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Investigating residue dissolution of insensitive high explosives in two sandy soil types: A predictive modelling approach

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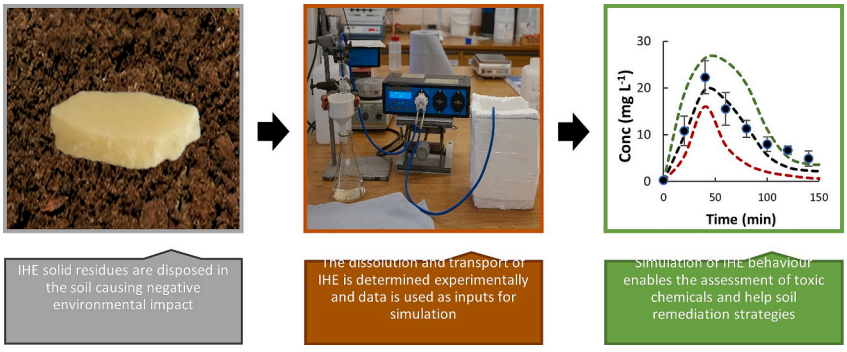
HIGHLIGHTS

- A stochastic model to simulate the concentration of IHE in leachate was developed.
- Dissolution rates for three constituent explosives were derived experimentally.
- Dissolution rates varied with temperature and pH, except for 5-nitro-1,2,4-triazol-3-one.
- Experimentally derived dissolution rates were used to model leachate concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

The demand for munitions that are less likely to detonate accidentally has led to an increased use of Insensitive High Explosives (IHE), which contain substances like 2,4-dinitroanisole (DNAN) and 5-nitro-1,2,4-triazol-3-one (NTO). These substances have different properties compared to traditional explosives, and their potential environmental impact is not well understood. When these explosives are used in live-fire training exercises, their residues end up in the soil. It is important to determine how these residues dissolve and enter the soil. This study aimed to experimentally measure the rate at which an IHE formulation dissolves when exposed to rainwater with pH levels of 5.0 and 6.5, and to simulate how these residues dissolve and move through two different soil types. The dissolution rates were determined by conducting experiments in which IHE particles (30–60 mg) were exposed to water with varying pH levels and temperatures. The results showed that the dissolution rate of NTO did not vary with pH, while the dissolution rate of DNAN and RDX decreased with decreasing pH. Specifically, the dissolution rate of DNAN decreased from 18 ± 40 μg min^{-1} at pH 6.5 to 6 ± 4 μg min^{-1} at pH 5.0, while the dissolution rate of RDX decreased from 8 ± 4 to 3 ± 1 μg min^{-1}. These findings were used to develop a stochastic model that successfully simulated the concentration of IHE in the leachate from soil columns over time. A sensitivity analysis revealed that while dissolution rates determined the amount of mass entering the soil, they

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did not significantly regulate the amount of mass that migrated through the soil and leached out of the soil columns.

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. However, early work suggests that NTO is significantly more soluble than previously used explosive constituents and is acidic at environmental pH raising concerns that rapid transport of this constituent may also increase rate of lead leaching from existing contaminated soils at ranges (Walsh et al., 2014). In addition, DNAN appears to be more toxic than its predecessor TNT (DNAN: 199 mg kg^{-1} (Dodd and McDougal, 2001) vs. TNT: 600–800 mg kg^{-1} (Reddy et al., 2000)), and is slightly more soluble (DNAN: 276 mg L^{-1} (Taylor et al., 2017) vs. TNT: 130 mg L^{-1} (Monteil-Rivera et al., 2009), which may enable higher concentrations with greater toxicity to migrate to groundwater. These unknowns raise the challenge of how to assess the potential environmental impact of IHE residues in soil.

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 migrate through soil (Dortch, 2018). 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) (Zahradník, 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 objective of this study was to investigate the dissolution rates of the constituents of Insensitive High Explosives (IHE) from solid residues when subjected to various rainwater types. Furthermore, the study aimed to predict the dissolution process of DNAN and NTO and their movement through sandy soils using GoldSim model. The impact of the dissolution rate of DNAN and NTO on their breakthrough curves was also investigated in two sandy soils with varying organic matter content and particle size distributions. The findings of this study provide valuable insights into the environmental and physicochemical factors that affect the dissolution process and offer an initial dataset to support the management and remediation of soils contaminated by IHE residues.

2. Material and methods

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.

2.2. Soils

Soils were purchased from a local building merchant (Swindon, UK). They were spread in trays and left air 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 1). Bulk density, porosity and NTO and DNAN soil water partition coefficients (K_d) were experimentally measured (Table 1). The percentage of particle size was also determined in triplicates using several sieves with different mesh size, as described in the United States Department of Agriculture (USDA) (Table 2).

2.3. Dissolution drip tests of the IHE formulation

Three particles (30–60 mg each, length between 5 and 10 mm, width and depth below 3 mm) of the IHE were placed in separated Pyrex Buchner funnels, held by a support stand and clamps (Fig. 1). The particles were exposed to a continuous flow of water at 40 mL min^{-1} (Kramoer Dosing Pump, China) for 100 min, 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 339 mm h^{-1}. The rainwater

Table 1
Physicochemical characterisation of the two soils and partition coefficient of IHE components.

	Soil 1	Soil 2
Description	UK Sand	UK topsoil
Soil type	Sand	Sandy loam
TOC[a]	0.09	12.65
C (%)[b]	1.35	12.92
C/N	135	22.7
pH[c]	9.5	7.2
Electrical conductivity[c] (dS/cm)	93.6	55.6
Bulk density (g cm^{-3})	1.93 ± 0.03	1.31 ± 0.14
Porosity (%)	38 ± 1	45 ± 5
NTO K_d (L kg^{-1})[d]	0.33 ± 0.03	0.40 ± 0.08
DNAN K_d (L kg^{-1})[d]	0.24 ± 0.17	9.3 ± 1.5

[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.
[d] K_ds obtained from Gutierrez-Carazo et al., 2022. (Gutierrez-Carazo et al., 2022).

Table 2
Percentage of particle size measured in the sand and sandy loam soils.

Sieve size	Sand (%)	Sandy loam (%)
>2.36 mm	0.0	22.3
>1.18 mm	0.1	15.3
>600 μm	0.9	22.0
>500 μm	2.7	5.7
>300 μm	86.7	12.8
>150 μm	12.3	16.1
>63 μm	0.4	9.0
<63 μm	0.0	1.2

had an initial pH 6.5 ± 0.1 and acid rainwater was acidified with HCl 1 M until pH 5.0 ± 0.1 and both were kept at 12 °C (UK rainfall temperature average (Kumar et al., 2017, Met Office website). Leachate was collected every 5 min during the first 50 min and every 10 min over another 50 min 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). The same procedure was conducted in triplicate with rainwater (pH 6.5) at 12 °C and 20 °C.

2.4. Soil column experiments

Three plastic columns (radius 5 cm × 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). 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 min. Leachate coming out of the soil columns were collected every 20 min for the first 140 min and every 30 min 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.

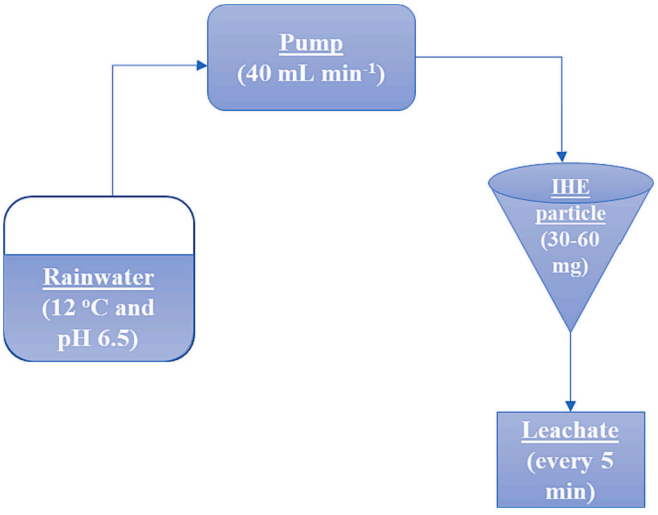

Fig. 1. Schematic illustration of the experimental setup for the study of the IHE formulation dissolution rate.

2.5. IHE component residues analysis

The analysis of IHE component residues was conducted using a Waters-Alliance 2696 high-performance liquid chromatography (HPLC) equipped with a Waters 996 photodiode array detector (USA). Separation of analytes was achieved on an Agilent Technologies ZORBAX Eclipse Plus C18 column (4.6 × 150 mm, i.d. 3.5 μm; Wilmington, DE, USA), maintained at a temperature of 30 °C. Samples were injected using a syringe loading injector with a 10 μL loop.

To achieve optimal chromatographic conditions, a linear gradient was employed with 40 % acetonitrile (solvent A) and 60 % water acidified with 0.1 % formic acid (solvent B), flowing at a rate of 1.5 mL min^{-1}. The analytes were quantified based on their UV absorbance, with peak sensitivity detected at 296 nm for DNAN, 245 nm for RDX, and 315 nm for NTO. Retention times for NTO, RDX, and DNAN were 1.01 min, 3.15 min, and 4.96 min, respectively (Temple et al., 2018). The calibration curve was obtained by plotting the concentration against corresponding peak area for each analyte. Both the peak areas of samples and standards were determined using Empower 2 software from Waters. The limit of quantification (LOQ) of the method 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).

2.6. Stochastic simulation in GoldSim

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. 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 (obtained experimentally) 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 (Eq. (1)) with some modifications over time.

$$\frac{dm}{dt} = m_o - k^{*}t \quad (1)$$

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.

For the transport process, a Pipe Pathway element was defined along with the main dimensions of the soil columns (Fig. 2. 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 (Table 3). This simulated set up looks very similar to Fig. 1 but it also includes a soil column between the IHE particles and the leachate.

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 to carry out probabilistic simulations. The model was run for 101 iterations, each of which generated a different output as different dissolution rates were sampled in each iteration. Last, the model performance was assessed by linearly comparing the experimental concentration against the simulated one and determining the linear coefficient (R).

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 et al., 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 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). The remaining inputted data displayed in Section 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 2.6.

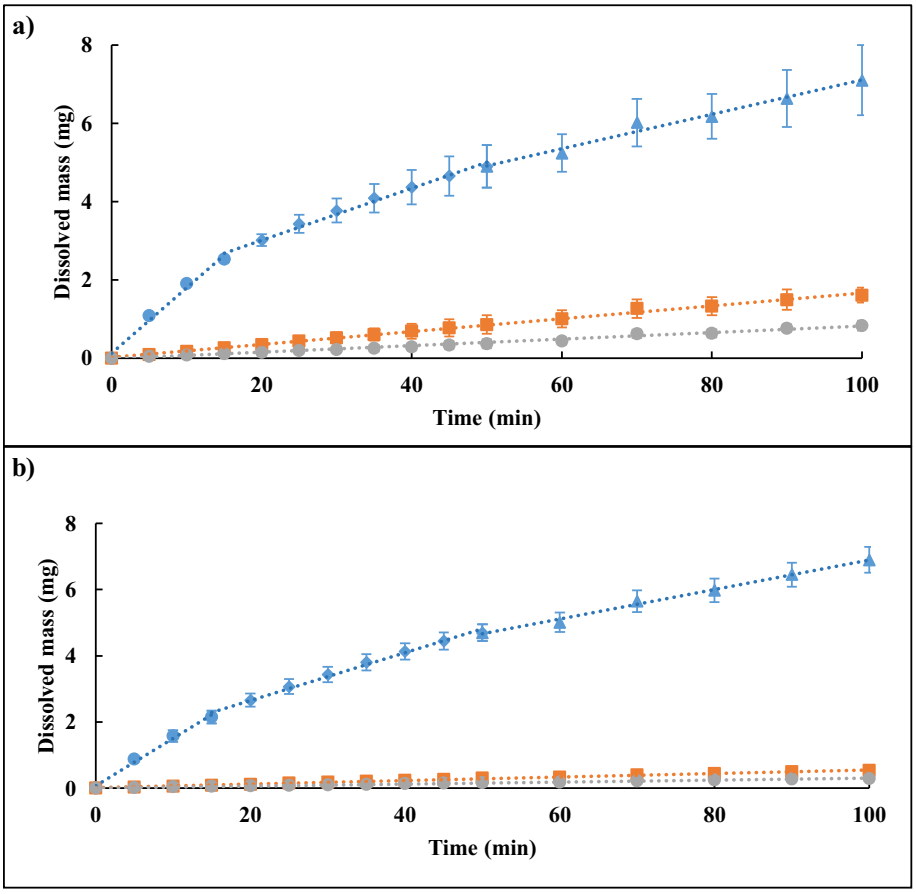

Fig. 2. Dissolution curve of NTO (blue), DNAN (orange) and RDX (grey) in an explosive formulation using a) rainwater pH 6.5 at 12 °C and b) acid rainwater pH 5.0 at 12 °C.

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

Table 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) μg min^{-1}
Constant pH (6.5)	Temperature (12 °C)	NTO (0–15 min)	170
		NTO (15–50 min)	70
		NTO (50–300 min)	50
		DNAN (0–300 min)	18
	Temperature (20 °C)	NTO (0–15 min)	264
		NTO (15–50 min)	105
		NTO (50–300 min)	57
		DNAN (0–300 min)	44
Constant temperature (12 °C)	pH 5.0	NTO (0–15 min)	143
		NTO (15–50 min)	72
		NTO (50–300 min)	45
		DNAN (0–300 min)	6.3
	pH 6.5	NTO (0–15 min)	170
		NTO (15–50 min)	70
		NTO (50–300 min)	50
		DNAN (0–300 min)	18

3. Results and discussion

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

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 (Fig. 2).

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 cases, 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. This is most likely due to the NTO elevated solubility, which is 45 and 210 times higher than DNAN and RDX respectively. 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. However, due to the low solubility of DNAN and RDX the solubility rates are low and the difference most likely arises from variations in processing of the explosive compound, and slight variations in particle size and available surface area.

After 100 min, 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, which is likely due to the manufacturing process wherein DNAN is used as a binder for the powdered NTO and RDX. This results in NTO and RDX coated in a DNAN 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 dissolution rates of DNAN and RDX confirming previous work in the field (Taylor et al., 2013).

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 (Eq. (2)) and it is usually integrated under specific terms that provide a first order equation (Hattori et al., 2013).

$$\frac{dm}{dt} = A^{*}\frac{D}{d}^{*}(C_s - C_b) \quad (2)$$

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 Eq. (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 5). NTO experimental dissolution rates were similar in both rainwaters, being only 20 % higher in acid rainwater (pH 5.0) over the first 15 min 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 min. Dissolution rates decreased slightly reaching a constant rate 40 ± 10 μg min^{-1} for NTO, 13 ± 5 μg min^{-1} 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 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.

Compound	Time (min)	Dissolution rate (μg min^{-1})	
		Rainwater pH 6.5	Rainwater pH 5.0
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

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. 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 min.

Simulated and experimental NTO and DNAN concentrations measured in the leachate coming out of the sand and sandy loam columns were plotted over time (Fig. 3), and the linear coefficient (R) was calculated to assess the performance of the model. 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 min 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 min reaching a maximum concentration between 15 and 25 mg L^{-1} at 40 min. 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 min, 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).

In sandy loam, experimental NTO breakthrough reached a maximum concentration between 15 and 27 mg L^{-1} after 50 min, although in this case NTO needed more time to travel along the sandy loam 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 results asDNAN was not detected in the leachate from the soil column over the 300 min duration of the experiment. Given the late elution in the simulation, a predicted 150 min prior to elution, the duration of the experiment was too short to determine the cause of the divergence between simulated and experimental results. The short timescale, and very low concentrations can also contribute to the discrepancy observed which can be attributed to experimental error. Overall the discrepancy is more likely due to errors in simulating the interaction of DNAN with the organic matter in the soil than the dissolution simulation as simulation of DNAN

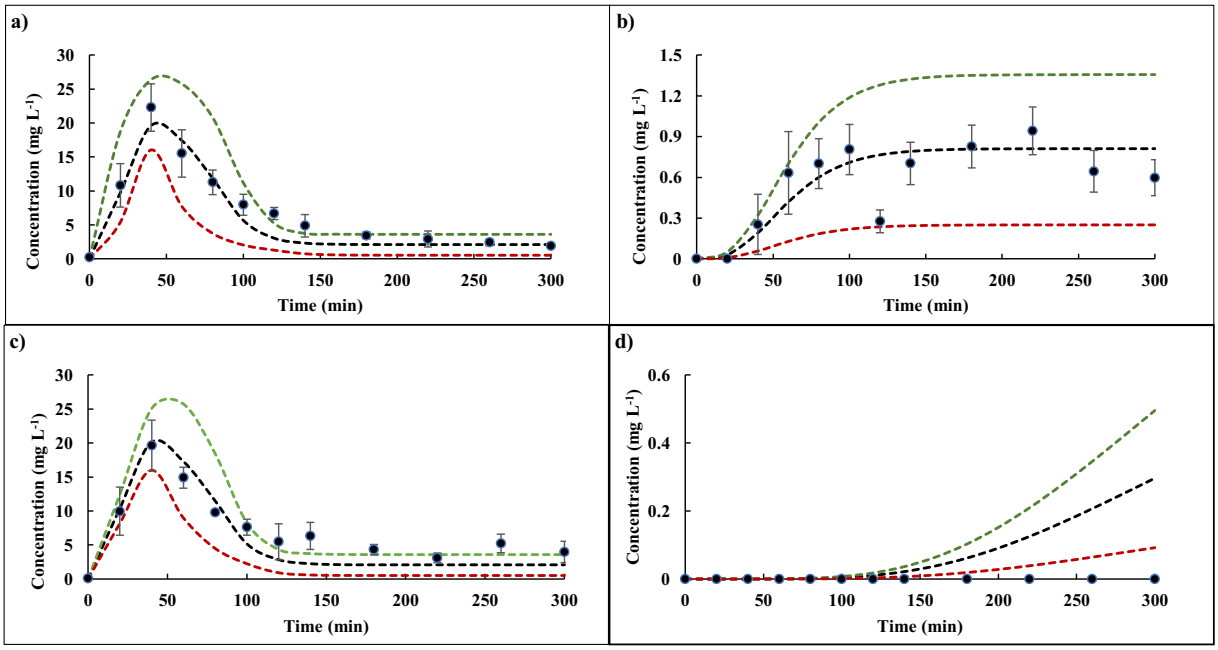

Fig. 3. Experimental and simulated breakthrough of a) NTO in sand b) DNAN in sand c) NTO in sandy loam and d) DNAN in sandy loam. Dashed lines indicate the maximum (green), mean (black) and minimum (red) breakthrough simulated in GoldSim, whereas dots) indicate measured values from experimental soil columns.

in sand soil shows good correlation (Fig. 3b).

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 solutes that enter the soil system over time, whereas the K_d, along with the dispersion and diffusion equations, regulated the velocity that contaminants travelled through the 20 cm of soil. The stochastic simulation also enabled the assessment of the maximum and minimum concentration limits expected for each compound based on the initial mass of the IHE formulation and the dissolution flow rate. In addition, the stochastic simulation was assessed for each compound and soil, providing R values of 0.984 for NTO in sand, 0.957 for DNAN in sand, and 0.971 for NTO in sandy loam, which is an indicator of "very strong correlation" according to conventional approaches (Schober and Schwarte, 2018). It was not possible to calculate the correlation for DNAN in sandy loam, as there were no detected concentrations in the experiment.

However, the model did not account for degradation, which is an important process that has been reported to occur rapidly for DNAN in soils rich in organic matter (Perreault et al., 2012; Temple et al., 2018). Although it is very unlikely that a significant concentration of DNAN degraded within 300 min. A more likely explanation is adsorption of DNAN to the organic matter, as a consequence of their highly strong

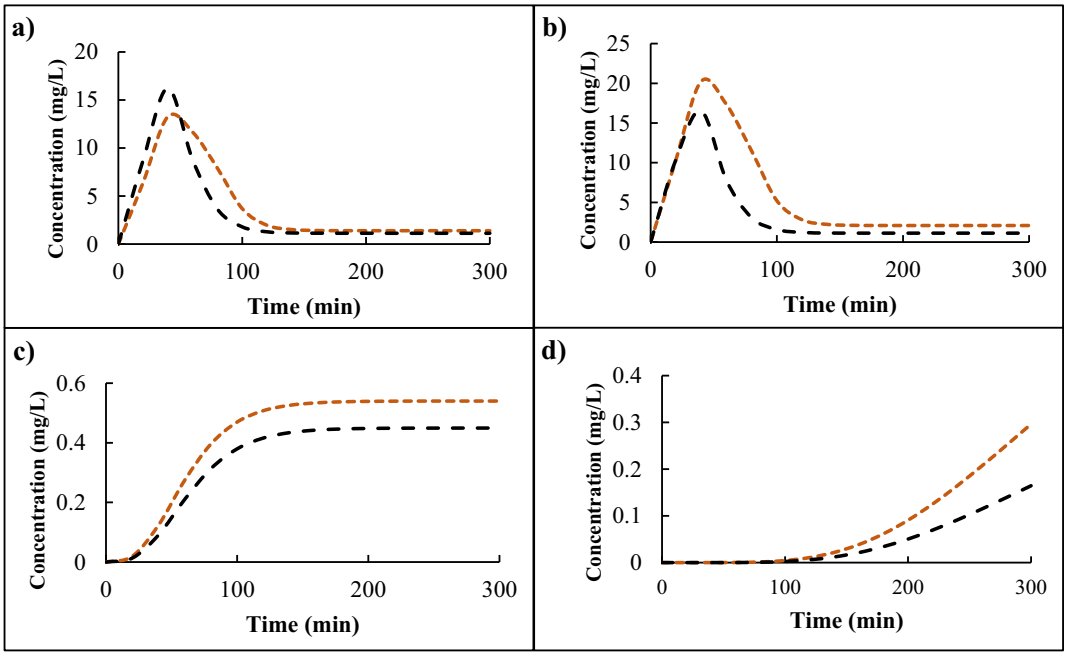

Fig. 4. Sensitivity analysis of NTO breakthrough in a) sand and b) sandy loam; and DNAN breakthrough in c) sand and d) sandy loam using rainwater at pH 5.0 (brown dotted line —) and pH 6.5 (black dotted line - - -).

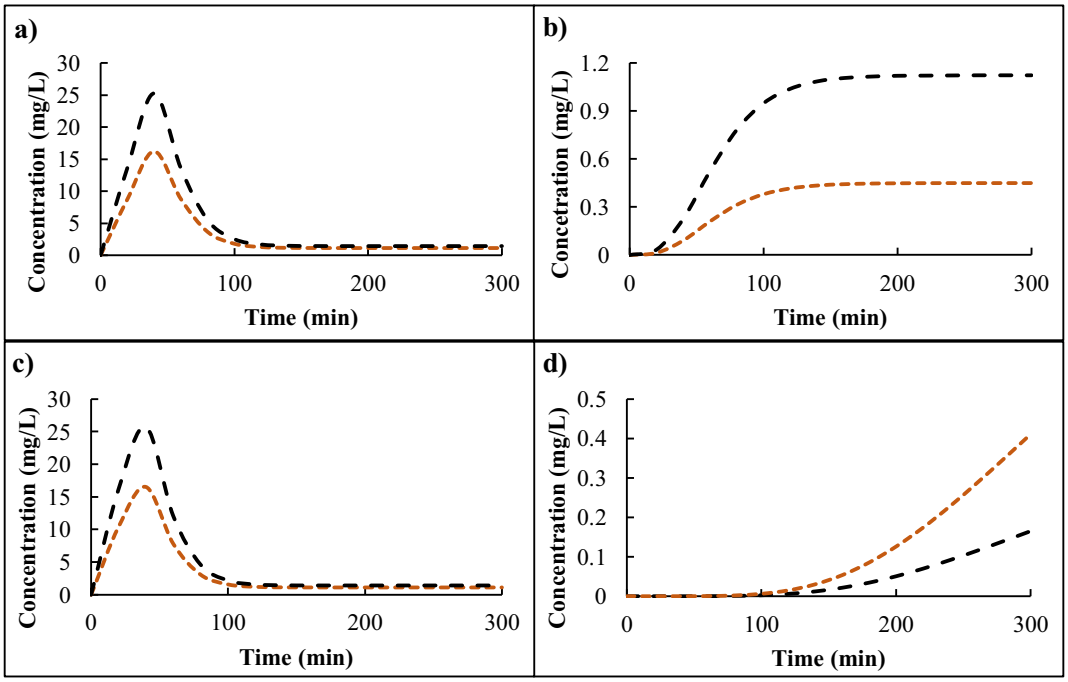

Fig. 5. Sensitivity analysis of NTO breakthrough in a) sand and c) sandy loam; and DNAN breakthrough in b) sand and d) sandy loam using rainwater at 12 °C (brown dotted line —) and 20 °C (black dotted line - - -).

bonding to organic substrates (Fuller et al., 2021). DNAN K_d in 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.

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 end, concentration leached out of the column was plotted over time by using empirical dissolution data determined at variable pH (Fig. 4) and temperatures (Fig. 5), while other relevant transport inputs remained unchanged (i.e., soil parameters and physico-chemical properties).

Overall, the sensitivity analysis for pH (Fig. 4) showed that the NTO and DNAN breakthrough were very similar in both sand and sandy soils. This phenomenum 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 dissolution rates had the same order of magnitude and this, along with the high interaction with the soils showed little impact on the overall breakthrough and concentration in the leachate. Thus, at these pHs, NTO concentration in sand and sandy loam leachate was between 13 and 23 mg L^{-1}, whereas DNAN concentration 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 (Fig. 5) 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 occurred 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 dissolution 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.

4. Conclusions

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 accumulation 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.

While the developed model successfully (R^2 = 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 dissolve more representatively. It could then be used to simulate the fate and transport of IHE in larger systems loaded with higher masses 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.

CRediT authorship contribution statement

Encina Gutierrez-Carazo: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Validation, Visualization, Writing – original draft, Writing – review & editing. **James Dowle:** Formal analysis, Software, Writing – review & editing. **Frederic Coulon:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. **Tracey Temple:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Melissa Ladyman:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Encina Gutierrez Carazo reports financial support was provided by Engineering and Physical Sciences Research Council. James Dowle reports a relationship with Golder Associates that includes: employment. Co-Author, Frederic Coulon, is an Associate Editor for STOTEN.

Data availability

Data will be made available on request.

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Investigating residue dissolution of insensitive high explosives in two sandy soil types: a predictive modelling approach

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