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Fate of CL-20 in sandy soils: Degradation products as potential markers of natural attenuation

Fanny Monteil-Rivera [a,*], Annamaria Halasz [a], Dominic Manno [a], Roman G. Kuperman [b], Sonia Thiboutot [c], Guy Ampleman [c], Jalal Hawari [a]

[a] Biotechnology Research Institute, National Research Council of Canada, 6100 Royalmount Avenue, Montréal, Québec, Canada H4P 2R2

[b] Edgewood Chemical Biological Center, 5183 Blackhawk Road, Aberdeen Proving Ground, MD 21010-5424, USA

[c] Defence Research and Development Canada, Valcartier, Canadian Ministry of National Defense, 2459 Pie IX Boulevard, Val Bélair, Quebec, Canada G3J 1X5

Two key intermediates of CL-20 degradation are potential markers of its natural attenuation in soil.

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ABSTRACT

Hexanitrohexaazaisowurtzitane (CL-20) is an emerging explosive that may replace the currently used explosives such as RDX and HMX, but little is known about its fate in soil. The present study was conducted to determine degradation products of CL-20 in two sandy soils under abiotic and biotic anaerobic conditions. Biotic degradation was prevalent in the slightly acidic VT soil, which contained a greater organic C content, while the slightly alkaline SAC soil favored hydrolysis. CL-20 degradation was accompanied by the formation of formate, glyoxal, nitrite, ammonium, and nitrous oxide. Biotic degradation of CL-20 occurred through the formation of its denitrohydrogenated derivative (m/z 393 Da) while hydrolysis occurred through the formation of a ring cleavage product (m/z 156 Da) that was tentatively identified as $CH_2{=}N{-}C({=}N{-}NO_2){-}CH{=}N{-}CHO$ or its isomer $N(NO_2){=}CH{-}CH{=}N{-}CO{-}CH{=}NH$. Due to their chemical specificity, these two intermediates may be considered as markers of *in situ* attenuation of CL-20 in soil.

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1. Introduction

The polycyclic nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (China Lake 20; CL-20), is one of the most powerful high energy materials and is being considered as a possible replacement for the currently used cyclic nitramine explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (Geetha et al., 2003; Simpson et al., 1997). The manufacturing and usage of munitions has resulted in severe contamination of both soils and groundwater (Pennington and Brannon, 2002; Best et al., 2006). Toxicological studies showed that CL-20 did not adversely affect terrestrial plants and indigenous soil microorganisms (Gong et al., 2004) but was highly toxic to the earthworm *Eisenia andrei* (Robidoux et al., 2004) and potworms *Enchytraeus crypticus* and *Enchytraeus albidus* (Dodard et al., 2005; Kuperman et al., 2006). These findings suggested that the fate of CL-20 in soil required investigation prior to its large-scale production in order to determine the potential adverse impacts of accidental release of CL-20 in the environment.

Several studies have investigated the abiotic and biotic degradation of CL-20 in aqueous media (Table 1, Fig. 1). These studies showed consistently the formation of nitrite and formate ions, usually at respective stoichiometries of ∼2 and ≤2. Although less reported in the literature other products of CL-20 include ammonia (NH_3), nitrous oxide (N_2O), glyoxal (CHOCHO), and glycolate ($CH_2(OH)COO^-$) (Table 1). In addition to these end products, early intermediates have been tentatively identified using a combination of LC/MS and amino- or nitro-labeled [^{15}N]-CL-20 (Fig. 1). The detection of these intermediates allowed proposing three initial CL-20 transformation routes prior to ring cleavage (Fig. 1): (1) the loss of one nitro group (denitration), (2) the reduction of one or two nitro group(s) to nitroso group(s) (nitroreduction), and (3) the transformation of a nitramine group into an amino group (denitrohydrogenation).

Although degradation of CL-20 in aqueous media, including formation of degradation products has been studied extensively, only little information is available on the degradation products of CL-20 in soil. CL-20 was reported to biodegrade in soil under aerobic (Trott et al., 2003; Crocker et al., 2005; Panikov et al., 2007) and anaerobic (Strigul et al., 2006; Panikov et al., 2007) conditions. Several strains capable of degrading CL-20, including *Agrobacterium* sp. strain JS71 (Trott et al., 2003), *Pseudomonas* sp. strain FA1 (Bhushan et al., 2003), and *Clostridium* sp. EDB2 (Bhushan et al.,

* Corresponding author. Tel.: +1 514 496 6259; fax: +1 514 496 6265.
E-mail address: fanny.monteil@cnrc-nrc.gc.ca (F. Monteil-Rivera).

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Table 1
CL-20 products and their normalized molar yields obtained after chemical or enzymatic degradation[a]

Reaction	Products						Reference
	NO_2^-	N_2O	NH_3	$HCOO^-$	CH_2OHCOO^-	CHOCHO	
In water							
Hydrolysis (pH 10)	1.9	0.9	0.8	0.5	ND[b]	ND	Balakrishnan et al. (2003)
Hydrolysis (pH 9.5)	2.2–3.5	ND	ND	0.75	ND	ND	Szecsody et al. (2004)
Alkaline hydrolysis	2	ND	ND	ND	ND	ND	Karakaya et al. (2005)
Photolysis (300 nm)	3.9[c]	ND	0.8	2.0	ND	ND	Hawari et al. (2004)
Reduction by Fe^0	0.04[d]	2.3	1.1	0.4	0.4	0.4	Balakrishnan et al. (2004b)
Nitroreductase	1.8	3.3	1.3	1.6	ND	1.0	Bhushan et al. (2004a)
Monooxygenase	1.7	3.2	0.6	1.5	ND	ND	Bhushan et al. (2004b)
In soil/water							
Alkaline sterile soil	2	ND	ND	+[e]	ND	ND	Balakrishnan et al. (2004a)
Subsurface sediments	1.4–5.0	ND	ND	0.4–1.9	ND	ND	Szecsody et al. (2004)

[a] Values were calculated from the product concentrations obtained at the end of each experiment, and the stoichiometries are calculated based on the number of moles of product observed for each mole of reactant consumed.
[b] ND, not determined.
[c] $NO_2^- + NO_3^-$.
[d] Two equivalents of NO_2^- were initially formed but subsequently reduced by Fe^0.
[e] Detected but not quantified.

2004c), have been isolated from soils and sediments. Beside its susceptibility to microbial degradation, CL-20 can also degrade abiotically in soils that are alkaline (Balakrishnan et al., 2004a) or that contain ferrous iron or clays (Szecsody et al., 2004). However, only formate ($HCOO^-$) and nitrite (NO_2^-) have been identified as CL-20 products in two of these studies with soil (Balakrishnan et al., 2004a; Szecsody et al., 2004).

Our objective was to determine the fate of CL-20 under abiotic and biotic conditions in two sandy soils that differ in organic carbon content and pH. We aimed at elucidating the degradation pathway(s) of CL-20 by identifying the intermediate and end products formed during its degradation in soil, and selecting those products, which could be used as markers for monitoring the natural attenuation of CL-20 in soil in case of its accidental release in the environment.

2. Materials and methods

2.1. Chemicals

Crystalline CL-20 (CAS 135285-90-4; ε-isomer, purity 99.3%, as determined by HPLC), amino-labeled and nitro-labeled [^{15}N]-CL-20, and uniformly labeled [^{14}C]-CL-20 (radiochemical purity, 98.8%; chemical purity 96.7%, specific activity of 0.75 mCi/

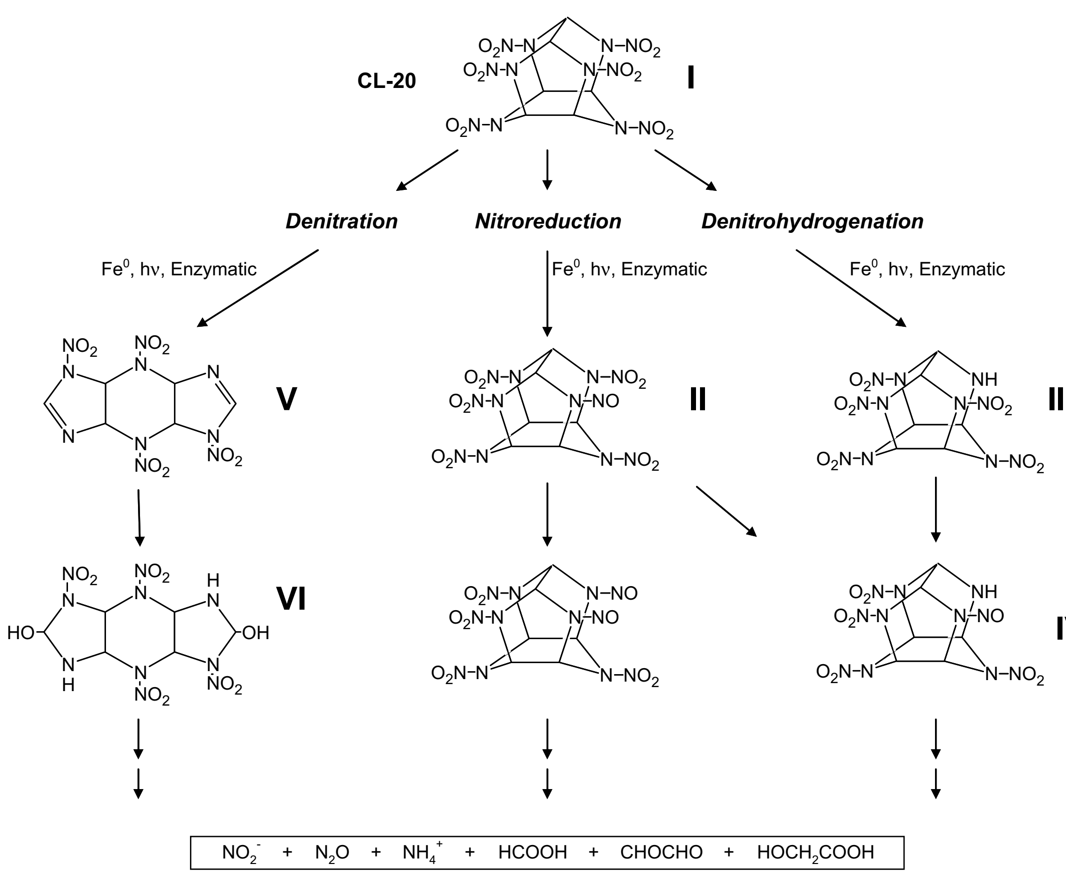

Fig. 1. Potential transformation routes for CL-20 degradation (data from Balakrishnan et al. (2004b), Bhushan et al. (2004a–c) and Hawari et al. (2004)).

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