Full Paper

Quantitative environmental assessment of explosive residues from the detonation of Insensitive High Explosive filled 155 mm artillery shell

Federica Persico^[a],Tracey Temple*^[a] Melissa Ladyman^[a],William Gilroy-Hirst^[a], Encina Guiterrez-Carazo^[a], Frederic Coulon ^[b]

Abstract: Insensitive High-Explosive (IHE) typically comprise up to five constituents including 2,4-dinitroanisle (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), which are mixed in various ratios to achieve desired performance and increase insensitivity. Insensitive munitions, which are designated to detonate on command and not accidentally, are currently in use in military operations and in training areas around the world. However, there is minimal literature available on the physiochemical behavior of these materials in the environment, therefore the actual consequence of residues being deposited post detonation is still an unexplored area of research. Three 155 mm artillery shells filled with an IHE mixture of 53% NTO, 54% DNAN and 13% RDX were detonated in an inert sand arena to collect and quantify residues. Post detonation, approximately 0.02% NTO and 0.07% DNAN are deposited in the environment which may rapidly accumulate dependent on the number of rounds fired. This is of concern due to the toxicity of DNAN and its degradation products, and the potential for increased acidity of soil and discoloration of watercourses from NTO contamination.

Keywords: 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanilisole (DNAN), 3, 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), Explosive residue, Multi-Increment sampling

1 Introduction

Energetic compounds are regularly deposited on military ranges following live-fire training activities [1]. The use of traditional explosives in various training areas has led to the contamination of soil and groundwater with recalcitrant and persistent hazardous chemicals which can render the sites unusable, therefore adversely affecting military readiness due to accumulation over time [2-5]. New generation Insensitive High Explosive (IHE) formulations consisting 3-nitro-1,2,4-triazol-5-one (NTO) (55%),(DNAN) (32%)dinitroanilisole and 1,3,5trinitroperhydro-1,3,5-triazine (RDX) (13%), increasingly being introduced into military service due to their improved safety profile [6]. For example, the United States (US) Department of Defence have investigated the use of 61 mm and 80 mm mortars filled with PAX-21 (RDX, DNAN and Ammonium Perchlorate) and Insensitive Munitions Explosive (IMX)-104 (DNAN, NTO, RDX) to replace legacy explosive fills [5,7]. However, IHE's contain chemical compounds and formulations not previously used in munitions e.g. NTO, and therefore their environmental consequences are not fully understood.

There have been limited studies into the deposition of explosives residues from munitions due to the challenges in efficiently sampling an area post-detonation. However, quantification of explosive residue deposition has been achieved using the Multi Increment Sampling (MIS) method on snow covered ranges [8]. MIS has been proven to be reproduceable

and representative, particularly for a non-homogeneous contamination [8,9]. This method has been used to residue deposition from investigate containing traditional explosive fills such as mortars, artillery rounds and grenades containing Composition B, and has shown that very small quantities of explosive residues are deposited from first order detonations (~0.00003% RDX from Comp B filled 61 mm mortar). While the most significant source of contamination is likely to be from blow-in-place disposals or partial detonations [3,10,11], residue from first order detonations may accumulate over time depending on the number of rounds fired [3,12]. For some live-fire ranges this may be tens of thousands of rounds per year resulting in significant accumulation of explosive residue, and the potential for soil and water contamination. However, research suggests that IHE filled munitions may deposit more explosive residue compared to conventional munitions. For example,

[a] F. Persico, Dr. T. Temple, Dr. M. Ladyman, W. Gilroy-Hirst, E. Guitierrez-Carazo Centre for Defence Chemistry Cranfield University Defence Academy of the United Kingdom, Shrivenham, SN6 7LA, UK E-mail: federica.persico@cranfield.ac.uk t.temple@cranfield.ac.uk m.ladyman@cranfield.ac.uk

(b) Prof F. Coulon School of Water, Energy and Environment Cranfield University Cranfield, MK43 0AL, UK RDX/HMX residues from IMX-104 filled 60 and 81 mm mortars may be as high as 0.006% and 0.001% respectively [13]. This equates to tens of milligrams per round. The percentage of DNAN residue deposited from the two IMX-104 filled rounds is comparable to the percentage of RDX (0.005% and 0.001% respectively), though this equates to a higher mass of DNAN per round due to the higher DNAN percentage in the formulation [13]. However, it is the percentage of NTO deposition that is most cause for concern (1.2% and 0.4% respectively), resulting in thousands of milligrams deposited per round. The tested rounds have relatively small explosive load (360 g and 831 g) compared to the 155 mm artillery shell which has a Net Explosive Quantity (NEQ) of 11.2 kg and therefore may deposit significant quantities of DNAN and NTO if used frequently at military training ranges [13].

The deposition of increased quantities of explosive residue from IHE filled munitions may increase accumulation rates, and therefore increase the likelihood of environmental consequences. RDX contamination has previously been of concern, however in many locations effective environmental management procedures have been implemented [14]. In addition, due to the low quantity of RDX in the IMX-104 formulation (13%) RDX is not the main contaminant of concern. Conversely, DNAN and NTO have not been used in significant quantities in munitions to date and environments where they are in use may require additional environmental monitoring and management in the future. NTO is of particular concern due to the potentially large quantities that may be deposited, as well as its acidity (pKa 3.76) and solubility (16.6 g L-1 at 25°C) [15,16], which means it may rapidly dissolve and transport into soil and ultimately to ground or surface waters where it may cause discoloration [17-19]. The behavior of NTO in the environment has not been fully investigated with uncertainty surrounding the chemical and toxicological properties of degradation products such as 5-amino-1,2,4-triazol-3-one (ATO) [20-23]. However, early indications suggest that ATO may be more toxic than NTO toward specific organisms [24]. While NTO has particularly low toxicity (LD₅₀ 5 g kg⁻¹ in rats), and sublethal toxicity (oligospermia), the uncertainty of its environmental behavior and the potential for deposition of significant quantities make it a particular concern [25, 26].

Understanding of the environmental fate of DNAN is more comprehensive than that of NTO. While DNAN is a nitrobenzene similar in structure to TNT, it is slightly more soluble (198.1 mg L⁻¹) and more toxic (LD₅₀ 199 mg kg⁻¹) and therefore may present a comparatively greater risk to the environment [27–31]. In addition, several of the ammino degradation products, such as 2-amino-4-nitroanisole (2-ANAN), have similar toxicity and may also present a risk to groundwater and local human and animal receptors [26,32,33]. The chemicophysical properties of DNAN, NTO, RDX and TNT are summarized in Table 1.

Table 1: Summary of the physicochemical and environmentally relevant properties of RDX, NTO and DNAN compared to TNT

DNAN compared to TNT.						
Name	Formula	Solubility ^b mg L ⁻¹	Log K₀c°	pKa	Toxicity LD₅₀ mg kg-¹	
TNT	C ₆ H ₃ CH ₃	100	1.10 ^d	NA	607-767 ⁹	
RDX	$C_3H_6N_6O_6$	60	0.88-2.4	NA	119 ^f	
NTO	$C_2H_2N_4O_3$	16,642	2.1 0.60-1.79	3.76 ^f	5000 ^f	
DNAN	C ₇ H ₆ N ₂ O ₅	276	1.79-1.92 1.62 1.58	NA	199 ^f	

^a Akhavan J. The Chemistry of Explosives. Third Edit. Norfolk: Biddles Ltd., Kings Lynn, Norfolk; 2011; b Taylor S., Ringelberg DB., Dontsova K., Daghlian CP., Walsh ME., Walsh MR. Chemosphere. 2013; 93(9): 1782–1788; ^c Arthur JD., Mark NW., Taylor S., Šimůnek J., Brusseau ML., Dontsova KM. Science of The Total 2018: 624: 758-768: d Environment. Amaral HIF., Claú Dia Gama. Α., Gonçalves, Cláudia... Fernandes J., João Batista M., Abreu M. Environmental Science. 2016; f Nandi AK., SK., Kunjir GM., Singh J., Mandal AK., Pandey RK. Central European Journal of Energetic Materials. 2013; 10(1): 113-122. f Arthur JD., Mark NW., Taylor S., Šimůnek J., Brusseau ML., Dontsova KM. 2018; 624: 758-768; 9 Reddy G., Chandra SAM., Lish JW., Qualls CW. International Journal of Toxicology. 2000; 19(3): 169-177.

The fate of explosive compounds is highly dependent on the local environment, however, to inform environmental assessment it is essential to understand the potential for accumulation of explosive residues from commonly used munitions such as the 155 mm artillery shell. In addition, understanding the potential for contamination may enable a more proactive approach to environmental management ensuring that live-fire training with new generation munitions does not result in significant contamination incidents as has already occurred with legacy explosives [2,34,35]. Therefore, the aim of this work was to quantify the percentage of DNAN, NTO and RDX residue remaining on the soil surface after detonation of an IMX-104 filled 155 mm artillery shell to determine the potential accumulation rate at military training areas.

2 Experimental Section

2.1 Explosive residue collection

2.1.1 Preparation of sampling arena

A sampling arena was created by levelling 11,900 Kg of inert fine particle sand to a depth of 5 cm in a semi-circular area (radius 10 m) on top of an impermeable plastic groundsheet. The arena was contained with flexible wooden edging panels around the external circumference (62 m). A 155 mm IMX-104 filled artillery

shell was placed at the centre of the arena, at a hight of 1 m, and detonated by a simulation fuze that closely approximated the live-firing initiation mechanism. A total of three detonations were carried out, two with the artillery shell in horizontal orientation and one with the artillery shell in a vertical orientation to comprehensively assess the residue distribution. Following each detonation, the sand was cleared away and fresh sand (11,900 kg) was levelled on top of new clean groundsheets.

2.1.2 Explosive residue sampling

Residue was collected post detonation using the Multi-(MIS) method. Increment Sampling In brief. approximately 100 increments of sand (100 x 10 g) were collected in triplicate from discrete Decision Units (DU) within the sampling arena using a metal scoop [8]. Two different DU layouts were used for the two horizontal orientation detonations, an arc layout and a radial layout (Figure 1a-b). For the vertical orientation detonation, the arc pattern was repeated (Figure 1a). All collected samples were double bagged and stored in a freezer at (-18°C) until analysis (~3 months). In addition, the entire arena was sampled after each detonation as one DU to ensure comprehensive coverage.

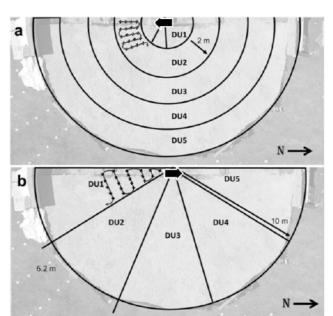


Figure 1: Decision Units (DU) for each detonation a) Detonation 1 and 3: arc DU's; b) detonation 2: radial DU's. Black arrows with white outline denotes orientation of the 155 mm shell for horizonal detonations (arrow point = nose). An example of how increments were collected is shown by the location of crosses on a sampling route, repeated three times on different routes for each DU.

2.1.3 Field controls

Control samples of the inert sand were taken prior to preparing the sampling area to ensure the sand used during the experimental phase was free from explosive contamination. Control samples were also taken from the soil underneath the groundsheet to baseline for cross-contamination and random samples within the DU's were collected as positive controls (PC) to validate

the sampling method and reproducibility of the results (Supplementary data). Additional controls samples were collected from outside the immediate sampling area prior to and post-detonation to ensure no DNAN, NTO or RDX residues were missed during analysis and to detect any potential cross-contamination from outside of the sampling area. This area was extended by 6 m from the boundary of the sampling area. All control samples were collected by using MIS in triplicate, with sand samples collected using a metal scoop and soil collected using a coring tool.

2.2 Laboratory Sample analysis

2.2.1 Sample processing

Collected samples were defrosted and air dried over 5-7 days before being passed through a 2.00 mm sieve to remove any foliage or large fragments. Samples were mechanically mixed and sub-sampled in triplicate by taking increments (~0.5 g) from a 5 by 5 grid to a mass of ~20 g.

2.2.2 Sample extraction

Sub-samples were extracted with acetonitrile/water (1:1) (40 mL) by shaking for 18 hours at 180 rpm in amber glass vials [36]. Samples were left to stand for 30 minutes before filtration through a 0.2 µm PES filter and analysed by HPLC. To confirm very low levels of NTO, DNAN and RDX residue the bulk liquid (5 mL) from a sub-selection of extractions was concentrated 5 times by evaporation at 35°C and quantified by HPLC. Resulting concentrations were used to determine the mass deposited.

2.3 HPLC analysis

Samples were analysed by High Pressure Liquid Chromatography (HPLC) using a 150 x 4.6 mm Agilent Zorbax Eclipse Plus C18 column in a Waters Alliance 2695 with a Waters 996 photodiode array detector [37]. The mobile phase was a 40:60 acetonitrile/water mix at a flow rate of 1.5 mL min-1 and a constant temperature of 30oC. Residue concentration (NTO, DNAN, RDX and common degradation products ATO, DNP, 2-ANAN, 4-ANAN and 2,4-ANAN) was determined by calibration to an IMX-104 standard calibration curve.

2.5 Quality controls

Play sand was artificially spiked with NTO, DNAN and RDX (12.5 ppm) and extracted after 24h, 48h and 6 days with 100% efficiency. Previous work has shown that in sand at ambient temperature (18 °C) NTO, DNAN and RDX remain stable for up to four months in the absence of light, and no degradation was detected in samples stored in the freezer for 3 months.

3 Results and Discussion

3.1 Determination of mass of explosive residue from detonation of 155 mm artillery shell

To quantify the explosive residues from detonation of the 155 mm artillery shells the detonation area was sampled using the MIS method. The published protocols for MIS were followed, with the exception of mechanical grinding of the samples due to the potential for initiation caused by friction between the sand and explosive residue [8]. Therefore, the sand was manually mixed prior to analysis to maximise homogeneity. As it has been shown that improved mixing (grinding) increases representativeness of samples, an increased error was accepted [9]. Analysis of control samples taken prior to the detonations confirmed that the groundsheet and 5 cm sand layer was sufficient to prevent cross-contamination from the surrounding and underlying soil.

There was concern that the detonation may significantly disrupt the sand and render it impossible to sample, however after the first detonation it was clear that only the centre of the arena was disrupted (Supplementary data). Therefore, the entire arena was sampled after each detonation by MIS. No explosive residues were detected in the entire arena samples for either detonation in the horizontal plane, nor for the detonation in the vertical plane. Samples concentrated by a factor of five also resulted in non-detect of any NTO, DNAN or RDX, suggesting that as expected the total residue deposition from a single 155 mm artillery shell was below the limit of detection (0.5 µl ml⁻¹) due to

the mass of sand diluting the explosive residue. However, quantifiable concentrations of DNAN were detected in several of the smaller DU's for all detonations (Table 2). The errors reported reflect the heterogeneity of results wherein some samples had significantly higher concentration of DNAN, and in other samples no DNAN was detected. Therefore, the results have been used as a broad estimate of potential residue deposition.

NTO was only detected in quantifiable concentrations in detonation 2, DU2, although characteristic NTO peaks were observed in samples from all DU's from all three detonations, suggesting that NTO was concentrations were below the limit of quantification of NTO (1.4 mg L-1)[17]. This was confirmed by concentrating select sample extracts i.e. in one of the replicates for detonation 3, decision unit 3 0.002 mg kg⁻¹ NTO was detected. Evaporating samples was considered to be too time consuming to achieve for samples. and therefore unquantifiable concentrations of NTO have been reported as 'trace' (Table 2).

RDX was detected in the 'area control' sample i.e. the soil directly beneath the sampling area, but was not detected in the sampling area, including in the concentrated samples. Previous work in the literature suggests it is likely that RDX is deposited, but the concentrations were too low to be detected by the methods used (Table 2). This was expected due to the low percentage of RDX in the IMX-104 composition (13%), other compositions have much higher concentrations of RDX (> 60%) making deposition of detectable concentrations much more likely [38].

Table 2: Summary of results from IMX-104 filled 155 mm artillery shell detonations. Standard deviation reported.

Decision Unit	Horizontal orientation- DU Arcs			Horizon	Horizontal orientation- DU Radial		Vertical orientation- DU Arcs		
	NTO mg kg ⁻¹	DNAN mg kg ⁻¹	RDX mg kg ⁻¹	NTO mg kg ⁻¹	DNAN mg kg ⁻¹	RDX mg kg ⁻¹	NTO mg kg ⁻¹	DNAN mg kg ⁻¹	RDX mg kg ⁻¹
Blank (sand)	0	0	0	0	0	0	0	0	0
Area control	0	0	Detect	0	0	Detect	0	0	Detect
DU1	Trace	0.24 ± 0.39	0	Trace	0	0	Trace	0	0
DU2	Trace	0.0009 ± 0.002	0	Trace	0.055± 0.1	0	Trace	0.0008 ±0.002	0
DU3	Trace	0.11 ± 0.2	0	Trace	0	0	Tracea	0	0
DU4	Trace	0	0	Trace	0	0	0	0	0
DU5	Trace	0.24 ± 0.42	0	0.16 ± 0.27	0	0	0	0.16 ±0.27	0
PC1	Trace	0.002 ± 0.001	0	Trace	0.17 ± 0.31	0	Trace	0	0
PC2	Trace	0	0	Trace	0	0	0	0	0
PC3	Trace	0.0008 ± 0.003	0	Trace	0	0	Trace	0	0
Whole area	0	0	0	0	0	0	0	0	0

^a Upon concentrating replicate 2, concentration of NTO was quantified as 0.002 mg kg-1.

3.1.1 Mass of DNAN residue deposition

Concentrations of DNAN were detected in four of the five DU's for detonation 1 (arcs), confirmed by trace

detection of DNAN in the positive controls in DU 1 (PC3) and DU 5 (PC1), and the non-detect in the positive control within DU4 (PC2). Conversely, in the second detonation DNAN was only detected in DU2 (radial),

confirmed by detection of DNAN in the random positive control. It is interesting to note that DNAN was only detected in the second radial DU in detonation 2 (South-Easterly) and it is likely that DNAN identified in detonation 1 was concentrated in a North-Easterly direction corresponding to DU2 in detonation 2, and the rear of the 155 mm shell (Figure 1). To ensure all explosive residues were accounted for, samples were also analysed for DNAN degradation products 2-ANAN, 4-ANAN, 2,4-ANAN and DNP, but these were not detected in any samples.

From the results of the horizontal detonations, it was expected that DNAN deposition from the third detonation would be similar, but possibly more uniformly distributed due to the vertical orientation. This is because in the vertical position, the shell was positioned nose-up meaning any increased DNAN deposition at the rear-end of the shell would be evenly distributed in the sampling area. While DNAN was detected in DU5 (furthest from the detonation centre), and very low levels detected in DU2, DNAN was not detected in any other DU's. In the vertical position, it is possible that residues were deposited beyond the sampling area, although no DNAN was detected in these control samples, very low concentrations may have been masked in the HPLC trace by the noise from soil organic matter.

The constructed sampling arena was semi-circular as it was assumed that the deposition would be symmetrical about the long axis of the projectile (nose to tail) and estimates of mass of residue deposited could be doubled to account for both halves. In reality, doubling the mass is unlikely to give a perfect estimate as deposition could be affected by slight variations in weather conditions and slight misalignments of the 155 mm artillery shell. A number of other assumptions were also made to enable estimation of the deposited mass of DNAN per kilogram of soil. For example, the mass of soil was determined by assuming DNAN would be deposited on the soil surface and no deeper than the sampling depth of 5 cm, and that the density of soil is similar to that of sand. As the concentration of DNAN recovered from the three detonations was significantly different, the mass of DNAN deposited was calculated from a) the combined concentrations from all DU's in detonation 1; b) DU5 in detonation 2; and c) DU5 in detonation 3 to provide upper and lower estimates. The total estimated mass of DNAN from each detonation was calculated by multiplying the concentration (mg kg-1) by double the mass of sand in the DU's where DNAN was found (Equation 1).

Estimated mass of DNAN in $DU = C_{residue} \times M_{sand}$ Eq. 1

Where C is the concentration in soil (mg kg⁻¹) and M is the mass of sand in the decision unit.

From the data obtained from Equation 1, the total estimated mass of DNAN from the three detonations accounted for between 0.006% and 0.07% of the total DNAN content in the 155 mm shell (Table 3). The upper estimate is slightly higher than previously published literature on the residue from 60 mm and 81 mm IMX-

104 shells which found 0.006% and 0.001% DNAN deposited respectively [13]. An increase in deposited residue may be due to the significant increase in the Net Explosive Quantity between the three shell sizes (approximately 11 kg (155 mm) vs 339 g (61 mm) and 807 g (81 mm)).

Table 3: Mass DNAN deposited from detonation of 155

mm artillery shell.

min artificity chem:					
Detonation	Concentration	Total Mass	% Mass		
	mg kg ⁻¹	g			
1	0.22 +0.0009 + 0.11	2.63	0.07		
	+0.24				
2	0.049	0.23	0.006		
	0.40	4.00	0.00		
3	0.16	1.23	0.03		

As expected from previously published literature, the mass of DNAN deposited from detonation of an IMX-104 filled 155 mm artillery shell is higher than for commensurate legacy munitions, such as TNT from Comp B filled 155 mm shells [13,39,40]. This is of note, as DNAN is a nitrobenzene with similar properties to TNT, although it is slightly more toxic (199 mg kg-1 vs 607-767 mg kg-1). DNAN's environmental behaviour may therefore be similar to TNT i.e. mineralisation by photo and bio-degradation before significant exposure to environmental receptors. However, this may not be true of all environments as it is highly dependent on soil type and weather conditions, and it may be possible for residues to accumulate to potentially hazardous levels. This is unlikely to be a problem for operational use as the incident rate is low, and in localised areas i.e. DNAN is likely to be diluted through environmental action such as infiltration with rainwater, surface run off and degradation. Therefore, in the absence of additional incident DNAN the concentration of this compound in the environment will rapidly decrease. However, the accumulation of DNAN may need to be considered for training with IMX-104 filled 155 mm artillery shells.

3.1.2 Mass of NTO deposition

One sample from the detonation 2, DU5, contained detectable quantities of NTO (0.16 ± 0.17 mg kg⁻¹). and detection of NTO was consistent in all DU samples, suggesting that during the detonation NTO was evenly distributed across the arena. Using Equation 1 and assuming a) the highest level of deposition (0.16 mg kg-1) in detonation 2, DU5 and b) assuming an average deposition of 0.03 mg kg-1 across the entire area, the mass deposited from a single detonation was between 71 mg and 762 mg (Table 4). This equates to between 0.001% and 0.01% of the mass of NTO in the 155 mm shell. This is significantly lower than the estimated deposition mass in the published literature from the detonation of 60 mm and 81 mm munitions on snow (0.4 - 1.2 %), suggesting that the mass of NTO deposited is lower for the 155 mm artillery shell [5].

Whilst NTO is significantly less toxic than DNAN (5000 mg kg⁻¹ vs 199 mg kg⁻¹), there is limited research into its wider environmental impact. One potential issue is that NTO may be acidic when solubilised i.e. after rainfall, which may increase leaching of nutrients and

metals from the existing contamination in soil [18]. For example, many explosive test and impact areas are contaminated with lead, which is known to leach more rapidly in soils with pH lower than 4 [39]. In addition, NTO discolours water at low concentrations (10 ppm), which would be considered pollution under multiple UK and European regulations, even if there were no associated toxicity [42].

Table 4: Mass NTO deposited from detonation of 155 mm artillery shell.

mm artillery snell.

Detonation	Concentration	Total Mass	% Mass
	mg kg ⁻¹	g	
2	0.16	762	0.01
1&3	0.003	71	0.001

3.2 Potential environmental impact of IMX-104 155 mm artillery shells

As RDX was not detected in appreciable concentrations the accumulation rate of hazardous concentrations of IMX-104 residues in the environment was based on the deposition of DNAN and NTO. Therefore, assuming the masses of DNAN and NTO residue per detonation as calculated above (Table 3 and Table 4) the estimated rate of accumulation during training was calculated using the Circular Error Probable (CEP) i.e. the radius of the area in which 50% of the rounds are likely to land. For the 155 mm artillery shell the CEP is 94 m - 267 m depending on the distance fired (15-30 km). The calculation takes into account that only 50% of rounds are likely to land within the CEP, with the remaining 50% distributed in an even larger area of diminishing soil concentration. The area increases with increasing distance. Using this calculation, after 1000 detonations the concentration of DNAN on the surface soil could be as high as 2.37 mg kg-1 (assuming lower CEP and higher mass deposited) but is more likely to fall between 0.21 and 2.37 mg kg⁻¹. Table 5 outlines the potential maximum concentration of DNAN and NTO in soil at CEP 94 m and CEP 267 m for detonation of 1000 and 10,000 IMX-104 filled 155 mm shells in the absence of other environmental processes such as adsorption, degradation and surface run off.

Table 5: The potential accumulation of DNAN and NTO in soil for 1000 and 10,000 firings for CEP 94 m and 267

<u>m.</u>					
Explosive residue	Estimated soil		Estimated soil		
deposited from	concentration 1000		concentration 10,000		
155 mm shell	detonations (mg kg ⁻¹)		detonations (mg kg ⁻¹)		
	CEP 94 m	CEP 267 m	CEP 94 m	CEP 267 m	
DNAN 0.006%	0.21	0.03	2.10	0.26	
DNAN 0.02%	0.72	0.09	7.24	0.90	
DNAN 0.07%	2.37	0.29	23.68	2.93	
NTO 0.001%	0.06	0.00	0.64	80.0	
NTO 0.01%	0.69	0.09	6.86	0.85	

Unfortunately, there are no current legal Soil Screening Level (SSL) for DNAN or NTO in soil although health-based environmental screening levels are in development [43]. However for the US EPA has given a residential and industrial SSL of 19 and 79 mg kg⁻¹ respectively for TNT, which has similar properties

to DNAN (United States Environmental Protection Agency, 2014). Although it is unlikely that the SSL for DNAN would be the same as for TNT, as DNAN is more toxic, it does give a guideline figure for concentrations of concern which are potentially exceeded at localised areas of soil on training ranges within as few as 10,000 firings. In addition, this figure does not consider the number of partially detonated or non-functioning ordnance which may be disposed by blow-in-place or left in the environment. Both methods known to deposit significant concentrations of explosives in the environment therefore contributing to the accumulation of residues [13,43].

The results in Table 5 suggest that the concentration of DNAN in soil could increase rapidly at training areas where 155 mm shells are in use. However, this calculation assumes that there is no transport beyond the first 5 cm of soil and that the training targets do not change. In reality, training is likely to take place over a much larger area further reducing the accumulation rate, and over a significant period of time. For example, if 10,000 155 mm shells are fired within a year, it is likely that a significant quantity of deposited DNAN will be dissolved by incident rainfall and transported into soil where it may to be rapidly degraded, especially in high organic content soils (50% within 3 months) [17]. While some degradation products are equally as toxic as DNAN, these are also likely to be further degraded to mineralised products such as nitrates and nitrites before exposure to a receptor. Therefore, while the contamination of soil is a concern, it may be managed by rotating training areas and avoiding areas with sensitive groundwater resources.

Accumulation of NTO is also of concern as the behaviour of NTO in the environment is still under investigation. For example, whilst some NTO degradation products have been speculated, such as ATO. thev have not yet been identified in environmentally representative samples such as soil studies [45]. In addition, there are limited toxicity studies on NTO and its degradation/decomposition products making it difficult to assess its environmental impact. From the findings in this work, and previous work indicating the rapid degradation of NTO in the environment, it is likely that NTO will be deposited in the environment from the use of IMX-104 filled 155 mm artillery shells, therefore, further investigation into the degradation products and their toxicity is required [17,46].

4 Conclusion

It is clear that DNAN and NTO residues were deposited from the detonation of an IMX-104 filled 155 mm artillery shell in slightly higher concentrations than has been recorded for legacy (RDX/TNT) filled munitions. While the deposited concentrations may not be of immediate concern after a single detonation, care must be taken if large quantities of IMX-104 filled munitions are to be used for training to manage accumulation and minimise environmental impact. The training environment is particularly relevant as the accumulation of DNAN and

NTO will be highly dependent on rate of infiltration into soil with rainfall, and the rate of degradation and therefore environmental management techniques must be chosen for their suitability to the local environment. Finally, it must be noted that this residue deposition investigation was relatively small scale, with only three detonations for comparison. To increase confidence in results, additional studies should be undertaken such as an accumulation study wherein samples are collected after 5 to 10 detonations.

Acknowledgements

The authors would like to thank Antony Grimes, Bonny Thawani, Charich Chuenta, Ana Paula Lopes, Jacopo Bonifacio, Lara Temple, Cait Gilroy-Hirst and Ruben Moya for their help with setting up the detonation arena and collecting samples. In addition, the authors thank Bj Clarke and Trevor Lawrence for their support during the practical phase of the work, and Karl Norris for making the surrounding barrier and pegs. With thanks to RWM Italia for funding.

References

- [1] R. Zentelis, S. Banks, J.D. Roberts, S. Dovers, D. Lindenmayer, Managing military training-related environmental disturbance, J. Environ. Manage. 204, 2017, 486–493.
 - https://doi.org/10.1016/J.JENVMAN.2017.09.029.
- J. Clausen, J. Robb, D. Curry, N. Korte, A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA, *Environ. Pollut*. 2004, 129, 13–21. https://doi.org/10.1016/j.envpol.2003.10.002.
- [3] A.D. Hewitt, T.F. Jenkins, M.E. Walsh, M.R. Walsh, S. Taylor, RDX and TNT residues from live-fire and blow-in-place detonations, Chemosphere. 2005, 61, 888–894. https://doi.org/10.1016/J.CHEMOSPHERE.2005.0 4.058.
- [4] M.R. Walsh, S. Thiboutot, M.E. Walsh, G. Ampleman, Controlled expedient disposal of excess gun propellant, J. Hazard. Mater. 2012, 219–220, 89–94. https://doi.org/10.1016/J.JHAZMAT.2012.03.060.
- [5] M.R. Walsh, M.E. Walsh, C.A. Ramsey, S. Thiboutot, G. Ampleman, E. Diaz, J.E. Zufelt, Energetic Residues from the Detonation of IMX-104 Insensitive Munitions, *Propellants, Explos. Pyrotech.* 2014, 39, 243–250. https://doi.org/10.1002/prep.201300095.
- [6] S. Singh, L. Jelinek, P. Samuels, A. Di Stasio, L. Zunino, IMX-104 Characterization for DoD Qualification, in: 2010 Insensitive Munitions

- Energ. Mater. Technol. Symp., Munich, Germany, October, 2010. https://imemg.org/wp-content/uploads/IMEMTS 2010/papers/Singh-10555_IMX-104 Qualification_IMEMTS2010-Paper.pdf.
- [7] M.R. Walsh, T. Temple, M.F. Bigl, S.F. Tshabalala, N. Mai, M. Ladyman, Investigation of Energetic Particle Distribution from High-Order Detonations of Munitions, *Propellants, Explos. Pyrotech.* 2017, 42. https://doi.org/10.1002/prep.201700089.
- [8] T.F. Jenkins, A.D. Hewitt, M.E. Walsh, T.A. Ranney, C.A. Ramsey, C.L. Grant, K.L. Bjella, Representative Sampling for Energetic Compounds at Military Training Ranges, *Environ. Forensics.* 2005, 6, 45–55. https://doi.org/10.1080/15275920590913912.
- [9] M.E. Walsh, C.A. Ramsey, T.F. Jenkins, The effect of particle size reduction by grinding on subsampling variance for explosives residues in soil, *Chemosphere*. 2002, 49, 1267–1273. https://doi.org/10.1016/S0045-6535(02)00528-3.
- [10] M.R. Walsh, C.M. Collins, A.D. Hewitt, Energetic Residues from Blow-in Place detonations of 60mm and 120mm Fuzed High-Explosive Mortar Cartridges, Report ERDC/CRREL TR-08-19, Cold Regions Research and Engineering Laboratory, Hanover, 2008.
- [11] S. Taylor, J. Lever, M. Walsh, M.E. Walsh, B. Bostick, B. Packer, Underground UXO: Are They a Significant Source of Explosives in Soil Compared to Low-and High-Order Detonations? Report TR-04-23, Cold Regions Research and Engineering Laboratory, Hanover, 2004.
- [12] A.D. Hewitt, T.F. Jenkins, T. Ranney, J. Stark, M.E. Walsh, S. Taylor, M.R. Walsh, D.J. Lambert, N.M. Perron, N.H. Collins, R. Karn, *Estimates for Explosives Residue from the Detonation of Army Munitions*, 2003.
- [13] M.R. Walsh, M.E. Walsh, C.A. Ramsey, S. Thiboutot, G. Ampleman, E. Diaz, J.E. Zufelt, Energetic Residues from the Detonation of IMX-104 Insensitive Munitions, *Propellants, Explos. Pyrotech.* 2014, 39 243–250. https://doi.org/10.1002/prep.201300095.
- [14] H. Ryu, J.K. Han, J.W. Jung, B. Bae, K. Nam, Human health risk assessment of explosives and heavy metals at a military gunnery range, *Environ. Geochem. Health*, Springer, 2007: pp. 259–269. https://doi.org/10.1007/s10653-007-9101-5.
- [15] J.D. Arthur, N.W. Mark, S. Taylor, J. Šimůnek, M.L. Brusseau, K.M. Dontsova, Dissolution and transport of insensitive munitions formulations

- IMX-101 and IMX-104 in saturated soil columns, Sci. Total Environ. **2018**, 624 758–768. https://doi.org/10.1016/J.SCITOTENV.2017.11.30 7.
- [16] A.K. Nandi, S.K. Singh, G.M. Kunjir, J. Singh, A.K. Mandal, R.K. Pandey, Assay of the insensitive high explosive 3-Nitro-1,2,4-triazol-5-one (NTO) by acid-base titration, *Cent. Eur. J. Energ. Mater.* 2013, 10, 113–122.
- [17] T. Temple, M. Ladyman, N. Mai, E. Galante, M. Ricamora, R. Shirazi, F. Coulon, Investigation into the environmental fate of the combined Insensitive High Explosive constituents 2,4-dinitroanisole (DNAN), 1-nitroguanidine (NQ) and nitrotriazolone (NTO) in soil, Sci. Total Environ. 2018, 625, 1264–1271. https://doi.org/10.1016/j.scitotenv.2017.12.264.
- [18] N.W. Mark, Batch and Column Transport Studies of Environmental Fate of 3-nitro-1,2,4-triazol-5one (NTO) in Soils. The University of Arizona, 2014.
- [19] N. Mark, J. Arthur, K. Dontsova, M. Brusseau, S. Taylor, J. Šimůnek, Column transport studies of 3-nitro-1,2,4-triazol-5-one (NTO) in soils, Chemosphere. 2017,171 427–434. https://doi.org/10.1016/j.chemosphere.2016.12.06 7.
- [20] L. Le Campion, A. Vandais, J. Ouazzani, N.N. Amerkhanova, R.P. Naumova, A. Becuwe, A. Delclos, D. Bruns-Nagel, J. Breitung, E. Von Löw, K. Steinbach, T. Gorontzy, M.W. Kahl, K.H.K.-H. Blotevogel, D. Gemsa, R.L. Crawford, G.I. Chipen, R.P. Bokalder, V.Y. Grinshtein, S.B. Funk, D.J. Roberts, D.L. Crawford, R.L. Crawford, P. Goldman, T. Gorontzy, O. Drzyzga, M.W. Kahl, D. Bruns-Nagel, . Breitung, E. Von Loew, K.H.K.-H. Blotevogel, W.H. Griest, A.J. Stewart, R.L. Tyndall, J.E. Caton, C.H. Ho, K.S. Ironside, W.M. Caldwell, E. Tan, K. Hankenson, D.J. Schaeffer, R.L. Koch, E.J.T. Chrystal, B.B. Beaulieu, P. Goldman, C. Kohl, P. Morgan, A. Geschler, D. La, J. Froines, L. Le Campion, M.T. Adeline, J. Ouazzani, L. Le Campion, M. Delaforge, J.P. Noel, J. Ouazzani, K.Y. Lee, L.B. Chapman, M.D. Coburn, J.O. London, D.M. Smith, E.C. McCoy, H.S. Rosenkranz, R. Mermelstein, S. Nikolic, M. Medic-Saric, S. Rendic, N. Trinajstic, P.-G. Rieger, H.-J. Knackmus, D.J. Roberts, R.H. Kaake, S.B. Funk, D.L. Crawford, R.L. Crawford, R.R. Scheline, N.R. Schneider, L.B. Sharon, M.E. Andersen, W.F. Von Oettigen, D.D. Donahue, H. Yagoda, A.R. Monaco, M.R. Harris, M.I. Walton, P. Workman, W.D. Won, L.H. DiSalo, J. Ng,

- Microbial remediation of NTO in aqueous industrial wastes. *FEMS Microbiology Letters*, **1999**, 176, 197–203. https://doi.org/10.1111/j.1574-6968.1999.tb13662.x.
- [21] N. Mark, J. Arthur, K. Dontsova, M. Brusseau, S. Taylor, Adsorption and attenuation behavior of 3-nitro-1,2,4-triazol-5-one (NTO) in eleven soils, Chemosphere. 2016,144, 1249–1255. https://doi.org/10.1016/j.chemosphere.2015.09.10 1.
- [22] C. Madeira, J. Field, M. Simonich, R. Tanguay, J. Chorover, R. Sierra-Alvarez, R. Sierra-Alvarez, R. Sierra-Alvarez, 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)., J Hazard Mater. 2018.
- [23] M.J. Krzmarzick, R. Khatiwada, C.I. Olivares, L. Abrell, R. Sierra-Alvarez, J. Chorover, J.A. Field, Biotransformation and Degradation of the Insensitive Munitions Compound, 3-Nitro-1,2,4-triazol-5-one, by Soil Bacterial Communities, *Environ. Sci. Technol.* 2015, 49. https://doi.org/10.1021/acs.est.5b00511.
- [24] L. Le Campion, M. Delaforge, J.P. Noel, J. Ouazzani, Metabolism of 14C-labelled 5-nitro-1,2,4-triazol-3-one (NTO): comparison between rat liver microsomes and bacterial metabolic pathways, J. Mol. Catal. B Enzym. 1998, 5, 395– 402. https://doi.org/10.1016/S1381-1177(98)00103-9.
- [25] L.C.B. Crouse, E.M. Lent, G.J. Leach, Oral Toxicity of 3-Nitro-1,2,4-triazol-5-one in Rats, *Int. J. Toxicol.* 2015, 34, 55–66. https://doi.org/10.1177/1091581814567177.
- [26] E.M Lent, L.C.B. Crouse, A.M. Jackovitz, E.E. Carroll, M.S. Johnson, An extended onegeneration reproductive toxicity test of 1,2,4-Triazol-5-one (NTO) in rats, *J. Toxicol. Environ. Health Part A.* 2016, 24, 1159-1178. https://doi.org/10.1080/15287394.2016.1219893.
- [27] E.M. Lent, L.C.B. Crouse, T. Hanna, S. Wallace, The Subchronic Oral Toxicity of DNAN and NTO in rats. Report: 87-XE-0DBP-10., US Army Institute of Public Health, 2012.
- [28] J. V. Dilley, C.A. Tyson, R.J. Spanggord, D.P. Sasmore, G.W. Newell, J.C. Dacre, Short-term oral toxicity of 2,4,6-trinitrotoluene in mice, rats, and dogs, *J. Toxicol. Environ. Health.* 1982, 9, 565–585. https://doi.org/10.1080/15287398209530188.

- [29] S. Taylor, D.B. Ringelberg, K. Dontsova, C.P. Daghlian, M.E. Walsh, M.R. Walsh, Insights into the dissolution and the three-dimensional structure of insensitive munitions formulations., *Chemosphere.* 2013, 93, 1782–8. https://doi.org/10.1016/j.chemosphere.2013.06.01 1.
- [30] K.S. Ro, A. Venugopal, D.D. Adrian, D. Constant, K. Qaisi, K.T. Valsaraj, L.J. Thibodeaux, D. Roy, Solubility of 2,4,6-trinitrotoluene (TNT) in water. *J. Chem. Eng. Data.* 1996, 41, 758–761. https://doi.org/10.1021/je950322w.
- [31] J.Hawari, F.Monteil- Rivera, N.N.Perreault,
 A.Halasz, L.Paquet, Z.Radovic-Hrapovic,
 S.Deschamps, S.Thiboutot, G.Ampleman,
 Environmental fate of 2,4-dinitroanisole (DNAN)
 and its reduced products. Chemosphere. 2015,
 119, 16-23.
 https://doi.org/10.1016/j.chemosphere.2014.05.04
 7.
- [32] S.G. Dodard, M. Sarrazin, J. Hawari, L. Paquet, G. Ampleman, S. Thiboutot, G.I. Sunahara, Ecotoxicological assessment of a high energetic and insensitive munitions compound: 2,4-Dinitroanisole (DNAN). J. Hazard. Mater. 2013, 262, 143–150. https://doi.org/10.1016/j.jhazmat.2013.08.043.
- [33] S. Taylor, M.E. Walsh, J.B. Becher, D.B. Ringelberg, P.Z. Mannes, G.W. Gribble, Photodegradation of 2,4-dinitroanisole (DNAN): An emerging munitions compound. *Chemosphere*. 2017, 167, 193–203. https://doi.org/10.1016/j.chemosphere.2016.09.14 2.
- [34] C.H. Racine, M.E. Walsh, B.D. Roebuck, C.M. Collins, D. Calkins, L. Reitsma, P. Buchli, G. Goldfarb, White Phosphorus Poisoning of Waterfowl in an Alaskan Salt Marsh, *J. Wildl. Dis.* 1992, 28, 669–673. https://doi.org/10.7589/0090-3558-28.4.669.
- [35] G. Bordeleau, M.M. Savard, R. Martel, G. Ampleman, S. Thiboutot, Determination of the origin of groundwater nitrate at an air weapons range using the dual isotope approach. *J. Contam. Hydrol.* 2008, 98, 97–105. https://doi.org/10.1016/j.jconhyd.2008.03.004.

- [36] T. Temple, S. Cipullo, E. Galante, M. Ladyman, N. Mai, T. Parry, F. Coulon, The effect of soil type on the extraction of insensitive high explosive constituents using four conventional methods, *Sci. Total Environ.* 2019, 668. https://doi.org/10.1016/j.scitotenv.2019.02.359.
- [37] W. Fawcett-Hirst, T.J. Temple, M.K. Ladyman, F. Coulon, 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*. 2020, 255, 126848. https://doi.org/10.1016/j.chemosphere.2020.126848.
- [38] S. Taylor, E. Campbell, L. Perovich, J. Lever, J. Pennington, Characteristics of Composition B particles from blow-in-place detonations, *Chemosphere*. 2006, 65, 1405–1413. https://doi.org/10.1016/J.CHEMOSPHERE.2006.0 3.077.
- [39] M.R. Walsh, M.E. Walsh, C.A. Ramsey, Measuring Energetic Contaminant Deposition Rates on Snow. Water Air Soil Pollut. 2012, 223, 3689–3699. https://doi.org/10.1007/s11270-012-1141-5.
- [40] M.R. Walsh, M.E. Walsh, C.A. Ramsey, S. Brochu, S. Thiboutot, G. Ampleman, Perchlorate contamination from the detonation of insensitive high-explosive rounds, *J. Hazard. Mater.* 2013, 262, 228–233. https://doi.org/10.1016/j.jhazmat.2013.08.045.
- [41] E. Mariussen, I.V. Johnsen, A.E. Strømseng, Distribution and mobility of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) from ammunition residues on shooting ranges for small arms located on mires. https://doi.org/10.1007/s11356-017-8647-8.
- [42] M. Tennant, S.C. Chew, T. Krämer, N. Mai, D. McAteer, J. Pons, Practical Colorimetry of 3-Nitro-1,2,4-Triazol-5-One, *Propellants, Explos. Pyrotech.* 2018, 44, 198–202. https://doi.org/10.1002/prep.201800239.
- [43] E.M. Lent, G. Leach, M.S. Johnson, Development of health-based environmental screening levels for insensitive munitions constituents, *Hum. Ecol. Risk Assess.* 2021, 6, 1543 –1567. https://doi.org/10.1080/10807039.2020.1859352

- [44] S. Taylor, J. Lever, M. Walsh, M.E. Walsh, B. Bostick, B. Packer, Underground UXO: Are They a Significant Source of Explosives in Soil Compared to Low-and High-Order Detonations? TR-04-23, Hanover, 2004. https://apps.dtic.mil/dtic/tr/fulltext/u2/b308065.pdf.
- [45] L.C. Moores, S.J. Jones, G.W.George, D.L. Henderson, T.C.Schutt, <u>Photo degradation</u> <u>kinetics of insensitive munitions constituents</u> <u>nitroquanidine, nitrotriazolone, and dinitroanisole</u> <u>in natural waters, J. Photochem. Photobiol. A</u> 2020, 386, 112094. https://doi.org/10.1016/j.jphotochem.2019.112094
- [46] M.J. Krzmarzick, R. Khatiwada, C.I. Olivares, L. Abrell, R. Sierra-Alvarez, J. Chorover, J.A. Field, Biotransformation and degradation of the insensitive munitions compound, 3-nitro-1,2,4-triazol-5-one, by soil bacterial communities, *Environ. Sci. Technol.* 2015, 49, 5681–5688. https://doi.org/10.1021/acs.est.5b00511.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))

Quantitative environmental assessment of explosive residues from the detonation of Insensitive High Explosive filled 155 mm artillery shell

Federica Persico^[a],Tracey Temple*^[a] Melissa Ladyman^[a],William Gilroy-Hirst^[a], Encina Guiterrez-Carazo^[a], Frederic Coulon ^[b]

Supplementary data

 Random DUs were selected to validate the sampling method and reproducibility of the results. Each random area was selected using a random generator number.

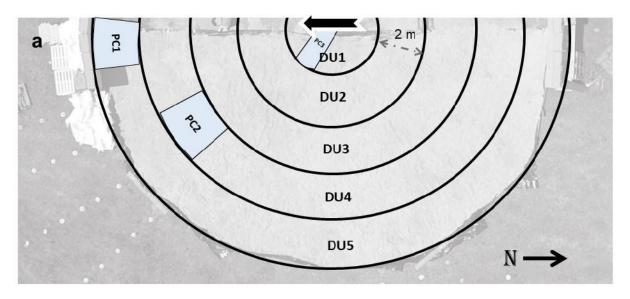


Figure 1. Random areas from Detonation 1.

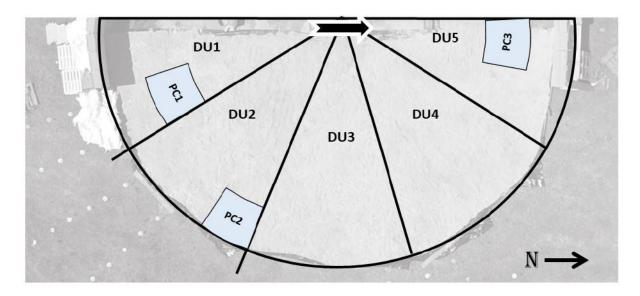


Figure 2. Random areas from Detonation 2.

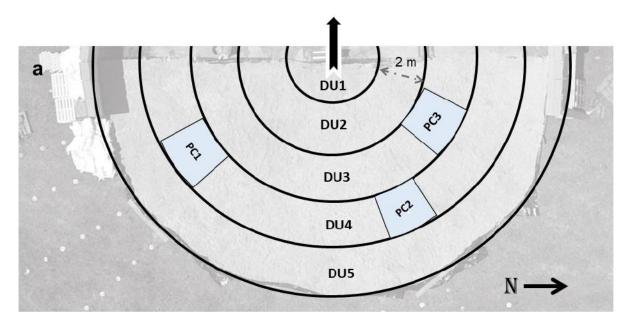


Figure 3. Random areas from Detonation 3.

• Picture were taken before and after the detonation occured.



Figure 4. Aerial picture before detonation 1.



Figure 5. Picture after detonation 1



Figure 6. Aerial picture after detonation 1.