to be an inert material in which the contaminant interactions with the soil was negligible.

To achieve more representative simulations, it was possible to correct the retardation in breakthrough manually by experimentally measuring the time taken for influent to travel the length of the column during saturation and including this in the model using the function element ‘Selector.’ This allowed a more representative simulation of the experimental breakthrough curves for both DNAN and NTO in quartz sand. However, it was preferable to improve the model by including additional physico-chemical parameters of the soil and contaminants so that fewer manual corrections would have to be made. Therefore, to further develop the simulations of DNAN and NTO transport model, the inclusion of additional parameters for more complex soils was investigated.

3.3.2 Simulating NTO and DNAN transport in sandy soils

Two soils classified as sand and sandy loam were used to investigate the most influential parameters required to simulate the transport of DNAN and NTO. Both soils had similar pH, although they showed differences in their particle size distribution and different organic matter content. These two soils were chosen to increase the complexity of the simulation as DNAN adsorbs significantly to soils with high organic content, and NTO is known to rapidly leach out of soils (Arthur et al., 2018; Terracciano et al., 2018). In addition, the organic matter content is key for sorption processes as organic particles in the soil can interact with DNAN and NTO by hydrogen bonding, covalent and donor/acceptor binding, polarity, and van der Waals forces (Landrum et al., 1984). The nitro groups of the explosive compounds promote polar interactions, as well as van der Waals forces between polar groups (such as –COOH, -OH and -H) found in organic matter particles (Vitale and Di Guardo, 2019). This promotes chemical sorption to the soil and retards its transport through soil matrices.

The presence of organic matter and inorganic elements such as nitrogen in the soils created more complex interaction between DNAN and NTO and the soil, which were difficult to simulate due to the simplicity of the model. To identify the key variables required for modelling these more complex scenarios, the simulation was initially run

with the same inputs as described in section 3.1, although soil inputted data elements were substituted by those obtained experimentally for the sandy and sandy loam soil: bulk density and porosity. The other inputted data elements (such as molecular weight or explosive initial concentration) remained invariable. As before, both simulated and experimental NTO and DNAN breakthrough curves were plotted over time (**Figure 3.4**).

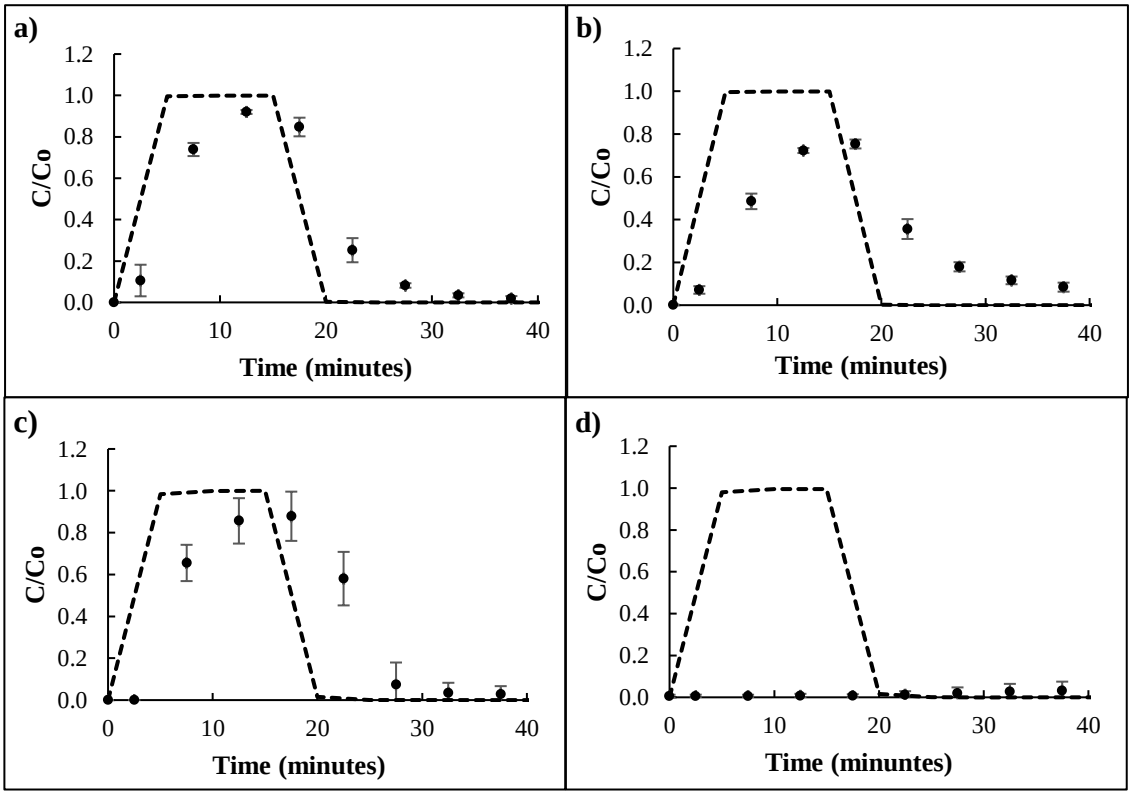


Figure 3. 4 Comparison between the GoldSim simulation and laboratory experiment breakthrough curves for a) NTO in sand b) DNAN in sand c) NTO in sandy loam and d) DNAN in sandy loam. The dots indicate experimental results and the discontinuous line is the simulated

For the sandy soil, the NTO experimental concentration peaked at 15 min at 93% of the influent concentration (**Figure 3.4 a**). DNAN concentration peaked between at 20 min with a maximum concentration of 87% of the influent. However, the GoldSim model simulated the peak concentration for both DNAN and NTO to be after 5 minutes, the same as for quartz sand, suggesting that inputted parameters had the same drawback as in quartz sand simulations (**Figure 3.4 b**). For comparison, sand density and porosity were similar to quartz sand (varying only 8% and 2% respectively), thus, the simulations were expected to be similar disregarding all other

interactions. Experimentally, total recovery of NTO and DNAN was 100 and 99% respectively, which matched GoldSim simulations, (100% after 55 minutes). Therefore, it was unlikely that degradation or sorption of DNAN and NTO to the soil influenced the transport of these compounds in the sand as all the contaminant mass leached out of the columns within the time of the experiment.

As expected in the sandy loam soil with higher organic matter content, the retention of DNAN and NTO was more significant. NTO peak concentration was detected between 15 and 20 min, five minutes later than in both quartz and sandy soil (**Figure 3.4 c**). In addition, the peak concentration was only 72% of the influent concentration, compared to 100% as simulated. Experimentally, total NTO mass recovered from the soil was only 76% of the initial, indicating possible irreversible adsorption due to the interactions between the contaminant and organic matter. The DNAN simulation was even less representative for sandy loam soil as experimental DNAN did not break through the column at all and was not detected in the leachate. Though the simulation estimated the first DNAN to be detected in the leachate after only 5 minutes, which suggested that DNAN strongly interacted with the soil particles. DNAN has been reported to degrade in sandy loam (Temple et al., 2018), yet it is unlikely that significant degradation would have taken place within the timescale of the soil column (55 minutes). Therefore, the retardation of DNAN transport and low recovery in effluent is most likely due to sorption (**Figure 3.4 d**).

The simulations performed by GoldSim showed rapid DNAN and NTO elution time, while experimentally, it took significantly longer for DNAN and NTO to elute from contaminated soil. The results suggest that under these environmental conditions, NTO may dissolve quickly and easily reach groundwater, resulting in a rapid influx of high concentration that may cause acute toxic effects. However, DNAN might undergo a lower and longer dosing leading to more chronic effects (O'Doherty et al., 2013; Vila, Lorber-Pascal and Laurent, 2008). Previous work has shown that, for the same soil, DNAN sorption of DNAN is much stronger than NTO to soil particles, which is supported by the more significant retention of DNAN on sandy loam soil even within the short timeframe of the experiment (Arthur et al., 2018; Mark et al., 2016). Although the simulations performed in sandy loam were not significantly representative, the model was used as a prototype for further simulations. In order to

determine which key parameters influenced on the NTO and DNAN breakthrough curve, it was necessary to carry out a sensitivity analysis.

3.3.3 Sensitivity analysis

A sensitivity analysis was performed for the main three physical parameters related to the soil already included in the model: density, porosity and tortuosity. These properties were chosen as they did not depend on the environmental conditions unlike flow rate or column dimensions but were integral to the system and vary dependant on the matrix used. However, given the significant retention of DNAN and NTO observed in sandy loam, it was evident that K_d was also influential. The sensitivity analysis was performed by simulating NTO breakthrough in sand and the results were compared by providing different values for the parameters listed in section 3.2.7 (**Figure 3.5**).

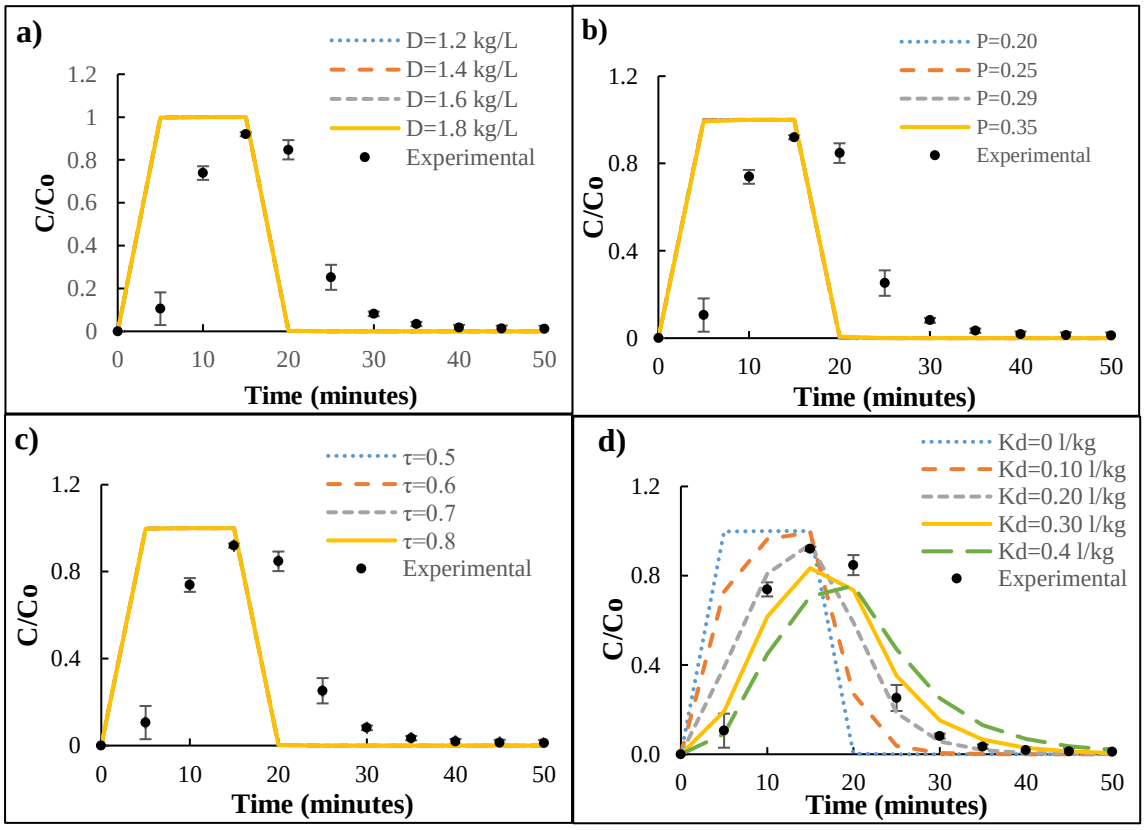


Figure 3. 5 Sensitivity analysis. Variation of NTO breakthrough curve (C/Co over time) in sandy soil when modifying the value of a) soil density, b) soil porosity, c) tortuosity and d) Kd of NTO in sand

The sensitivity analysis was undertaken for sandy soil and NTO as a representative system. Whereas soil bulk density, porosity and tortuosity did not influence NTO breakthrough the partition coefficient showed significant differences in peak breakthrough concentration time, with increasing K_d improving correlation to the experimental data. This was as expected as K_d tends to increase with increasing organic matter content, and the organic matter content of the sand (4.9 %) was equivalent to literature values for soils with higher partition coefficients.

However, due to the simplicity of the model, the sensitivity analysis did not take into account any parameter regarding the hydrodynamic dispersivity process or the structural effects caused by the of the soil (sieved, repacked and saturated with water) (Adhav et al., 2019). The aim was to create an “efficient” or “representative” model with the minimum required parameters. In addition, it is a challenging variable to quantify under experimental conditions, as it is not a simple calculation and requires parameters such as the pore water velocity quantified by tracers. Though this parameter may improve the simulation performance, it also adds complexity to the model which contradicts the simplicity of the approach.

As K_d was the key parameter that regulated the transport of NTO (and potentially of DNAN) in sand, it was concluded that an experimentally derived K_d for the specific soil-contaminant combination was essential for achieving more representative simulations. As a result, K_d coefficients were inputted as stochastic data elements in the model to achieve more representative DNAN and NTO breakthrough curves in the sandy soils.

3.3.4 Simulating NTO and DNAN transport in soil using K_d and Monte Carlo method

During the sensitivity analysis, it was concluded that K_d was necessary to achieve more representative simulations, and therefore, measured experimental K_d values were inputted to the model as stochastic values. The stochastic element allows the definition of a maximum and minimum partition coefficient value instead of a unique value, enabling the user to assess the uncertainty of the breakthrough curve outcomes. All previous simulations were deterministic and produced one single output, which was unlikely to be representative of the real environment. The

remaining inputs were conducted as described in section 3.2 and were added as 'data elements' (single values).

To assess the performance of the model, experimental breakthrough curves were plotted over time along with the maximum, mean and minimum breakthrough curves simulated by GoldSim for each IHE constituent in the sandy soils (**Figure 3.6)**. From these results, it was evident that the simulation of NTO and DNAN transport was significantly more representative of experimental values in sandy loam and sand when experimental K_d was included in the model. The inclusion of K_d reduced the simulated length of time of peak concentration outflow from a plateau equal in time to the contaminant influent, to a peak that much more closely resembled the experimental data. In particular, the addition of K_d for DNAN concentration in sandy loam soil was able to simulate the complete retention of DNAN within the experimental timeframe in three out of four cases.

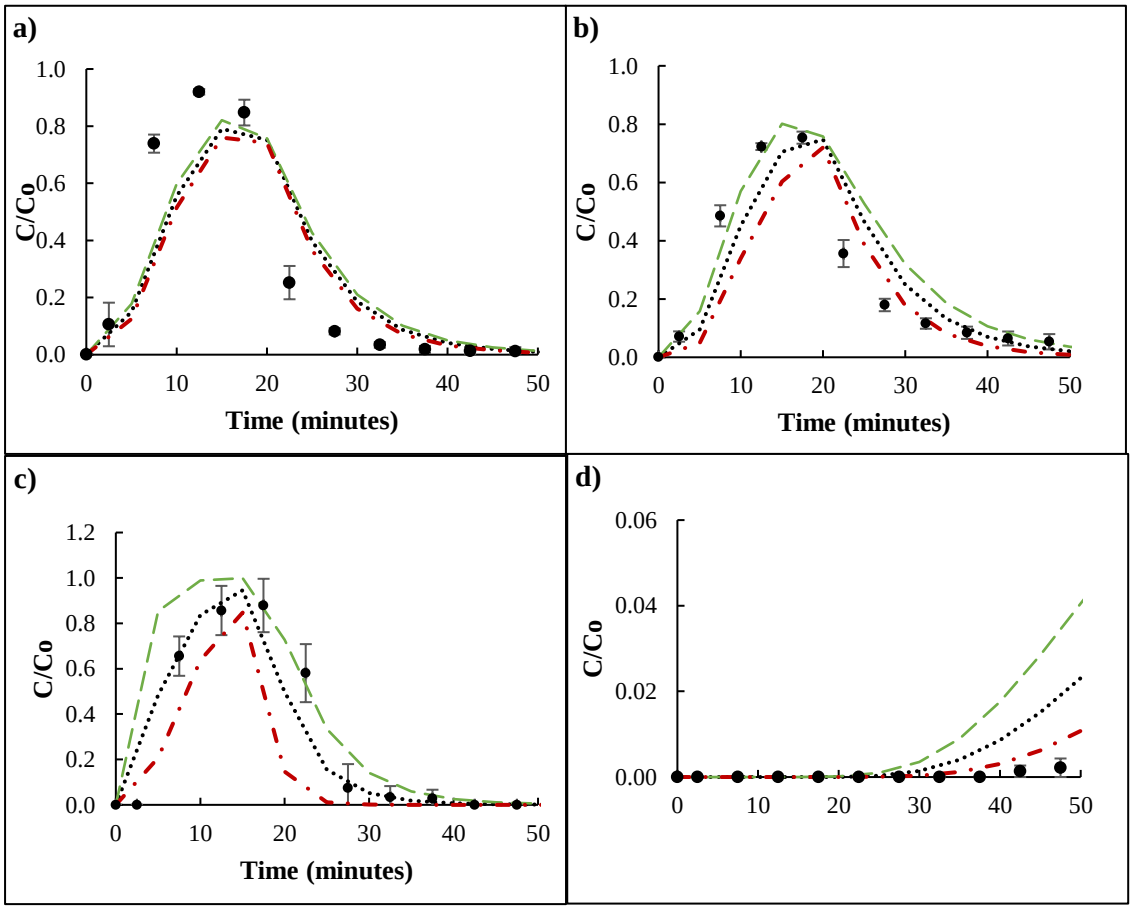


Figure 3. 6 Comparison between the GoldSim simulation, including Kd as a distribution element and 101 realizations using Monte Carlo, and laboratory experiment breakthrough curves for a) NTO in sand b) DNAN in sand c) NTO in sandy loam and d) DNAN in sandy loam. Dashed lines indicate the maximum (- - -), mean (…) and minimum (-.-.) breakthrough simulated in GoldSim, whereas dots indicate measured values from experimental soil columns.

Though similar, the simulation of NTO in sand did not compare as well to the experimental values as in other simulations. Experimentally, peak breakthrough concentration was between 10 and 15 minutes, similar to the simulations, which predicted a peak at 15 minutes. The maximum concentration was 90% of the initial experimentally compared to 87% in the model, which was within the margins of the experimental error. This could also be due to the absence of dispersion in the simulation, that might be influencing NTO transport through this soil type. For DNAN breakthrough concentration peaked at the same time as simulation (between 15 and 20 minutes and 15 minutes respectively) at 78% and 80% of the influent concentration. The addition of a variable K_d was clearly an improvement on the model as its simulations were more representative than those in section 3.2.

In sandy loam, NTO experimental concentration and time were within the simulated maximum and minimum breakthrough which suggested that the model could representatively simulate the behaviour of this constituent in soils with low organic content. DNAN K_{OC} was very high indicating strong adsorption to the soil, which explained why inclusion of experimentally derived K_d significantly improved simulation performance. Although the experimental breakthrough concentration was lower than the lower limit of the GoldSim estimated minimum breakthrough, DNAN concentrations reported were so low that the difference was marginal. These results corroborated the results of other studies in which DNAN was strongly sorbed to soils rich in organic matter (Linker et al., 2015; Olivares et al., 2016; Todde et al., 2018). This may be due to irreversible binding to quinones contained in the humic acids under aerobic conditions (Beck et al.,2018). In addition, DNAN has been reported to undergo reductive transformation to aromatic amines soil matrices (Kadoya et al., 2021). Another study reported that aromatic amines tend to covalently bind to carbonyl groups in natural organic matter through nucleophilic and possibly radical coupling reactions (Menezes et al., 2021). Although degradation processes have not yet been included in the model, it could explain the lack of experimental detection. However, due to the short timeframe of the soil columns it is unlikely that degradation is responsible for the observed retardation in this case.

The experimental K_ds for DNAN and NTO are significantly lower in the sandy soil, which explains the minimal interaction between these compounds and the organic

carbon content of the soil. In addition, preparation of the soil in the laboratory facilities (sieved, saturated and repacked) removed the natural structure of the sand, which might have modified the real bulk density and porosity that the soils initial had. This issue is notable in sandy loam, where the organic content was high, increasing K_{OC} and thus, interactions with contaminants particularly DNAN. If this parameter was included, it would potentially have further retarded the analytes in the studied soils. Further to this, while NTO and DNAN have been reported to adsorb to mineral surfaces such as birnesite or ferrihydrite (Khatiwada et al., 2018; Linker et al., 2015), this was not observed for NTO, as over 90% of this chemical was leached from the column in both sand and sandy loam. The sorption of DNAN to mineral surfaces might explain its absence in the experimental leachate in sandy loam, although if this process was governing the system, it would be expected to participate more in sand, as it has a higher mineral content than sandy loam. Therefore, although mineral complexation could be a key process on the IHE breakthrough in soil, the study revealed it was not necessary to include it distinctly from K_d in this model.

Overall, the simulations were significantly more representative of experimental results when K_d was included using the Monte Carlo method. Despite the short experimental timeframe (only 55 minutes in total), K_d is likely to be an essential parameter for simulating longer transport times as soil columns are dynamic systems in which the contaminant is in continuous movement, preventing equilibrium. For longer exposure experiments, inputs related to exposure time will need to be altered, although other parameters such as K_d should be similar unless there is a drastic variation in environmental conditions such as temperature. The same would happen with larger soil columns, in which the participation of processes such as horizontal transport or matrix diffusion zones and dispersivity may increase and would require modifications in the GoldSim model. K_d is, therefore, a key parameter for modelling DNAN and NTO transport in soils and to achieve representative results, it must be experimentally derived for the specific soil-contaminant matrix rather than estimated from literature.

3.4 Conclusion

With the increasing drive for replacement of legacy explosive fills with IHE, it is likely that DNAN and NTO filled munitions will progressively be used for training and defence purposes. Therefore, understanding the behaviour of these IHE in various environments prior to their extensive use is essential. The developed GoldSim transport model representatively simulated the transport of two key IHE components, DNAN and NTO, in two soil types using relatively few parameters. However, the model accounted for certain simplistic experimental conditions in order to study the transport of explosive material residues that might be less representative of real environments. In addition, the model does not include hydrodynamic dispersivity, a mechanism which might have improved the representativeness of the model outcome in comparison to the experimental results. Despite these limitations, the study proved that the model can be suitable to simulate the transport of dissolved explosive materials in sandy soils.

The sensitivity analysis concluded that that the K_d was particularly important for representative simulation and must be experimentally determined for the soil-contaminant system of interest. Although it is necessary to experimentally determine key parameters for the system of interest for the model to be representative, these values are far quicker to obtain than running long environmentally representative laboratory experiments. In addition, the use of stochastic modelling enabled the uncertainty inherent in environmental systems to be embedded in the simulation further increasing its representativeness. The next stage will be to continue increasing the complexity of the system by testing larger systems, mixtures of soil types, mixtures of contaminants and different exposure scenarios e.g., IHE leaching from a solid mixture. However, the GoldSim model developed is the first of its kind to representatively simulate the transport of DNAN and NTO in actual soils.

This study has meaningful applicability in the environmental management of IHE. First, the empirically determined soil and explosive physicochemical data can be used as inputs for models developed under similar conditions. For instance, K_d can be extrapolated to other studies with similar soil properties, avoiding the performance of tedious and time-consuming experiments. In addition, the outcome of the simulation can serve as a basis for other modellers to compare their simulations and

make more representative predictions. Further to this, explosive breakthrough curve in the sand and sandy loam columns can be used to validate the simulations and performed by other modellers, which will be less time consuming and more economic in future research. Nonetheless, the most important applicability of the study relies on the probabilistic simulations, which can assist decision makers to evaluate the risks posed by IHE in the soil and to develop efficient remediation strategies in contaminated areas by IHE.

CHAPTER 4. Simulation of the dissolution process of Insensitive High Explosive residues in rainwater.

ABSTRACT

The need for new munitions less sensitive to accidental detonation has increased the use of Insensitive High Explosives (IHE), which contain combinations of constituents such as 2,4-dinitroanisole (DNAN) and 5-nitro-1,2,4-triazol-3-one (NTO). These compounds have significantly different physicochemical properties compared to legacy explosives and currently there is a limited understanding of the environmental impact posed by their residues. As these residues are deposited in the soil after live-fire training activities, it is essential to determine how they dissolve and enter the soil before breaking through the soil matrix. Therefore, this work aimed to experimentally determine the dissolution rates of an IHE formulation when exposed to pH 5.0 and pH 6.5 rainwater and to representatively simulate the dissolution and mobility of IHE residues in two soil types. The dissolution rates were obtained by conducting dripping experiments at different water pH and temperature on IHE particles (30-60 mg), which found that NTO dissolution rate slowed down as the IHE particles decreased in mass, whereas DNAN dissolution remained constant over time. Specifically, NTO decreased from 170 ± 20 μg min^{-1} over the first 15 minutes to 48 ± 10 μg min^{-1} after 50 minutes, whereas DNAN dissolution rate was 18 ± 4 μg min^{-1}. These data were used to build a stochastic model to simulate dissolution of NTO and DNAN from IHE particles, which was able to simulate the concentration of IHE in soil column leachate over time successfully. Finally, a sensitivity analysis revealed that whereas dissolution rates controlled the mass entering the soil, it did not significantly regulate the mass breaking through the soil and leaching out of the soil columns.

4.1 Introduction

The need for safer munitions has driven the replacement of traditional explosive fills such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) with Insensitive High Explosives (IHE) (Walsh et al., 2014). This new generation contains chemical constituents such as 2,4-dinitroanisole (DNAN) and 5-nitro-1,2,4-triazol-3-one (NTO), which are less likely to be accidentally detonated. The use of IHE for military training purposes can deposit kilos of explosive per hectare after multiple detonations (Walsh et al., 2018), and due to their novelty, little is still known about the toxicity and persistence of their constituents in soil. This poses the challenge of how to assess the environmental impact posed by IHE residues in contaminated soils.

The first step to analyse environmental impact of IHE is by understanding how they behave after deposition. Once explosive residues are deposited into the soil, they tend to dissolve when exposed to rainfall and enter the soil matrix (Pichtel, 2012). This process is known as dissolution, and it is the first step to understanding explosive fate and transport in the environment as it indicates the concentration of a chemical that can break through soil (Dortch, 2018). In order to understand how IHEs enter the soil matrix, it is necessary to determine the kinetics behind their dissolution process. This is determined by the dissolution rate, which defines the speed at which an IHE particle dissolve in a specific solvent. It is dependent on the area of the solid exposed to the solvent and the characteristics of the solvent (temperature, pH and polarity) (Flowers et al., 2002).

The solubility of some IHE constituents has been investigated, as well as their transport through soils. For instance, NTO is highly soluble in water (12.8 g L^{-1}) and is also an acidic compound (pKa 3.76), which quickly dissolves during periods of rainfall and therefore may easily travel through unsaturated and saturated porous media (Richard and Weidhaas, 2014; Taylor et al., 2013). DNAN has moderate water solubility (278 mg L^{-1}) and its dissolution from IHE formulations has been reported to be slow (Taylor et al., 2015), tending to accumulate on the top layers of the soil (Temple et al., 2018). Finally, RDX,

which may also be included in some IHE formulations (Galante et al., 2021), has low water solubility (60 mg L^{-1}), which reduces ingress to the soil matrix (Pichtel, 2012). While new generation of explosives have chemicals, which have been qualified for use, their dissolution rates are not fully investigated, especially, when they dissolve as an IHE formulation.

In the literature, IHE dissolution rates have been experimentally obtained by performing dripping tests to mimic conditions on training ranges where spatially isolated explosive particles, scattered by partial detonations, are dissolved by rainfall (Dontsova et al., 2014; Taylor et al., 2015). The results indicated that the solubility of the individual constituents of IHE formulations differed by orders of magnitude, dissolving sequentially and in the order predicted by their solubility. However, these studies did not account for water temperature or pH, that can affect the dissolution of the IHE in the formulation (Lynch et al., 2001). In addition, the dripping tests were conducted with distilled water, which is clearly cleaner, ion free and not representative of rainwater. The determination of dissolution rates is an essential parameter used in computational modelling to study fate and transport as it quantifies the contaminant inflow rate in the soil system (Dortch, 2018). However, modelling these rates is challenging, as it is necessary to select the correct dissolution process and the required value for each variable supporting the model (Lynch et al., 2003). To that, stochastic simulations can help to simulate representative scenarios as they allow the study of the uncertainty associated to the system (GoldSim Technology Group LLC, 2021). However, simulating IHE dissolution rates poses additional challenges when modelling the fate and transport of explosive residues as a) there is a lack of empirical data for dissolution rates to be used in the simulations and b) not many computational models have been used for studying explosive transport in soil.

The aim of this study was to determine the dissolution rates of IHE constituents from a solid residue under different types of rainwater and to extend the GoldSim model developed in Chapter 3, by simulating the dissolution process of DNAN and NTO and their breakthrough in sandy soils. Further to this, the influence of DNAN and NTO dissolution rate on their breakthrough curves was

investigated in two sandy soils with different organic matter content and particle size distributions. As a result, this study sheds light on the environmental and physico-chemical factors that influence the dissolution process and provides a first data set that can aid in the environmental management and remediation of soils contaminated by IHE residues.

4.2 Material and methods

4.2.1 IHE formulation particles and solvents

An IHE formulation containing NTO, DNAN and RDX (53, 32 and 15% respectively) was already available at Cranfield University. Rainwater was collected over 6 months, filtered (Whatman, filter paper sheet grade 1) and stored in plastic bottles in the fridge (4°C). Initial rainwater pH was 6.5, which was higher than natural rainwater (pH 5.6). Hydrochloric acid (HCl) and acetonitrile were purchased from Sigma Aldrich, and ultra-pure water was obtained from Merck-Millipore.

4.2.2 Soils

Soils were purchased from a local building merchant (Swindon, UK). They were spread in trays and left drying form 7 days until constant weight. Then, they were sieved through a 2 mm sieve and bigger particles, sticks and stones were removed. A small sample of soil was taken to perform a physicochemical soil analysis (**Table 4.1**). Last, bulk density, porosity and NTO and DNAN soil water partition coefficients were experimentally measured (**Table 4.2**).

Table 4. 1 Chemical characterisation of sandy and sandy loam soils. Total Organic Content (TOC), Total Carbon and Nitrogen (TCN).

Soil	Description	TOC [a]	TCN (%) [b]		pH [c]	Electrical conductivity [c] (dS/cm)
			C	C/N		
Sand	UK Sand	0.09	1.35	135	9.5	93.6
Sandy loam	UK topsoil	12.65	12.92	22.7	7.2	55.6

[a] Determined by BS 7755-3.8:1995, ISO 10694:1995 Soil quality. [b] Determined by BS EN 16168:2012 Sludge, treated biowaste and soil. Determination of total nitrogen using dry combustion method. [c] Determined by Jenway pH and conductometer (1:5) soil: water.

Table 4. 2 Soil bulk density, soil porosity and soil water partition coefficient for NTO and DNAN in each soil

Soil	Bulk density (g cm^{-3})	Porosity (%)	NTO partition coefficient	DNAN partition coefficient (L kg^{-1})
Sand	1.93 ± 0.03	38 ± 1	0.33 ± 0.03	0.40 ± 0.08
Sandy loam	1.31 ± 0.14	45 ± 5	0.24 ± 0.17	9.3 ± 1.5

4.2.3 Dissolution drip tests of the IHE formulation

Three particles (30-60 mg each) of the IHE were placed in separated Pyrex Buchner funnels, held by a support stand and clamps (**Figure 4.1**). The particles were exposed to a continuous flow of water at 40 mL min^{-1} (Kramoer Dosing Pump, China) for 100 minutes, with a total volume of 4 L of rainwater to simulate rainfall. The water flow was directed onto the particles using a frame to keep the influent tube steady with a 1.5 radius, providing an accelerated. rainfall rate of 3395 mm h^{-1}. The rainwater had an initial pH 6.5 ± 0.1 and pH 5.0 rainwater was acidified with HCl 1M until pH 5.0 ± 0.1. Both types of rainwater were kept at 12°C, to reproduce the average rainfall temperature in UK (Kumar et al., 2017, Met Office website). Leachate was collected every 5 minutes during the first 50 minutes and every 10 minutes over another 50 minutes using 300 mL amber glass jars placed under the funnels. 2 mL aliquots were filtered through a 0.2 µm polyethylene terephthalate (PET) filters and stored at 4°C until analysis (within 2 days).

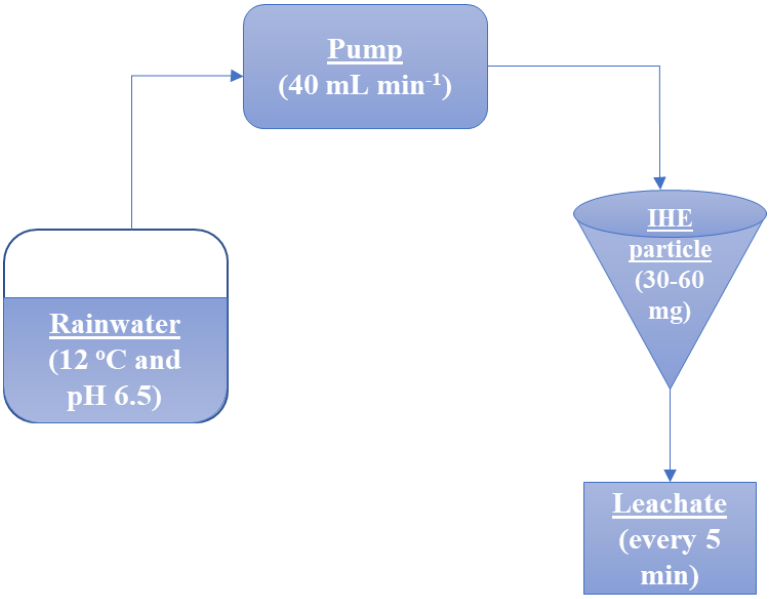


Figure 4. 1 Schematic illustration of the experimental setup for the study of the IHE formulation dissolution rate

The same experiment was conducted in triplicate with rainwater (pH 6.5) at 12°C and 20°C to use the results for the sensitivity analysis (section 4.2.7).

4.2.4 Soil column experiments

Three plastic columns (radius 5 cm x height 20 cm) were filled with air dried sand or sandy loam soil (2400 ± 5 g and 1159 ± 3 g, respectively) and gently compacted with a weight tool until no visible gaps were observed. The columns were saturated with distilled water (up to 1000 mL) and allowed to settle for one day. Five IHE particles with a total mass between 240 and 300 mg were placed on top of the soil columns in a 3D printed support (radius 1.5 cm) (**Figure 4.2**). The support was attached to first avoid the IHE particles direct contact with the soil matrix and to enclose the particles to ensure water was in constant contact with the explosive particle surface. A mesh was incorporated to the support to allow water and dissolved IHE compounds drop on top of the soil. Rainwater pH 6.5 at 12°C was pumped (Kramoer Dosing Pump, China) on top of the particle at a continuous flowrate of 40 mL min^{-1} for 300 minutes. Leachate coming out of the soil columns were collected every 20 minutes for the first 140 minutes and every 30 minutes after that. Samples were filtered with 0.2 µm polyethylene

terephthalate (PET) filters and stored at 4°C, until analysis. Analysis by HPLC was normally done within 2 days.



Figure 4. 2 Experimental set up of the construction of the soil columns and the 3D printer support (golden) containing the IHE particles

4.2.5 High Performance Liquid Chromatography with Diode Array Detector (HPLC-DAD)

HPLC was performed using a Waters-Alliance 2696 equipped with a Waters 996 photodiode array detector (USA). The analytes were separated on a ZORBAX Eclipse Plus C18 column (4.6 x 150 mm, i.d. 3.5 µm) from Agilent Technologies (Wilmington, DE, USA) maintained at 30°C. Samples were injected with a syringe loading injector fitted with 10 µL loop. Optimum chromatographic conditions were obtained with a linear gradient of 40% CAN (solvent A) and 60% water acidified 0.1% with formic acid (solvent B) with a flow rate of 1.5 mL min^{-1} The analytes were quantified via UV absorbance with optimum sensitivity detected at 296 nm for DNAN, 245 nm for RDX and 315 nm for NTO. Retention times were 1.01 minutes for NTO, 3.15 minutes for RDX and 4.96 minutes for DNAN (Temple et al., 2018). The calibration curve was

obtained by plotting the concentration against corresponding peak area for each analyte and both peak areas of samples and standards were determined by Empower 2 software (Waters). For this method, the limit of quantification (LOQ) was 0.42, 0.45 and 0.40 mg L^{-1} for NTO, DNAN and RDX. The limit of detection (LOD) was 0.04, 0.05 and 0.04 mg L^{-1} for NTO, DNAN and RDX respectively (Fawcett-Hirst et al., 2020).

4.2.6 Dissolution process in the stochastic simulation

The Contaminant Transport Module in GoldSim version 14.0 (GoldSim Technology Group LLC, 2021) was used to simulate IHE dissolution and transport in soil over time. The properties of the water and explosive constituents were defined using the 'Material' element which includes molecular mass and solubility of NTO and DNAN in water. Then, the soil media was defined by adding the soil water partition coefficient, soil bulk density and soil porosity experimentally obtained previously in Chapter 3 (**Table 4.3**).

For the dissolution process, initial parameters of the formulation such as percentage of explosive chemicals and initial mass were specified and linked using the Data and Expression elements. Individual dissolution rates were added as a Stochastic element with their respective standard deviation and linked to the system with a 'Selector' element that allowed the definition of the specific dissolution rate for each compound over time. The addition of the dissolution rates was inputted in the model following a zero order kinetic equation (**Equation 4.1**) with some modifications over time.

$$\frac{dm}{dt} = m_o - k * t \qquad \textbf{(Equation 4. 1)}$$

where *dm/dt* is the mass difference over time, m_o is the initial mass (mg), *k* is the dissolution rate (mg min^{-1}) and *t* is time (min).

The dissolution rate of DNAN was defined constant over time and the dissolution rate of NTO was variable, taking three different values over time. RDX was not included in the model as its persistence in the environment has been fully understood (Beck et al., 2018; Brannon et al., 2005; Fuller et al., 2012) and its percentage in the IHE particle was minimal, which hampered its

detection and comparison by analytical methods. The dissolution constants for IHE constituent were normalised according to the IHE initial mass.

Table 4. 3 Model parameters used in GoldSim to simulate the transport of NTO and DNAN in sand and sandy loam soils. All the inputted data was experimentally measured to replicate experimental conditions.

Section	Parameter	Value	Type
Column dimensions	Height Radius	20 cm 5 cm	Deterministic
IHE particle	Initial mass % NTO % DNAN	270 mg 53% 32%	Deterministic
Sand properties	Density Porosity Kd (NTO) Kd (DNAN)	1.93 g cm^{-3} 38 % 0.33 ± 0.03 L kg^{-1} 0.40 ± 0.08 L kg^{-1}	Deterministic Deterministic Stochastic Stochastic
Sandy loam properties	Density Porosity Kd (NTO) Kd (DNAN)	1.31 g cm^{-3} 45 % 0.24 ± 0.17 L kg^{-1} 9.3 ± 1.5 L kg^{-1}	Deterministic Deterministic Stochastic Stochastic
Water flux	Inflow / Outflow	40 ml min^{-1}	Deterministic
Dissolution rate in rainwater (pH 6.5)	NTO (0-15min) NTO (15-50 min) NTO (50-300 min) DNAN	170 ± 10 µg min^{-1} 70 ± 20 µg min^{-1} 50 ± 15 µg min^{-1} 18 ± 4 µg min^{-1}	Stochastic (uniform distribution)
Simulation settings	Simulation time Simulation sampling Realisations	300 minutes 20 minutes 101 realisations	-

For the transport process, a Pipe Pathway element was defined along with the main dimensions of the soil columns. The column element was linked to the soil and compounds were introduced at the specific rate over time described in the previous paragraph. The column was attached to a Cell Pathway that simulated the leachate coming out of the system. The Contaminant Transport Module used one dimensional advection dispersion equations to simulate the breakthrough of the contaminants in soil (Lee and Hwang, 2009; Pulkkanen and Nordman, 2010) and the flux of each compound leaving the column was

represented as function of time. Finally, a Result element was defined to show the IHE mass in the leachate over time.

In order to factor in the uncertainty caused by the impact of environmental conditions to the results, the Monte Carlo method was used. This method enables the sampling of stochastic elements in order to carry out probabilistic simulations. The model was run for 101 iterations, (as explained in Chapter 3) each of which generated a different output as different dissolution rates were sampled in each iteration.

4.2.7 Sensitivity analysis

A sensitivity analysis in an environmental model is commonly performed to assess the effect that different parameters have on the output (Jackson, Trebitz and Cottingham, 2000). This type of analysis was performed on the model to show how different dissolution rates affected the breakthrough curve of the IHE constituents in the sand and sandy loam. To do so, a similar experiment as described in section 4.2.3 was performed but this time, using a) rainwater at 12°C and 20°C (maintaining a constant pH 6.5) and b) rainwater at pH 5.0 and 6.5 (maintaining a constant temperature of 12°C) (**Table 4.4**). The remaining inputted data displayed in section 4.2.6 remained invariable to assess to what extent, the dissolution rates would determine the IHE breakthrough in each soil and mass in found in the soil column. Therefore, the inputted data for the analysis was the different dissolution rates experimentally obtained for NTO and DNAN when the IHE particles were dissolved under different a) rainwater temperature and b) at different water pH and the outputted data was the concentration found leached out of the soil column. In this case, the variable data were inputted as deterministic elements as the aim was to compare average concentration in the leachate. Further to this, no formulas or other elements in the model were altered neither the simulating settings described in section 4.2.6.

Table 4. 4 Experimental dissolution rates for DNAN and NTO measured at different rainwater pH and temperature and used in the sensitivity analysis

Scenario	Variable	Constituent (and period)	Dissolution rate (inputted value)
1 Constant pH (6.5)	Temperature (12°C)	NTO (0-15min) NTO (15-50 min) NTO (50-300 min) DNAN (0-300 min)	170 µg min^{-1} 70 µg min^{-1} 50 µg min^{-1} 18 µg min^{-1}
	Temperature (20°C)	NTO (0-15min) NTO (15-50 min) NTO (50-300 min) DNAN (0-300 min)	264 µg min^{-1} 105 µg min^{-1} 57 µg min^{-1} 44 µg min^{-1}
2 Constant temperature (12°C)	pH 5.0	NTO (0-15min) NTO (15-50 min) NTO (50-300 min) DNAN (0-300 min)	143 µg min^{-1} 72 µg min^{-1} 45 µg min^{-1} 6.3 µg min^{-1}
	pH 6.5	NTO (0-15min) NTO (15-50 min) NTO (50-300 min) DNAN (0-300 min)	170 µg min^{-1} 70 µg min^{-1} 50 µg min^{-1} 18 µg min^{-1}

4.3 Results and discussion

4.3.1 Effect of water pH on the dissolution curves for DNAN, NTO and RDX in an IHE formulation

In order to provide insight on how IHE constituents dissolve when they are in a formulation, dripping tests were performed on small 30-60 mg IHE particles using rainwater at pH 6.5 and 5.0. The reason why these pHs were chosen was to assess differences on IHE dissolution between 6.5 and slight acid rainwater (5.0), two possible pH that are commonly found in rainwater in the environment (USEPA, https://www.epa.gov/acidrain/what-acid-rain). Initial rainwater pH was 6.5, which was higher than natural rainwater (pH 5.6). Typically, rainwater is acidic as it interacts with the environmental carbon dioxide and produces carbonic $acid^{-}$, which lowers the dissolution pH up to 5.6. For that comparison, cumulative dissolved mass of each constituent in the IHE formulation was plotted over time to compare the influence of the rainwater pH on the dissolution of the constituents (**Figure 4.3**).

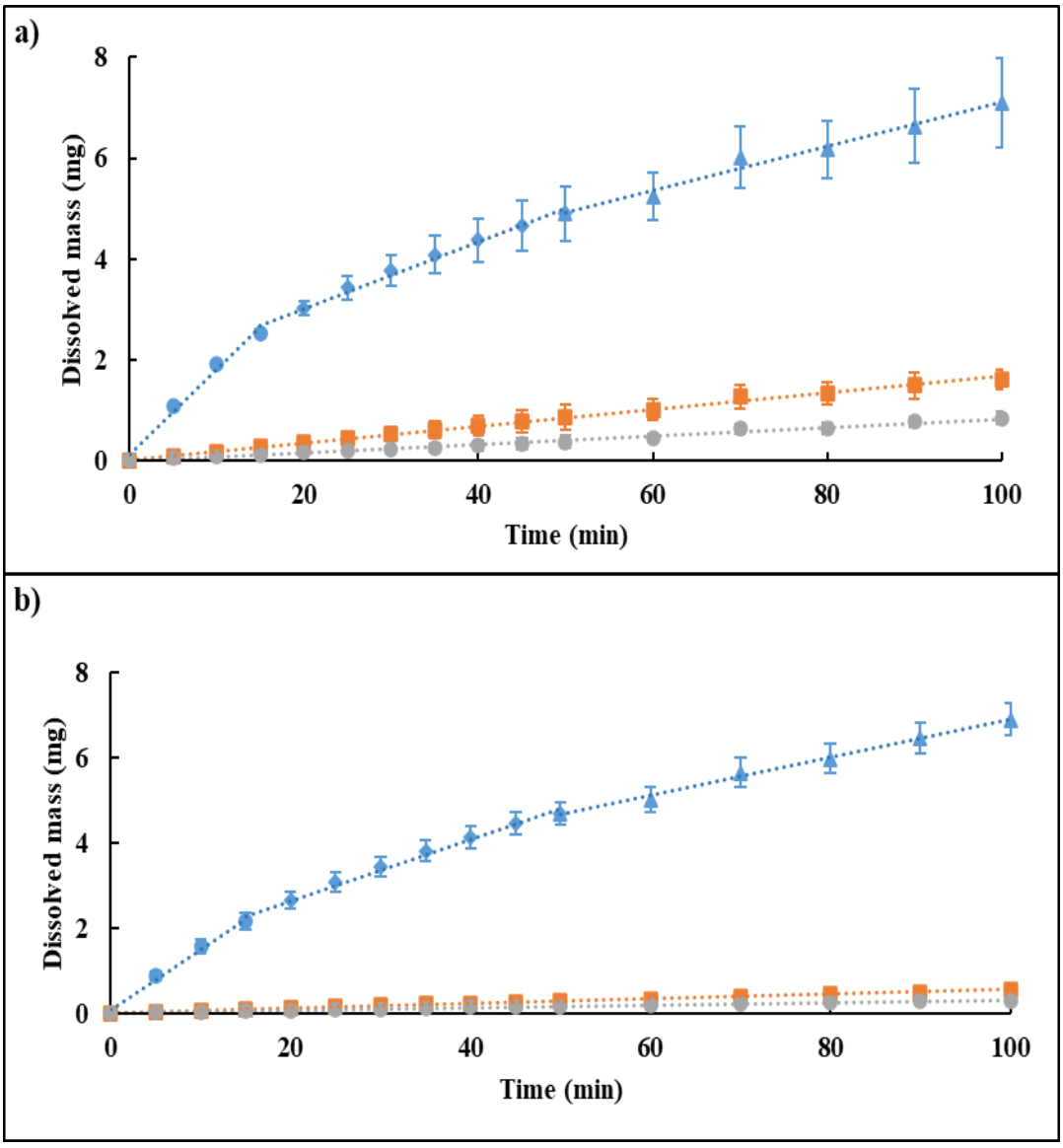


Figure 4. 3 Dissolution curves of NTO (blue), DNAN (orange) and RDX (grey) in a explosive formulation at 12°C using a) rainwater pH 6.5 and b) rainwater pH 5.0.

Over the course of the experiment, the IHE particles lost their characteristic yellow colour and showed tiny pores on the surface. This indicated that NTO, the main constituent which gives this characteristic colour, was rapidly dissolving from the IHE particle. Conversely, most of the DNAN, which is used as an energetic binder for melt cast formulations due to its low melting temperature (95°C) (Davies and Provatas, 2006), remained in the IHE matrix along with the RDX. The fact that NTO was rapidly dissolved at the beginning whereas DNAN and RDX remained in the formulation, suggested that the

constituents in the IHE formulation dissolved sequentially and in the order predicted by their solubility (Dontsova et al., 2014; Taylor et al., 2015).

In both scenarios, NTO dissolution rate slowed when the IHE particles shrank, demonstrating that its dissolution was not constant over time. However, NTO dissolution had a similar behaviour when it was dissolved in both types of water, suggesting that NTO dissolution does not change with minor changes in pH (5.0 and 6.5). This was unexpected, as some previous studies have pointed out that NTO solubility was up to 100 times higher at acidic pH (Tennant et al., 2019). In the case of DNAN and RDX, their dissolution showed linearity over time, and they dissolved significantly slower than NTO most likely due to the 45 and 210 times respectively higher solubility of NTO in water. DNAN and RDX dissolved concentrations were twice higher over time in rainwater than in acidic rainwater, which was unexpected as neither DNAN nor RDX has an acidic isomer. One possible explanation was that the acidification of the rainwater with HCl affected the rate of DNAN and RDX due to a salting out effect (Gorgenyi et al., 2006; Turner and Rawling, 2001). This effect explains that water solubility of organic compounds usually decreases in the presence of inorganic salts, as a competition between the ions of the salt and the organic compounds for available water molecules is created. This effect might not be very impactful in NTO due to its high water solubility, but it may influence the dissolution of DNAN and RDX, as their solubilities in water are considered medium and low respectively (Boddu et al., 2008).

After 100 minutes, the dissolved IHE mass in rainwater (27% ± 1%) and acid rainwater (23% ± 1%) showed little difference. The percentages were surprisingly low for a formulation that contained 53% of NTO, although it can be explained as over its synthesis, DNAN (the binder) is firstly melted before adding the other constituents as powder. This makes the binder coat NTO and RDX in the matrix, creating a homogeneous formulation (Frem, 2022). This, along with the shape of the dissolution curves, suggests the NTO available on the top layer of the IHE particle undergoes a rapid dissolution. However, once this first layer its dissolved, the remaining NTO in the IHE particle is regulated by the presence of DNAN and RDX.

4.3.2 Determination of dissolution rates

The dissolution rates of the IHE constituents were estimated from the dissolution curves plotted in the previous section to quantify how much mass was dissolved over time. Typically, the contaminant dissolution follows the Noyes- Whitney equation (**Equation 4.2**) and it is usually integrated under specific terms that provide a first order equation (Hattori, Haruna and Otsuka, 2013).

$$\frac{dm}{dt} = A * \frac{D}{d} * (C_s - C_b) \qquad \textbf{(Equation 4. 2)}$$

where *dm/dt* is the dissolution rate (kg s^{-1}); *A* is the contact area (m^2), *D* is the diffusion coefficient which is related to the viscosity of the solvent (m^2 s^{-1}), *d* is the thickness of the concentration gradient (m); C_s is the solute surface maximum concentration (solubility) (kg m^{-3}) and C_b is the concentration of solute in the bulk solvent solution (kg m^{-3}).

Among the IHE constituents studied, only NTO showed a behaviour that could be described by a first order equation. Conversely, DNAN and RDX dissolution was constant over time (zero order) and thus, their dissolution rates could not be assumed to follow this type of equation. In addition, as the dissolution rates were used firstly to compare how the IHE dissolved and secondly, as inputs in the model to simulate IHE dissolution, it was necessary to calculate these rates in a way that could be easily understood and simulated. Thus, dissolution rates of each IHE compound were determined experimentally using the already mentioned **Equation 4.1** and calculating the slope of the cumulative dissolved mass over time. As NTO dissolution rate was not constant over time, it was decided to estimate different rates over different periods of time, as done in other studies (Morley et al., 2006) (**Table 4.5**). NTO experimental dissolution rates were similar in both rainwaters, being only 20% higher in acid rainwater (pH 5.0) over the first 15 minutes in comparison to neural rainwater (pH 6.5). However, differences were more remarkable in DNAN and RDX, whose dissolution rate was three and two times higher in unacidified rainwater than in acid rainwater respectively.

Once the dripping test was finished and results were compared, dissolution rates obtained with unacidified rainwater were selected for the modelling, as that type of rain is more similar to actual rainfall in the area the experiment was conducted. To obtain more information about the dissolution rate, the same IHE particles continued being dissolved in unacidified rainwater for another 120 minutes. Dissolution rates decreased slightly reaching a constant rate 40 ± 10 µg min^{-1} for NTO, 13 ± 5 µg min^{-1} for DNAN and 7 ± 3 µg min^{-1} for RDX. On this second part of the dripping test, 44% of the total IHE formulation particle weight was dissolved, finding in the leachate 59% of the NTO, 27% of the DNAN and only 23% of the RDX. The dissolution rates were assumed constant over time and were used as inputs in the stochastic simulation developed in the next section.

Table 4. 5 Experimental dissolution rates of NTO, DNAN and RDX over time (µg min-1) obtained with rainwater at pH 6.5 and acid rainwater at pH 5.0 at 12°C

		Dissolution rate (µg min^{-1})	
Compound	**Time (min)**	**Rainwater**	**Acid rainwater**
NTO	0 - 15	170 ± 10	140 ± 30
	15 - 50	70 ± 20	72 ± 8
	50 - 100	50 ± 15	45 ± 6
DNAN	0 - 100	18 ± 4	6 ± 1
RDX	0 – 100	8 ± 4	3 ± 1

4.3.3 Comparison of simulated and experimental dissolution and transport of IHE particles in soils

A computational model was developed in GoldSim using soil and compound key physicochemical parameters as well as the dissolution rates obtained from the dripping tests. The values were inputted as stochastic elements, which allowed the calculation of the maximum and minimum concentrations expected to be found in the soil and leachate. In order to assess the performance of the model, a longer and larger dimension-scale experiment was performed by

placing solid IHE formulations on top of columns filled with two different soils and irrigating the particles with rainwater at 40 mL min^{-1} over 300 minutes.

Simulated and experimental NTO and DNAN concentrations measured in the leachate coming out of the sand and sandy loam columns were plotted over time (**Figure 4.4**). To simulate dissolution of five IHE particles, some correction factors were needed to be applied to the model. NTO and DNAN dissolution rates over the first 100 minutes needed to be normalised by multiplying them by the ratio between the mass used for dripping tests (45 mg in average) and the mass used for the soil column experiments (280 mg in average). Although the addition of the dissolution rates by this method worked for the simulation, it might need further mass normalisation, for instance, 1 kg. Ultimately, except for DNAN breakthrough in sandy loam, the stochastic simulation successfully modelled NTO and DNAN dissolution and transport through soil in combination.

NTO in sand dissolved rapidly over the first 100 minutes reaching a maximum concentration between 15 and 25 mg L^{-1} at 40 minutes. The experimental concentration was between the maximum and the minimum simulated by the model, highlighting the variability in the concentration due to the stochastic nature of the simulation. Simulated NTO concentration also matched the experimental one over time, indicating that the soil parameters controlling NTO transport through the soil were representative enough for the simulation. Both the simulated and the experimental concentrations reached their minimum values (between 3 and 5 mg L^{-1}) after 150 minutes, as expected from the dissolution rates obtained in section 3.2. In contrast, DNAN breakthrough did not reach a maximum value. Instead, it remained steady between 0.4 and 1.4 mg L^{-1}. This model behaviour is mainly due to the constant dissolution rate assumed in the model and the interaction of DNAN with the inorganic and organic particles present in soils (Hawari et al., 2015). Even though this sand soil only contained 2.3% of organic matter content, the inorganic minerals have been reported to affect electrostatic or covalent bonding in the aromatic compounds, containing charged or polar functionalities which are sufficient to irreversibly adsorb DNAN to the sand (Linker et al., 2015).

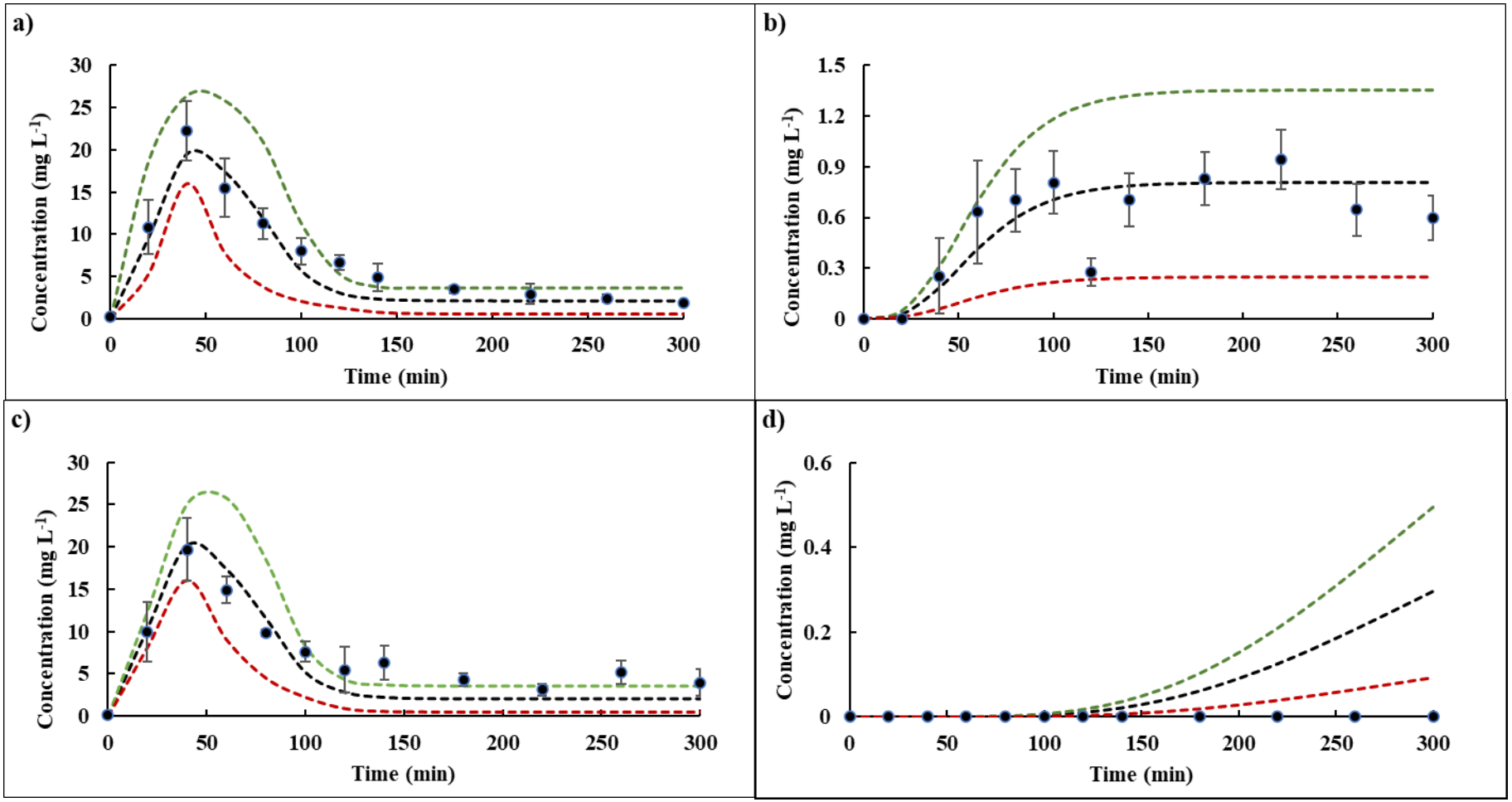


Figure 4. 4 Experimental and simulated breakthrough of a) NTO in sand b) DNAN in sand c) NTO in sandy loam and d) DNAN in sandy loam. Dashed lines indicate the maximum (- - -), mean (- - -) and minimum (- - -) breakthrough simulated in GoldSim, whereas dots indicate measured values from experimental soil columns.

In sandy loam, experimental NTO breakthrough reached a maximum concentration between 15 and 27 mg L^{-1} after 50 minutes, although in this case NTO needed more time to travel along the sandy soil than in sand. As the NTO dissolution rates are the same for both soils, this retention was justified by its 20% higher soil water partition coefficient (K_d) compared with the sandy soil. Conversely, simulated DNAN breakthrough was not representative of the experimental one, DNAN was not detected in the leachate coming out of the soil column over the 300 minutes the experiment took place. A possible explanation is that experimental concentrations were below the limit of detection by HPLC for DNAN (less than 0.5 mg L^{-1}) (Fawcett-Hirst et al., 2020).

The stochastic simulation of dissolution and transport of IHE compounds in soil allowed a better understanding of how these two processes worked together. Dissolution rates controlled the amount of IHE residues that enter the soil system over time, whereas the K_d, along with the dispersion and diffusion equations, regulated the velocity that contaminants travelled with along the 20 cm of soil. The stochastic simulation also enabled the assessment of the maximum and minimum concentration limits expected for each compound considering the initial mass of the IHE formulation and the dissolution flow rate.

However, the model did not account for degradation and/or biodegradation, which is an important process that has been reported to occur simultaneously for DNAN in soils rich in organic matter (Perreault et al., 2012; Temple et al., 2018). Although it is very unlikely that DNAN degraded that fast in only 300 minutes, the absence of this compound in the leachate highlighted that the assumption that degradation did not occur so rapidly might not be accurate. Another explanation could be an irreversibly adsorption process of DNAN to the organic matter, as a consequence of their highly strong bonding to organic substrates (Fuller et al., 2021). DNAN K_d in sandy loam was obtained in equilibrium, and it might not be representative enough for dynamic scenarios. To overcome this imitation, it would be really useful to replace in those cases K_d by other partition coefficients that include percentage of organic matter such as organic carbon water partition coefficient (K_{OC}) (Bronner and Goss, 2011; Jarvis, 2016). Thus, there are still open questions about which parameters can

achieve representative simulations in complex scenarios, in which degradation and strong adsorption are big factors when modelling IHE fate and transport.

4.3.4 Sensitivity analysis using water at different pH and temperature

A sensitivity analysis was performed in GoldSim to gain further insights into how the IHE dissolution rates were affected by the rainwater pH and temperature and how they regulated the concentrations released of NTO and DNAN released to the soil system. To that, concentration leached out of the column was plotted over time by using empirical dissolution data determined at variable pH (**Figure 4.5**) and temperatures (**Figure 4.6**), while other relevant transport inputs remained unchanged (i.e., soil parameters and physico-chemical properties)

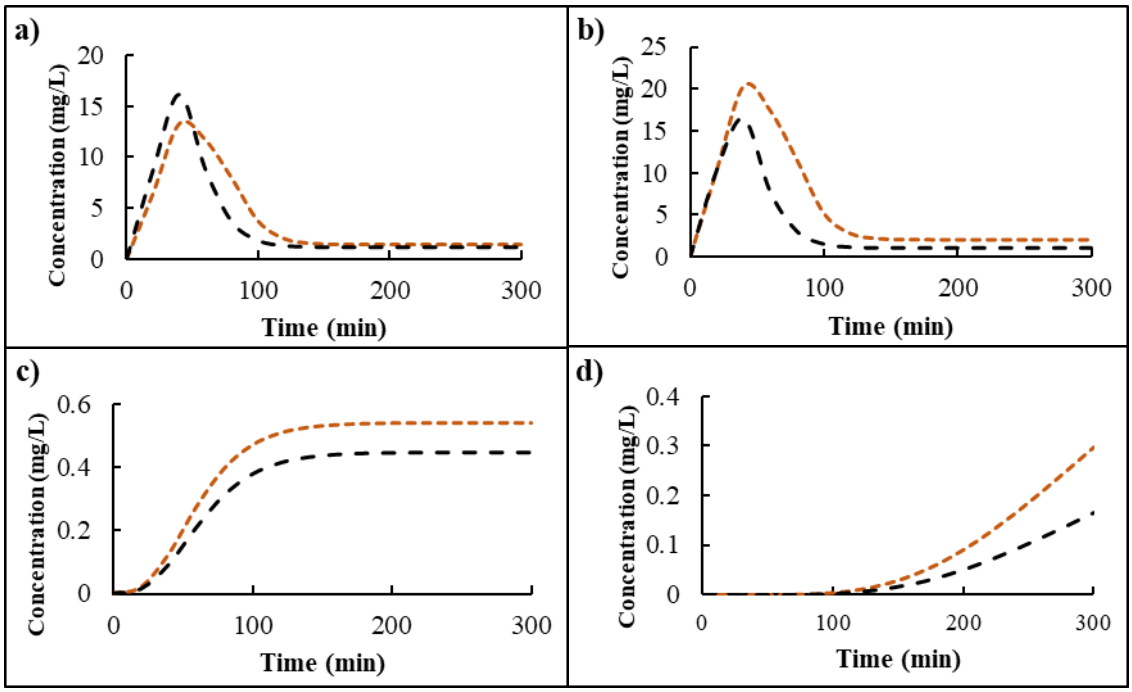


Figure 4. 5 Sensitivity analysis of NTO breakthrough in a) sand and b) sandy loam; and DNAN breakthrough in c) sand and d) sandy loam using rainwater at pH 5.0 (brown dotted line) and pH 6.5 (black dotted line).

Overall, the sensitivity analysis for pH (**Figure 4.5**) showed that the NTO and DNAN breakthrough were very similar in both sand and sandy soils. This phenomenum was was expected for NTO as the dissolution rates were similar, but unexpected for DNAN, as it dissolved three times slower at pH 5.0 than at pH 6.5. However, the inputted DNAN disolution rates had the same order of magnitude and this, along with

the high interaction with the soils showed ittle difference in the overall brekathough and concentration in the leachate. Thus, at these pH, NTO concentration in sand and sandy loam was between 13 and 23 mg L^{-1}, whereas DNAN concnetration was below 0.5 mg L^{-1}. Thus, the IHE concentrations simulated in the analysis were very similar in both soils and at both water pH.

The sensitivity analysis (**Figure 4.6**) showed how the IHE dissolution rates (affected by the water temperature) influenced the IHE breakthrough and peak concentrations in the soils. For NTO, the maximum concentration was 30% higher at 20°C than at 12°C. This phenomenon ocurred in both sand and sandy loam, although NTO travelled equally fast through both soils mainly due to the low K_d and low adsorption to the soils (Mark et al., 2016). In the case of DNAN, the dissoluton rate was 3 times higher when using water at 20°C than at 12°C in sand. However, due to the slow movement of DNAN through the sandy loam soil, the simulated maximum concentration did not differ significantly from the sandy loam.

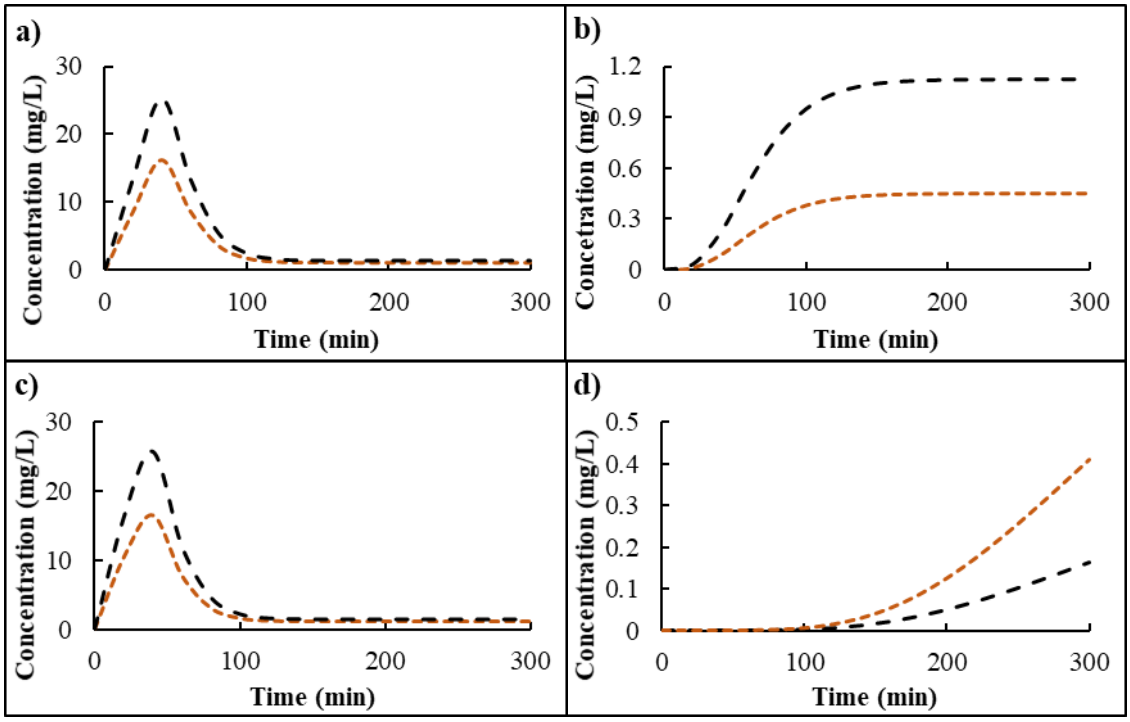


Figure 4. 6 Sensitivity analysis of NTO breakthrough in a) sand and c) sandy loam; and DNAN breakthrough in b) sand and d) sandy loam using rainwater at 12°C (brown dotted line) and 20°C (black dotted line).

4.4 Conclusions and recommendations

The dissolution rates of DNAN and NTO in an IHE formulation were experimentally determined to investigate the rate at which post detonation solid residues dissolve in the soil matrix. The rates increased when using higher water temperature and decreased with higher water pH, except for NTO which remained unaffected. After dissolving the first layer of NTO in the particle, NTO dissolution was regulated by the dissolution rate of DNAN (binder) and NTO availability on the particle surface. This phenomenon showed the dependency of the constituents inside the formulation on the rate of dissolution of the outer layers, which limited NTO dissolution over time, resulting in requiring four different rates to describe dissolution.

The stochastic dissolution model was combined with the soil transport model already developed, to produce a simulation of the dissolution and transport through sandy soils of DNAN and NTO from an IHE formulation. The simulations showed that NTO has a fast dissolution rate in soil, meaning than NTO can easily spread through the environment aquatic pathways and potentially reach further receptors. However, DNAN dissolved slower and remained in the soil for longer periods, boosting its acummulation in land contaminated by IHE and potentially affecting receptors in the soil. As a recommendation, it would be interesting to determine whether DNAN remains adsorbed to the soil or degrades into toxic metabolites, as these mechanisms might influence concentrations of DNAN reaching receptors.

Whilst the developed model successfully (R = 0.91 - 0.95) simulated the dissolution of DNAN and NTO in an IHE formulation, the modelling of the dissolution rates could be further developed, for instance by introducing a first order equation which may describe how the IHE constituents disolve more representaively. It could then be used to simulate the fate and transport of IHE in larger systems loaded with higher massess of explosive residues, where it is not practical to specify different dissolution rates for different time intervals. In addition, the model will require validation over longer periods of time in order to make reliable predictions that can inform the long-term assessment of the risks posed by IHE formulations. It is hoped this model will provide a baseline to assist with decisions on the appropriate use and disposal of new generation insensitive munitions containing IHE formulations, in

particular enabling estimation of likely concentrations in soil to ensure they remain below harmful levels.

CHAPTER 5. Determination of the influence of temperature on the degradation of Insensitive High Explosive residues

ABSTRACT

Insensitive High Explosives (IHE) are of interest to replace traditional explosive fills as they are safer to manipulate and store. Due to their novelty, little is known about the persistence of IHE residues in soil, and there are concerns around the toxicity of some IHE degradation products. In this study, the degradation of an IHE formulation comprised of 53% 5-nitro-1,2,4-triazol-3-one (NTO), 32% 2,4-dinitroanisole (DNAN) and 15% hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) was investigated in two sandy soils with different particle size distributions (sand and sandy loam) and organic matter content (0.92% and 12.7% respectively). Firstly, the influence of abiotic and biotic processes on the IHE mass loss in soil was investigated in soil batch tests to understand how the constituents degraded and the contribution of biodegradation to the total degradation process. In sand and sandy loam, 9% and 11% respectively of the IHE initial mass was biodegraded over two months. Among the three IHE constituents, NTO was the most sensitive to biodegradation whereas DNAN was only biodegraded in the sandy soil and RDX did not undergo significant biodegradation. Secondly, the influence of soil temperature was assessed on the degradation of IHE mass, which showed lower percentages of IHE mass loss in soils stored at 4°C and 12°C than at 20°C. The half-life of the IHE chemicals showed that they degraded between 2 and 4 times slower at 4°C compared to 20°C for both sandy soils. The estimated half-lives showed that these chemicals can persist in the soil between 40 days and 2 years, depending on the soil type and temperature. Next, activation energy for degradation was derived by fitting the Arrhenius equation to individual IHE concentrations, showing values between 44 and 62 kJ mol^{-1}. This study is the first to report the kinetic mechanisms behind the degradation of an IHE formulation as a function of temperature, providing meaningful data that can be used to assess the persistence of IHE residues from polar to tropical regions.

5.1 Introduction

The need for new explosive formulations that are less sensitive to accidental detonation has driven the replacement of traditional explosive fills with Insensitive High Explosive (IHE) fills containing mixtures of chemical constituents. Over the years, IHE have been used for military purposes, depositing residues in the environment that can negatively impact the soil and groundwater biosphere. Recent studies have shown that a single blow-in-place detonation or partial detonation can deposit substantial explosive residues in the environment (Hewitt et al., 2005; Walsh et al., 2017). In addition, even so named 'full-order' detonations deposit several milligrams per m^2 of explosive residues after each detonation (Persico et al., 2022). Whilst this may seem insignificant, residues can rapidly accumulate over time where thousands of rounds may be used during routine military training (Galante et al., 2017). This fact along with improper management and disposal practices of explosive formulations and munitions have led to soil contamination by both energetic materials and their by-products to levels that threaten human health, livestock and ecosystems (Pichtel, 2012). Thus, IHE accumulation in the environment (especially in soil and water) must be managed and, ideally, minimized.

One of the most promising IHE fills includes 5-nitro-1,2,4-triazol-3-one (NTO) and 2,4-dinitroanisole (DNAN), which are used in combination with the more traditional explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). NTO is a thermally stable explosive constituent with similar performance to RDX. Among its chemical properties, NTO has been reported to be highly soluble in water and toxic to small animals (Crouse, Lent and Leach, 2015; Reddy et al., 2011). In addition, NTO degrades to 3-amino-1,2,4-triazol-5-one (ATO) via 3- hydroxylamino-1,2,4-triazol-5-one (HTO) under anaerobic conditions and to nitrogen ions (NO_2^- and NO_3^-) under aerobic conditions by soil bacteria colonies (Krzmarzick et al., 2015). DNAN is used as an energetic binder for melt cast formulations due to its low melting temperature (95°C), and in the environment has been shown to undergo degradation to more toxic constituents such as 2-amino-4-nitroanisole (2-ANAN), 4-amino-2-nitroanisole (4-ANAN), 2,4-diaminoanisole (DAAN), 2-methoxy-5-nitroaniline (MENA) and 2,4-dinitrophenol (DNP) (Indest et al., 2017; Qin et al., 2021; Temple and Ladyman, 2019). Finally, while the environmental fate and degradation of RDX has been

extensively investigated, little has been studied in combination with other IHE constituents. RDX is known to be relatively stable to biodegradation, though will degrade to the mono- di and tri- nitroso degradation products (MNX, DNX and TNX respectively) over long periods of time. However, due to its stability it is more likely to accumulate in plant leaves and migrate to ground water, and its exposure over long time periods has been reported to be toxic for humans and animals (Harvey et al., 1991; Kaplan et al., 1965; Lotufo et al., 2015). Due to its novelty, little has been investigated about this IHE formulation and this raises the challenge on how its residues degrade in the soil.

To date, most biodegradation studies have focused on aerobic bioaugmentation strategies in which specific bacterial stains that can efficiently degrade explosive residues were used (Karthikeyan and Spain, 2016; Khan et al., 2013; Perreault et al., 2012). Examples of this include bacterial colonies that contain nitroreductase enzymes specifically to degrade NTO (Fuller et al., 2021) and demethylase for DNAN biotransformation into 2-ANAN and 4-ANAN (Fida et al., 2014). In contrast, there have been fewer investigations into biodegradation of IHE under anaerobic conditions, although DNAN biodegradation has been studied in bed reactors with bacteria and ethanol as electron acceptor (Arnett, Rodriguez and Maloney, 2009; Platten et al., 2010). Degradation of IHE residues has also been reported to occur under chemical and physical factors such as UV light (photodegradation) in which the DNAN main degradation pathways were o-demethylation, denitration and nitro reduction resulting in degradation products with greater environmental toxicity (Kennedy et al., 2017; Yang et al., 2018).

An important factor that influences the degradation of contaminants in soil is temperature. For instance, a study revealed that NTO degraded 30% faster in soils at 30°C than at 21°C, (Madeira et al., 2019b). These studies can be useful for assessing the impact of IHE in soils of Mediterranean and Oceanic climates. However, little has been described about IHE behaviour in cold regions such as the United States, Norway and Canada, where military organizations and researchers regularly undertake live fire training that deposits IHE residues to the soil (Ladyman, Mai and Temple, 2017). In addition, there is a lack of information about the kinetics that drive IHE degradation processes, and no studies have investigated degradation

of IHE formulations at such low temperatures, as studies have focused on investigating each component individually. This raises the question of what the real impact of IHE residues in soils is in cold regions.

The aim of this study was to provide insight into the mechanistic understanding of how IHE constituents degrade when in a formulation in two different soil types in varying climates. To achieve this, the degradation of IHE constituents was investigated in two sandy soils a) to study the influence of particle size distribution, organic matter content and the contribution of biotic and abiotic degradation processes and b) to study the influence of low temperatures. This is the first study that investigates the effect of low soil temperature on the degradation of a IHE formulation and will provide insight on the environmental risk posed by explosive formulations in cold climates.

5.2 Materials and methods

5.2.1 Soil characteristics, IHE solution and solvents

Acetonitrile was purchased from Merck, Germany, and high purity water prepared using the Millipore Milli Q plus purification system (18.2 MΩ.cm at 25 °C) was used for all experiments. The solid IHE formulation containing 53% NTO, 32% DNAN and 15% RDX (w/w) was obtained from BAE systems.

Stock solution (200 mg L^{-1}) was prepared by dissolving 400 mg of the above IHE formulation in 2 L of distilled water at room temperature. This concentration was chosen as it was the maximum concentration at which RDX (limiting solute) could be dissolved in water at 20°C. The dissolution was stirred at room temperature for two days to ensure complete dissolution.

Two soils (same as Chapter 3 and Chapter 4) were purchased from a building merchant in Oxfordshire (UK), classified as ‘sandy loam’ and ‘sandy’ soils by their particle size distribution. Soils were air-dried for 2 weeks and passed through a 2-mm sieve to remove the largest fractions. Soil pH and electric conductivity were determined according to British Standards (BS 13039:2001). Total Carbon Nitrogen (TCN) content and Total Organic Carbon (TOC) were determined using Elementar

Vario ELIII (**Table 5.1**) and the C/N was estimated from their ratio (Temple et al., 2018) on a single subsample.

Table 5. 1 Characterisation of the sand and sandy loam soil.

Soil	pH [a]	Electrical conductivity [b] ($\mu S\ cm^{-1}$)	Total organic carbon content [b] (%)	C/N [b]	Dry matter content [c] (% m/m)
Sand	7.9	0.012	0.92	601	99.7
Sandy loam	8.0	0.30	12.65	17	97.2

[a] Determined by Griffin pH meter model 80 at room temperature, (1:5) in water; [b] Determined by Elementar Vario ELIII; [c] Determined by incineration at 400°C for three days.

5.2.2 Evaluation of the contribution of the abiotic and biotic processes on the degradation of the IHE formulation

To study degradation of an IHE formulation, soil (sand or sandy loam [10 g]) was added to amber glass tubes (60 mL volume). Half the amber vials (48 vials) were then separated and placed in a wet autoclave at 120°C for 20 min while the other half (48 vials) did not undergo sterilization. IHE stock solution was added to the amber vials containing either sand (3 mL) or sandy loam (5 mL). The moisture content was adjusted to a saturation of 30% and 50% respectively to mimic humid conditions without completely submerging the soil in water. The vials were placed in a dark environment and incubated at 20°C for the duration of the experiment. Each batch experiment was carried out in triplicate and samples were sacrificed at 0, 7, 14, 28 and 56 days for extraction and analysis by High Performance Liquid Chromatography (HPLC). Further to this, negative controls (soil with distilled water) and positive controls (stock solution) were incubated in triplicates simultaneously with the samples and were included in the analysis.

5.2.3 Influence of temperature on the degradation of the IHE formulation in soil

Investigation of degradation at low temperatures followed the same protocol as Section 5.2.2 without sterilisation. Samples were stored at 12°C and 4°C for 0, 7, 14, 28 or 56 days before extraction and analysis.

5.2.4 Extraction method for IHE constituents in soil

IHE constituents were extracted from the soil samples according to Temple et al (2019). Briefly, soil (10 g) was mixed with acetonitrile: water (1:1) (20 mL) and shaken for 24 hours at 150 rpm. The supernatant was then collected and filtered through a 2 nm nylon filter and stored at 4°C for up to two days until analysis. Each extraction was performed in triplicate.

Extraction efficiency was determined by incubating soils with stock solution for 1 hour (day 0) before extraction (**Table 5.2**). These extractions were performed in triplicate and all results were corrected to these extraction efficiencies.

Table 5. 2 Mass recovery (%) of IHE compounds at day 0 in each soil and treatment using acetonitrile: water (1:1)

Soil	Temperature (°C)	Treatment	Mass recovered (%)		
			NTO	DNAN	RDX
Sand	20	Sterilization	83 ± 5	86 ± 1	88 ± 3
	20	Natural	82 ± 1	85 ± 1	87 ± 1
	12	Natural	68 ± 1	68 ± 1	68 ± 5
	4	Natural	67 ± 1	66 ± 1	65 ± 1
Sandy loam	20	Sterilization	71 ± 2	47 ± 8	53 ± 6
	20	Natural	49 ± 3	50 ± 7	51 ± 5
	12	Natural	30 ± 8	40 ± 6	34 ± 4
	4	Natural	30 ± 2	33 ± 4	30 ± 1

5.2.5 High Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD)

Analysis was performed using an HPLC Waters-Alliance 2696 equipped with a Waters 996 photodiode array detector (USA). The IHE constituents were separated on a ZORBAX Eclipse plus C18 column (100 mm × 4.6 mm, Ø 3.5 µm) maintained at 30°C. Samples were injected with a syringe loading injector with 20 µL loop. The eluent mixture contained 40% acetonitrile and 60% MilliQ water acidified 0.1% with formic acid passed at a flowrate of 1.5 mL min^{-1}. The analytes were quantified via UV absorbance with optimum sensitivity detected at 235 nm for RDX, 296 nm for DNAN and 315 nm for NTO. With these conditions, retention times were 1.01 min for NTO, 3.16 min for RDX and 4.96 min for DNAN. The calibration curve (**Figure 5.1**) was obtained by plotting the concentration against corresponding peak area for each analyte and both peak areas of samples and standards were determined by Empower 2 software (Waters). The limit of detection (LoD) was 0.5 mg L^{-1} and limit of quantification (LoQ) was 1.4 mg L^{-1} for both DNAN and NTO (Fawcett-Hirst et al., 2020; Temple et al., 2018).

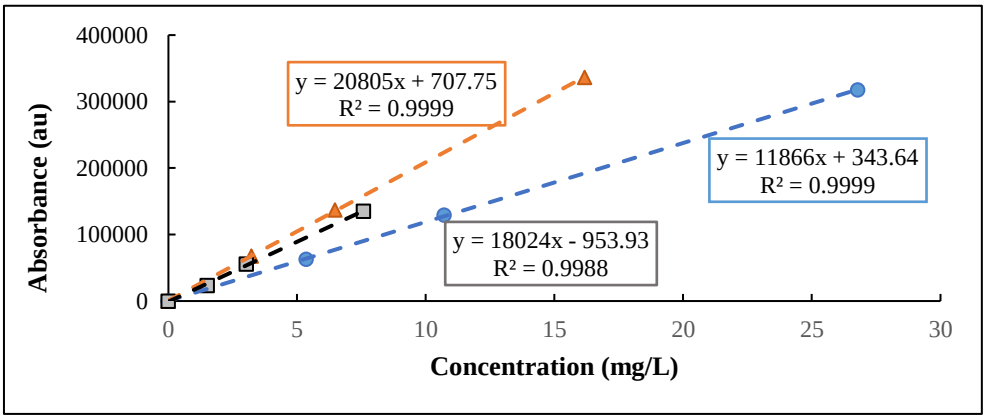


Figure 5. 1 Calibration curve of the IHE constituents in the HPLC: NTO (blue circles), DNAN (orange triangles) and RDX (grey squares).

5.3 Results and discussion

5.3.1 Influence of the abiotic and biotic processes on the degradation of the IHE formulation

The soils were spiked with an IHE formulation and samples were sacrificed over 56 days. Then, the individual mass of each IHE constituent was plotted over time for each sandy soil, comparing the differences between biotic and abiotic soils (**Figure 5.2**).

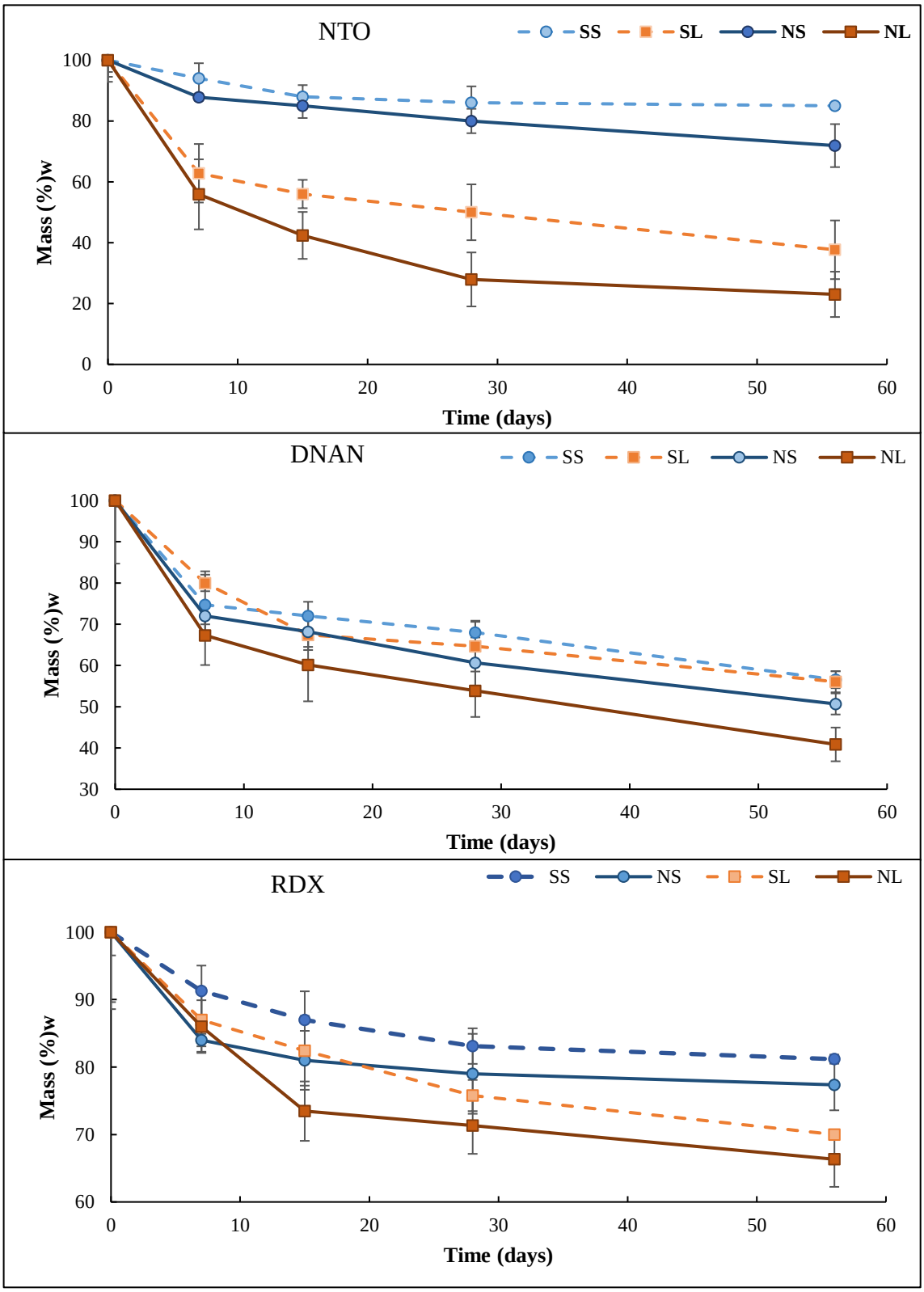


Figure 5. 2 Residual mass $(\%)_w$ over time of NTO, DNAN and RDX in sterilised sand (SS), natural sand (NS), sterilised sandy loam (SL) and natural sandy loam (NL).

Overall, the mass loss of the compounds was between 5 and 10% higher in the natural soils (in which both chemical and biological degradation occurred) than in their respective sterilised soils. In addition, the compound mass loss was around 10% lower in the sandy soil than in the sandy loam, which was expected as the sandy loam had more organic matter content and therefore, more interactions occurred between the organic matter and the IHE constituent. However, the mass loss of each IHE constituent was different in sand than in loam, which suggested that the IHE constituents underwent different biodegradation process in each of the two soil types.

NTO constitutes 53% of the IHE composition and thus its behavior in soil contributes to a considerable part of the total behavior of IHE. Although significant NTO mass was detected in sand, little difference was observed between biotic (72% ± 7%) and abiotic sand (85% ± 5%) after 56 days. This difference indicated that the percentage of NTO that underwent biodegradation was only 13% ± 2%, which was low compared to that expected from literature (Temple et al., 2018). In sandy loam, the total NTO mass loss was greater than in sand, although there was little change observed between abiotic (38% ± 9%) and biotic (23% ± 7%) sandy loam after 56 days. This was unexpected, as frequently soils with high organic content promote suitable conditions for endogenous bacterial growth (Hayat et al., 2010) and thus, NTO biodegradation was expected to be higher in the sandy loam. In addition, NTO has been reported to weakly undergo sorption processes to soils (Mark et al., 2017; Temple et al., 2018), but it has been reported to rapidly degrade in the presence of bacterial strains rich in nitroreductase enzymes (Le Campion, Vandais and Ouazzani, 1999; Madeira et al., 2019a). This suggests that the selected soils did not contain any such bacterial strains able to degrade NTO as described in literature. Further to this, the main degradation by-products (such as HTO or ATO) described in literature were not detected over the course of the experiment (Fuller et al., 2021; Madeira et al., 2019b), and this may be due to the potential low concentrations of degradatoin products (< 1.5 mg L^{-1}) which would be below the limit of detection of the HPLC.

After 56 days, DNAN detected mass in sand was above 50% of the initial mass, although in this case there was little difference between biotic (51% ± 3%) and

abiotic (57% ± 2%) soils. This may be due to a slow but irreversible adsorption of DNAN to inorganic soil particles rather than chemical degradation, as sand contains high mineral content and DNAN has been reported to strongly interact with ferrous complexes (Khatiwada et al., 2018; Oh et al., 2018). Conversely, DNAN mass in abiotic (56% ± 3%) and biotic (41 ± 4%) sandy loam was slighlty lower, however, it biodegraded mass was twice higher than in sand. This could be due to the rapid DNAN mass loss in the sandy loam soil (around 35% in only 7 days) that could promote sorption to organic particles in the soil such quinones and humic acids. Specifically through covalent bonding between the nitro groups in DNAN and aromatic amines and carbonyl groups in natural organic matter, which is a potential mechanism for non-reversible sorption (Ariyarathna et al., 2016; Kadoya et al., 2021; Menezes et al., 2021a). In addition, reported DNAN degradation products (2-ANAN, 4-ANAN and DNP) were not identified in the soil extraction, most likely due to similar reasons that none of the NTO by-products were detected.

Lastly, RDX comprised only 15% of the formulation, and thus, its mass loss contributed less than NTO and DNAN to the total mass loss. After 56 days, RDX detected mass was very similar in abiotic (81% ± 1%) and biotic (77% ± 3%) sand, which indicated that RDX barely underwent biodegradation. This was expected, as RDX has not been reported to significantly biodegrade in soils with bacterial strains (Sagi-Ben Moshe et al., 2012). The mass detected in the sand after 56 days was suggested that RDX did undergo sorption to the sand, which was unexpected as RDX has a low sorption coefficient in sandy soils (Larson et al., 2008). In the sandy loam, little difference was observed between RDX detected mass in biotic (66% ± 4%) and abiotic (70% ± 1%) sandy loam, which suggested that RDX did not undergo biodegradation. However, RDX underwent more chemical and physical proceses in sandy loam than in sand, which was expected due to the high organic content that might promote interaction between the compoun and with the organic soil partices (Sharma, Mayes and Tang, 2013).

The comparison between IHE compound mass measured under biotic and abiotic soils suggested little participation (< 15%) of biodegradation by endogeneous baterial strains in both soils. The low participation of the biodegradation could be explained due to the experimental saturation of the natural soils with the IHE

dissolution, which might have led to anaerobiosis (medium with no oxygen). If this could happen, only anaerobic bateria could be active in absence of oxygent, which would have limited the bacterial colonies available in the soil and would explain why, overall, the biodegradation was so low in comparison to chemical degradation and sorption processes (Jog, Sierra and Jim, 2020). Despite this limitation, the study showed great influence of abiotic proceses, which are often controlled by environmental conditions such as soil temperature. This study was conducted at 20°C and thus, it shred light on how IHE behaved at such temperature. In order to provide insight on the IHE degradation in field soils, IHE degradation was also investigated at different low temperatures.

5.3.2 Influence of temperature on the degradation of the IHE constituents in soil

Analysis of the influence of biodegradation on IHE compounds in sandy soils provided an overview of their behaviour at 20°C, in which the most significant IHE mass loss over time was observed in biotic soils. Typically, temperature influences chemical and physical processes and thus, to determine its impact on the degradation of explosive material residues in cold environments such as the UK, the detected mass of the IHE compounds over 56 days was analysed in soils stored at low temperatures (4°C and 12°C) and 20°C. In this study, mass was calculated with no distinction between biotic and abiotic degradation, although once again, masses were corrected by extraction efficiency. Hence, the mass losses of NTO, DNAN and RDX in each sandy soil were plotted over time and compared at 4°C, 12°C and 20°C (**Figure 5.3**).

In sand, NTO degraded smoothly over time at 20°C, maintaining 72% ± 7% of its initial mass after 56 days, whereas at low temperatures there was a higher percentage of mass remaining, reaching 94% ± 4% and 89% ± 5% at 4°C and 12°C respectively. The similarity between NTO mass loss at low temperatures suggested that although soil type indeed affects NTO interactions with the soil, these interactions did not take place due to the lack of energy available at cold temperatures. Therefore, between 4°C and 12°C, the effect of temperature on the NTO was barely existent in both soils. Conversely, in the sandy loam, there was a

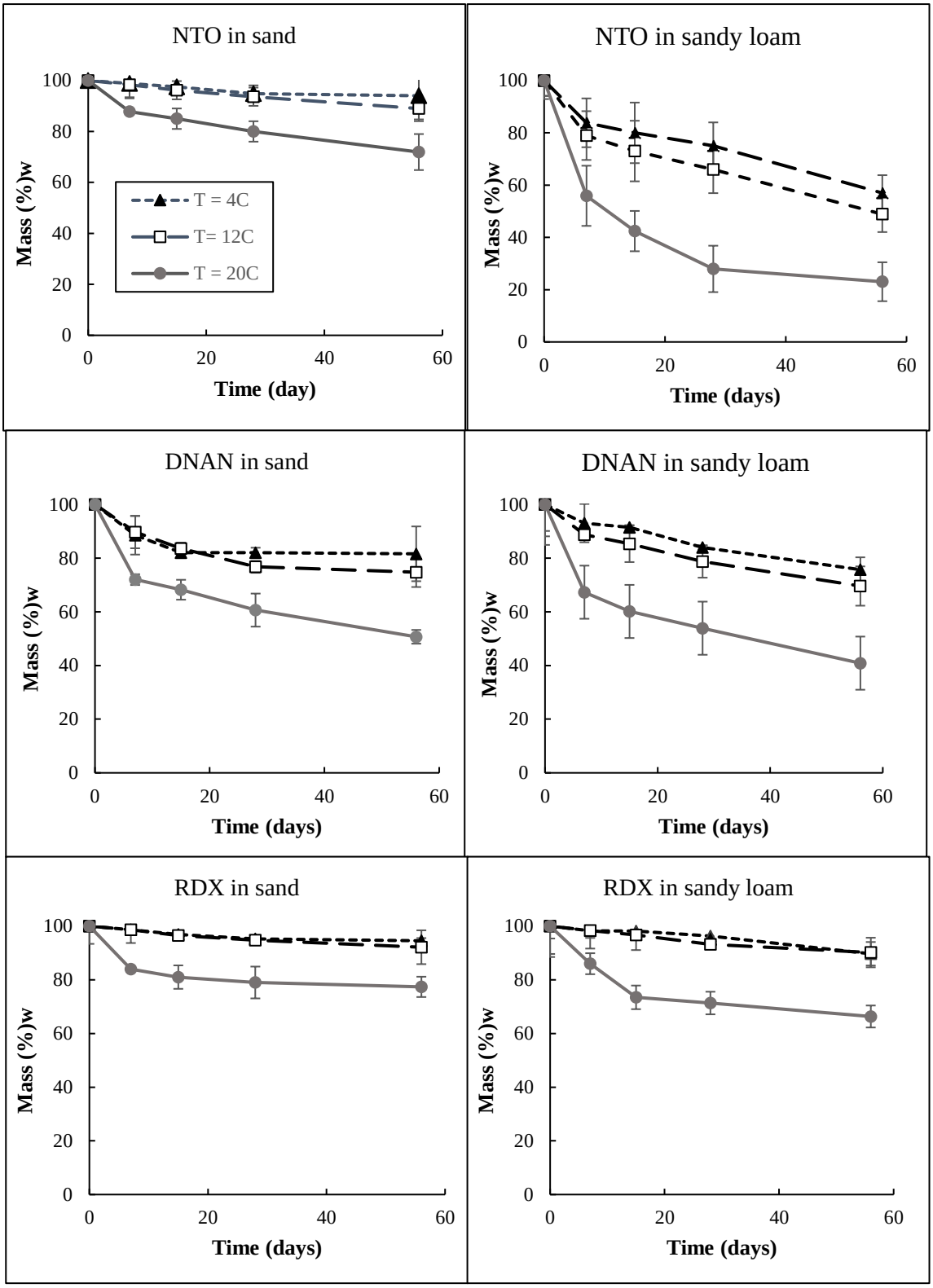


Figure 5. 3 Comparison of NTO, DNAN and RDX mass degradation over 56 days in sand and sandy loam at different temperature: 4°C (triangles), 12°C (squares) and 20°C (dots).

lower amount of NTO remaining in the soil at all temperatures, with 57% ± 7% of the initial mass at 4 C, 49% ± 8% at 12°C and 23% ± 7% at 20°C. While these results corroborate the effect of low temperature on constituent degradation, it also demonstrates the influence of the organic soil particles in the process.

DNAN degradation profile in sand was similar to NTO, although the mass remaining in soil was lower after 56 days; at 20 °C there was 51 ± 3% % of mass remaining, at 12 °C 75% ± 6%, and at 4 °C 82% ± 9%. In sandy loam, the detected mass after 56 days was 41 ± 4% % at 20 °C, 70% ± 5% at 12 °C, and 76% ± 7% at 4 °C. These values were similar to the ones observed in sandy soil, which suggested that the degradation of this constituent was not as influenced by its interaction with the organic particles of the soil as NTO was. Nevertheless, lower temperatures had a visible impact on the degradation process of DNAN, which suggests that the elevated interactions between DNAN and the quinones and humic acids in high organic content soils described in literature for temperatures above 20°C (Menezes et al., 2021b) might also occur at low temperatures.

Lastly, little difference was observed in RDX mass remaining at low temperatures after 56 days, detecting 95% ± 6% of the initial mass at 4°C and 92% ± 1% at 12°C for sand, and 90% ± 5% at both temperatures for sandy loam. This suggest that RDX has greater stability at low temperatures in sandy soils. Conversely, the remaining mass at 20°C was lower (77% ± 4% in sand and 66% ± 4% in sandy loam), which was significantly reduced in comparison to results reported by similar studies, in which RDX mass remained more stable over time (Yu et al., 2017). A possible explanation could be the difference in organic content present in the soils used in this study. As for the difference between RDX mass loss at low temperatures and 20°C, it suggests that low temperature has a great impact on the interaction between RDX and soil particles, and these interactions are likely similar in sand and sandy loam. Although RDX only comprises 15% of the formulation and thus, its impact in soil would be small, it has been reported to increase the mass loss of other explosive constituents (Sagi-Ben Moshe et al., 2009), which is why its presence needed to be considered in this study.

It is important to note that this study did not account for soil bacteria acclimation, a process under which certain bacterial colonies require time to adapt to environmental changes (e.g., temperature, pH) and may not actively participate in chemical processes in the soil (Leroi et al., 1994). For this study, soils were stored at low temperature after the dissolution containing IHE was added, and as such a limitation may have been introduced to the degradation process. Previous literature showed that providing extra time for the soil to acclimate, hampers the proliferation of colonies and promotes bioaugmentation and increases the capacity of bacteria to degrade (Gu et al., 2023, He et al., 2023). Therefore, in future studies, it would be advised to modify the experimental setup by storing the soil at the target temperature before introducing the IHE formulation to the medium.

5.3.3 Calculation of kinetic parameters for each IHE constituents in soil

As it was observed that temperature influences IHE degradation in soils, the kinetics of degradation processes for the IHE were investigated to obtain a better understanding of the constituent behaviour and to extract numerical data that can be used to assess their persistence. In this section, degradation rates, half-lives and the activation energy for each constituent and soil are calculated.

There are several mathematical equations to estimate the rate of mass loss of a compound after its deposition in soil, however, the most common approaches utilize a zero (**Equation 5.1**), first (**Equation 5.2)** or second (**Equation 5.3**) order equation (Burnell et al., 2018; Sanz-Prat et al., 2020; Wang, Guo and Yates, 2006).

$$[A]_t = -k_0 * t + [A]_o \qquad \textbf{(Equation 5. 1)}$$

$$Ln[A]_t = -k_1 * t + Ln[A]_o \qquad \textbf{(Equation 5. 2)}$$

$$\frac{1}{[A]_t} = k_2 * t + \frac{1}{[A]_o} \qquad \textbf{(Equation 5. 3)}$$

where $[A]_t$ is the IHE mass over time, (mg), k_0, k_1, and k_2 are the degradation constants for each equation (mg day^{-1}, day^{-1} and mg^{-1} day^{-1} respectively), t is time (days) and $[A]_o$ is the IHE initial mass (mg).

In order to determine which of the above equations best fits the measured compound mass over time, linear regression was performed, and the regression coefficient was calculated. In this study, degradation of NTO in sand at 20°C was chosen as a representative sample as its degradation was high over time, allowing a better comparison between different linear fits (**Figure 5.4**). In this example and for all the other IHE compounds, soil and temperature, degradation showed a near-optimum adjustment to the first order equation. Thus, degradation rate (*k*) was calculated using the slope of the linear adjustment to that equation. Then, half-life ($\tau_{1/2}$) was calculated using the formula for first order degradation (**Equation 5.4**).

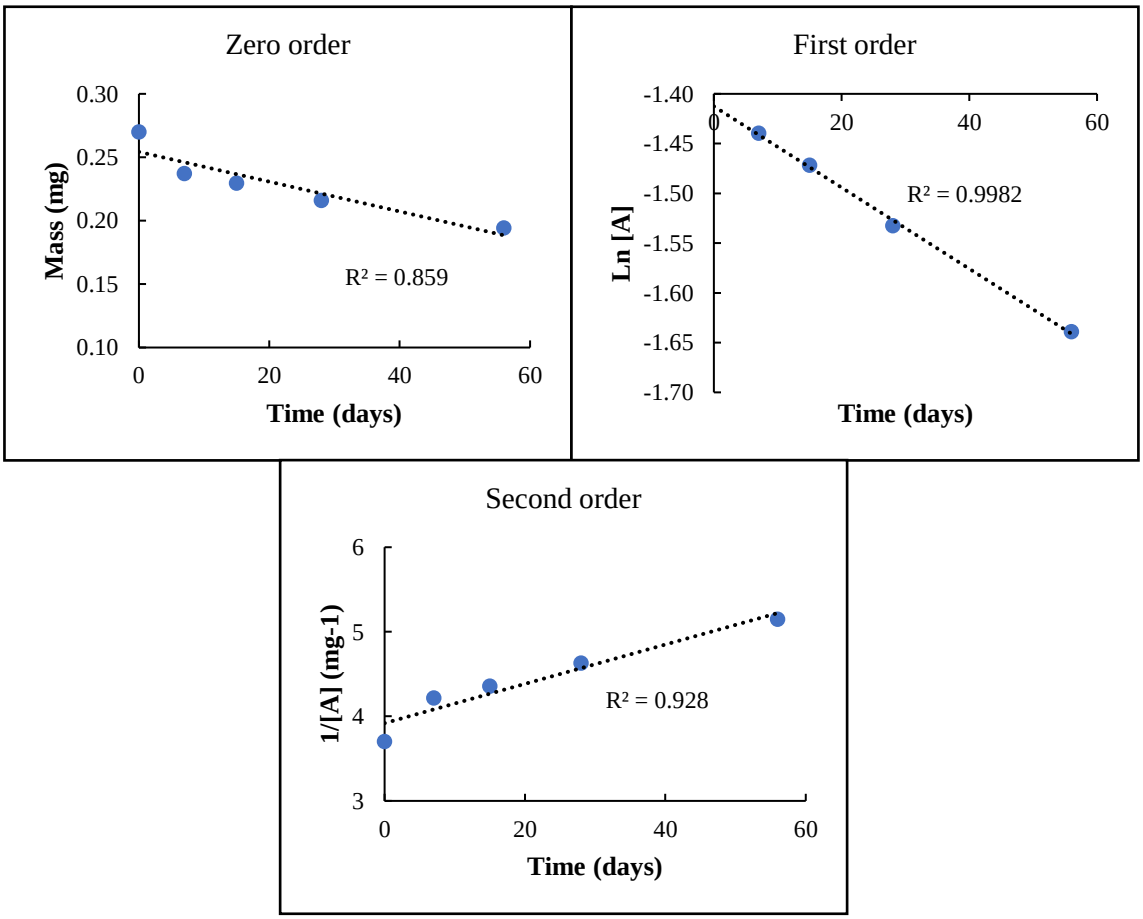


Figure 5. 4 Comparison of the NTO degradation in sand at 20°C by adjustment to zero, first and second degradation order equations

$$\tau_{1/2} = Ln(2)/k \qquad \textbf{(Equation 5. 4)}$$

where $\tau_{1/2}$ is half lifetime (days) and k is the degradation constant (days^{-1}).

Therefore, Equation 5.2 and Equation 5.4 were then applied to calculate the degradation rate and half life for each IHE compound at different soil temperatures (**Table 5.3).**

Table 5. 3 IHE formulation half-life and degradation rates calculated in each soil at different temperature.

IHE compound	Temperature (°C)	Soil	Degradation rate (day^{-1}) (10^{-3})	Half-life (days)
NTO	4	Sand	1.1 ± 0.2	620 ± 130
		Sandy loam	4 ± 2	250 ± 140
	12	Sand	2.38 ± 0.04	291 ± 5
		Sandy loam	6 ± 3	180 ± 90
	20	Sand	4.1 ± 0.1	170 ± 5
		Sandy loam	17 ± 5	40 ± 9
DNAN	4	Sand	2.8 ± 1.6	250 ± 140
		Sandy loam	5 ± 1	150 ± 40
	12	Sand	4.8 ± 1.4	150 ± 40
		Sandy loam	5.9 ± 0.9	120 ± 20
	20	Sand	10 ± 3	70 ± 20
		Sandy loam	14 ± 3	50 ± 10
RDX	4	Sand	1.0 ± 0.3	700 ± 200
		Sandy loam	1.9 ± 0.2	370 ± 40
	12	Sand	1.4 ± 0.2	480 ± 60
		Sandy loam	1.9 ± 0.2	370 ± 40
	20	Sand	4 ± 2	200 ± 90
		Sandy loam	6 ± 2	110 ± 40

Using the degradation rates at different T, Arrhenius activation energy was calculated following **Equation 5.5**

$$k = A * e^{-\frac{E}{RT}}$$ **(Equation 5. 5)**

where *k* is the degradation constant (scalar), *A* is the Arrhenius constant (scalar), *E* is Arrhenius activation energy (KJ mol^{-1}) *T* is temperature (K) and *R* is the gas constant (KJ K^{-1} mol^{-1}).

The activation energy was then, calculated from **Equation 5.6** by plotting 1/T against ln(k) (**Figure 5.3**) and multiplying the slope of that linear adjustment by R, following and **Equation 5.7**. The numerical values were displayed in **Table 5.4** for each soil and chemical compound, and the results are discussed in the next section.

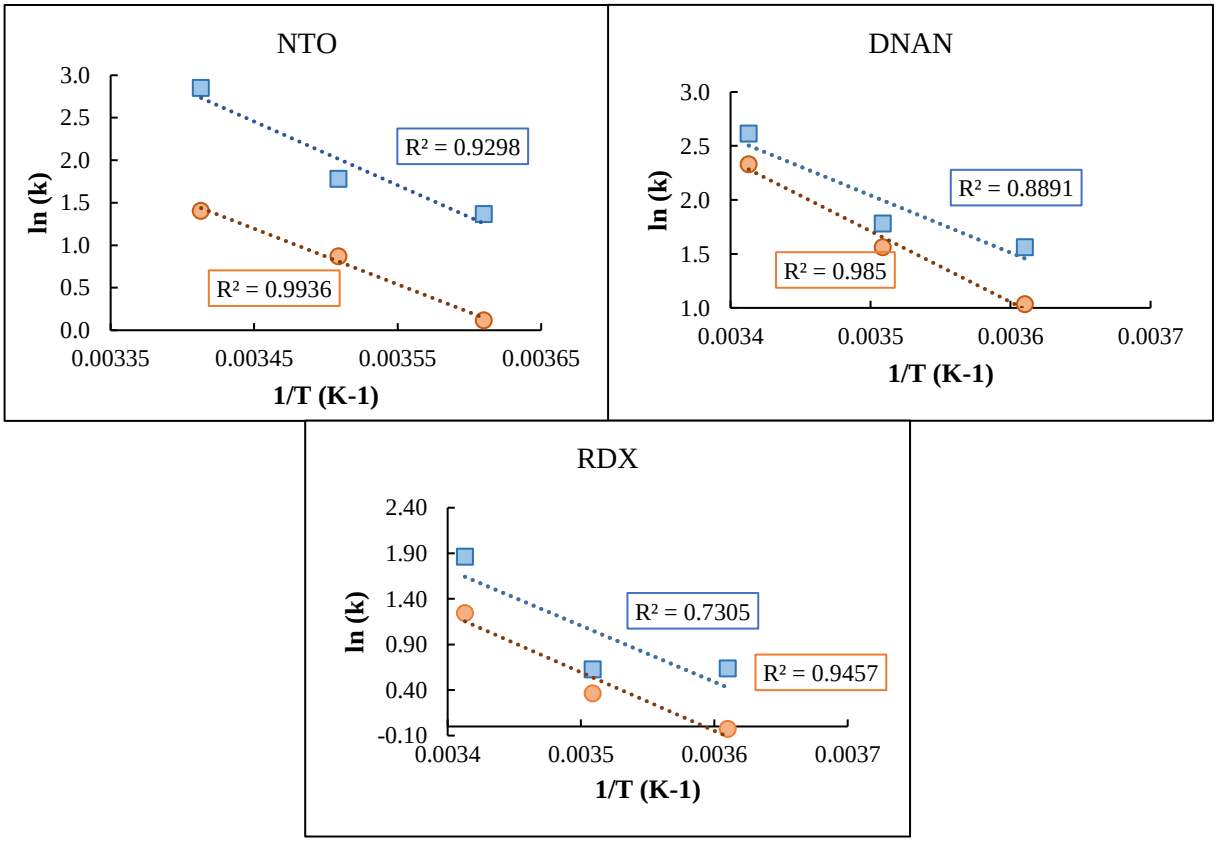


Figure 5. 5 Rate constant against temperature for ach IHE compound in sand (orange circles) and sandy loam (blue squares).

$$\ln(k) = \frac{-E}{R} * \frac{1}{T} + \ln(A) \qquad \textbf{(Equation 5. 6)}$$

$$E = -\text{slope} * \text{R} \qquad \textbf{(Equation 5. 7)}$$

Table 5. 4 Arrhenius activation energy (kJ mol^{-1}) for each IHE compound in each soil

	Sand	Loam
NTO	54 ± 4	62 ± 17
DNAN	55 ± 7	44 ± 16
RDX	53 ± 13	51 ± 31

5.3.4 Discussion of the degradation kinetics and activation energy

The data displayed in the previous section provides numerical information about how the IHE chemicals degrade in sand and sandy loam and under different temperatures. In addition, activation energy was estimated to better understand how much energy they required to start their degradation and provide numerical data to understand and quantify how likely was for them to degrade in different sandy soils.

Among the three compounds in the formulation, NTO had the lowest half-lives overall for each soil type and temperature, which indicates that it was the fastest to degrade. In sand, NTO degraded 4 times faster at 20°C than at 4°C, showing a broad half-life between 170 and 617 days respectively. Conversely, in sandy loam, NTO degraded 5 times faster at 20°C than at 4°C, although the half-lives (40 and 176 days) where noticeably lower than in sand. However, its activation energy was 13% higher in sand than in loam, which pointed out that despite its rapid kinetics, it required more energy to start degradation. In addition, these activation energy results were similar to other alternative heterocyclic ketone reported in literature (Taylor-Lovell, Sims and Wax, 2002).

DNAN was the second IHE constituent to rapidly degrade in soil after NTO. It degraded 3 and 4 times faster at 20°C than at 4°C in sand and sandy soil respectively, which was slightly lower than for NTO. Further to this, DNAN half-lives in sand and sandy were quite similar at 20°C (67 and 51 days respectively) but slightly different at 4°C (246 and 145 respectively). This indicated that although DNAN seems to degrade similarly in both soils at 20°C , this rule does not apply at lower temperatures. Further to this, DNAN activation energy in sand is 20% higher than in loam, which was the opposite to NTO. The activation energies in sand and sandy loam (55 kJ mol^{-1} and 44 kJ mol^{-1}) were slightly higher than expected for an aromatic compound (Whelan et al., 2015), nonetheless, the two nitro groups could

potentially be increasing the energy required to start the degradation process of the chemical compound.

Finally, RDX was the most stable compound in the formulation, showing the lowest degradation rates and highest half-lives for each soil. It degraded 3 times faster at 20°C than at 4°C in both soils, which was the lowest degradation rate among the three IHE constituents. In addition, RDX half-lives were twice higher in sand than in sandy loam, being between 200 and 713 days in sand at 20°C and 4°C respectively and 108 and 386 days respectively in sandy loam. Further to this, the activation energy was very similar for both soils, which suggested that maybe it undergo similar degradation processes despite the difference in organic matter.

Overall, the data provided in this study are assumed to be appropriate for the constituents despite the absence of similar literature. In addition, it has shed light on how these chemicals behave in low temperature environments and how long they would persist in the soil. In conclusion, the persistence of this formulation in soil was not as high as other explosive chemicals such as TNT and HMX which have been reported to remain at greater than 90% for more than 5 years in different soils (Becker, 1995). As the continuous deposition of IHE residues in soils constantly prolongs their persistence, especially in cold regions, it might require years for the soil to self-remediate and reach a healthy state. However, the initial concentrations used were relatively low to extrapolate to what it might occur in military ranges, and as a recommendation, the degradation of higher quantities of explosive residues would need to be studied to complement this study. Until that time, its presence in the ecosystem will continue to pose risks to human health and ecological sustainability, as some of the IHE constituents can reach groundwater.

5.4 Conclusions and recommendations

This study provided insights into the degradation of IHE constituents in soil when they are deposited in combination as part of a formulation. Firstly, the IHE compound mass loss due to biodegradation was similar and low (around 10%) in both soils, which was unexpected as usually, soils with higher organic matter content (such as sandy loam) facilitate bacterial growth and thus a higher rate of biodegradation in comparison to more inorganic soils (such as sand). As a recommendation, additional

investigation should be conducted using soils from more representative locations, as opposed to the soils obtained for this study, which may have come from more sterile environments. These soils might contain higher endogenous bacterial strains and could potentially provide more information on the influence of biotic processes on the IHE mass loss over time.

Secondly, the study of chemical and physical degradation of the IHE residues in soil showed that after two months, IHE mass loss was lower in sand (43%) than in sandy loam (63%). The difference in mass loss indicated a high dependence on the soil type and organic matter content, signifying that soils richer in organic matter content are more likely to interact with IHE residues and thus contribute more to IHE mass loss. Furthermore, low temperature ended up decreasing IHE mass loss, albeit at a different rate depending on the soil type. Low temperatures significantly reduced the NTO mass loss in sandy loam and DNAN mass loss in sand, whereas RDX had similar mass loss in both soils. The total IHE degradation rates showed that the IHE constituents degraded 3 times slower at 4°C compared to 20°C in sand and 4 times slower in sandy loam for the same temperature values. The experimental IHE half-lives showed a high persistence (from months to years) of IHE in the soil matrix especially at low temperatures. This could lead to potential toxicity issues, especially in cold regions such as Norway, Canada, or USA in which IHE are commonly used and their residues tend to accumulate on the top layers of the soil.

Overall, the results of this study demonstrate how residual concentrations of IHE constituents that are likely to accumulate after multiple detonations can be estimated and inform the environmental risk posed by their deposition in soil. This can enhance decision making on how to evaluate contaminated soils and improve explosive management systems in the environment. In addition, the data provided in this study shows the basal degradation rates of IHE residues in two types of soil. This can be useful for assisting soil remediation strategies by establishing the natural periods of time the explosive residues need to degrade before any amend is added.

CHAPTER 6. Assessment of the performance of a stochastic model for the simulation of Insensitive High Explosive fate and transport

ABSTRACT

The use of a new generation of less sensitive explosives known as Insensitive High Explosive (IHE) has been increasing as they are safer to handle and store. However, their environmental impact is not as fully understood as the impact of traditional explosives, which have been linked to several serious contamination incidents. Therefore, there is an opportunity to avoid past mistakes by investigating the potential issues that can be caused by the deposition of IHE residues in the soil. Historically, this has been challenging and has required extensive and time-consuming empirical experimentation closely replicating environmental conditions. However, it is now possible to simulate these complex interactions using computational software. In this study, degradation rates were included in a previously developed stochastic computational model using the GoldSim software to simulate the fate and transport of IHE residues containing 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dinitroanilisole (DNAN). The developed model was then validated by simulating breakthrough time and concentration for DNAN and NTO for two independent experimental soil column studies under a) controlled laboratory conditions and b) outdoor weathering conditions. Overall, the model demonstrated successful simulation of indoor conditions ($R > 0.5$). However, its performance in simulating outdoor conditions, particularly in soils with high organic content, was relatively less effective ($R > 0.25$ and $R > 0.1$ for NTO and DNAN, respectively). This limitation can be attributed to the complex interactions inherent in such soil types, posing challenges for accurate simulation. Nevertheless, the model was still capable of simulating low concentration levels comparable to experimental data for both indoor and outdoor conditions. Furthermore, the study critically evaluated the applicability of the model for risk assessment and remediation strategies in contaminated areas. As such, it is proposed that this model is used as a foundation for future investigations on the fate and transport of explosives in soil.

6.1 Introduction

The need for military readiness demands manufacture and use of explosively filled munitions to ensure adequate stockpiles and maintain training, which can lead to environmental contamination and toxicity from explosive residue contamination (Walsh et al., 2017). To that end, the study of the behaviour of explosive residues in soil has been typically conducted empirically, attempting to reproduce what might happen in military ranges or contaminated lands and often under controlled conditions (such as consistent temperature or water exposure). For instance, field lysimeters and soil column studies have been used to discretely investigate the mobility and sorption of explosive munitions in the soil (Mark et al., 2017; Molina et al., 2006; Won and Borden, 2017). Parameters such as soil-water partition coefficient (K_d) and organic carbon water partition coefficient (K_{OC}) have been measured to determine explosive adsorption to soil particles and organic matter respectively (Bronner and Goss, 2011; Linker et al., 2015). In addition, dripping tests reproducing rainfall have been used to measure dissolution rates and water solubility of explosives under different pH, and temperature (Lynch et al., 2001; Taylor et al., 2015). Further to this, degradation experiments have been conducted to study explosive persistence in soil under aerobic and anaerobic processes as well as degradation rates, metabolic pathways and by-products (Le Campion, Vandais and Ouazzani, 1999; Fuller et al., 2021; Perreault et al., 2012). However, the replication of environmental conditions can be complex and often difficult to achieve in aggregate when multiple processes occur simultaneously, which poses limitations when investigating the fate and transport of explosive residues in real settings.

To overcome these limitations, the use of computational modelling is gaining traction, as it enables the study of contaminants for which intuitive and analytical solutions are not readily available (Bhattacharyya, Sahara and Ohno, 2019). For instance, computational programs such as HYDRUS and TREECS have been used to simulate explosive breakthrough curves in soil and water respectively to determine the rate at which explosive residues are transferred to groundwater (Alavi et al., 2011; Dortch, 2018). HYDRUS has also been used to determine explosive parameters such as dissolution rates, decay constants or K_d, which can be used to estimate mobility and persistence in soil (Arthur et al., 2018; Mark et al., 2017).

Further to this, the dissolution of ‘green’ explosives (those manufactured using environmentally benign processes) in saline water has been simulated by COSMO-RS, which modelled their dissolution at different temperatures and salt concentrations (Alnemrat and Hooper, 2014). Although the data provided in these studies can be useful to understand explosive residue behaviour, a) only one explosive chemical is investigated in a study, which is not representative of formulations containing combinations of chemical compounds and b) few processes are studied simultaneously providing a poor overview of the real contamination issues. On top of that, the simulations performed have been deterministic, providing an invariable outcome once initial conditions are defined. Thus, the models cannot account for uncertainty associated with environmental conditions, which made them less representative of real environments.

GoldSim is a computational programme that allows the user to dynamically simulate and visualize complex systems in engineering, science, and business (GoldSim Technology Group LLC, 2021). Through its ability to define inputs as stochastic elements, the output produced is a probability distribution of the expected outcome, which facilitates the simulation of systems that contain high levels of uncertainty. It is also user-friendly, which enables easy manipulation of the features described and facilitates the presentation of the simulation to decision-makers and stakeholders. These features make GoldSim suitable for simulating contaminant transport in different media (e.g., water, soil, vadose zone, etc.), as well as allowing the user to link the processes occurring between different media, whose interactions are frequently ignored or poorly understood.

To date, GoldSim has been used to simulate the transport of organic compounds in soil, such as aromatic and aliphatic hydrocarbon fractions in chalk (Cao et al., 2015), or spent nuclear fuel in crystalline rock (Lee, Choi and Kim, 2016). Further to this, GoldSim has been used to simulate the transport of inorganic elements such as potassium and nickel residues in a field (Lu et al., 2012) and radioactive elements from a uranium mining facility (Plagnes et al., 2017). Although GoldSim has not been used to simulate environmental fate and transport of explosive compounds yet, these examples suggest that it could be suitable for this purpose.

In Chapter 3, a stochastic model was developed using GoldSim to study the mobility of 3-nitro-1,2,4-triazole-5-one (NTO) and 2,4-dinitroanisole (DNAN) in sandy soils, by inputting the key explosive and soil parameters. This model was further extended in Chapter 4, by specifying the dissolution rates of explosive residues in rainwater. Finally, to accurately depict the degradation of constituents in the soil, it was essential to incorporate the half-lives of the compounds into the model. These half-lives were determined in Chapter 5, providing the necessary information for simulating the degradation processes within the model. As a result, a model that simulates fate and transport in soil of an IHE containing DNAN and NTO was developed. In this Chapter, the performance of the model developed in GoldSim was assessed to determine to what extent it can representatively simulate the overall fate and transport of IHE residues. This was achieved by simulating previously conducted experiments (Jenkins, 2018; Paula, 2018), using known parameters from the initial set up and assessing the similarity of results to validate the developed model. In addition, the study demonstrates the model's ability to predict IHE contaminant transport rate and peak concentration under controlled and non-controlled (outdoor) conditions. This proves the applicability of the model to assess the risk posed to the environment from explosive contamination and assist development of remediation strategies.

6.2 Experimental design for comparison to simulation

In order to assess the performance of the model, the results of two independent studies, designed to assess transport of a IHE formulation (1g) containing NTO (53%) and DNAN (32%) through soils under a) controlled (Paula, 2018) and b) field conditions (Jenkins, 2018), were compared against the simulation output. Both independent studies used soil columns (r = 5 cm, h = 20 cm) with solid IHE residues scattered over the top. In addition, both studies measured the concentration of NTO and DNAN leaching out of the column over time. The soils used for this experiment were categorised as sand and sandy loam and had similar physico-chemical properties (density, porosity, soil structure) to the ones described in Chapter 3, 4 and 5 of this thesis.

6.2.1 Experimental design for indoor soil columns

Soil columns were irrigated with distilled water using a pumping system to replicate annual UK rainfall volume in an accelerated timescale of 42 days. To minimise variability, the experiment did not account for seasonal rainfall and assumed a constant flow rate (30 mm day^{-1}) throughout the experimental period. The leachate was analysed every 7 days by HPLC to determine NTO and DNAN concentrations in both sand and sandy loam.

6.2.2 Experimental design for outdoor soil columns

The second experimental setup was carried out under outdoor weathering conditions over 12 months. The experiment was run from the 31st of March 2017 to the 31st of March 2018, allowing rainfall to irrigate the soil column naturally. The rainfall rate was assumed to be the same as reported by Windrush Weather (https://www.windrushweather.co.uk/) for that period in Marlborough, Wiltshire, UK. In this case, the leachate was collected every 4 weeks and the contaminant concentrations were measured by HPLC.

6.3 Development of the model in GoldSim

The fate and transport of NTO and DNAN was simulated using GoldSim version 14.0 and the Contaminant Transport Module. This module is an add-on extension to the GoldSim simulation software framework that allows the user to dynamically model mass transport processes in different scenarios.

The model framework consisted of the following elements:

- Material: Fluid (water), Soil (sand or sandy loam) and Species (NTO and DNAN)
- Pathway: Cell Pathway (leachate) and Pipe Pathway (soil column)
- Input: Data (e.g., soil parameters, indoor inflow, DNAN and NTO initial mass), Stochastic (e.g., degradation rates, dissolution rates, K_d) and Time Series (outdoor inflow)
- Function: Selector (choosing dissolution rates over time) and Expression (equations describing different fate and transport processes)

- Result: Time History result (NTO and DNAN concentration in leachate).

The dimensions of the experiment and the time scale were specified for each scenario (based on the experimental conditions) and linked by the inflow of water in the system. For the simulation, three main processes were included: transport through soil (Chapter 3), dissolution in rainwater (Chapter 4) and degradation in soil (Chapter 5). Lastly, the simulation settings were based on the duration and the sampling timestep as well as the number of realisations performed with the Monte Carlo method.

6.3.1 Model dimensions, timescale, and water inflow

The developed model contained three main elements that computationally replicated the experimental set up: IHE particles, soil column and leachate. The initial IHE mass (1 g) was inputted using a Cell Pathway in which the percentage of NTO (53%) and DNAN (32%) was specified as well as their individual masses. This element was linked to a Pipe Pathway that simulated the soil columns (height =20 cm; radius = 5 cm) in which DNAN and NTO masses were added as input rates coming from the dissolution of the IHE particles with the rain. Lastly, the Pipe Pathway was linked to another Cell Pathway that simulated the concentration of DNAN and NTO leaching out of the soil column over time. These three elements were connected by the water inflow that dripped on to the column, dissolved the IHE formulation and passed through the soil into leachate.

The water inflow was simulated in GoldSim by manually adding it to the model and linking them to the Pipe Pathway element. The study performed in indoor conditions attempted to reproduce annual rainfall in 42 days, irrigating the soil columns containing IHE particles on top with distilled water (30 mm day^{-1}) at 20°C. The parameter was inputted to the model as a constant value over time, as it best simulated the use of a pump which provides controlled water inflow. Conversely, for the outdoor soil columns water ingress was added as a Time Series element to account for the seasonal rainfall based on data from Windrush Weather Station (Wiltshire, UK) as a seasonal average of the UK's annual rainfall (**Table 6.1**). The outdoor model also accounted for evapotranspiration, which was included as a Time Series element attached to the Pipe (soil column) as a drainage outflow. For this

process, the inputted data was obtained from Crondall Weather Station (Hampshire, UK). (https://crondallweather.co.uk/daily-monthly-and-seasonal-evapotranspiration-statistics-for-crondall/). All parameters of this section were added to the model as deterministic values.

Table 6. 1 Rainfall and evapotranspiration values used per season (3 months) to simulate water balance in outdoor conditions. All inputted data were added as deterministic values.

Month	Season	Rainfall* (mm mon^{-1})	Evaporation* (mm mon^{-1})
Apr - Jun	Spring	25	6
July - Sep	Summer	45	2
Oct - Dec	Autumn	74	1
Jan - Mar	Winter	89	1

* estimated for a circular section r = 5 cm (soil column)

6.3.2 Simulating transport (advection and sorption)

The Contaminant Transport Module integrated in GoldSim enabled the definition of the soil, water and IHE constituent properties in the Material. In it, NTO and DNAN were added as Species elements specifying their molecular weight (130 and 198 mg/mol respectively) and water solubility (16500 and 275 mg L^{-1} respectively) (Fawcett-Hirst et al., 2020). The sandy soils were added as “Solid” elements, and their main characteristics, which were previously experimentally measured in Chapter 3, were inputted in the model (**Table 6.2**). The equations used in GoldSim to describe contaminant sorption and mobility were the same as the ones displayed in Chapter 3 (Equations 3.2, 3.3 and 3.4).

Table 6. 2 Parameters inputted in GoldSim to simulate advection and sorption processes of DNAN and NTO in soil

Soil property	Value	Sand	Sandy loam
Bulk density (kg m^{-3}) [a]	Deterministic	1.81	1.27
Porosity (a.u) [b]	Deterministic	0.29	0.44
Tortuosity (a.u) [c]	Deterministic	0.50	0.50
K_d (NTO) (L kg^{-1}) [b]	Probabilistic (uniform)	0.334 ± 0.025	0.242 ± 0.17
K_d (DNAN) (L kg^{-1}) [b]	Probabilistic (uniform)	0.401 ± 0.082	9.51 ± 1.51

[a] Data collected from Temple et al., 2018; [b] Data collected experimentally in Chapter 3; [c] Data estimated from Alaoui et al., 2003.

6.3.3 Simulating dissolution rate of the IHE formulation

Dissolution rates as determined in Chapter 4 were manually inputted in the simulation by following the Noyes-Whitney equation that describes IHE dissolution over time (Equation 4.1). Dissolution rates needed to be adjusted to the NTO and DNAN initial mass and rainfall time relevant to the model. The time was corrected assuming that total annual rainfall in Wiltshire, UK in 2018 was around 825 mm (Windrush Weather Station). Thus, 200 mL of rainwater falling over the IHE particles were equal to the rainfall estimated in 0.92 days in indoor conditions and 15 days in outdoor conditions. The dissolution rates were normalised to account for the new IHE mass (1 g), as they were obtained in Chapter 4 at a different mass (45 mg). The new dissolution rates were added to the model as stochastic data elements with uniform distribution (**Table 6.3**).

Table 6. 3 Dissolution rates of DNAN and NTO for indoor and outdoor conditions.

INDOOR CONDITIONS	**Dissolution rates (mg day^{-1})**	
Time interval (days)	**NTO**	**DNAN**
0 - 3 days	34.4 ± 14.0	5.9 ± 2.0
3 - 10 days	13.7 ± 3.8	
10 - 42 days	7.4 ± 3.3	

OUTDOOR CONDITIONS	Dissolution rates (mg mon-^{1})	
Time interval	**NTO**	**DNAN**
0 - 0.5 months	29.8 ± 2.1	2.8 ± 0.8
0.5 – 2 months	12.3 ± 3.8	
2 - 12 months	7.2 ± 2.1	

6.3.4 Simulating degradation rates

Individual degradation rates of NTO and DNAN were derived from the experimental work carried out in Chapter 5 and followed a first order degradation equation (**Equation 5.2**). These rates were added to the model as stochastic values with uniform distribution in the DNAN and NTO Species elements, by defining its half-life (**Table 6.4**).

Table 6. 4 Degradation rates of NTO and DNAN determined at 12°C (outdoor) and 20°C (indoor) in sandy soils.

Soil	Temperature	Half-life (days)	
		NTO	**DNAN**
Sand	12 ^{o}C	291 ± 5	150 ± 40
	20 ^{o}C	170 ± 5	70 ± 20
Sandy loam	12 ^{o}C	180 ± 90	120 ± 20
	20 ^{o}C	40 ± 9	50 ± 10

6.3.5 Run settings and stochastic simulation

The duration specified for each simulation was set according to the timeframe reported by each of the two experiments. For the indoor soil columns simulation, it was 42 days with a timestep of 7 days, whereas for the outdoor soil columns simulation, it was 1 year with a timestep of 1 month.

The stochastic simulations were carried out by applying the Monte Carlo method in GoldSim, as it enabled the probabilistic calculation of different NTO and DNAN breakthrough curves in the soils. The method settings were adjusted to perform 101

realizations, as it was considered sufficient number of samples to generate representative results for this study without (GoldSim Technology Group LLC, 2021). In addition, the ‘Latin Hypercube Sampling’ method was selected to ensure a near-random set of samples from the probability distributions were chosen. Lastly, the option ‘Repeat sampling sequence’ was selected to ensure that every subsequent run of the simulation used the same randomly selected data values, and so the simulations could be re-run with the same input.

6.4 Results and discussion

6.4.1 Assessing the performance of the model for simulating IHE fate and transport in indoor sandy soil columns

The GoldSim model developed in Chapters 3 and 4 with the addition of degradation processes from Chapter 5 was used to simulate the total fate and transport process of NTO and DNAN in sand and sandy loam. To assess the performance of the model, the simulated NTO and DNAN concentrations in the leachate of each soil were compared against the experimental data for indoor conditions. The experiment consisted of soil columns (20 cm x 5 cm) in triplicate containing an IHE formulation (1 g) and they were exposed to accelerated rainfall for 42 days. The model performance was analysed using the direct correlation comparison between simulated and experimental output (**Figure 6.1**) by discussing the correlation coefficient and the slope.

The four scenarios showed a correlation factor (R) above 0.65, which indicates a “strong correlation” using a conventional approach (Schober and Schwarte, 2018). Nevertheless, the performance of the model cannot be assessed just with this parameter, and therefore the slope of the graphs was also assessed, which provided information on the adjustment between the experimental and simulated data, where the closer to one the better the similarity. In this case, the best adjustment was for the compounds in sand (**Figure 6.1a** and **Figure 6.1b**) followed by the simulation of DNAN in sandy loam (**Figure 6.1d**). This indicated that the model was able to simulate slow breakthroughs in which IHE constituents are found in low concentrations (< 2 mg L-1).

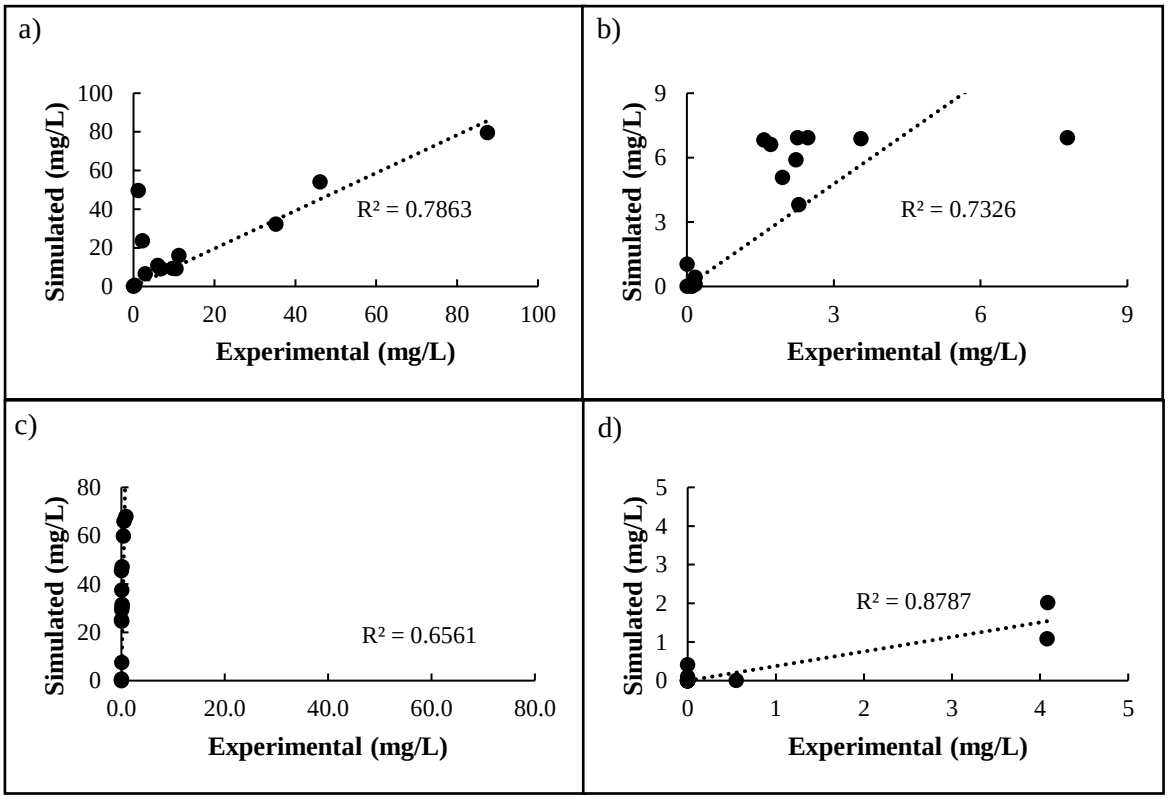


Figure 6. 1 Comparison between the simulated and measured breakthrough concentrations found in leachate in indoor soil columns of a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam. "y" is the slope of the tendency line and "R" is the correlation factor.

However, in the case of NTO in sandy loam (**Figure 6.1c**), the slope was 100 times higher than expected, mainly due to the absence of NTO in the experimental leachate, which was translated into a poor model performance, despite the strong correlation factor. It is possible the assumptions made in the model influenced the inputted data and the approach used to simulate the processes in the model. As an example, some of the parameters experimentally measured (such as the absence of K_{OC} in sandy loam or the seasonal rainfall data inputted instead of a monthly one) might not have been representative enough and this might have biased how the contaminates behaved in the model.

Further to this, the variance between the simulated and experimental concentrations was reported by comparing the correlation coefficient squared (R^2) and the root mean square error (RMSE), two different approaches to report goodness of fit (**Table 6.5**). In this case, RMSE was measured following **Equation 6.1**.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} ||y(i) - x(i)||^2}{N}}$$ (**Equation 6.1**)

where *N* is the number of data points, *y(i)* is the experimental measurement and *x(i)* is its corresponding prediction.

Table 6.5. Absolute RMSE and R^2 for the values of simulated and experimental concentrations of DNAN and NTO in sand and sandy loam in indoor conditions.

Soil	Compound	RMSE	R^2
Sand	NTO	149	0.783
	DNAN	4	0.733
Sandy loam	NTO	55	0.656
	DNAN	11	0.879

The RMSE provides information on the average difference between the experimental and simulated result values. The closest to 0 indicates the best correlation (and model performance). The R^2 identifies the percentage of variance in the simulated data compared to the experimental output and the closer to 1 the better adjustment. From the values calculated in **Table 6.5**, it is observed that overall, the model performed best for DNAN in both soils, however this may simply be due to the very low concentrations of DNAN found in the leachate Although, the R^2 showed a better correlation for NTO in sand than DNAN in sand, the RMSE suggested the correlation was not as significant. This variation may be due to the higher solubility of NTO which results in significantly higher concentrations of NTO in leachate and therefore a wider margin for error. Finally, the simulation of NTO in sandy loam had the lowest R^2 and an elevated RMSE, which indicated that among the four simulations, this was the least accurate. This might be due to the total absence of NTO concentrations in the leachate in the experiments, as can be visualised when plotting and comparing experimental and simulated concentration in the leachate over time.

Once the correlation between the simulated and experimental concentrations was established, a comparison between experimental and simulated concentrations over time was performed to visually compare and assess how representative the simulated outcome was. The Monte Carlo method enabled the estimation of the contaminant breakthrough curve based on the selected data range for each realization. Hence, the experimental and simulated maximum, mean and minimum breakthrough curves of NTO and DNAN for each soil were plotted over time (**Figure 6.2**).

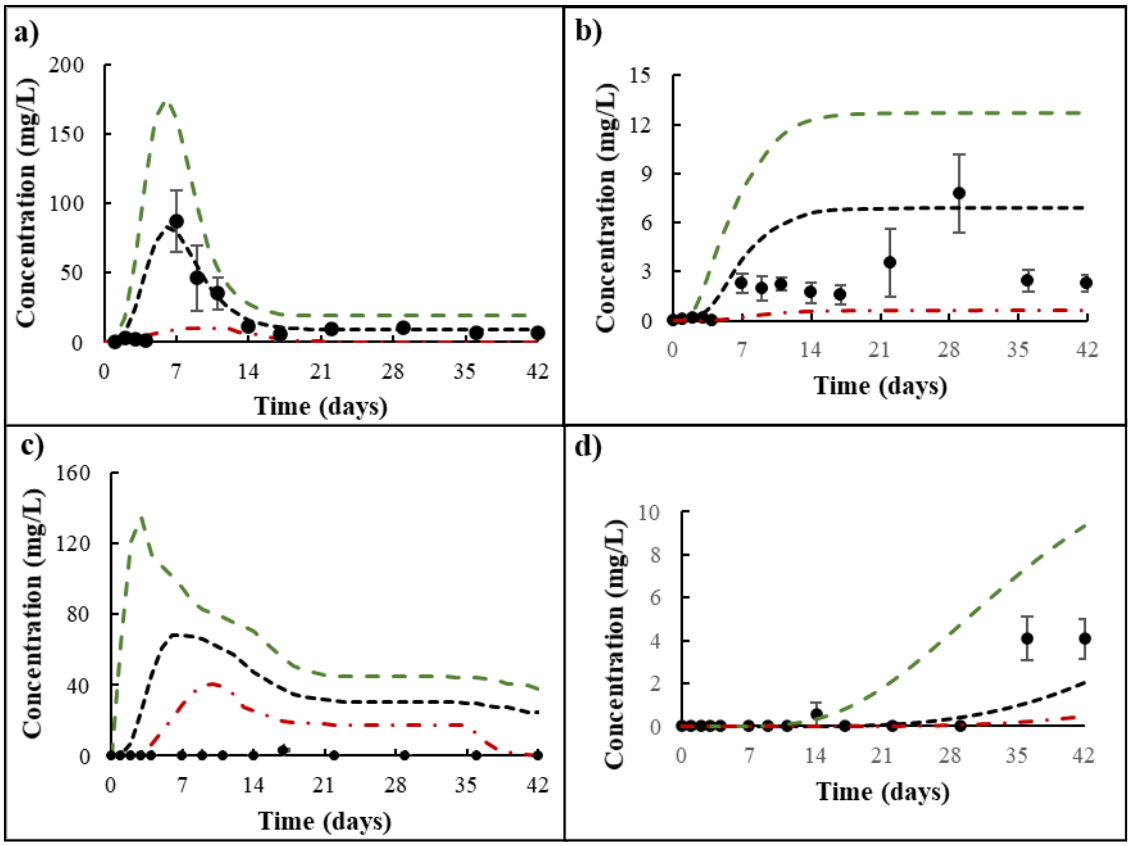


Figure 6. 2. Breakthrough curves for a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam in accelerated indoor experiments. Dashed lines indicate the maximum (- - -), mean (**---**) and minimum (**-.-.**) breakthrough simulated in GoldSim, whereas dots indicate measured values from experimental soil columns.

Overall, the simulations of NTO and DNAN breakthrough curves in the sandy soil (**Figure 6.2 a and b**) effectively simulated the peak concentrations in soil. The simulated NTO peak concentration (82 mg L^{-1}) was very similar to the experimental one (88 ± 22 mg L^{-1}), and they both reached a plateau after 14 days with an average

of between 6 and 11 mg L^{-1} per week. However, the model was less representative in simulating the minimum time required for NTO to leach out of the column as, in the experimental results, NTO did not leach out until day 5, whereas the model simulated concentration leaching out after 2 days. In the case of DNAN, simulated concentration showed a plateau (6 mg L^{-1}) after two weeks, that coincided with the experimental concentration (8 ± 2 mg L^{-1}) after 29 days, providing an average between 4 and 6 mg L^{-1} over the duration of the experiment. In addition, DNAN experimental concentrations found in the leachate were 2 times lower than the average simulated ones, except for the one obtained at day 28. However, these differences fell between the maximum and minimum simulated concentrations predicted in GoldSim which indicated that the dissolution rates, K_d and soil properties inputted in the model were suitable to provide representative simulation and the NTO and DNAN followed the formulas used to describe dissolution, adsorption and advection in soil. These results suggest that it may be possible to progress the model to larger scales, in which the soil system replicates scenarios such as contaminated military ranges.

As previously noted, when discussing simulated concentrations, the breakthrough of NTO in sandy loam (**Figure 6.2 c**) was less representative than in sandy soil, most likely due to a large percentage of NTO unexpectedly not found in any of the portions (solid particle, soil and leachate) of the experiment. According to the simulation, NTO peak breakthrough concentration (68 mg L^{-1}) was expected at 5 days, however this was not observed experimentally. In fact, NTO was not detected for 42 days, and even then, only at very low concentrations (0.87 mg L^{-1}). Post experimental extraction of the remaining formulation showed that 75% of the NTO had dissolved from the IHE matrix, and a further 1.2% was found in the soil. Thus while 73.7% NTO leached into soil from the IHE matrix, only 16.0% was detected in leachate meaning that 57% NTO was ‘lost’. The ‘lost’ mass could potentially have been either irreversibly adsorbed in the sandy loam or rapidly degraded by soil bacteria. At the time, it was assumed that NTO had degraded, although no degradation products were identified, yet degradation studies in Chapter 5 and previously published work (Krzmarzick et al., 2015; Mark et al., 2017; Temple et al., 2018) suggested that NTO is unlikely to completely degrade within 42 days. This suggests the existence of

some unknown parameter that relates to adsorption which was not included in the model.

The comparison between simulated and experimental DNAN breakthrough curves in sandy loam (**Figure 6.2 d**) showed high correlation (R = 0.87), despite DNAN being persistent in the soil with a tendency to be adsorbed into the topsoil layers. The simulated peak concentration (2 mg L^{-1}) was very similar to the experimental one (4 mg L^{-1}) which indicated that the model could representatively simulate DNAN breakthrough over 42 days in sandy loam. As shown in Chapter 3, the DNAN breakthrough curve in sandy loam is particularly low due to the high adsorption of DNAN to the organic particles (such as quinones and humic acids) of the soil (Menezes et al., 2021). The K_d*s* of the sandy loam soils used were not measured when the experiment work was carried out and the K_d inputted in GoldSim was an estimation calculated from similar soils (measured in Chapter 3). However, for this case, K_d effectively represented DNAN adsorption to soil, suggesting that in lieu of experimental data, K_d values could be obtained by calculation from other soils with similar organic matter content and particle size distribution (as well as other parameters such as pH and soil temperature).

Even though the simulations of the breakthrough of NTO and DNAN in sandy soils were representative, the outcome suggested that some of the key parameters (especially related to soil adsorption) could be modified. Other studies containing soil contaminant modelling include the organic carbon-water partition coefficient (K_{OC}), linking the organic content in the soil with the contaminant transport (Bronner and Goss, 2011; Jarvis, 2016) and this might result in more representative simulations. Hence, it would be beneficial to investigate the relationship between K_{OC} and K_d and potentially include it in the GoldSim model. This could yield more representative results for soils such as sandy loam, where the percentage of organic matter is considered high (> 6%). With this adjustment, GoldSim could improve the description of advection processes and could include mathematically the influence or relation between the soil organic content and the IHE constituents.

6.4.2 Assessing the performance of the model for simulating the fate and transport of IHE in outdoor sandy soil columns.

To assess the performance of the model against a more representative scenario, an outdoor soil column weathering experiment was simulated. The experiment consisted of soil columns (20 cm × 5 cm) in triplicate containing an IHE formulation (1g), which were then exposed to natural weather conditions for twelve months. This setup was considered a more representative experiment to reproduce IHE environmental impact in contaminated lands. During the experiment, the concentration of NTO and DNAN in the leachate of each soil column was different, most likely due to the variable volume of rainfall that each soil column was exposed to and therefore the volume of water incident on the solid IHE formulation. This was corroborated by the experimental volumes collected from the leachate, as they varied significantly between the three columns and did not match the expected volume of rainfall. This reinforced the idea of using probabilistic modelling to simulate these scenarios, as these simulations can embed the uncertainty associated with variable environmental conditions. As with indoor conditions, the model performance was analysed by the RMSE (**Table 6.6**). and by direct correlation comparison between the simulated (mean) concentrations found in the leachate against the experimental concentration for each IHE constituent and soil (**Figure 6.3**).

Overall, the comparison between simulated and experimental concentrations for outdoor soil columns showed an overestimation of the simulated concentrations against experimental ones, yet the model provided valuable data for NTO and DNAN behaviour in the soil. In sand, the correlations for NTO (R = 0.660) and DNAN (R = 0.726) were lower than the ones for the same soil in indoor conditions, but the values of the concentration in leachate were in the same order of magnitude which would be sufficient to enable an estimation of risk. The conventional approach classified the relations experimental/simulated as “strong correlation” for DNAN in sand, “moderate correlation” for NTO in both soils and “weak correlation” for DNAN in sandy loam. The slopes followed the same trend showing that DNAN in sand was the best fit, followed by NTO in both soils and DNAN in sandy loam, which indicates poor relationship between simulated and experimental concentrations. However, this last one was due to the almost total absence of experimental DNAN in the leachate.

Therefore, the model performance assessment was not as representative as expected which can be potentially explained due to the uncontrolled nature of outdoor conditions and the limitations of the model discussed below.

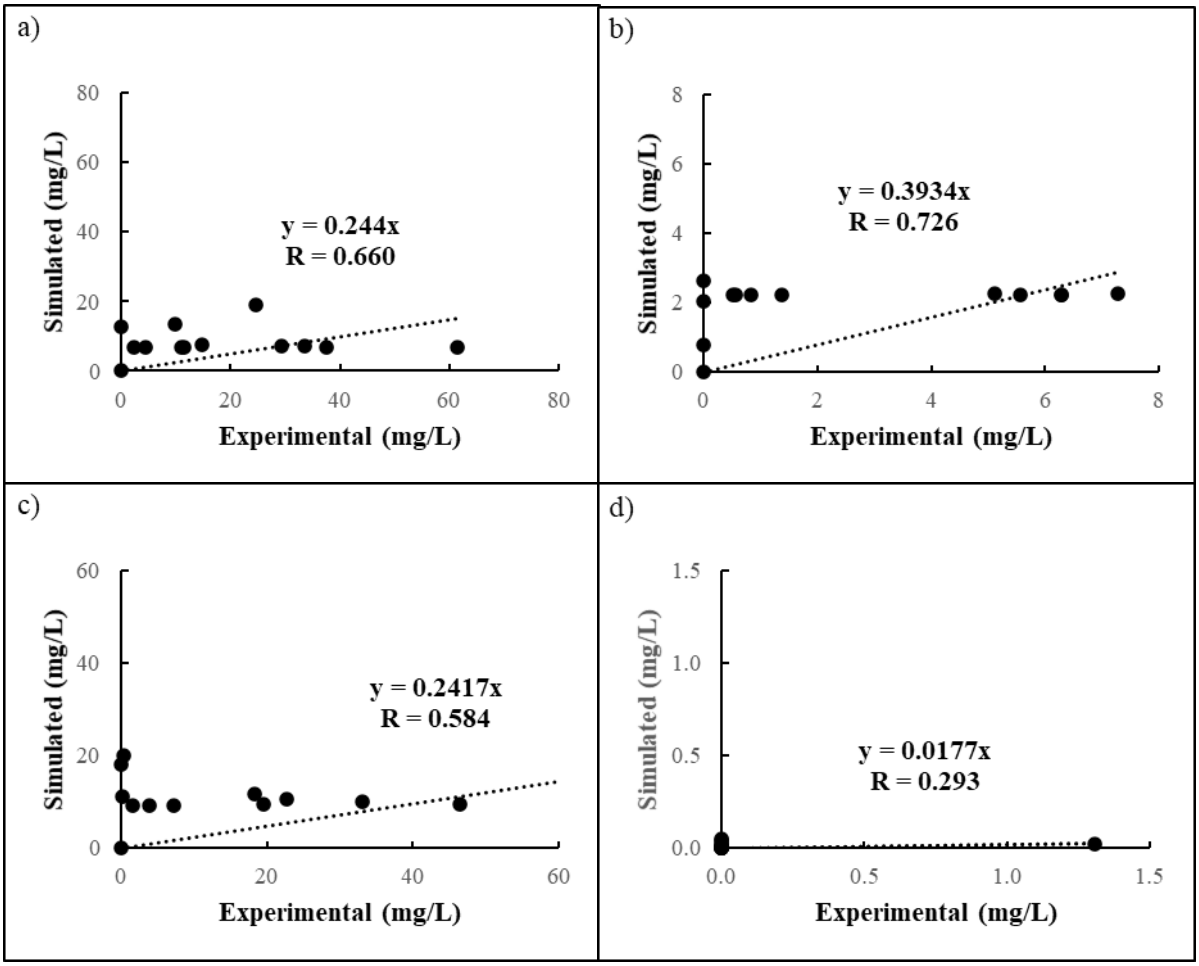


Figure 6. 3 Comparison between the simulated and measured plume concentrations found in leachate in outdoor soil columns of a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam.

The results from the RMSE and R^2 (**Table 6.6**) differed from the results obtained from the indoor column comparison. The lowest variance was obtained for DNAN in sandy loam and was mainly due to the low concentrations (0 in most of the cases) detected in the leachate, followed by DNAN in sandy soil due to the same reason. However, the simulation of NTO in sand and sandy loam had a higher variance in comparison to the experimental results, which can be explained due to the higher differences between simulated and experimental concentrations in the leachate. The R^2 approach showed higher variance of the model performance for DNAN and NTO

in sandy loam in comparison to the correlation of these chemicals in sandy loam. This issue might be due to the total absence of experimental concentrations in the leachate, which was better understood, once again, when visually comparing both outputs over time.

Table 6.6. Absolute RMSE and R^2 for the values of simulated and experimental concentrations of DNAN and NTO in sand and sandy loam in indoor conditions.

Soil	Compound	RMSE	R^2
Sand	NTO	74	0.436
	DNAN	10	0.527
Sandy loam	NTO	79	0.301
	DNAN	1	0.086

As in the previous section, in order to obtain a visual comparison between the experimental and simulated concentrations over time, the experimental and simulated maximum, mean and minimum breakthrough curves of NTO and DNAN for each soil were plotted over time (**Figure 6.4)**.

In sand, the NTO simulated breakthrough curves (**Figure 6.4 a**) were on average lower than the experimental ones, however due to the very large error bars between the three triplicates there was significant overlap between the two sets of data. The simulated peak concentration of NTO (15 mg L^{-1}) was observed to leach out within 2 months, whereas the experimental peak concentrations (60 mg L^{-1}) were detected after 8 months. However, when taking into account the potential errors in the experimental data, it is plausible that the peak breakthrough might have occurred much earlier, possibly around 4 months. This adjustment brings the experimental data more in line with the simulation results.

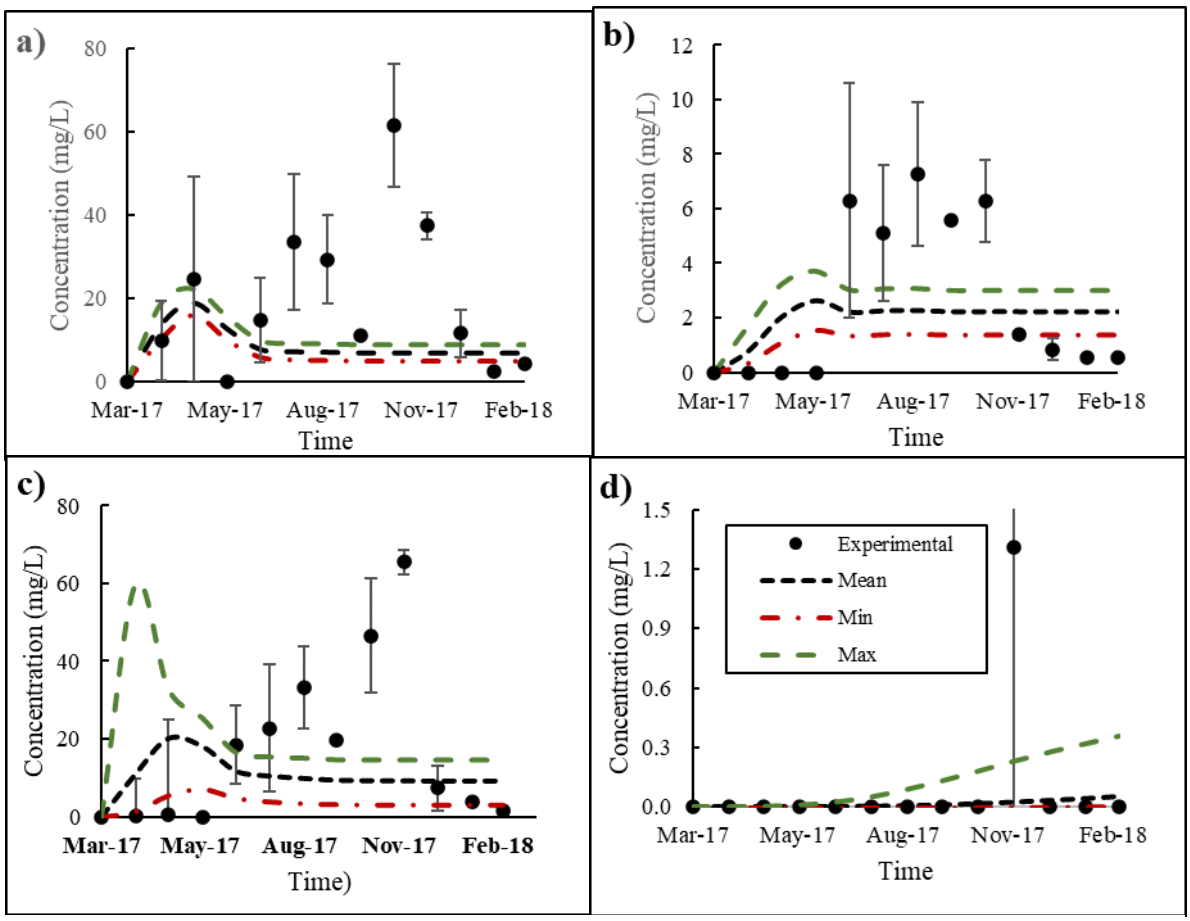


Figure 6. 4 Breakthrough curves for a) NTO in sand, b) DNAN in sand, c) NTO in sandy loam and d) DNAN in sandy loam in outdoor experiments. Dashed lines indicate the maximum (- - -), mean (---) and minimum (-.-.) breakthrough simulated in GoldSim, where dots indicated measured values from experimental soil columns.

A similar trend was observed in the DNAN breakthrough curve in the sand (**Figure 6.4b**), where the simulated concentrations exhibited a consistent DNAN concentration (2 - 4 mg L^{-1}) leaching out of the columns. In contrast, the experimental concentrations displayed more fluctuations (ranging from 4 - 7 mg L^{-1}), with notable drops (< 2 mg L^{-1}) coinciding with the onset of the winter season, specifically during the fourth and ninth months. This variation in the experimental data is most likely due to the high variability of rainfall entering into the columns. The columns were high sided with at least 15 cm between the top layer or the soil and the top of the column which may have blocked rain from entering the columns, particularly if the rain was not falling directly vertically onto them. In addition, it is suspected that some blocking between the columns also occurred, with columns first in line in the direction of the rain receiving most rainfall and blocking columns in the

second row. The simulation cannot take these factors into account and assumes consistent and comprehensive rainfall coverage on the modelled columns which may account for the smoothing of the data.

The disparity observed between the experimental and simulated leached concentrations of NTO and DNAN in the sand could potentially be attributed to the mechanism used for simulating rainfall in the model. For instance, if the estimated volume of rainwater expected to be in contact with the IHE particles was uneven throughout the year, it would cause inconsistency with laboratory determined dissolution rates and would explain why simulated concentrations did not align to experimental values. However, the simulated NTO and DNAN concentrations were in the same order of magnitude suggesting that the model data could be beneficial for estimating contaminant behaviour in sand and to provide approximate concentrations in leachate.

In the outdoor sandy loam columns, the simulated breakthrough curve of NTO did not closely align with the experimental data during the summer and autumn seasons. However, it exhibited a closer representation during the winter and spring seasons. (**Figure 6.4 c**). The simulated NTO peak concentration (12 mg L^{-1}) was achieved after 3 months (June 2017), whereas experimental NTO peak concentration (60 mg L^{-1}) was detected at 9 months (December 2017). The delayed experimental breakthrough of NTO was not expected in the sandy loam soil due to NTO high solubility in water and low K_d (reported in Chapter 3). It is possible that the high organic content in the sandy loam (12%) could be facilitating a higher irreversible adsorption to the quinones and humic acids in the soil. For sorption processes, only K_d, soil density and soil porosity were inputted in the model. This suggests that the discrepancies could be due to preferential flow paths made in the soil column that would avoid the sorption of NTO to the soil and would make it leach more rapidly from the soil column. Thus, the simulation in soils with high organic content might need an extra parameter that links sorption to organic matter with DNAN and NTO concentration over time, as suggested in the simulations of NTO and DNAN in indoor sandy loam columns.

Finally, the simulated DNAN peak concentration was very low (0.2 mg L^{-1}) and was detected at the end of the simulation (12 months) (**Figure 6.4 d**). However, DNAN

was not detected in any of the experimental sandy loam columns in the leachate, except for one sample after 9 months (December 2017) which had 1.4 mg L^{-1}. An explanation for the absence of DNAN in the experimental sandy soil column leachate could be due to the low concentration levels close to the limit of detection of the HPLC (LoD = 0.5 and LoQ = 1.5 mg L^{-1}). This effect would hamper a correct and reliable measurement of the analytes and would provide erroneous or misleading concentrations that might not match the simulated ones, which are, over the 12 months, below 0.5 mg L^{-1}. Another explanation could be related to extreme weather conditions that may happen outdoors, which were not factored into the model. Intense rainfall, changes in temperature, snowfall and sun exposure are a few of the environmental factors that may cause an extreme reaction of the contaminant in the leachate. Lastly, the observed discrepancy may also be attributed to the significant interactions between DNAN and the soil particles present in the soil (Kadoya et al., 2021; Olivares et al., 2017; Richard and Weidhaas, 2014), which was not accounted enough with the K_d inputted in the model. Thus, further investigation into the impact of these interactions may lead to the development of a more representative model.

Another aspect to consider is the timestep selected to display the contaminate concentration in the leachate. The small-time steps allow the model to handle the detailed short-term leaching behaviour seen in aggregated soils (Rose et al., 1991). However, in this model, the time step was 1 month, which can be considered very large. This issue was not contemplated when the experiment was designed and therefore, could not be extended *a posteriori*. It is possible that shorter timesteps could have shown different results, modifying the quality of the numerical simulation. A larger number of measures would definitely have enabled a more descriptive comparison and model performance analysis, and this must be considered in further research. However, for this thesis, the timestep had to be equal to the experimental one to be representative and that is the reason why it only provided 13 measures over 12 months. Nevertheless, this number provided enough data to compare the simulated and experimental work and to provide an overview of the evolution of the explosive material traces in the soil.

Although the soil column did not have any vegetation, it included soil evaporation, and water drainage, which are the main two flow processes when modelling

groundwater flow and transport (Rahman et al., 2019). However, one of the limitations of the model was the lack of column hydrology or lateral water fluxes, which influence the dynamic evolution of the soil moisture profile (Maquin et al., 2017). This was especially important in months between May and July, in which there was little rainfall, and the warm temperatures may have influenced the soil moisture and therefore, the transport of DNAN and NTO. However, this was not reflected in the experimental results as the months with more analyte collected in the leachate were from August to November, whereas the model predicted higher concentrations around spring. To achieve more accurate estimations of concentrations in simulations, future simulations may need to incorporate a specific parameter of randomness associated with rainfall. Currently, the model assumes a varying rate of continuous rainfall for each month. However, in reality, rainfall intensity varies greatly, ranging from light drizzles to heavy downpours. Accounting for this variability could have a significant impact on generating more representative simulations.

Overall, the simulations of NTO and DNAN breakthrough in sandy soils maintained in outdoor spaces and in contact with environmental conditions were less representative than indoor. In the case of sand, the primary challenges stemmed from the use of a non-representative K_d (distribution coefficient) for the soil and the utilisation of dissolution rates derived from annual rainfall estimates in the UK, which proved to be misleading. On the other hand, in sandy loam, the major discrepancies were attributed to the substantial influence of high organic content, which led to strong interactions with the analytes, impeding their mobility through the soil particles. In these long experimental studies that are performed over a year, degradation undoubtedly participates more than in short period experiments where IHE constituents do not have enough time to degrade. Although the model did account for seasonal rainfall and evapotranspiration, it did not include parameters such as the variable soil moisture, which would have been beneficial to describe soil water related processes and column hydrology. Lastly, the degradation rates that were selected for the simulation, were derived without taking outdoor weather conditions (e.g., rain, drought, snow, etc.) into consideration, which may have impacted the model performance.

6.4.3 Applicability of the model developed in GoldSim

In the previous sections, the performance of the model was assessed by using two different experimental data sets from independent studies and trying to simulate the fate and transport of IHE constituents under different soil types and environmental conditions. Overall, the model demonstrated reasonable accuracy simulating the behaviour of IHE constituents in indoor conditions. The correlation between the simulated and experimental concentrations was considered “strong” for three out of four scenarios, being able to simulate concentration values in the same order of magnitude. While the conditions simulated are not necessarily representative of real conditions, it is a first step forward to simulating what would happen on military training ranges. When simulating fate and transport for the outdoor conditions study, the model underestimated NTO concentrations in both sandy soils. However, the concentrations reported by the study were at levels too low to be considered toxic to receptors (Crouse, Lent and Leach, 2015; Reddy et al., 2011), therefore, the values predicted by the model would lead to the same conclusion in both soil types i.e., that there is limited risk of negative impacts from the contaminants.

In the case of DNAN, the model was able to representatively simulate breakthrough curve in sandy soils. Although some of the experimental concentrations were beyond the limits established for the simulated ones, both breakthroughs were within the same order of magnitude (1 - 6 mg L^{-1}), which on a scale of environmental risks is not a significant difference. It would be interesting, then, to investigate whether the variability scales with increasing mass of IHE by conducting a significantly larger scale experiment for comparison i.e., tens of grams of IHE. Furthermore, in sandy soil, simulated DNAN concentration values were very low suggesting that the presence of DNAN may not be a risk to soil and groundwater, as 1) the dissolution rate was quite slow, 2) DNAN was strongly adsorbed in the soil and 3) DNAN half-life in sand loamy soil at 12°C (134 days) would promote the degradation of the compound meaning there would be less available mass for impact on receptors.

Based on these findings, one potential application of the model is to provide support for decision-making in risk assessment scenarios concerning the deposition of Insensitive High Explosive (IHE) residues in contaminated areas. By understanding the persistence and mobility of IHE in the environment, it becomes possible to

determine whether substances like NTO and DNAN (along with their by-products) pose a risk to soil and human health, enabling proactive measures to be taken. In this regard, the model has effectively simulated the fate and transport of IHE constituents, demonstrating its representativeness. Furthermore, the model can be employed to assist in devising remediation strategies for contaminated areas, particularly military ranges. By accurately simulating the behavior of IHE substances, the model aids in formulating effective approaches for mitigating the environmental impact and addressing contamination issues. Given the model's capability to provide insights into the concentration of NTO and DNAN breakthrough, as well as their degradation and accumulation in the upper layers of soil, it becomes possible to predict their concentrations in the environment. This information can be utilized to develop decontamination plans, such as employing specific plant crops known to effectively remove contaminants (Terzaghi et al., 2015), or utilizing bacterial strains with degradation mechanisms that can break down IHE constituents into less toxic metabolites (Prommer and Barry, 2014). Furthermore, the model can serve as a foundational tool that can be extended and adapted by other modelers for their own simulations involving different explosive formulations in soil environments. Certain modifications would be necessary to account for varying soil parameters (e.g., pH, organic matter), and the modeler would need to specify the key parameters relevant to the specific simulation. The flexibility of GoldSim in terms of visualization and parameter customization makes it easy to tailor the model to suit individual requirements. By being utilized appropriately, the model can withstand the test of time and remain a valuable tool in the field.

6.5. Conclusions and recommendations

The performance of a model developed in GoldSim to predict the fate and transport of IHE residues in sandy soils has been assessed. This was carried out by comparing NTO and DNAN concentrations reported by two previously conducted independent soil column experiments to the ones simulated by the model in two types of sandy soil. The first experiment was performed in soil columns placed indoors, in which environmental conditions were stable and thus could be easily reproduced in the model. As a result, the model was able to representatively

simulate the NTO and DNAN fate and transport in the soils. The second experiment was performed in sandy soil columns placed outdoors, where the soil and its constituents underwent weathering processes, making it challenging to simulate them. While the NTO and DNAN concentrations were not simulated within an acceptable threshold, the simulated values were within the same order of magnitude, which in both cases would lead to the same result in terms of risk assessment.

The model developed in GoldSim has been proven to work on sandy soils under very specific environmental conditions. In order to improve the simulations and to broaden the scope of usability, other soil types would need to be modelled, especially soils with a higher silt content and bacterial activity. There was clearly a challenge remaining on how to include column hydrology, yet the addition of seasonal rainfall and evapotranspiration was a step towards achieving more representative results. This could be potentially important in months in which the lack of rainfall and the high environmental temperatures could extremely affect the water balance of the system. In addition, it could be useful to include further IHE formulations or IHE formulations with different proportion of chemical constituents as lack of information is currently an ongoing issue for modellers. Thus, a stronger collaboration between experimenters and modellers is recommended to achieve this goal and to create computational frameworks to study the fate and transport of IHE residues in contaminated lands.

CHAPTER 7. Conclusions and recommendations for future work

7.1 Overview of the key findings and contribution to knowledge

The use of explosives for military training and demolition activities has driven the change of traditional explosive fills to a new generation of Insensitive High Explosives (IHE). These new formulations are less likely to be accidentally detonated, making them safer to store, transport and manipulate. IHE fills often comprise of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dianisole (DNAN), two new constituents whose physico-chemical properties differ from traditional explosive compounds, and thus, their mobility and persistence in the environment is less well known. NTO has been reported to easily break through the soil and reach groundwater (Arthur et al., 2018; Khatiwada et al., 2018), whereas DNAN has been proven to accumulate in the soil and be shown to surrounding organisms (Lotufo et al., 2015; Moores et al., 2020). However, due to the novelty of these explosive fills and the lack of environmental impact studies, little is still known about the overall behaviour of IHE formulations in soil, which highlighted the challenge on how to assess the risks posed by their residues in contaminated areas.

This thesis aimed to contribute to this issue by providing insight on the main processes that participate in the fate and transport of explosive residues in the soil and by building a computational model to simulate the fate and transport of IHE compounds in sandy soils and with different environmental conditions (e.g., soil temperature, water pH). The literature review (**Chapter 2**) identified that advection, diffusion and dispersion as well as sorption and dissolution were key processes influencing the transport of explosive residues through the soil, while chemical degradation and biodegradation were the key processes describing the environmental fate of explosive residues. Once established, the most predominant and successful computational programmes described in the literature to assess similar contaminant impact (e.g., pesticides in soil) were selected and discussed. Although most of the programmes could efficiently simulate contaminant behaviour, they were able to do so in deterministic systems. In addition, they did not show evidence of success in the study of combination of contaminants, making them

inappropriate for simulating IHE formulations. Ultimately, GoldSim was chosen due to its stochastic approach for studying dynamic systems which allowed the assessment of uncertainty associated with environmental conditions (e.g., soil temperature). It also enabled the manual addition of inputs and mathematical equations within the system, providing enough freedom to representatively simulate environmental conditions and complex scenarios.

Based on the literature review, it was noted that the breakthrough of IHE residues in soil was the first step to understanding how they behaved in soil. The literature divided the contaminant transport into three main processes: advection, diffusion and dispersion and described them by the advection-dispersion equation and Flick's law. Here, it was assumed that advection was the main transport process occurring as it described the bulk movement of the IHE dissolved particles in water. In addition, soil sorption was another process that explained the interactions of IHE constituents to the inorganic and organic particles in the soil and was especially remarkable in soils with high organic content. In order to assess the influence of organic matter on the breakthrough of IHE constituents, two sandy soils with different organic content were chosen: one with a low organic content (sand) and the other with high organic content (sandy loam).

To study the influence of the soil type on the overall breakthrough of IHE constituents, an initial soil column experiment (using sand and sandy loam) was conducted and outlined in **Chapter** 3 where the IHE constituents were added to the system in dissolution. The aim was to reproduce how IHE constituents would break through the soil in case of spillage in a manufacturing facility. The work showed that NTO rapidly broke through the first 10 cm of soil in seconds which meant than NTO could easily reach unsaturated soil zones and quickly spread in the environment through water media. DNAN showed similar behaviour to NTO in the sand, but it remained adsorbed to the sandy loam soil particles for the duration of the experimental work, which suggested that it could accumulate on the topsoil layers and could potentially be a threat for any living organisms present in the sandy soil.

Simultaneously, soil properties (e.g., bulk density, porosity) were experimentally measured as well as the NTO and DNAN soil water partition coefficient (K_d). All these parameters were required for building a model in GoldSim that could

representatively simulate NTO and DNAN breakthrough in the aforementioned soils. This model was created to determine what parameters participated during the breakthrough of DNAN and NTO and to support the experimental work mentioned above. Once built, the output (IHE concentrations in the leachate) was compared to the ones obtained in the soil column experiments to validate the model and to ensure sufficient data quality and representativeness of a real system. The initial parameters required by GoldSim to simulate the breakthrough of IHE compounds in a dynamic soil system were IHE initial mass, inflow conditions and soil and IHE physico-chemical properties. Once introduced, a sensitivity analysis revealed that K_d was the most significant input among the ones tested, followed by soil density and thus, the inputted data to describe them needed to be reliable. This implied that K_d could not be estimated from the literature and was required to be empirically measured to ensure sufficient representativeness of the system under study. However, two assumptions were made when building the model, a) K_d was constant over the studied range of temperature (15 ^{o}C - 20^{o}C) and K_d was linear for the studied IHE concentrations. Further to this, the initial model did not account for column hydrology, which could have made a difference on the simulations.

The simulation of transport processes of IHE chemicals was a first start to understand how IHE behave when they are already dispersed in the soil in dissolution, for instance, a spillage from an explosive manufacturing site. However, in most situations, IHE residues are released into the environment from partial detonations as homogeneous solid residues. In **Chapter 4**, IHE dissolution rates were investigated under different types of rainwater to determine when the constituents enter the soil matrix and at which concentrations. This was necessary because, while there are existing studies on the solubility of IHE in water, only few investigated the dissolution rate of these formulations. In addition, none of them provided reliable data like the UK's environmental conditions that could be used to dynamically simulate IHE dissolution in GoldSim. Once again empirical work was required to describe how the three compounds dissolved from the solid formulation over time and how their dissolution was influenced by different types of rainwater.

The empirical data showed that the dissolution rate of NTO from the formulation was not constant over time, with a rapid initial dissolution phase over the first 15 minutes

which was halved over the following 35 minutes and was 3 times reduced after 50 minutes. On the other hand, DNAN dissolution rates was linear over the studied time (200 minutes), which suggested that DNAN was the constituent limiting the overall IHE dissolution rate of the formulation. This meant that 30mg - 60mg of IHE formulation required 15 minutes to fully dissolve the exposed NTO on the surface of the formulation, after which time the NTO mass rate in the system was regulated by the slower dissolution of DNAN. Thus, the total IHE mass rate entering the soil matrix was dependant on the time, water flow and presence of DNAN in the particle. Further to this, rainwater temperature and pH were proven to modify the rate of IHE compounds. High temperature (20°C) increased the dissolution rates of the compounds in the formulation in comparison to environmental temperature (12°C). However, a rain pH 5.0 did not significantly affect the dissolution rate of NTO (in comparison to pH 6.5), although it reduced the DNAN dissolution rate three times. This effect was unexpected as the DNAN chemical structure is the same over the pH range and it does not have any acidic proton to release that would explain such change over 1.5 pH units.

In the model, the dissolution process was added following a variant of the Noyes-Whitney equation. As the dissolution rates were not constant over time, they were inputted in the model using a Selector element, which allowed the model to use different dissolution rates as a function of time. In the IHE formulation, NTO was assumed to have three dissolution rates over the first 100 minutes, whereas DNAN was assumed to have only one. In this case, it was also assumed that after 100 minutes and due to the small IHE particles (30mg - 60mg) the dissolution rates were constant over time. The last assumption was that the dissolution rates would increase or decrease depending on the initial IHE particle mass and the number of IHE that underwent dissolution. All of the assumptions led to inputting the dissolution rates in the model as ‘Stochastic elements’ with uniform distributions, as the variability on these key parameters would provide further information on the IHE dissolution.

The combination of IHE dissolution and breakthrough simulations provided a more complete overview of how NTO and DNAN interacted with the environment and what concentrations were expected to be found in the soil to assist risk assessment. The

addition of the dissolution rates as stochastic elements provided an estimated mass rate entering the soil system, however, K_d was still dominant when assessing the NTO and DNAN breakthrough in combined dissolution and transport processes in the soil. This key finding led the research to determine whether the IHE breakthrough would still be controlled by K_d over longer periods of time, or if, by contrast, other processes such as degradation would participate more.

The study of IHE degradation in soil is a particularly challenging problem as soils contain mixtures of both organic and inorganic compounds that can interact with NTO and DNAN. In addition, soils with high organic content promote the growth of bacterial colonies that can biodegrade the IHE constituents through different metabolic pathways, releasing new chemical compounds to the soil. To better understand how long IHE persist in soil, laboratory experiments were conducted **in Chapter 5** to investigate the degradation of an IHE formulation in sand and sandy loam under biotic and abiotic conditions. According to the results, the mass loss of IHE chemical residues was between 20% and 50% in the sandy soils. However, the IHE mass loss in abiotic sandy soils was in both cases 15% lower, which indicated that the biodegradation caused by endogenous microorganisms present in the soils accounted only for 15% of the initial mass. This result was unexpected as loamy sand had a higher organic matter content and thus, a higher rate of biodegradation was anticipated. It was clear that the conditions of the soil (e.g., organic matter and endogenous bacteria) influenced the degradation and sorption of the IHE residues. As a result, IHE residues in sand were more likely to remain in the soil matrix and undergo transport processes, whereas in sandy loam, IHE residues were more prone to either be irreversibly adsorbed in the soil or undergo degradation, accumulating in the top layers of the soil.

Once established that IHE biodegradation in soil was limited, the research focused on what other parameters could influence IHE degradation. The literature indicated that degradation is highly dependent on temperature, and thus, the study continued by assessing the influence of soil temperature on the degradation of IHE residues. As the previous study was conducted at 20°C, it was necessary to perform similar studies at different soil temperatures in order to compare results. The average temperature in the UK is 12°C, and this data linked to the fact that no publications

reported IHE degradation at low temperature led the research to select 12°C and 4°C as the temperatures to compare to the results of IHE degradation in soils at 20°C.

The effect of the soil temperature on the degradation of IHE residues proved that IHE residues barely degraded in sand at low temperatures in comparison to the same soils stored at 20°C. Low temperatures clearly affected the interaction between the soil particles and the IHE compounds and this effect was more noticeable in the sandy soil as the IHE formulation mass was almost invariable over time, likely to be due to the low organic matter content (< 2%). In addition, the research provided estimated degradation rates and half-lives of the IHE chemical traces in the sand and sandy loam, offering an overview of the persistence of IHE residues in the soil. This persistence which varied from months to 2 years depending on the chemical, soil and temperature selected, being especially remarkable in sand at 4°C and 12°C, which could lead to potential accumulation of IHE residues at live fire ranges located in low temperature regions. Therefore, the data provided can help risk assessment posed by IHE residues in cold regions such as Canada (e.g., British Army Training Unit Suffield, a military training range), USA (e.g., Cold Regions Research and Engineering Laboratory, an explosive research laboratory) or Norway (e.g., Raufoss, a munition manufacturing facility).

Combining the findings of Chapters 3 to 5 enabled development of a simulation for persistence and breakthrough of IHE in soil. The simulation was validated in **Chapter 6** by comparing IHE concentrations in leachate from previously conducted soil column studies to their simulated values. The simulation of leachate concentrations in the indoor soil columns showed a strong correlation ($R > 0.65$) with the empirical values confirming the representativeness of the model. In all these cases, the experimental concentrations were equal to or less than the simulated ones and even in the weakest cases, both concentrations shared the same order of magnitude, suggesting that the model was effective under these conditions. Outdoor simulations showed further changes, but these were mainly due to the difference in rainwater volume and the high organic matter present in the loamy sand, which was not initially included in the model.

The collection of the experimental data was obtained from two MSc theses undertaken separately to this work, in which studies were performed in slightly different soils. This fact highlights the robustness of the model to simulate IHE behaviour in slightly different soils. It also indicates the importance of representative data, as for instance, IHE K_ds were estimated from **Chapter 3** and this issue undoubtedly lowered the representativeness of the simulations. Further to this, the model provided enough data to be used to computationally simulate the behaviour of an IHE formulation, allowing the prediction of peak concentrations and persistence in the soils.

However, as mentioned throughout the chapters, the developed model had some limitations in simulating contaminant fate and transport. Firstly, it did not account for contaminant hydrology, which would have helped to understand the water flow balance and lateral water fluxes within the column. Additionally, although the model considered soil-chemical interactions by including an experimental K_d value, it lacked a specific parameter accounting for soil organic matter content. Consequently, the model might not be representative for organic rich soils where parameters such as K_{OC} play an important role in sorption processes. Moreover, despite utilising experimentally measured data as input, the model did not incorporate pH and temperature parameter dependencies. Instead, it relied on the modeller's knowledge to determine the more accurate values for each scenario, potentially leading to inadequate simulations if used by other users unaware of these dependencies. Lastly, although the model has been tested in small-scale scenarios, its intended purpose was to aid in understanding chemicals behaviour in larger soil areas. Nonetheless, it remains uncertain whether the results obtained from these small scenarios can be extrapolated to locations such as military training ranges, and further improvements might be necessary to achieve representative simulations.

However, the model created has high potential to be used for risk assessment purposes and eventually, to partially replace empirical work. It is unlikely to be possible to simulate IHE behaviour in the environment based on wholly computational data as it requires accurate empirical data, in particular, IHE compound K_ds for the specific soils of interest, dissolution rates and degradation rates. In most cases, it is still necessary to conduct short and precise experimental

work to obtain the inputs required to achieve representative simulations. Further to this, the model will need routine validation to ensure reliable outcomes and to that, it will need to be compared to empirical works. Although computational modelling seems to be the solution to understanding and potentially predicting IHE behaviour in the soil, it will always require a minimum number of experimental works. However, development of a framework detailing the main key parameters and their values for different scenarios would significantly aid environmental risk assessment for IHE.

The stochastic model developed in GoldSim allowed the understanding of how two IHE constituents behave under two different environmental conditions and in two different sandy soils, where the interactions among the different elements were complex and difficult to explain. The addition of key inputs as stochastic elements in the simulations led to representative outputs that showed a probabilistic distribution of the breakthrough concentrations over time instead of a single value. This approach is clearly an advantage for risk assessment purposes, and thus, it could be interesting for use in other environments. However, the model is simply a means to understand the behaviour of contaminants in complex soil systems. The modellers and the scientific community in general are responsible for interpreting the outcome and deciding on a course of action.

The applications of this thesis can be summarised into three main points. Firstly, the data provided and the model developed in this work can be used to create a baseline for evaluating the hazards and potential consequences of the use of IHE at military ranges, demolition areas and manufacturing facilities under different environmental conditions. This will enhance decision making on how to evaluate contaminated lands and will improve explosive management systems in the environment. The second application is to serve as a baseline for studying contaminated areas by IHE residues and to support decision making on soil remediation strategies. In addition, it will establish the natural periods of time for the explosive residues to degrade before any amend is added. Lastly, the model can be used as a baseline and extended by other modellers conducting environmental studies to run their own simulations with other explosive contaminants in soil. Therefore, the work conducted in this thesis can be used as a steppingstone to recover soil sustainability.

7.2 Recommendations for future work

The use of computational methods to assess the risks posed by IHE in the soil is an advantage for scientists and decision makers as it enables the gathering of essential information very quickly in comparison to time consuming experimental work. The models developed so far for this purpose require a high knowledge of the environment and good understanding of the processes governing the fate and transport of IHE residues. Therefore, recommended further work is as follows:

- The understanding, investigation and addition of further biological and chemical processes that IHE residues can undergo when disposed in the soil such as plant uptake and run-off;
- The study of long-term concentrations of IHE in soil to complete risk assessment posed by IHE formulations;
- The implementation of a framework with representative values of key parameters used for modelling in different soil types and explosive formulations;
- The study of the interaction between IHE formulations (containing chemicals in different proportions) and types of soil on the texture triangle (e.g., silty, clay);
- The inclusion of alternative parameters (e.g., K_{OC}) or formulas (e.g., Freundlich isotherm, second-order degradation) that improves the representativeness of the simulations;
- Identification threshold limits for IHE residues in soil in the UK and linkage with the model developed in GoldSim to assess the toxic and threshold doses of the IHE to potential receptors;
- Extension of the model developed in this work to build standardised computational models to representatively predict the behaviour of IHE residues in soil, similar to existing models for other chemical compounds such as pesticides in agriculture.

REFERENCES

Adriaanse, P.I., Boesten, J.J. and Crum, S.J. (2013) ‘Estimating degradation rates in outdoor stagnant water by inverse modelling with TOXSWA: A case study with prosulfocarb’, *Pest Management Science*, 69(6), pp. 755–767.

Åkesson, M., Bendz, D., Carlsson, C., Sparrenbom, C.J. and Kreuger, J. (2014) ‘Modelling pesticide transport in a shallow groundwater catchment using tritium and helium-3 data’, *Applied Geochemistry*, 50, pp. 231–239.

Alaoui, A., Germann, P., Jarvis, N. and Acutis, M. (2003) ‘Dual-porosity and kinematic wave approaches to assess the degree of preferential flow in an unsaturated soil’, *Hydrological Sciences Journal*, 48(3), pp. 455–472.

Alavi, G., Chung, M., Lichwa, J., D’Alessio, M. and Ray, C. (2011) ‘The fate and transport of RDX, HMX, TNT and DNT in the volcanic soils of Hawaii: A laboratory and modeling study’, *Journal of Hazardous Materials*, 185(2–3), pp. 1600–1604.

Amaral, H.I.F., Gama, A.C., Gonçalves, C., Fernandes, J., Batista, M.J. and Abreu, M. (2016) ‘Long-term TNT and DNT contamination: 1-D modeling of natural attenuation in the vadose zone: case study, Portugal’, *Environmental Earth Sciences*, 75(1), pp. 1–15.

Ariyarathna, T., Vlahos, P., Tobias, C. and Smith, R. (2016) ‘Sorption kinetics of TNT and RDX in anaerobic freshwater and marine sediments: Batch studies’, *Environmental Toxicology and Chemistry*, 35, pp. 47–55.

Arnett, C.M., Rodriguez, G. and Maloney, S.W. (2009) ‘Analysis of bacterial community diversity in anaerobic fluidized bed bioreactors treating 2, 4-dinitroanisole (DNAN) and n-Methyl-4-nitroaniline (MNA) using 16S rRNA gene clone libraries’, *Microbes and Environments*, 24(1), pp. 72–75.

Arthur, J.D., Mark, N.W., Taylor, S., Šimunek, J., Brusseau, M.L. and Dontsova, K.M. (2017) ‘Batch soil adsorption and column transport studies of 2,4-dinitroanisole (DNAN) in soils’, *Journal of Contaminant Hydrology*, 199, pp. 14–23.

Arthur, J.D., Mark, N.W., Taylor, S., Šimůnek, J., Brusseau, M.L. and Dontsova, K.M. (2018) ‘Dissolution and transport of insensitive munitions formulations IMX-101 and IMX-104 in saturated soil columns’, *Science of the Total Environment*, 624, pp. 758–

768.

Ayawei, N., Ebelegi, A.N. and Wankasi, D. (2017) ‘Modelling and Interpretation of Adsorption Isotherms’, *Journal of Chemistry*, 2017

Balakrishnan, S., Roy, A., Ierapetritou, M.G., Flach, G.P. and Georgopoulos, P.G. (2005) ‘A comparative assessment of efficient uncertainty analysis techniques for environmental fate and transport models: Application to the FACT model’, *Journal of Hydrology*, 307(1–4), pp. 204–218.

Bear, J. and Cheng, A.H.D. (2010) *Modelling Groundwater Flow and Contaminant Transport*. New York: Springer US.

Bear, J. and Verruijt, A. (1987) *Modeling groundwater flow and pollution.*

Beck, A.J., Gledhill, M., Schlosser, C., Stamer, B., Böttcher, C., Sternheim, J., Greinert, J. and Achterberg, E.P. (2018) ‘Spread, Behavior, and Ecosystem Consequences of Conventional Munitions Compounds in Coastal Marine Waters’, *Frontiers in Marine Science*, 5, p. Article 141.

Becker, N.M. (1995) *Fate of Selected High Explosives in the Environment: a Literature Review*. California, USA.

Beegum, S., Šimůnek, J., Szymkiewicz, A., Sudheer, K.P. and Nambi, I.M. (2018) ‘Implementation of Solute Transport in the Vadose Zone into the “HYDRUS Package for MODFLOW”’, *Groundwater*, 57(3), pp. 392–408.

Beltman, W.H.J. and Adriaanse, P.I. (1999) *User’s manual TOXSWA 1.2.* Winand Staring Centre, Wageningen

Bernstein, A., Adar, E., Nejidat, A. and Ronen, Z. (2011) ‘Isolation and characterization of RDX-degrading Rhodococcus species from a contaminated aquifer’, *Biodegradation*, 22(5), pp. 997–1005.

Beven, K. (2002) ‘Towards a coherent philosophy for modelling the environment’, *Proceedings of the Royal Society*, (458), pp. 1–20.

Blythe, S.P., Nisbet, R.M. and Gurney, W.S.C. (1982) ‘Instability and complex dynamic behaviour in population models with long time delays’, *Theoretical Population Biology*, 22(2), pp. 147–176.

Boddu, V.M., Abburi, K., Maloney, S.W. and Damavarapu, R. (2008) ‘Physicochemical properties of an insensitive munitions compound , N -methyl-4-nitroaniline (MNA)’, *Journal of Hazardous Materials*, 155, pp. 288–294.

Bordeleau, G., Savard, M.M., Martel, R., Ampleman, G. and Thiboutot, S. (2008) ‘Determination of the origin of groundwater nitrate at an air weapons range using the dual isotope approach’, *Journal of Contaminant Hydrology*, 98(3–4), pp. 97–105.

Borgesen, C.D., Fomsgaard, I.S., Plauborg, F., Schelde, K. and Spliid, N.H. (2015) *Fate of pesticides in agricultural soils*.

Braida, W.J., Wazne, M., Ogundipe, A., Tuna, G.S., Pavlov, J. and Koutsospyros, A. (2012) ‘Transport of Nitrotriazolone (NTO) in Soil Lysimeters’, *Protection and Restoration of the Environment Conference XI*, (July)

Brannon, J.M., Price, C.B., Hayes, C. and Yost, S.L. (2002) ‘Aquifer Soil Cation Substitution and Adsorption of TNT, RDX, and HMX’, *Soil and Sediment Contamination: An International Journal*, 11(3), pp. 327–388.

Brannon, J.M., Price, C.B., Yost, S.L., Hayes, C. and Porter, B. (2005) ‘Comparison of environmental fate and transport process descriptors of explosives in saline and freshwater systems’, *Marine Pollution Bulletin*, 50(3), pp. 247–251.

Bronner, G. and Goss, K.U. (2011) ‘Sorption of organic chemicals to soil organic matter: Influence of soil variability and ph dependence’, *Environmental Science and Technology*, 45, pp. 1307–1312.

Brown, D.M., Bonte, M., Gill, R., Dawick, J. and Boogaard, P.J. (2017) ‘Heavy hydrocarbon fate and transport in the environment’, *Quarterly Journal of Engineering Geology and Hydrogeology*, 50(3), pp. 333–346.

Burnell, D.K., Xu, J., Hansen, S.K., Sims, L.S. and Faust, C.R. (2018) ‘A Practical Modeling Framework for Non-Fickian Transport and Multi-Species Sequential First-Order Reaction’, *Groundwater*, 56(4), pp. 524–540.

Byrn, S.R., Zografi, G. and Chen, X.S. (2017) *Solubility and Dissolution*.

Le Campion, L., Vandais, A. and Ouazzani, J. (1999) ‘Microbial remediation of NTO in aqueous industrial wastes’, *FEMS Microbiology Letters*, 176(1), pp. 197–203.

Cao, X., Temple, T., Li, X., Coulon, F. and Sui, H. (2015) ‘Influence of particle size and organic carbon content on distribution and fate of aliphatic and aromatic hydrocarbon fractions in chalks’, *Environmental Technology and Innovation*, 4, pp. 227–239.

Carsel, R.F., Mulkey, L.A., Lorber, M.N. and Baskin, L.B. (1985) ‘The pesticide root zone model (przm): a procedure for evaluating pesticide leaching threats to groundwater’, *Ecological Modelling*, 30, pp. 49–69.

Carsel, R.F., Smith, C.N., Mulkey, L.A., Dean, J.D. and Jowise, P. (1984) *Users Manual for the Pesticide Root Zone Model (PRZM), Release 1*. Athens, Georgia.

Chen, H., Zhang, X., Demars, C. and Zhang, M. (2017) ‘Numerical simulation of agricultural sediment and pesticide runoff : RZWQM and PRZM comparison’, *Hydrological Processes*, 31, pp. 2464–2476.

Chiu, M.C., Hunt, L. and Resh, V.H. (2016) ‘Response of macroinvertebrate communities to temporal dynamics of pesticide mixtures: A case study from the Sacramento River watershed, California’, *Environmental Pollution*, 219, pp. 89–98.

Clark, B. and Boopathy, R. (2007) ‘Evaluation of bioremediation methods for the treatment of soil contaminated with explosives in Louisiana Army Ammunition Plant, Minden, Louisiana’, *Journal of Hazardous Materials*, 143(3), pp. 643–648.

Clausen, J., Robb, J., Curry, D. and Korte, N. (2004) ‘A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA’, *Environmental Pollution*, 129(1), pp. 13–21.

Connon, R.E., Geist, J. and Werner, I. (2012) ‘Effect-based tools for monitoring and predicting the ecotoxicological effects of chemicals in the aquatic environment’, *Sensors (Switzerland)*, 12(9), pp. 12741–12771.

Crouse, L.C.B., Lent, E.M. and Leach, G.J. (2015) ‘Oral toxicity of 3-nitro-1,2,4-triazol-5-one in rats’, *International Journal of Toxicology*, 34(1), pp. 55–66.

Davies, P.J. and Provatas, A. (2006) ‘Characterisation of 2 ,4-Dinitroanisole : An Ingredient for use in Low Sensitivity Melt Cast Formulations’, *Weapons systems division. Defence Science and Technology Organisation, DSTO-TR-1904*, , pp. 1–22.

Detrick, F. (1991) ‘Environmental Chemistry Short Communication’, *Environmental Toxicology*, 10, pp. 5–8.

Diamantopoulos, E., Šimůnek, J., Oberdörster, C., Hammel, K., Jene, B., Schröder, T. and Harter, T. (2017) ‘Assessing the Potential Exposure of Groundwater to Pesticides: A Model Comparison’, *Vadose Zone Journal*, 16(11), pp. 1–13.

Diersch, H.-J.G. (2014) *FEFLOW: Finite Element Modelling of Flow, Mass and Heat Transport in Porous and Fractured Media*

Dontsova, K., Taylor, S., Pesce-Rodriguez, R., Brusseau, M., Arthur, J., Mark, N., Walsh, M., Lever, J. and Šimůnek, J. (2014) *Dissolution of NTO, DNAN and Insensitive Munitions Formulations and Their Fates in Soils*. Tucson, Arizona, USA.

Dontsova, K.M., Yost, S.L., Šimunek, J., Pennington, J.C. and Williford, C.W. (2006) ‘Dissolution and Transport of TNT, RDX, and Composition B in Saturated Soil Columns’, *Journal of Environment Quality*, 35, pp. 2043–2054.

Dorn, A., Hammel, K., Dalkmann, P., Faber, D., Hellpointner, E., Lamshoeft, M., Telscher, M., Bruns, E., Seidel, E. and Hollert, H. (2021) ‘What is the actual exposure of organic compounds on Chironomus riparius? - A novel methodology enabling the depth-related analysis in sediment microcosms’, *Chemosphere*, 279, ID. 130424.

Dortch, M.S. (2018) ‘Modeling Dissolution of High Explosive Formulations’, *Soil and Sediment Contamination*, 27(4), pp. 280–310.

Dubus, I.G. and Brown, C.D. (2002) ‘Volatile Organic Compounds in the Environment’, *Journal of Environmental Quality*, 31, pp. 227–240.

Earl, N., Cartwright, C.D., Horrocks, S.J., Worboys, M., Swift, S., Kirton, J.A., Askan, A.U., Kelleher, H. and Nancarrow, D.J. (2003) *Review of the Fate and Transport of Selected Contaminants in the Soil Environment*.

Ebrahimian, H. and Noory, H. (2015) ‘Modeling paddy field subsurface drainage using HYDRUS-2D’, *Paddy and Water Environment*, 13(4), pp. 477–485.

Egeghy, P.P., Sheldon, L.S., Isaacs, K.K., Özkaynak, H., Goldsmith, M.R., Wambaugh, J.F., Judson, R.S. and Buckley, T.J. (2016) ‘Computational exposure science: An emerging discipline to support 21st-century risk assessment’,

Environmental Health Perspectives, 124(6), pp. 697–702.

El-Kilani, R.M.M. and Belal, M.H. (2010) 'Modelling an environmental pollutant transport from the stacks to and through the soil', *Journal of Advanced Research*, 1(3) University of Cairo., pp. 243–253.

Etnier, A.L. (1989) 'Water Quality Criteria for Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)', *Regulatory Toxicology and Pharmacology*, 157, pp. 147–157.

Eum, J., Kwak, J., Kim, H.J., Ki, S. and Lee, K. (2016) '3D Visualization of Developmental Toxicity of 2 , 4 , 6-Trinitrotoluene in Zebrafish Embryogenesis Using Light-Sheet Microscopy', *International Jorunal of Molecular Sciences*, 17(November), p. 1925.

Falone, S.Z., Vieira, E.M. and Onuska, F.I. (2006) 'Adsorption study of RDX and TNT explosives in soils by HPLC', *Journal of Liquid Chromatography and Related Technologies*, 29, pp. 1645–1662.

Fawcett-Hirst, W., Temple, T.J., Ladyman, M.K. and Coulon, F. (2020) 'Adsorption behaviour of 1,3,5-trinitroperhydro-1,3,5-triazine, 2,4-dinitroanisole and 3-nitro-1,2,4-triazol-5-one on commercial activated carbons', *Chemosphere*, 255, p. 126848.

Ferreira, C., Ribeiro, J., Almada, S. and Freire, F. (2017) 'Environmental Assessment of Ammunition: the Importance of a Life-Cycle Approach', *Propellants, Explosives, Pyrotechnics*, 42(1), pp. 44–53.

Fida, T.T., Palamuru, S., Pandey, G. and Spain, J.C. (2014) 'Aerobic biodegradation of 2,4-dinitroanisole by Nocardioides sp. strain JS1661', *Applied and Environmental Microbiology*, 80(24), pp. 7725–7731.

Firestone, M., Fenner-Crisp, P., Barry, T., Bennett, D., Chang, S. and Callahan, M. (1997) *Guiding Principles for Monte Carlo Analysis*. Washington DC.

Francois, E., Tasker, D., Burritt, R. and Bowden, P. (2018) 'Initiation of insensitive high explosives using multiple wave interactions Initiation of Insensitive High Explosives Using Multiple Wave Interactions', *AIP Conference Proceedings 1979*.

Frem, D. (2022) 'A Review on IMX-101 and IMX-104 Melt-Cast Explosives: Insensitive Formulations for the Next-Generation Munition Systems', *Propellants, Explosives, Pyrotechnics*, (e202100312), pp. 1–17.

Fuller, M.E., Rezes, R.T., Hedman, P.C., Jones, J.C., Sturchio, N.C. and Hatzinger, P.B. (2021) ‘Biotransformation of the insensitive munition constituents 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dinitroanisole (DNAN) by aerobic methane-oxidizing consortia and pure cultures.’, *Journal of Hazardous Materials*, 407., p. 124341.

Fuller, M.E., Schaefer, C.E., Andaya, C., Lazouskaya, V., Fallis, S., Wang, C. and Jin, Y. (2012) ‘Dissolution kinetics of sub-millimeter Composition B detonation residues: Role of particle size and particle wetting’, *Chemosphere*, 88(5), pp. 591–597.

Galante, E., Temple, T., Ladyman, M. and Gill, P.P. (2017) ‘The UK Ministry of Defence Project Orientated Environmental Management System (POEMS)’, *Propellants, Explosives, Pyrotechnics*, 42, pp. 36–43.

Galante, E.B.F., Mai, N., Ladyman, M.K., Gill, P.P., Temple, J., Coulon, F., Galante, E.B.F., Mai, N., Ladyman, M.K. and Gill, P.P. (2021) ‘Evaluation of small-scale combustion of an insensitive high explosive formulation containing 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanisole (DNAN), and 1,3,5-triazine (RDX)’, *Journal of Energetic Materials*, 39(1) Taylor & Francis, pp. 85–99.

Gharbi, M., Soualmia, A., Dartus, D. and Masbernat, L. (2016) ‘Comparison of 1D and 2D hydraulic models for floods simulation on the medjerda riverin tunisia’, *Journal of Materials and Environmental Science*, 7(8), pp. 3017–3026.

GoldSim Technology Group LLC (2021) *GoldSim User’s Guide (Version 14.0)*. Seattle, Washington USA.

González-Forero, R. (2014) ‘Partitioning model of the adsorption of explosives from soils to determine its environmental fate.’, *Revista Criminalidad*, 56, pp. 139–152.

Gorgenyi, M., Dewulf, J., Langenhove, H. Van and Herberger, K. (2006) ‘Aqueous salting-out effect of inorganic cations and anions on non-electrolytes’, *Chemosphere*, 65, pp. 802–810.

Groom, C.A., Halasz, A., Paquet, L., Morris, N., Olivier, L. and Dubois, C. (2002) ‘Accumulation of HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) in Indigenous and Agricultural Plants Grown in Firing-Range Soil’, *Environmental Science and Technology*, 36, pp. 112–118.

Hao, Q. long, Qiao, H., Zhou, C.Z., Peng, W., Zhang, K. and Lu, S. (2018) ‘Effects of Fulvic Acid on TNT Adsorption in Soil’, *Soil and Sediment Contamination,* 27(3), pp. 186-199.

Harvey, S.D., Fellows, R.J., Cataldo, D. and Bean, R.M. (1991) ‘Fate of the explosive hexahydro-1,3,4-triniyto-1,3,5-triazine (RDX) in soil ans bioaccumulation in bush bean hydroponic plants’, *Environmental Chemistry*, 10, pp. 845–855.

Hattori, Y., Haruna, Y. and Otsuka, M. (2013) ‘Dissolution process analysis using model-free Noyes-Whitney integral equation’, *Colloids and Surfaces B: Biointerfaces*, 102, pp. 227–231.

Havlová, V. and Vopálka, D. (2010) ‘HTO as a conservative tracer used for characterization of contaminant migration in porous rock environment’, *Journal of Radioanalytical and Nuclear Chemistry*, 286(3), pp. 785–791.

Hawari, J., Monteil-Rivera, F., Perreault, N.N., Halasz, A., Paquet, L., Radovic-Hrapovic, Z., Deschamps, S., Thiboutot, S. and Ampleman, G. (2015) ‘Environmental fate of 2,4-dinitroanisole (DNAN) and its reduced products’, *Chemosphere*, 119, pp. 16–23.

Hayat, R., Ali, S., Amara, U., Khalid, R. and Ahmed, I. (2010) ‘Soil beneficial bacteria and their role in plant growth promotion: A review’, *Annals of Microbiology*, 60(4), pp. 579–598.

Hewitt, A.D., Jenkins, T.F., Walsh, M.E., Walsh, M.R. and Taylor, S. (2005) ‘RDX and TNT residues from live-fire and blow-in-place detonations’, *Chemosphere*, 61(6), pp. 888–894.

Indest, K.J., Hancock, D.E., Crocker, F.H., Eberly, J.O., Jung, C.M., Blakeney, G.A., Brame, J. and Chappell, M.A. (2017) ‘Biodegradation of insensitive munition formulations IMX101 and IMX104 in surface soils’, *Journal of Industrial Microbiology and Biotechnology*, 44, pp. 987–995.

Inglezakis, V.J. and Zorpas, A. (2011) ‘Industrial hazardous waste in the framework of EU and international legislation’, *Management of Environmental Quality: An International Journal*, 22(5), pp. 566–580.

Jackson, L.J., Trebitz, A.S. and Cottingham, K.L. (2000) ‘An Introduction to the

Practice of Ecological Modeling', *BioScience*, 50(8), pp. 694–706.

Jacques, D., Šimůnek, J., Mallants, D. and van Genuchten, M.T. (2008) 'Modelling coupled water flow, solute transport and geochemical reactions affecting heavy metal migration in a podzol soil', *Geoderma*, 145(3–4), pp. 449–461.

Janney, P. and Jenkins, J. (2019) 'A Systems Approach to Modeling Watershed Ecohydrology and Pesticide Transport', *Journal of Environmental Quality*, 48(4), pp. 1047–1056.

Jarvis, N. (2016) 'Extended sorption partitioning models for pesticide leaching risk assessments: Can we improve upon the Koc concept?', *Science of the Total Environment*, 539, pp. 294–303.

Jarvis, N.J. (1995) 'Simulation of soil water dynamics and herbicide persistence in a silt loam soil using the MACRO model', *Ecological Modelling*, 81(1–3), pp. 97–109.

Jarvis, N.J., Hollis, J.M., Nicholls, P.H., Mayr, T. and Evans, S.P. (1997) 'MACRO - DB: A decision-support tool for assessing pesticide fate and mobility in soils', *Environmental Modelling and Software*, 12(2–3), pp. 251–265.

Jarvis, N.J., Stahli, M., Bergstrom, L. and Johnsson, H. (1994) 'Simulation of Dichlorprop and Bentazon Leaching in Soils of Contrasting Texture Using the MACRO Model', *Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology*, 29(6), pp. 1255–1277.

Jarvis, N.J., Villholth, K.G. and Ulen, B. (1999) 'Modelling particle mobilization and leaching in macroporous soil', *European Journal of Soil Science*, 50(4), pp. 621–632.

Jenkins, D.E. (2018) '*Fate and transport of insensitive high explosives in outdoor soil columns'*. MSc thesis from Explosives Ordnance Engineering course. Cranfield University. Shrivenham campus, UK.

Jog, K. V, Sierra, R. and Jim, A. (2020) 'Rapid biotransformation of the insensitive munitions compound' *World Journal of Microbiology and Biotechnology*, 36, pp. 1–10.

Johnson, M.S. and Reddy, G. (2015) 'Chapter 3- Wildlife Toxicity Assessment for 2,4,6-TRinitrotoluene (TNT). Book *Wildlife Toxicity Assessments for Chemicals of Military Concern*. Department of Defence (USA). Amsterdam: Elsevier

Kadoya, W.M., Sierra-Alvarez, R., Jagadish, B., Wong, S., Abrell, L., Mash, E.A. and Field, J.A. (2021) ‘Covalent bonding of aromatic amine daughter products of 2,4-dinitroanisole (DNAN) with model quinone compounds representing humus via nucleophilic addition’, *Environmental Pollution*, 268, ID 115862.

Kalderis, D., Juhasz, A.L., Boopathy, R. and Comfort, S. (2011) ‘Soils contaminated with explosives: Environmental fate and evaluation of state-of-the-art remediation processes (IUPAC Technical Report)’, *Pure and Applied Chemistry*, 83(7), pp. 1407–1484.

Kaplan, A.S., Bsce, C.F.B., Col, L. and Peczenik, A. (1965) ‘Archives of Environmental Health : An International Human Intoxication From RDX’, *Archives of Environmental Health: An International Journal*, 10(6), pp. 877–883.

Karthikeyan, S. and Spain, J.C. (2016) ‘Biodegradation of 2,4-dinitroanisole (DNAN) by Nocardioides sp. JS1661 in water, soil and bioreactors’, *Journal of Hazardous Materials*, 312, pp. 37–44.

Kasaraneni, V., Kohm, S.E., Eberle, D., Boving, T. and Oyanedel-Craver, V. (2014) ‘Enhanced containment of polycyclic aromatic hydrocarbons through organic modification of soils’, *Environmental Progress and Sustainable Energy*, 33(1), pp. 47–54.

Kennedy, A.J., Poda, A.R., Melby, N.L., Moores, L.C., Jordan, S.M., Gust, K.A. and Bednar, A.J. (2017) ‘Aquatic toxicity of photo-degraded insensitive munition 101 (IMX-101) constituents’, *Environmental Toxicology and Chemistry*, 36(8), pp. 2050–2057.

Khan, F., Pal, D., Ghosh, A. and Cameotra, S.S. (2013) ‘Degradation of 2,4-dinitroanisole (DNAN) by metabolic cooperative activity of Pseudomonas sp. strain FK357and Rhodococcus imtechensis strain RKJ300’, *Chemosphere*, 93(11), pp. 2883–2888.

Khatiwada, R., Abrell, L., Li, G., Root, R.A., Sierra-Alvarez, R., Field, J.A. and Chorover, J. (2018) ‘Adsorption and oxidation of 3-nitro-1,2,4-triazole-5-one (NTO) and its transformation product (3-amino-1,2,4-triazole-5-one, ATO) at ferrihydrite and birnessite surfaces’, *Environmental Pollution*, 240, pp. 200–208.

Kitcher, E., Braida, W., Koutsospyros, A., Pavlov, J. and Su, T.L. (2017) ‘Characteristics and products of the reductive degradation of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dinitroanisole (DNAN) in a Fe-Cu bimetal system’, *Environmental Science and Pollution Research*, 24(3), pp. 2744–2753.

Klein, M. and Klöppel, H. (1993) ‘Usefulness of models for the prediction of run-off events - comparison with experimental data’, *Science of the Total Environment*, 134, pp. 1421–1428.

Kossik, R. and Miller, I. (2004) *A probabilistic total system approach to the simulation of complex environmental systems*. Proceedings of the 2004 Witer Simulation Conference. GoldSim Technology Group: Issaquah, Washington, USA.

Krzmarzick, M.J., Khatiwada, R., Olivares, C.I., Abrell, L., Sierra-Alvarez, R., Chorover, J. and Field, J.A. (2015) ‘Biotransformation and degradation of the insensitive munitions compound, 3-nitro-1,2,4-triazol-5-one, by soil bacterial communities’, *Environmental Science and Technology*, 49(9), pp. 5681–5688.

Kumar, M., Ladyman, M.K., Mai, N., Temple, T. and Coulon, F. (2017) ‘Release of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) from polymer-bonded explosives (PBXN-109) into water by artificial weathering’, *Chemosphere*, 169, pp. 604–608.

Kupfersberger, H., Klammler, G., Schumann, A., Brückner, L. and Kah, M. (2018) ‘Modeling Subsurface Fate of -Metolachlor and Metolachlor Ethane Sulfonic Acid in the Westliches Leibnitzer Feld Aquifer’, *Vadose Zone Journal*, 17(1), p. 1-5.

Ladyman, M.K., Mai, N. and Temple, T. (2017) Estimating explosive contamination from live-fire munitions using multi-increment sampling in Alaska, *Official Journal of the Institute of Explosive Engineering*, 12, p 29-30.

Lammel, G., Klopffer, W., V.S., S., Schmidt, E. and Lepi, A. (2007) ‘Multicompartmental Fate of Persistent Substances chemistry-atmospheric transport model’, *Environmental Science and Pollution Research*, 14(3), pp. 153–165.

Lammoglia, S.K., Brun, F., Quemar, T., Moeys, J., Barriuso, E., Gabrielle, B. and Mamy, L. (2018) ‘Modelling pesticides leaching in cropping systems: Effect of uncertainties in climate, agricultural practices, soil and pesticide properties’, *Environmental Modelling and Software*, 109, 342–352.

Larsbo, M. and Jarvis, N. (2010) ‘Simulating Solute Transport in a Structured Field Soil’, *Journal of Environment Quality*, 34(2), p. 621.

Larson, S.L., Martin, W.A., Escalon, B.L. and Thompson, M. (2008) ‘Dissolution, sorption, and kinetics involved in systems containing explosives, water, and soil’, *Environmental Science and Technology*, 42(3), pp. 786–792.

Lee, K.. and Coburn, M.. (1988) *3-Nitro-1,2,4-triazol-5-one, a less sensitive explosive*. Los Alamos National Laboratory report LA-10302-MS, New Mexico, USA.

Lee, Y.M., Choi, H.J. and Kim, K. (2016) ‘A preliminary comparison study of two options for disposal of high-level waste’, *Progress in Nuclear Energy*, 90, pp. 229–239.

Lee, Y.M. and Hwang, Y. (2009) ‘A GoldSim model for the safety assessment of an HLW repository’, *Progress in Nuclear Energy*, 51(6), pp. 746–759.

Leju, J., Ladu, C. and Zhang, D.-R. (2011) ‘Modeling atrazine transport in soil columns with HYDRUS-1D’, *Water Science and Engineering*, 4(3), pp. 258–269.

Levine, B.S., Furedi, E.M., Gordon, D.E., Barkley, J.J. and Lish, P.M. (1990) ‘Toxic Interactions of the Munitions Compounds TNT and RDX in F344 Rats’, *Fundamental and Applied Toxicology*, 380, pp. 373–380.

Lewis, T.A., Newcombe, D.A. and Crawford, R.L. (2004) Bioremediation of soils contaminated with explosives *Journal of Environmental Management*, 70, pp. 291-307.

Li, Y., Ren, X., Hill, R., Malonew, R. and Ying, Z. (2017) ‘Characteristics of Water Infiltration in Layered Water-Repellent Soils’, *Pedosphere*, 28(5), pp. 775–792.

Linker, B.R., Khatiwada, R., Perdrial, N., Abrell, L., Sierra-Alvarez, R., Field, J.A. and Chorover, J. (2015) ‘Adsorption of novel insensitive munitions compounds at clay mineral and metal oxide surfaces’, *Environmental Chemistry*, 12(1), pp. 74–84.

Lotufo, G.R., Biedenbach, J.M., Sims, J.G., Chappell, P., Stanley, J.K. and Gust, K.A. (2015) ‘Bioaccumulation kinetics of the conventional energetics TNT and RDX relative to insensitive munitions constituents DNAN and NTO in Rana pipiens tadpoles’, *Environmental Toxicology and Chemistry*, 34(4), pp. 880–886.

Lu, C., Samper, J., Luis Cormenzana, J., Ma, H., Montenegro, L. and Ángel Cuñado, M. (2012) 'Reactive transport model and apparent K d of Ni in the near field of a HLW repository in granite', *Computers and Geosciences*, 49, pp. 256–266.

Luo, Y. (2019) '*Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment and Management. Chapter 14: Modeling the Mitigating Effects of Conservation Practices for Pyrethroid Uses*'. Deartment of Pesticide Regulation, California, Environmental Protection Agency. Sacramento: American Chemical Society.

Luo, Y., Zhang, X., Liu, X., Ficklin, D. and Zhang, M. (2008) 'Dynamic modeling of organophosphate pesticide load in surface water in the northern San Joaquin Valley watershed of California', *Environmental Pollution*, 156(3), pp. 1171–1181.

Lynch, J.C., Brannon, J.M. and Delfino, J.J. (2002) 'Dissolution rates of three high explosive compounds: TNT, RDX, and HMX', *Chemosphere*, 47, pp. 725–734.

Lynch, J.C., Brannon, J.M., Hatfield, K. and Delfino, J.J. (2003) 'An exploratory approach to modeling explosive compound persistence and flux using dissolution kinetics', *Journal of Contaminant Hydrology*, 66(3–4), pp. 147–159.

Lynch, J.C., Myers, K.F., Brannon, J.M. and Delfino, J.J. (2001) 'Effects of pH and temperature on the aqueous solubility and dissolution rate of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)', *Journal of Chemical and Engineering Data*, 46(6), pp. 1549–1555.

Madeira, C.L., Field, J.A., Simonich, M.T., Tanguay, R.L., Chorover, J. and Sierra-Alvarez, R. (2018) 'Ecotoxicity of the insensitive munitions compound 3-nitro-1,2,4-triazol-5-one (NTO) and its reduced metabolite 3-amino-1,2,4-triazol-5-one (ATO)', *Journal of Hazardous Materials*, 343, pp. 340–346.

Madeira, C.L., Jog, K. V., Vanover, E.T., Brooks, M.D., Taylor, D.K., Sierra-Alvarez, R., Waidner, L.A., Spain, J.C., Krzmarzick, M.J. and Field, J.A. (2019a) 'Microbial Enrichment Culture Responsible for the Complete Oxidative Biodegradation of 3-Amino-1,2,4-triazol-5-one (ATO), the Reduced Daughter Product of the Insensitive Munitions Compound 3-Nitro-1,2,4-triazol-5-one (NTO)', *Environmental Science and Technology*, 53(21), pp. 12648–12656.

Madeira, C.L., Kadoya, W.M., Li, G., Wong, S., Sierra-Alvarez, R. and Field, J.A. (2019b) ‘Reductive biotransformation as a pretreatment to enhance in situ chemical oxidation of nitroaromatic and nitroheterocyclic explosives’, *Chemosphere*, 222, pp. 1025–1032.

Mallants, D., Šimůnek, J., van Genuchten, M.T. and Jacques, D. (2017) ‘Simulating the fate and transport of coal seam gas chemicals in variably-saturated soils using HYDRUS’, *Water (Switzerland)*, 9(6), ID 385.

Mamy, L., Gabrielle, B. and Barriuso, E. (2008) ‘Measurement and modelling of glyphosate fate compared with that of herbicides replaced as a result of the introduction of glyphosate-resistant oilseed rape’, *Pest Management Science*, 64, pp. 262–275.

Marín-Benito, J.M., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J. and Mamy, L. (2015) ‘Chemosphere Modeling fungicides mobility in undisturbed vineyard soil cores unamended and amended with spent mushroom substrates’, *Chemosphere*, 134, pp. 408–416.

Mark, N., Arthur, J., Dontsova, K., Brusseau, M. and Taylor, S. (2016) ‘Adsorption and attenuation behavior of 3-nitro-1,2,4-triazol-5-one (NTO) in eleven soils’, *Chemosphere*, 144, pp. 1249–1255.

Mark, N., Arthur, J., Dontsova, K., Brusseau, M., Taylor, S. and Šimůnek, J. (2017) ‘Column transport studies of 3-nitro-1,2,4-triazol-5-one (NTO) in soils’, *Chemosphere*, 171, pp. 427–434.

McGivern, B.B., Tfaily, M.M., Borton, M.A., Kosina, S.M., Daly, R.A., Nicora, C.D., Purvine, S.O., Wong, A.R., Lipton, M.S., Hoyt, D.W., Northen, T.R., Hagerman, A.E. and Wrighton, K.C. (2021) ‘Decrypting bacterial polyphenol metabolism in an anoxic wetland soil’, *Nature Communications*, 12(1), 1–16.

Menezes, O., Kadoya, W.M., Gavazza, S., Sierra-alvarez, R., Mash, A., Abrell, L. and Field, J.A. (2021) ‘Covalent binding with model quinone compounds unveils the environmental fate of the insensitive munitions reduced product 2 , 4-dia - minoanisole (DAAN) under anoxic conditions’, *Journal of Hazardous Materials*, 413, ID 125459.

Merdun, H. and Quisenberry, V.L. (2004) ‘Simulation of water and solute transport with MACRO model in Cecil loamy sand soil’, *Australian Journal of Soil Research*, 42(8), pp. 939–951.

Molina, G.M., Padilla, I., Pando, M. and Pérez, D.D. (2006) ‘Field lysimeters for the study of fate and transport of explosive chemicals in soils under variable environmental conditions’, *Detection and Remediation Technologies for Mines and Minelike Targets XI*, 6217, ID 62173A.

Monteil-Rivera, F., Paquet, L., Deschamps, S., Balakrishnan, V.K., Beaulieu, C. and Hawari, J. (2004) ‘Physico-chemical measurements of CL-20 for environmental applications: Comparison with RDX and HMX’, *Journal of Chromatography A*, 1025, pp. 125–132.

Moores, L.C., Kennedy, A.J., May, L., Jordan, S.M., Bednar, A.J., Jones, S.J., Henderson, D.L., Gurtowski, L. and Gust, K.A. (2020) ‘Identifying degradation products responsible for increased toxicity of UV-Degraded insensitive munitions’, *Chemosphere*, 240, ID 124958.

Morley, M.C., Yamamoto, H., Speitel, G.E. and Clausen, J. (2006) ‘Dissolution kinetics of high explosives particles in a saturated sandy soil’, *Journal of Contaminant Hydrology*, 85(3–4), pp. 141–158.

Neitsch, S.., Arnold, J.., Kiniry, J.. and Williams, J.. (2011) ‘*Soil & Water Assessment Tool Theoretical Documentation Version 2009*’, Texas Water Resources Institute Technical Report 406, Texas A&M University, USA.

Nham, H.T.T., Greskowiak, J., Nödler, K., Rahman, M.A., Spachos, T., Rusteberg, B., Massmann, G., Sauter, M. and Licha, T. (2015) ‘Modeling the transport behavior of 16 emerging organic contaminants during soil aquifer treatment’, *Science of the Total Environment*, 514, pp. 450–458.

Oh, J.A., Beltman, W.H.J., Ter Horst, M.M.S., Ham, S.N., Park, Y.K., Shin, J.Y. and Kyung, K.S. (2021) ‘Development of surface water exposure scenarios for risk assessment of pesticides in Korea’, *Science of the Total Environment*, 771, ID. 144790.

Oh, S.Y., Seo, Y.D., Jeong, T.Y. and Kim, S.D. (2018) ‘Sorption of Nitro Explosives

to Polymer/Biomass-Derived Biochar', *Journal of Environmental Quality*, 47, pp. 353–360.

Olivares, C.I., Abrell, L., Khatiwada, R., Chorover, J., Sierra-Alvarez, R. and Field, J.A. (2016) '(Bio)transformation of 2,4-dinitroanisole (DNAN) in soils', *Journal of Hazardous Materials*, 304, pp. 214–221.

Pachepsky, Y., Benson, D. and Rawls, W. (2000) 'Simulating scale-dependent solute transport in soils with the fractional advective-dispersive equation', *Soil Science Society of America Journal*, 64(4), pp. 1234–1243.

Panik, M. and Necas, V. (2013) 'GOLDSIM models of long-term radiation impact of conditionally cleared radioactive material', *Progress in Nuclear Energy*, 67, pp. 88–97.

Paszko, T. (2014a) 'Modeling of pH-dependent adsorption and leaching of MCPA in profiles of Polish mineral soils', *Science of the Total Environment*, 494–495, pp. 229–240.

Paszko, T. (2014b) 'Adsorption, degradation and mobility of carbendazim in profiles of Polish mineral soils', *Geoderma*, 226–227(1), pp. 160–169.

Patterson, D.A., Strehmel, A., Erzgräber, B. and Hammel, K. (2017) 'Modeling chemical accumulation in sediment of small waterbodies accounting for sediment transport and water-sediment exchange processes over long periods', *Environmental Toxicology and Chemistry*, 36(12), pp. 3223–3231.

Paula, P. (2018) '*Environmental transport studies of components of an insensitive high explosive formulation in soil*'. MSc thesis from Explosives Ordnance Engineering course. Cranfield University, Shrivenham campus, UK

Pennington, J.C. and Brannon, J.M. (2002) 'Environmental fate of explosives', *Thermochimica Acta*, 384, pp. 163–172.

Pereira, A.S., Cerejeira, M.J. and Daam, M.A. (2014) 'Comparing ecotoxicological standards of plant protection products potentially toxic to groundwater life with their measured and modelled concentrations', *Ecotoxicology and Environmental Safety*, 102(1), pp. 152–159.

Perreault, N.N., Manno, D., Halasz, A., Thiboutot, S., Ampleman, G. and Hawari, J.

(2012) ‘Aerobic biotransformation of 2,4-dinitroanisole in soil and soil Bacillus sp.’, *Biodegradation*, 23(2), pp. 287–295.

Persico, F., Temple, T., Ladyman, M., Gilroy-Hirst, W., Gutierrez-Carazo, E. and Coulon, F. (2022) ‘Quantitative Environmental Assessment of Explosive Residues from the Detonation of Insensitive High Explosive Filled 155 mm Artillery Shell’, *Propellants, Explosives, Pyrotechnics*, 47(3), e202100220.

Pichtel, J. (2012) ‘Distribution and Fate of Military Explosives and Propellants in Soil: A Review’, *Applied and Environmental Soil Science*, Article ID 617236, pp. 1–33.

Pistocchi, A., Sarigiannis, D.A. and Vizcaino, P. (2010) ‘Spatially explicit multimedia fate models for pollutants in Europe: State of the art and perspectives’, *Science of the Total Environment*, 408(18), pp. 3817–3830.

Plagnes, V., Schmid, B., Mitchell, B. and Judd-Henrey, I. (2017) ‘Water balance modelling of a uranium mill effluent management system’, *Journal of Hydrology*, 549, pp. 741–753.

Platten, W.E., Bailey, D., Suidan, M.T. and Maloney, S.W. (2010) ‘Biological transformation pathways of 2,4-dinitro anisole and N-methyl paranitro aniline in anaerobic fluidized-bed bioreactors’, *Chemosphere*, 81(9), pp. 1131–1136.

Pulkkanen, V.M. and Nordman H. (2010) *Modelling of Near-Field Radionuclide Transport Phenomena in a KBS-3V Type of Repository for Nuclear Waste with Goldsim Code – and Verification Against Previous Methods*. Working Report 2010-14, Posiva OY, Eurajoki, Finland.

Qin, C., Abrell, L., Troya, D., Hunt, E., Taylor, S. and Dontsova, K. (2021) ‘Outdoor dissolution and photodegradation of insensitive munitions formulations IMX-101 and IMX-104: Photolytic transformation pathway and mechanism study’, *Chemosphere*, ID 130672.

Racine, C.H., Walsh, M.E., Roebuck, B.D., Collins, C.M., Calkins, D., Reitsma, L., Buchli, P. and Goldfarb, G. (1992) ‘White phosphorus poisoning of waterfowl in an Alaskan salt marsh, *Journal of Wildlife Diseases*, 28(4), pp. 669–673.

Ramasamy, M., Power, C. and Mkandawire, M. (2018) ‘Numerical prediction of the long-term evolution of acid mine drainage at a waste rock pile site remediated with

an HDPE-lined cover system', *Journal of Contaminant Hydrology*, 216, pp. 10–26.

Reddy, G., Song, J., Kirby, P., Lent, E.M., Crouse, L.C.B. and Johnson, M.S. (2011) 'Genotoxicity assessment of an energetic propellant compound, 3-nitro-1,2,4-triazol-5-one (NTO)', *Mutation Research - Genetic Toxicology and Environmental Mutagenesis*, 719(1–2), pp. 35–40.

Regnery, J., Lee, J., Drumheller, Z.W., Drewes, J.E., Illangasekare, T.H., Kitanidis, P.K., McCray, J.E. and Smits, K.M. (2017) 'Trace organic chemical attenuation during managed aquifer recharge: Insights from a variably saturated 2D tank experiment', *Journal of Hydrology*, 548, pp. 641–651.

Reichenberger, S., Bach, M., Skitschak, A. and Frede, H.G. (2007) 'Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; A review', *Science of the Total Environment*, 384(1–3), pp. 1–35.

Richard, T. and Weidhaas, J. (2014) 'Dissolution, sorption, and phytoremediation of IMX-101 explosive formulation constituents: 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine', *Journal of Hazardous Materials*, 280, pp. 561–569.

Robidoux, P.Y., Hawari, J., Thiboutot, S., Ampleman, G. and Sunahara, G.I. (2001) 'Chronic toxicity of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in soil determined using the earthworm (Eisenia andrei) reproduction test', *Environmental Polution*, 111, pp. 283–292.

Rodrigo-Ilarri, J., Rodrigo-Clavero, M., Cassiraga, E. and Ballesteros-Almonacid, L. (2020) 'Assessment of Groundwater Contamination by Terbuthylazine Using Vadose Zone Numerical Models . Case Study of Valencia Province (Spain)', *Environmental Research and Public Health*, 17, ID 3280.

Sagi-Ben Moshe, S., Dahan, O., Weisbrod, N., Bernstein, A., Adar, E. and Ronen, Z. (2012) 'Biodegradation of explosives mixture in soil under different water-content conditions', *Journal of Hazardous Materials*, 203–204, pp. 333–340.

Sagi-Ben Moshe, S., Ronen, Z., Dahan, O., Weisbrod, N., Groisman, L., Adar, E. and Nativ, R. (2009) 'Sequential biodegradation of TNT, RDX and HMX in a mixture', *Environmental Pollution*, 157(8–9), pp. 2231–2238.

Saltelli, A. (2002) ‘Sensitivity analysis for importance assessment’, *Risk Analysis*, 22(3), pp. 579–590.

Sanz-Prat, A., Greskowiak, J., Burke, V., Rivera Villarreyes, C.A., Krause, J., Monninkhoff, B., Sperlich, A., Schimmelpfennig, S., Duennbier, U. and Massmann, G. (2020) ‘A model-based analysis of the reactive transport behaviour of 37 trace organic compounds during field-scale bank filtration’, *Water Research*, 173, ID 115523.

Scheringer, M., Salzmann, M., Stroebe, M., Wegmann, F., Fenner, K. and Hungerbühler, K. (2004) ‘Long-range transport and global fractionation of POPs: Insights from multimedia modeling studies’, *Environmental Pollution*, 128(1–2), pp. 177–188.

Seguí, M. del M.B., Hess, T., Sakrabani, R. and Tyrrel, S. (2017) ‘Long-term phosphorus removal in land treatment systems: Evaluation, experiences, and opportunities’, *Critical Reviews in Environmental Science and Technology*, 47(5), pp. 314–334.

Shahul Hameed, K.P. and Sadashiva Murthy, B.M. (2019) ‘Laboratory soil column studies on transport of petroleum VOCs in different subsoils’, *Indian Journal of Environmental Protection*, 39(9), pp. 825–833.

Sharma, P., Mayes, M.A. and Tang, G. (2013) ‘Role of soil organic carbon and colloids in sorption and transport of TNT, RDX and HMX in training range soils’, *Chemosphere*, 92(8), pp. 993–1000.

Shi, X., Lei, T., Yan, Y. and Zhang, F. (2016) ‘Determination and impact factor analysis of hydrodynamic dispersion coefficient within a gravel layer using an electrolyte tracer method’, *International Soil and Water Conservation Research*, 4(2), pp. 87–92.

Showalter, S.K., Prairie, M.R., Stange, B.M., Rodacy, P.J. and Leslie, P.K. (1994) *Photocatalysis for the Destruction of Aqueous TNT, RDX, and HMX.* Report Conf-941255-1, Sandia National Laboratoies, Albuquerque, New Mexico, USA.

Šimůnek, J., van Genuchten, M.T. and Šejna, M. (2016) ‘Recent Developments and Applications of the HYDRUS Computer Software Packages’, *Vadose Zone Journal,*

15(7), pp. 1-25.

Šimůnek, J., Jacques, D., Langergraber, G., Bradford, S.A., Šejna, M. and Van Genuchten, M.T. (2013) ‘Numerical modeling of contaminant transport using HYDRUS and its specialized modules’, *Journal of the Indian Institute of Science*, 93(2), pp. 265–284.

Skjetne, E. and Auriault, J.L. (1999) ‘High-velocity laminar and turbulent flow in porous media’, *Transport in Porous Media*, 36(2), pp. 131–147.

Steefel, C.I., Appelo, C.A.J., Arora, B., Jacques, D., Kalbacher, T., Kolditz, O., Lagneau, V., Lichtner, P.C., Mayer, K.U., Meeussen, J.C.L., Molins, S., Moulton, D., Shao, H., Šimůnek, J., Spycher, N., Yabusaki, S.B. and Yeh, G.T. (2015) 'Reactive transport codes for subsurface environmental simulation', *Computer Geoscience*, 19, pp. 445-478.

Su, C., Zhang, H., Cridge, C. and Liang, R. (2019) ‘A review of multimedia transport and fate models for chemicals: Principles, features and applicability’, *Science of the Total Environment*, 668, pp. 881–892.

Sweeney, L.M., Phillips, E.A., Goodwin, M.R. and Bannon, D.I. (2015) ‘Toxicokinetic Model Development for the Insensitive Munitions Component 3-Nitro-1,2,4-Triazol-5-One’, *International Journal of Toxicology*, 34(5), pp. 408–416.

Taylor-Lovell, S., Sims, G.K. and Wax, L.M. (2002) ‘Effects of moisture, temperature, and biological activity on the degradation of isoxaflutole in soil’, *Journal of Agricultural and Food Chemistry*, 50(20), pp. 5626–5633.

Taylor, S., Bigl, S. and Packer, B. (2015) ‘Condition of in situ unexploded ordnance’, *Science of the Total Environment*, 505, pp. 762–769.

Taylor, S., Park, E., Bullion, K. and Dontsova, K. (2015) ‘Dissolution of three insensitive munitions formulations’, *Chemosphere*, 119, pp. 342–348.

Taylor, S., Ringelberg, D.B., Dontsova, K., Daghlian, C.P., Walsh, M.E. and Walsh, M.R. (2013) ‘Insights into the dissolution and the three-dimensional structure of insensitive munitions formulations’, *Chemosphere*, 93, pp. 1782–1788.

Teklu, B.M., Adriaanse, P.I., Ter Horst, M.M.S., Deneer, J.W. and Van den Brink, P.J. (2015) ‘Surface water risk assessment of pesticides in Ethiopia’, *Science of the*

Total Environment, 508, pp. 566–574.

Temple, T., Ladyman, M., Mai, N., Galante, E., Ricamora, M., Shirazi, R. and Coulon, F. (2018) 'Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil', *Science of the Total Environment*, 625, pp. 1264–1271.

Temple, T.J. and Ladyman, M.K. (2019) *Global Approaches to Environmental Maagement on Military Training Ranges*.

Tennant, M., Chew, S.C., Krämer, T., Mai, N., Mcateer, D. and Pons, J. (2019) 'Practical colorimetry of 3-nitro-1,2,4-triazol-5-one', *Propellants, Explosives, Pyrotechnics*, 44(2), pp. 198–202.

Terzaghi, E., Zacchello, G., Scacchi, M., Raspa, G., Jones, K.C., Cerabolini, B. and Di Guardo, A. (2015) 'Towards more ecologically realistic scenarios of plant uptake modelling for chemicals: PAHs in a small forest', *Science of the Total Environment*, 505, pp. 329–337.

Tsuchiya, R., Kato, T., Jeong, J. and Arnold, J.G. (2018) 'Development of SWAT-paddy for simulating lowland paddy fields', *Sustainability (Switzerland)*, 10, ID 3246.

Turner, A. and Rawling, M.C. (2001) 'The influence of salting out on the sorption of neutral organic compounds in estuaries', *Water Research*, 35(18), pp. 4379–4389.

UK Government Office for Science (2018) *Computational modelling: Technological Futures*. Council for Science and Technology.

Uusitalo, L., Lehikoinen, A., Helle, I. and Myrberg, K. (2015) 'An overview of methods to evaluate uncertainty of deterministic models in decision support', *Environmental Modelling and Software*, 63, pp. 24–31.

Vila, M., Lorber-Pascal, S. and Laurent, F. (2008) 'Phytotoxicity to and uptake of TNT by rice', *Environmental Geochemistry and Health*, 30(2), pp. 199–203.

Walsh, M., Gullett, B., Walsh, M., Bigl, M. and Aurell, J. (2018) 'Improving post-detonation energetics residues estimations for the Life Cycle Environmental Assessment process for munitions', *Chemosphere*, 194, pp. 622–627.

Walsh, M.R., Temple, T., Bigl, M.F., Tshabalala, S.F., Mai, N. and Ladyman, M. (2017) ‘Investigation of Energetic Particle Distribution from High-Order Detonations of Munitions’, *Propellants, Explosives, Pyrotechnics,* 42, pp. 932-941.

Walsh, M.R., Walsh, M.E., Taylor, S., Ramsey, C.A., Ringelberg, D.B., Zufelt, J.E., Thiboutot, S., Ampleman, G. and Diaz, E. (2013) ‘*Characterization of PAX-21 Insensitive Munition Detonation Residues*’, 38(3), pp. 399–409.

Walsh, M.R.M.E., Walsh, M.R.M.E., Ramsey, C.A., Thiboutot, S., Ampleman, G., Diaz, E. and Zufelt, J.E. (2014) ‘Energetic Residues from the Detonation of IMX-104 Insensitive Munitions’, *Propellants, Explosives, Pyrotechnics*, 39(2), pp. 243–250.

Wang, C., Fuller, M.E., Schaefer, C., Caplan, J.L. and Jin, Y. (2012) ‘Dissolution of explosive compounds TNT, RDX, and HMX under continuous flow conditions’, *Journal of Hazardous Materials*, 217–218, pp. 187–193.

Wang, N., Jiang, Y., Xia, T., Xu, F., Zhang, C., Zhang, D. and Wu, Z. (2022) ‘Antimony Immobilization in Primary-Explosives-Contaminated Soils by Fe-Al Based Amendments’, *Environmental Research and Public Health*, 19(4), ID 1979.

Wang, Q., Guo, M. and Yates, S.R. (2006) ‘Degradation kinetics of manure-derived sulfadimethoxine in amended soil’, *Journal of Agricultural and Food Chemistry*, 54(1), pp. 157–163.

Wang, R., Yuan, Y., Yen, H., Grieneisen, M., Arnold, J., Wang, D., Wang, C. and Zhang, M. (2019) ‘A review of pesticide fate and transport simulation at watershed level using SWAT: Current status and research concerns’, *Science of the Total Environment*, 669, pp. 512–526.

Whelan, M.J., Coulon, F., Hince, G., Rayner, J., McWatters, R., Spedding, T. and Snape, I. (2015) ‘Fate and transport of petroleum hydrocarbons in engineered biopiles in polar regions’, *Chemosphere*, 131, pp. 232–240.

Wilson, R.C. and Collins, A.G.E. (2019) ‘Ten simple rules for the computational modeling of behavioral data’, *eLife*, 8, pp. 1–33.

Winchell, M.F., Peranginangin, N., Srinivasan, R. and Chen, W. (2018) ‘Soil and Water Assessment Tool model predictions of annual maximum pesticide concentrations in high vulnerability watersheds’, *Integrated Environmental*

Assessment and Management, 14(3), pp. 358–368.

Xu, X., He, J., Li, Y., Fang, Z. and Xu, S. (2014) ‘Adsorption and Transport of Ciprofloxacin in Quartz Sand at Different pH and Ionic Strength’, *Open Journal of Soil Science*, 4(12), pp. 407–416.

Yang, Y., Ji, Y., Yang, P., Wang, L., Lu, J., Ferronato, C. and Chovelon, J.M. (2018) ‘UV-activated persulfate oxidation of the insensitive munitions compound 2,4-dinitroanisole in water: Kinetics, products, and influence of natural photoinducers’, *Journal of Photochemistry and Photobiology A: Chemistry*, 360, pp. 188–195.

Yu, H.A., DeTata, D.A., Lewis, S.W. and Nic Daeid, N. (2017) ‘The stability of TNT, RDX and PETN in simulated post-explosion soils: Implications of sample preparation for analysis’, *Talanta*, (164), pp. 716–726.

Flowers, P., Theopold, K., Langley, R., Robinson, W.R. (2002) *Chemistry 2e*.*Chapter 11. Solutions and colloids*. OpenStax: Rice University, Houston, Texas, USA.

Zhang, J., Tang, H. and Chen, M. (2019) ‘Linear substitute model-based uncertainty analysis of complicated non-linear energy system performance (case study of an adaptive cycle engine)’, *Applied Energy*, 249, pp. 87–108.

Zhang, K., Zhong, S. and Zhang, H. (2020) ‘Predicting Aqueous Adsorption of Organic Compounds onto Biochars, Carbon Nanotubes, Granular Activated Carbons, and Resins with Machine Learning’, *Environmental Science and Technology*, 54(11), pp. 7008–7018.

Zhang, R., and Bennet, B.D. (1996) '*Applied Contaminant Transport Modeling: Theory and Practice'*. New York: Wiley.

Zhang, X. and Zhang, M. (2011) ‘Modeling effectiveness of agricultural BMPs to reduce sediment load and organophosphate pesticides in surface runoff’, *Science of the Total Environment*, 409(10), pp. 1949–1958.