Environmental Fate and Impact of Insensitive Energetic Materials

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ABSTRACT

Over the past few decades, new insensitive energetic compounds have been tested as potential replacements for TNT and RDX in insensitive munitions formulations. This paper summarizes the results of a multi-year study conducted in Canada to determine the environmental fate (transport and abiotic/biotic degradation) and ecological impact of nitroguanidine (NQ), 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), 1,1-diamino-2,2-dinitroethene (FOX-7), N-guanylurea-dinitramide (FOX-12), and their formulations. NQ, NTO, FOX-7 and FOX-12 were found to exhibit intermediate to high water solubility, low n-octanol/water partition coefficient (K_{ow}) and distribution coefficient (K_d < 0.3 L kg^{-1}), indicative of a high migration potential in soil. DNAN, with a lower aqueous solubility, higher K_{ow} (38.1) and K_d (2.3), should remain closer to the discharge point. Irradiation with simulated sunlight caused transformation of NQ to guanidine, O-demethylation and denitration of DNAN without breaking the aromatic ring and the fast degradation of the dinitramide in FOX-12. Removal of the compounds by a soil microbial community was accelerated when nutrients were provided. NQ and the guanylurea moiety of FOX-12 were completely mineralized by a bacterial strain that used them as the sole N source for growth. DNAN and NTO were mainly reduced at the nitro groups. In general, except for NTO in plants and DNAN in most receptors, the compounds displayed reduced toxicity compared to TNT. The plant was more sensitive than earthworms to the three IM formulations tested, in accordance with the toxicity of DNAN and NTO. Overall, the insensitive compounds appear to have a less detrimental environmental impact than the conventional explosives.

1.0 INTRODUCTION

Over the last century, organic nitrogen-based energetic chemicals 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) have been widely used by the Defense Industry. Extensive research has been done to understand the environmental fate and degradation pathways of RDX and TNT at DoD training ranges (Monteil-Rivera et al., 2009). Both RDX and TNT were found to be persistent and toxic, and Ranges and Training Areas (RTA) now contain residues of explosives that pose a potential risk to RTA users, local flora and fauna and the surrounding population (Jenkins et al., 2006). Thus far most research indicates that TNT can easily transform to its corresponding amino derivatives, which are even more toxic than TNT, and tend to either sorb irreversibly to soil humic matter or bioaccumulate in various aquatic and terrestrial receptors (Achtnich et al.,

2000; Fleishmann et al., 2004; Hawari et al., 2000; Kalderis et al., 2011). In the case of RDX, we found that the chemical can either be reduced to its corresponding toxic nitroso derivatives (MNX, DNX and TNX) or undergo denitration and subsequent decomposition to less toxic chemicals including 4-nitro-2,4-diazabutanal (NDAB), methylenedinitramine (MEDINA), nitrite, nitrate, ammonia, HCHO and HCOOH (Halasz et al., 2010; Paquet et al., 2011). Based on past experience with environmental issues associated with the use of traditional explosives, the need to be proactive and to assess environmental exposure and the risks associated with the manufacture and use of these compounds before putting them into service is now recognized.

Recently, there has been a global interest in many countries including Canada to test new insensitive energetic chemicals (IECs), or Insensitive High Explosives (IHE), for introduction in new insensitive munitions (IM) formulations. Nitroguanidine (NQ), 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), 1,1-diamino-2,2-dinitroethene (DADNE or FOX-7) and *N*-guanylurea-dinitramide (FOX-12) were amongst the candidate IECs that presented low sensitivity toward accidental stimuli, high thermal stability and high performance characteristics (Fig. 1). Although the primary goal of the IM formulations is to make the weapon systems they support safer to manufacture, transport and handle (Camp Doha in Kuwait and the USS Forrestal incident are rather graphic justification), their behaviour in the environment must also be considered and a favourable environmental impact has to be demonstrated compared to current formulations. Before large-scale replacement goes into effect in Canadian RTAs, it is important to understand the environmental fate, degradation pathways and impact of these chemicals, individually and in formulations. DNAN and NTO are key components in IM formulations IMX-101, IMX-104 and PAX-48, additionally containing NQ, RDX and HMX, respectively. The present study summarizes laboratory findings of a comprehensive research initiative that was undertaken to determine the environmental fate (transport and abiotic/biotic degradation) and ecological impact of IECs and their formulations prior to their wide use by the Canadian Army. These data should help site managers to know the potential environmental risk of these new munitions and to compare it to that of currently used munitions.

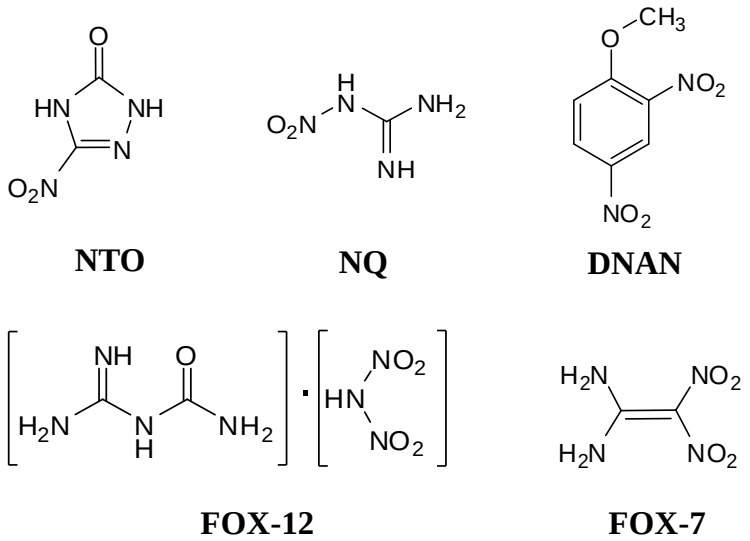

Figure 1. Chemical structures of studied insensitive energetic chemicals

2.0 MATERIALS AND METHODS

2.1 Chemicals

NTO, DNAN, FOX-7, FOX-12 and the IM formulations (IMX-101, IMX-104, PAX-48) were provided by Defence Research and Development Canada (DRDC)-Valcartier. NQ and 4-amino-2-nitroanisole (4-A-2-NAN) were purchased from Sigma-Aldrich, 2-amino-4-nitroanisole (2-A-4-NAN) from MP Biomedicals and 2,4-diaminoanisole (DAAN) from Fluka.

2.2 Soil Characteristics and Preparation

Three soils (DRDC-08, DRDC-09 and DRDC-10) sampled in 2008, 2009 and 2010, respectively, from a Canadian training range at DRDC, Valcartier, were used in this study. Specific characteristics of the soils are given in Table 1. The three soils were passed through a 2-mm sieve and kept at 4°C until use. Soil samples to be used as killed controls were sterilized by autoclaving (121°C, 20 min) on three consecutive days.

Table 1: Physicochemical properties of soils used in this study.

	Particle size distribution			Total Org. C (%)	pH	CEC (mequiv./100 g)
	% Clay (< 2 μm)	% Silt (2-53 μm)	% Sand (> 53 μm)			
DRDC-08	2	4	94	0.36	4.2	< 10
DRDC-09	1.5	25.2	73.3	2.08	6.7	13.2
DRDC-10	0.7	1.6	97.6	2.00	5.7	<10

CEC, Cationic Exchange Capacity

2.3 Physicochemical Measurements

The aqueous solubility of the five IECs was measured at 25°C, in triplicate, as described previously (Monteil-Rivera et al., 2004). Briefly, saturated suspensions of individual chemical were agitated and analyte concentration was measured in the supernatant until constant values were obtained. The octanol-water partition coefficient (K_{ow}) of the compounds was measured at 22 ± 2°C as previously reported using the traditional flask shaking method (OECD, 1981). Ionization constant (pK_a) of 2-ANAN, 4-ANAN and DAAN was measured spectrophotometrically as described by Albert and Serjeant (1971) using 10^{-2} M chloroacetic, formic, and chloroacetic and acetic buffers, respectively.

2.4 Sorption on Soil

Sorption and fate of the five IECs were studied in long-term batch experiments using the DRDC soils (Table 1) as described in Hawari et al. (2015). Sorption experiments were conducted over 2 months, triplicate samples were sacrificed at each sampling time and amount of IEC was measured by reverse HPLC is aqueous supernatant or soil extract. The soil-water distribution coefficient (K_d) in L kg^{-1} was calculated as the ratio $[EC]_s/[EC]_{eq}$, where $[EC]_s$ is the concentration of energetic chemical (EC) adsorbed on soil (in mg kg^{-1}) and $[EC]_{eq}$ is the concentration of EC in the aqueous phase at equilibrium (in mg L^{-1}).

2.5 Photolysis Experiments

In order to predict the degradability of the IECs in naturally occurring conditions, photolysis experiments were conducted in duplicate using artificial sunlight generated from a SolSim Solar Simulating Photoreactor

(Hawari et al., 2015). Initial IEC and degradation products were analyzed as described below.

2.6 Biotransformation in Soil Microcosms

The soil microcosms consisted of 10 g of DRDC-10 soil and 20 mL of mineral salts medium (MSM) in 100-mL sterile glass serum bottles. The MSM (pH 7.0) consisted of (per L of distilled water): 0.38 g K_2HPO_4, 0.2 g $MgSO_4.7H_2O$, 0.05 g $FeCl_3.6H_2O$. Energetic chemicals were added at a final concentration of 20 mg L^{-1}. Microcosms were prepared (i) unamended; (ii) amended with C sources (glucose and succinate); (iii) amended with C sources and an N source (NH_4Cl); and (IV) anaerobic (under argon) amended with 1% molasses. Each treatment was prepared in 3-5 replicates and the microcosm bottles were incubated at room temperature (22 ± 2°C) away from light. At periodic intervals, aliquots were collected from the aqueous phases to monitor the disappearance of the compounds and the formation of degradation products. Assays with pure bacterial strains were conducted in MSM or in Luria-Bertani (LB) medium.

2.7 Ecotoxicity Assays

Toxicity toward aquatic receptors was assessed by dissolving each IEC separately at or near their water solubility limit. The standard 30-min Microtox test (*Vibrio fischeri*) was performed on the aqueous samples as previously described (EC, 1992). Chronic toxicity to freshwater green algae was tested using the 72-h growth inhibition of *Pseudokirchneriella subcapitata* in 96-well microplate (EC, 2007). The terrestrial toxicity tests were conducted on earthworms (*Eisenia andrei*) and plants (ryegrass *Lolium perenne*) in a natural sandy soil (DRDC-10, Table 1). The 14-d earthworm lethality test was conducted as in EC 2007. Phytotoxicity was determined by the 7-d seedling emergence and 19-d shoot growth (dry mass) tests according to earlier methods (ASTM, 2002; USEPA, 1989).

2.8 Analytical Methods

All IECs were quantified by reversed-phase high performance liquid chromatography (HPLC) with UV detection using various mobile phases and columns and various optimal wavelengths (Hawari et al., 2015; Perreault et al., 2013). Degradation products were analyzed by liquid chromatography–mass spectrometry (LC-MS) using a mass spectrometer (MS, Bruker MicroTOFQ mass analyzer) attached to an HPLC system equipped with a diode array detector. Nitrite, nitrate, formate and ammonium were quantified by ion chromatography (Balakrishnan et al., 2004). Formaldehyde was analyzed by HPLC after derivatization with 2,4-pentanedione as described previously (Fournier et al., 2010).

3.0 RESULTS AND DISCUSSION

When released into the environment, most ECs do not migrate to the atmosphere due to their low volatility. However, they can be solubilized in water and migrate through subsurface soil at a rate that depends on their solubility in water, their rate of dissolution and the affinity they exhibit for stationary phases of the soil matrix. Physicochemical properties of chemicals thus play a major role in their transport in the environment. They are also crucial parameters when designing experiments and analytical methods to assess the environmental behavior of formulations.

3.1 Physicochemical Properties

Table 2 summarises the aqueous solubility and K_{ow} of the five IECs; data for other ECs are provided as reference. The aqueous solubility of ECs varies greatly from values below 5 mg L^{-1} to > 40,000 mg L^{-1}. Similarly, the affinity of these chemicals for organic matter varies significantly from compounds that have higher affinity for water than for organics (log K_{ow} < 0) to compounds that are favorably distributed into the organic phase (log K_{ow} > 0). Of all the ECs studied, NQ, NTO, FOX-7 and FOX-12 exhibited higher water

solubility and very low K_{ow}. Chemicals with a low K_{ow} value (log K_{ow} < 1) may be considered hydrophilic; they tend to have high water solubility, small soil adsorption coefficients and low bioaccumulation. Conversely, chemicals with a high K_{ow} (log K_{ow} > 4) are very hydrophobic. The above four chemicals will thus be more prone to migration through subsurface soil and groundwater contamination. In contrast, DNAN, like TNT, with its significantly lower aqueous solubility and higher K_{ow}, should remain closer to the discharge point at training range sites.

3.2 Sorption on Soils

Sorption of the 5 IECs on DRDC soils was studied through long-term batch experiments. Distribution coefficients (K_d) measured at the equilibrium are provided in Table 3. As demonstrated by the very low K_d values measured (Table 3: all K_d < 0.3 L kg^{-1}) and in line with their very low affinity for organic solvents (Table 2: log K_{ow} < 0), NTO, NQ, FOX-7 and FOX-12 are all polar compounds that will be prone to easy and fast migration in soil. In contrast and in agreement with its lower aqueous solubility and higher K_{ow}, DNAN was found to sorb slightly more to the DRDC-09 soil, with a K_d value of 2.3. More details on sorption of DNAN and its amino derivatives to various soils can be found in Hawari et al. (2015).

Table 2: Physicochemical properties of energetic chemicals.

Common name	Water solubility at 25°C (mg L^{-1})	Log K_{ow}	pKa	Reference
Aromatic nitro				
TNT	150	1.86-2.00	NA	Rosenblatt et al., 1991
2,4-DNT	200	1.98	NA	HSDB
2,6-DNT	204	2.10	NA	HSDB
DNAN	**210**	**1.58**	NA	Hawari et al., 2015
2-ANAN	250	1.47	2.55	Hawari et al., 2015
4-ANAN	4,430	0.80	3.50	Hawari et al., 2015
DAAN	> 40,000	< -1	2.61(*o*)	Hawari et al., 2015
			5.46(*p*)	Hawari et al., 2015
Nitramines				
RDX	56.4	0.90	NA	Monteil-R. et al., 2004
HMX	4.5	0.17	NA	Monteil-R. et al., 2004
CL-20	3.7	1.92	NA	Monteil-R. et al., 2004
IECs				
NQ	**3,250**	**-0.68**		This study
NTO	**17,200**	**-1.7**		This study
FOX-7	**320**	**-0.46**		This study
FOX-12	**4,920**	**< -2**		This study

NA, not applicable; HSDB, Hazardous Substances Data Bank

Table 3: Adsorption coefficients (K_d's) of energetic chemicals in soils from DRDC-Valcartier.

	Clay/Silt (%)	Sand (%)	TOC (%)	CEC cmol/kg	K_d (L kg^{-1})				
					DNAN	NQ	NTO	FOX-7	FOX-12
DRDC-08	6	94	0.36	< 10		< 0.1			
DRDC-09	26.7	73.3	2.08	13.2	2.3	-	< 0.1	0.24	< 0.1

3.3 Aqueous Photolysis

Exposure of IM formulations to sunlight in the field may lead to various extents of photodegradation in the solid form or in solution once individual components have leaked into the environment. In order to predict the degradability of formulations in naturally occurring conditions, irradiation experiments were conducted using artificial simulated sunlight.

NQ disappeared quickly (t½ = 14.6 h) during irradiation in the SolSim reactor. Guanidine, NH_4^+, NO_2^- and NO_3^- were identified as the ultimate products of photolysis formed upon the cleavage of N-N bond in NQ (Fig. 2a). DNAN degraded more slowly (t½ = 74.4 h) and the identification of 2,4-dinitrophenol, aminonitrophenols and hydroxynitroanisoles suggested the occurrence of O-demethylation and denitration without breaking the aromatic ring of DNAN (Fig. 2b). Interestingly, a half-life of 5.1 h was previously determined for 2,4-DNT, and it was shown in this study that the change of the methyl group to methoxy in 2,4-DNAN slowed down the photodegradation rate by 15-fold.

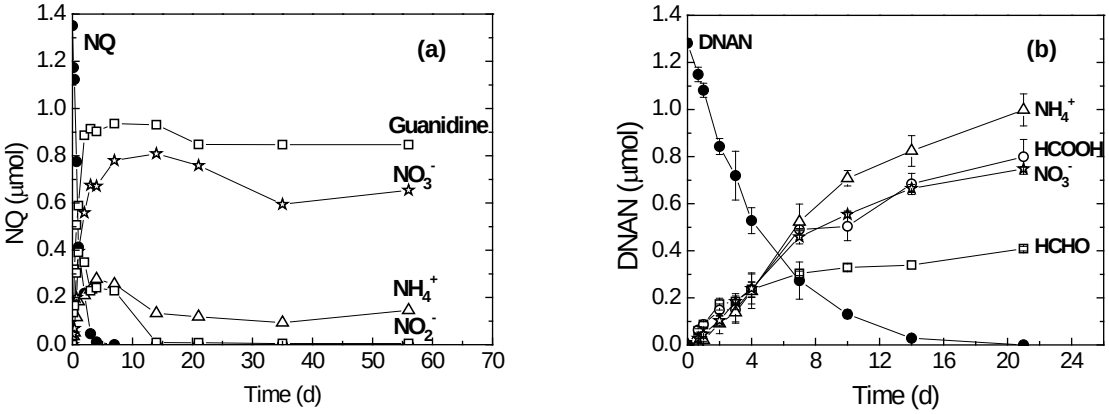

Figure 2: Time course for aqueous photolysis of (a) NQ and (b) DNAN under simulated sunlight.

More than 90% of NTO was degraded in 7 d in the SolSim photoreactor with concomitant formation of NO_2^-, NO_3^- and NH_4^+. The nonstoichiometric formation of nitrate and nitrite from disappearing NTO suggested that more than one initial degradation pathway occurred (Fig. 3). When NTO was photolyzed in the presence of ^{18}O-labeled water, about 20% of the expected ^{18}O was incorporated into two intermediate products. The formation of the intermediates without water involvement was best explained by the loss of nitric oxide (NO) from an initially formed photo-rearranged nitrite intermediate of NTO.

Complete photodegradation of FOX-7 was achieved in 1.9 days (t½ = 12 h). The average molar recovery of nitrite and nitrate combined for each mole of FOX-7 degraded was only 70%, suggesting that NO might have also been released by a nitro-to-nitrite rearrangement in FOX-7. The cleavage of O-NO bond is energetically more favorable than C-NO_2 bond cleavage. Finally, when the FOX-12 salt in water was subjected to artificial solar light, only the dinitramide part was photodegraded whereas guanylurea remained

intact. The very photoreactive dinitramide disappeared in 30 min (t½ = 0.17 h), producing NO_2^-, NO_3^- and NH_4^+. The above findings suggest that photolysis is a significant transformation process that could contribute to reduce the persistence of some IECs dispersed in surface water bodies.

Photolysis of the insensitive munition formulation IMX-101 was also determined (Halasz et al., 2018). Due to a large variance in the water solubility of its three constituents, DNAN, NQ and NTO, two solutions of IMX-101 were prepared: one with low concentration (109 mg L^{-1}) and another with high concentration (2,831 mg L^{-1}). In general, photolysis rates measured in the formulation were found to differ from the rates measured individually. In addition to the known degradation products, DNAN removal in IMX-101 was accompanied by the production of methoxydinitrophenols, which were not observed during photolysis of DNAN alone. One route for the formation of methoxydinitrophenols was suggested to involve photonitration of the DNAN photoproduct methoxynitrophenol during simultaneous photodenitration of NQ and NTO in IMX-101. Indeed, when DNAN was photolyzed in the presence of $^{15}NO_2$-labeled explosive CL-20, we detected methoxydinitrophenols with an increase of 1 mass unit, indicating that denitration of DNAN and renitration of products simultaneously occurred. As was the case with DNAN, we found that guanidine, a primary degradation product of NQ, also underwent renitration in the presence of NTO and the photocatalyst TiO_2 (Halasz et al., 2018). We concluded that the three constituents of IMX-101 can be photodegraded in surface water and that fate and primary degradation products of IMX-101 can be influenced by the interactions between the formulation ingredients and their degradation products.

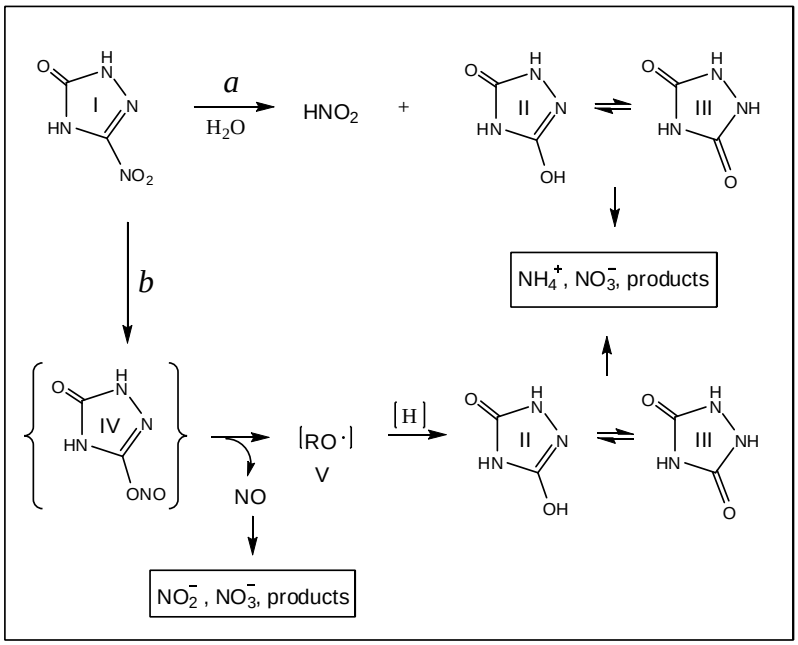

Figure 3: Proposed photodegradation routes of NTO in water by simulated sunlight.

3.4 Biotranformation

In soil microcosms, removal of the five IECs by the indigenous microbial community, under both aerobic and anaerobic conditions, was accelerated when nutrients were provided, suggesting a low potential for natural attenuation. The addition of ammonium (NH_4Cl), however, hindered the degradation of NQ and guanylurea (FOX-12), because biodegradation of these compounds is linked to their use as the N source. NQ was not degraded under anaerobic conditions. Using pure bacterial strains, transformation of DNAN was shown to occur *via* sequential reduction of the nitro groups. Under aerobic conditions, a strain of *Bacillus* (13G), isolated from the DRDC-10 soil, reduced DNAN to 2-ANAN and 4-ANAN *via* the intermediary

formation of the nitroso and hydroxylamino derivatives (Perreault et al., 2012*a*). Further reduction to DAAN was observed with *Shewanella oneidensis* strain MR-1 (ATCC 700550) and *Pseudomonas fluorescence* I-C under anaerobic conditions. Other products identified included acetylated and demethylated products and azoxy- and azo-dimers (Perreault et al., 2012*a*). In addition, the enzyme manganese peroxidase from the fungus *Phanerochaete chrysosporium*, efficiently transformed 4-ANAN, forming methanol, formaldehyde, ammonia and 4-formamido-2-nitroanisole. Transformation of NTO by a variety of bacterial strains was always limited to the reduction of the nitro group to form 3-amino-1,2,4-triazol-5-one (3-ATO) as end-product, under aerobic and anaerobic conditions.

Variovorax strain VC1, also isolated from the DRDC-10 soil, grew with NQ as the sole N source, forming NH_3, N_2O and CO_2, *via* the intermediary formation of nitrourea (Fig. 4) (Perreault et al., 2012*b*). NQ biodegradation was shown to involve initial enzymatic hydroxylation of the imine, -C=N- bond, leading first to the formation of the unstable α-hydroxynitroamine intermediate, $O_2NNHC(OH)(NH_2)_2$, whose decomposition in water leads to the formation of NH_3, N_2O and CO_2.

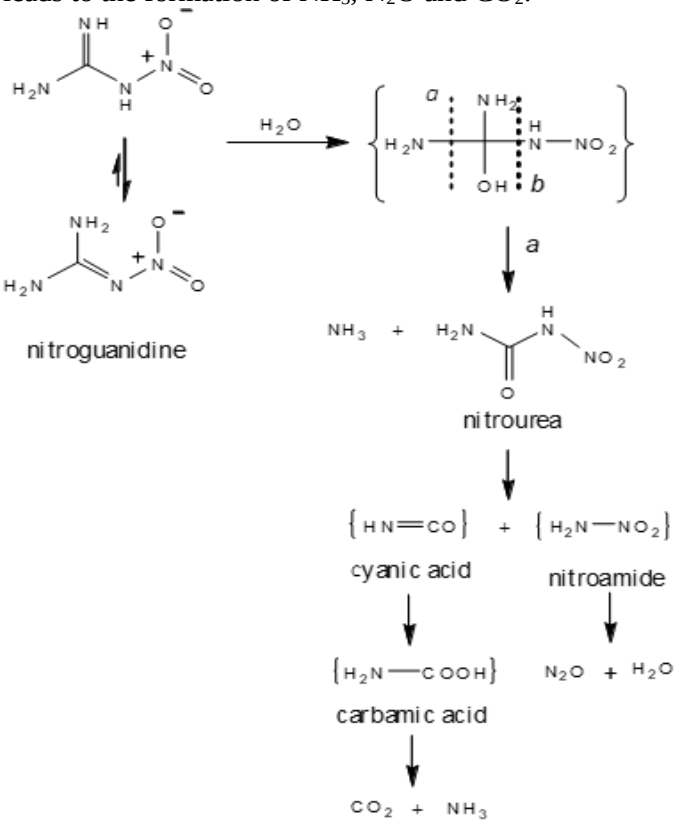

Figure 4: Proposed degradation route of NQ by *Variovorax* strain VC1. Compounds in bracket were not detected.

Strain VC1 also grew with FOX-12 as the sole N source, degrading the guanylurea moiety to guanidine and ammonia, without attacking the dinitramide (Perreault et al., 2013). *Bacillus* 13G was further able to degrade the dinitramide. As mentioned above, dinitramide is readily photodegraded. Combining bacteria and light (room lighting) allowed achieving total degradation of FOX-12. Under these conditions, guanylurea and dinitramide degraded simultaneously with almost similar rates. Finally, when FOX-7 was incubated with different bacterial isolates, the major N-product detected was always NO_3^- and NH_3, under aerobic and anaerobic conditions, respectively. Nitrite transiently accumulated and a small amount of formaldehyde was formed. Anaerobic transformation of FOX-7 by MR-1 produced ammonia at a molar ratio of ~1.5 moles

NH_3 per mole of FOX-7 degraded.

Biotransformation of IMX-101 by the DRDC-10 soil microbial community also indicated a limited potential for natural attenuation. In general, the biotransformation pattern of each formulation component was in agreement with the one of DNAN, NTO and NQ individually. NTO was similarly transformed under aerobic and anaerobic conditions when sugars were provided, NQ was readily degraded under aerobic conditions but persisted under anaerobic conditions, and 2-ANAN and 4-ANAN were both detected as DNAN transformation products.

3.5 Aquatic Ecotoxicity

The aquatic toxicity of the five IECs to the marine bacterium *V. fischeri* and to the freshwater microalgae *P. subcapitata* was tested after dissolving the chemicals in water (Table 4). Compared to conventional ECs, DNAN and its amino derivatives were less toxic than TNT, but more toxic than RDX. The four other IECs were much less toxic than DNAN. NTO and NQ were only toxic to the bacterium or the microalgae at very high concentrations ($EC_{50} \geq 3{,}727$ mg L^{-1} and $EC_{50} \geq 1{,}094$ mg L^{-1}, respectively). FOX-7 and FOX-12 had intermediate toxicity values in the Microtox test, but showed high toxicity in the algal growth inhibition test. The IM formulations led to more toxicity toward algae than earthworms, in accordance with their main ingredients, NTO and DNAN.

Table 4: Toxicity benchmark values (EC20 and EC50 in mg L-1) of energetic chemicals and IM formulations in the Microtox and algal growth inhibition tests.

	Microtox		Algae		Reference
	EC_{20}	EC_{50}	EC_{20}	EC_{50}	
TNT	0.11	0.95	0.09	0.73	Sunahara et al., 1998
RDX	23.2	> 40.2	> 40.2	> 40.2	Sunahara et al., 1998
DNAN	4.40	13.89	1.40	2.22	Dodard et al., 2013
2-ANAN	3.20	8.50	4.10	21.88	Dodard et al., 2013
4-ANAN	15.78	42.06	6.10	42.86	Dodard et al., 2013
NTO	2,405	5,100	1,587	2,324	This study
NQ	1,253	3,727	760	1,094	This study
FOX-7	> 128	> 128	9.4	21.8	This study
FOX-12	874	1,816	9.8	17.2	This study
IMX-101	37.45	217.01	9.51	13.49	This study
IMX-104	46.63	> 177.56	6.82	9.33	This study
PAX-48	55.73	> 213.85	8.21	10.8	This study

Figures 5 and 6 illustrate the trend of acute and subchronic toxicity of DNAN (and its amino derivatives) compared to other nitroaromatic compounds (NACs). NACs are generally highly toxic to aqueous receptors. Based on the EC values, the rank order from most toxic to least toxic is: TNT > 2,6-DNT > 2-ANAN = DNAN > 4A-DNT > 2A-DNT > 2,4-DNT > 4-ANAN in the Microtox assay, and TNT > DNAN > 2A-DNT = 2,4-DNT > 4A-DNT > 2-ANAN > 2,6-DNT > 4-ANAN in the algal assay. With some exceptions, the parent compounds (TNT, DNTs and DNAN) were more toxic than their reduced transformation products, indicating that toxicity of NACs is governed in part by the number of nitro groups.

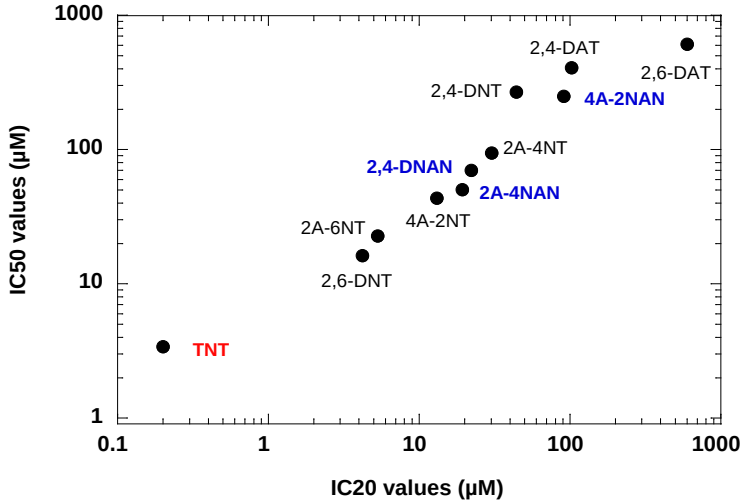

Figure 5: Trend of acute toxicity of NACs using the Microtox assay.

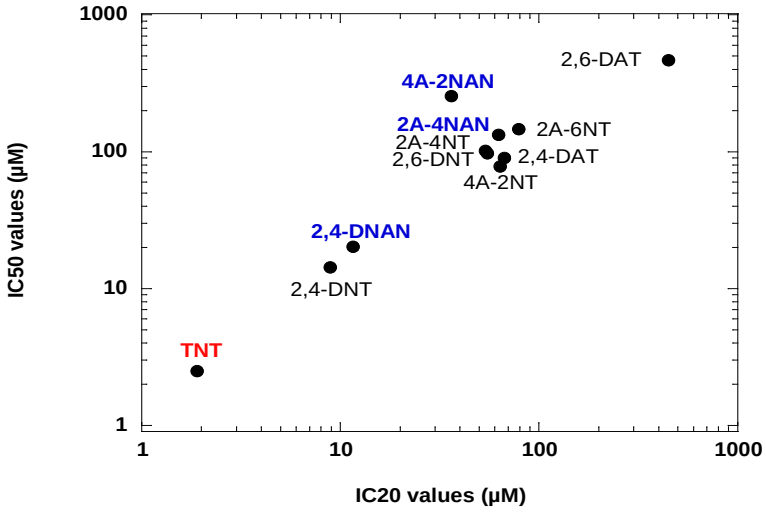

Figure 6: Trend of subchronic toxicity of NACs using the algal growth inhibition assay.

3.6 Terrestrial Ecotoxicity

The toxicological impacts of the IECs and formulations amended in soil are presented in Table 5. DNAN and 2-ANAN were shown to be highly lethal to earthworms, about 3 times more than TNT. At sub-lethal concentrations, DNAN caused an avoidance response (EC_{50} = 31 mg/kg). However while DNAN was also highly toxic to ryegrass (EC_{50} = 7 mg/kg), 2-ANAN was not phytotoxic at the maximum concentration tested (1,232 mg/kg), suggesting a detoxification or lowering of bioavailability upon reduction of a nitro group to an amino.

Table 5: Toxicity benchmark values (EC20 and EC50 in mg kg-1) of energetic chemicals and IM formulations amended in soil on earthworms (E. andrei) and ryegrass plants (L. perenne).

	Earthworm lethality test		Plant growth (dry mass)		Reference
	EC_{20}	EC_{50}	EC_{20}	EC_{50}	
TNT	110	143	61	86	a, b
DNAN	< 38	38	< 7	7	Dodard et al., 2013
2-ANAN	23.6	48.6	>1232	>1232	This study
RDX	> 1,671	> 1,671	> 9,586	> 9,586	a, c
NTO	1,687	2,768	0.7	1.9	This study
NQ	> 4,768	> 4,768	> 4,768	> 4,768	This study
FOX-7	1,108	6,463	> 4,768	> 4,768	This study
FOX-12	> 5,000	> 5,000	15	82	This study
IMX-101	140	200	4.2	15.3	This study
IMX-104	129	193	1.9	3.4	This study
PAX-48	129	193	2.9	4.7	This study

[a]Robidoux et al., 2002; [b]Rocheleau et al., 2006; [c]Rocheleau et al., 2008

4.0 CONCLUSION

The environmental fate of insensitive energetic compounds was investigated. Some experimental data were also gathered for the IM formulations IMX-101, IMX-104 and PAX-48. Except for DNAN that behaved similarly to other NACs, most IECs appeared to dissolve rapidly and extensively from formulations; they are also expected to be highly mobile in soil, in agreement with their high water solubility and low affinity for soil organic matter. Photolysis appeared as a significant transformation process and could contribute to reduce the persistence of IECs dispersed in surface water bodies and near the detonation points, where vegetation does not shade post-detonation residues. Conversely, hydrolysis of IECs, another abiotic process, was shown to occur mostly at high pH (pH 12) and temperature (50ºC) that are rather not susceptible to be encountered in nature; that is why it was not described in the present study. DNAN, like other NACs, was mainly reduced to its monoamino-derivatives, with complete nitroreduction achieved only under anaerobic conditions. Apart from NTO that was simply reduced to 3-ATO, NQ, FOX-7 and FOX-12 were readily biodegraded. However, since DNAN and NTO are the main ingredients of IM formulations, these should not be extensively decomposed by microorganisms in the environment. DNAN, recognized as a suitable alternative to TNT, was more toxic than TNT to terrestrial receptors, whereas it was significantly less toxic to aquatic species. The three IM formulations caused strong inhibition to plant growth with $EC_{50} \leq 15$ mg kg^{-1}. In general, the IECs displayed reduced toxic effects compared to conventional explosives. However, high dissolution rates and solubility will lead to pulses of IECs into the environment (Walsh et al., 2018), compounding the detrimental effects. Understanding the environmental fate and impact of IECs will help munitions suppliers, munitions acquirement managers, site managers and environmental officers to take the right decisions to manage their activities and training.

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