

# **Comparison of the Relative Risks of CL-20 and RDX**

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## Acronyms, Abbreviations, and Symbols

<b>ATSDR</b>	Agency for Toxic Substances and Disease Registry
<b>CL-20</b>	China Lake 20; hexanitrohexaazaisowurtzitane
<b>DoD</b>	Department of Defense
<b>EPA</b>	Environmental Protection Agency
<b>ESOH</b>	Environment, Safety, and Occupational Health
<b>g</b>	Gram
<b>HAL</b>	Health Advisory Limit
<b>Hg</b>	Mercury
<b>HMX</b>	Cyclotetramethylene-tetranitramine
<b>Kg</b>	Kilogram
<b>K<sub>d</sub></b>	Soil-water partition coefficient
<b>K<sub>oc</sub></b>	Soil organic carbon-water partition coefficient
<b>K<sub>ow</sub></b>	Octanol-water partition coefficient
<b>L</b>	Liter
<b>MCL</b>	Maximum Contaminant Level
<b>mg</b>	Milligrams
<b>mm</b>	Millimeter
<b>NA</b>	Not available
<b>ND</b>	Not determined
<b>PM</b>	Product Teams and their Program Managers
<b>PRG</b>	Preliminary Remedial Goal
<b>RBC</b>	Risk-Based Concentration
<b>RDX</b>	hexahydro-1,3,5-trinitro-1,3,5-triazine
<b>RfD</b>	Reference dose
<b>TNT</b>	2,4,6-trinitrotoluene
<b>USD(AT&amp;L)</b>	Under Secretary of Defense for Acquisition, Technology, and Logistics
<b>UXO</b>	Unexploded ordnance

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# 1 Introduction

Acquisition decisions by product teams and their program managers (PMs) on the specifications, design, and manufacture of munitions containing high explosives—such as China Lake 20 (CL-20) or hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)—frequently depend on evaluating technical performance, availability, and cost. The evaluation of the human health and ecological risks associated with the use of these materials is also a critical factor in acquisition decisions. The identification and management of Environment, Safety, and Occupational Health (ESOH) risks throughout an acquisition program minimizes technology risk during system development and testing and provides for the cost-effective, long-term sustainability of the system over its total life cycle.<sup>43</sup> Information and data important for evaluating risks for CL-20 and RDX are published in various sources, but they have not been comprehensively summarized and compared in a manner that allows PMs to fully evaluate these materials.

This document, *Comparison of the Relative Risks of CL-20 and RDX*, compares CL-20 with RDX and other munitions constituents in use and describes, where possible, potential environmental and human-health risks for each compound based on four likely exposure scenarios at active and closed testing and training ranges. A companion Noblis report, *Evaluation of the Relative Risk of China Lake 20 (CL-20) Based on Current Toxicity, Fate and Transport, and other Technical Information*,<sup>10</sup> provides a detailed review of the physicochemical properties, toxicity, and risks associated with the two compounds.

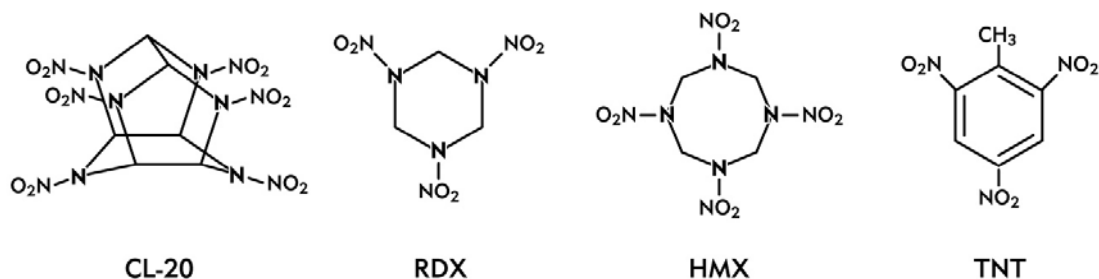
This document is designed to serve as a tool for PMs to inform the selection of energetic materials for use in Department of Defense (DoD) weapons systems. The discussion of the environmental, human-health, and programmatic risks for CL-20 and RDX is based on available data, including the physicochemical properties and information on the toxicities of these chemicals. The overall information reviewed suggests that CL-20 and RDX can display similar fate and transport characteristics in a wide variety of potential exposure scenarios. However, toxicity data needed to evaluate the human health risks associated with CL-20 are lacking.

## 2 Summary of Risk Information

### 2.1 Properties

Figure 2-1 depicts the chemical structures of CL-20, RDX, and cyclotetramethylene-tetranitramine (HMX), which are nitramine explosives, and of 2,4,6-trinitrotoluene (TNT), which is a nitroaromatic explosive. All of these energetic chemicals contain the same elements—carbon, nitrogen, hydrogen, and oxygen—arranged in ring complexes. The structural similarities among CL-20, RDX, and HMX suggest that CL-20, used in a manner similar to RDX, may yield similar environmental concerns in soil, sediment, and groundwater.<sup>9</sup>

On the other hand, CL-20 has the most complicated structure of all the explosives depicted in Figure 2-1, consisting of multiple strained rings. In addition, CL-20 has the highest molecular weight of all of these compounds (Table 2-1). The high density of CL-20 explains, in part, the higher explosive energy per pound of CL-20 relative to the other explosives listed in Table 2-1.



**Figure 2-1. Chemical Structure of CL-20, RDX, HMX, and TNT**

**Table 2-1. Basic Physicochemical Properties of CL-20, RDX, TNT, and HMX**

Compound	Molecular Weight	Density (20°C)	Water Solubility (mg/L at 5, 20, & 40°C)	Soil Sorption $K_d$	Log $K_{oc}$	Vapor Pressure Torr (mm Hg)
CL-20	438	2.04	2, 3-5, 7.4	0.22-3.8	2.4-3.2	ND
RDX	222	1.82	16, 35-52, 123	0.16-3.5	0.89-2.4	$4 \times 10^{-9}$
HMX	296	1.91	1.3, 3-7, 11.8	0.086-18	0.54-2.8	$3 \times 10^{-14}$
TNT	227	1.65	57, 100, 245	0.04-11	2.5-3.0	$2 \times 10^{-4}$

Densities are from Hoffman (2003), the Merck Index and ATSDR (1997); Density is for the pure  $\epsilon$  form of CL-20, and will vary by formulation. Solubility data are primarily from Monteil-Rivera et al. 2004 and Lynch 2002. The  $K_d$  values are from Brannon et al. (1999) and Szecsody et al. (2004).  $K_{oc}$  values are from ATSDR (1995b, 1997), Townsend and Myers (1996) and Hawari et al. (2003). Vapor pressures are from HSDB and Rosenblatt et al. (1991). ND = not determined

In addition, all of the nitramines listed in Table 2-1 have very low water solubilities. However, CL-20 generally has the lowest water solubility, and its solubility increases the least with increasing temperature. The lower solubility of CL-20 suggests that CL-20 is likely to remain in soils longer, and CL-20 groundwater plumes will have somewhat lower concentrations and smaller dimensions, compared with RDX and HMX under similar conditions and release concentrations. These differences are more likely to be noticeable at higher ambient temperatures.

Further, there are no substantial differences in the other environmentally relevant properties listed in Table 2-1 for CL-20 and RDX. In particular, the *soil-water partition coefficient* ( $K_d$ ) describes the equilibrium distribution of a chemical between soil and water. The greater the  $K_d$ , the greater the tendency of a chemical to attach to solid particles in a soil, sediment, or aquifer material, typically including organic matter, clays, or iron and manganese oxides. The *soil organic carbon–water partition coefficient* ( $K_{oc}$ ) is a similar parameter that describes the affinity of the chemical specifically to organic matter. Both CL-20 and RDX have low  $K_d$  and  $K_{oc}$  values, indicating that both adsorb weakly to solid matter. Thus, all other factors being equal, both will move essentially unhampered with groundwater through soil and sediment matrices.

Research indicates that CL-20 adsorption depends to a greater extent on organic matter in environmental matrices, while RDX adsorption correlates more closely with clay content.<sup>6,38</sup> Relatively high  $K_d$  values (up to ~300) were reported for CL-20 in soils with high organic content, depending on the type—as well as the amount—of organic matter in the soils.<sup>6,18</sup> Thus, there may be some differences in the movement of CL-20 and RDX through soils. However,

both CL-20 and RDX can generally be expected to be poorly immobilized in soil, sediment, and groundwater matrices.<sup>31</sup>

## 2.2 Environmental Degradation

Two other characteristics potentially distinguishing CL-20 from RDX include degradation rate in soil and groundwater and susceptibility to photolysis.

CL-20 will degrade faster than RDX in soil and groundwater under most circumstances. This has been attributed to the rigid, multi-ring cage structure of CL-20 molecule, which can reasonably be expected to be much more labile in the environment than the relatively simple planar ring structure of RDX.

CL-20 can be readily biodegraded in soil at concentrations on the order of 20 mg CL-20/kg soil.<sup>41</sup> Unlike RDX, CL-20 can degrade almost as well in near-surface soil under reducing conditions (for example, in the presence of ferrous iron) as it does under oxidizing conditions. In contrast, RDX may degrade significantly faster under reducing conditions than under the oxidizing conditions typical of most groundwater systems. Thus, the overall evidence suggests that CL-20 can degrade faster and under a wider variety of environmental conditions than RDX. The degradation rates of both CL-20 and RDX are likely to decrease as their concentrations increase in the soil.

However, the reported half-lives of CL-20 and RDX were similar in soils collected from three military training ranges and maintained under moist, unsaturated conditions in the dark, indicating that CL-20 and RDX will display similar stabilities and degradation rates in soils under these conditions.<sup>24</sup>

Photolysis is a common degradation mechanism in surface waters. The photolysis of CL-20 is much more rapid than the photolysis of RDX.<sup>19</sup> Thus, all other factors being equal, photolysis may result in detectable RDX concentrations in surface water extending farther from the point of release compared with CL-20. This effect will likely diminish with increasing depth of the surface water and will also vary depending on the time of year.<sup>1</sup>

## 2.3 Breakdown Products

Most of the initial intermediate environmental degradation products of both CL-20 and RDX are structures that are not expected to persist in the environment under most conditions. Many of the other intermediates and the end products of CL-20 and RDX are the same and, like the initial intermediate structures, none of them is expected to persist except in the driest environments.

The breakdown of CL-20 can yield glyoxal instead of the formaldehyde produced from RDX. This difference is not expected to be significant because both formaldehyde<sup>39</sup> and glyoxal<sup>13</sup> will rapidly break down to form carbon dioxide in moist soil and aqueous environments.<sup>5,23</sup> Further, neither of these substances is likely to be produced in sufficient quantities from the explosives to drive a human-health or ecological risk assessment on a military range.

## 2.4 Bioaccumulation

The *octanol-water partition coefficients* ( $K_{ow}$ ) and the available experimental data indicate that CL-20, RDX, HMX, and TNT have little potential to bioconcentrate or bioaccumulate in the plants and animals of an ecosystem.

The  $K_{ow}$  of a chemical is the ratio of the concentration of the chemical in the organic solvent octanol and in water at equilibrium and at a specified temperature. The low  $K_{ow}$  of the energetic chemicals<sup>44</sup> suggest that these substances have low lipid solubility and, therefore, little potential to bioconcentrate or bioaccumulate.

Bioconcentration and bioaccumulation factors derived from experimental studies in plants<sup>8,12,16,17,46</sup>, soil invertebrates<sup>25,26</sup>, fish<sup>42</sup>, birds<sup>7</sup>, and mammals<sup>3</sup> confirm this prediction.

Thus, neither CL-20 nor RDX are likely to bioconcentrate in the lower levels of the food chain (plants and invertebrates) or bioaccumulate at the higher food-chain levels (fish, birds, and mammals).

## 2.5 Toxicity

CL-20 is clearly and substantially more toxic than RDX to soil invertebrates. Toxicity studies in earthworms<sup>33</sup>, potworms<sup>14,27</sup>, and microarthropods (including insects) that live in soil<sup>28</sup> indicate that as little as 0.02 mg CL-20/kg soil can reduce the soil invertebrate population,<sup>33</sup> while 44-660 mg RDX/kg soil has no effect.<sup>14,25</sup> This is important because toxicity to invertebrates typically serves as the basis for the screening values used to determine whether a more advanced site-specific ecological risk assessment is needed. The substantially lower screening values expected for CL-20 from the results of these studies, compared with RDX, suggests that sites contaminated with CL-20 will be more likely to need follow-on site-specific assessments.

There is some limited evidence suggesting that CL-20 may be more toxic to fish and aquatic invertebrates than RDX.<sup>28,32,35</sup> For example, as little as 2 mg CL-20/L water can have a substantial impact on fathead minnows,<sup>28</sup> while 13 mg RDX/L water has no effect on zebrafish.<sup>32</sup> However, these comparisons are equivocal because none of these studies examined the toxicity of CL-20 and RDX in the same species.

In contrast, limited studies suggest that CL-20 is substantially less toxic than RDX to plants<sup>16,34,45</sup> and birds.<sup>7,15,22</sup> For example, up to 10,000 mg CL-20/kg soil had no effect on alfalfa or ryegrass,<sup>16</sup> while as little as 5.8 mg RDX/kg soil caused adverse effects in some plant species.<sup>45</sup>

Similarly, adult Japanese Quail fed up to 5,000 mg CL-20/kg body weight/day for 5 days or 1,000 mg CL-20/kg body weight for 42 days were unaffected,<sup>7</sup> while as little as a single 190 mg RDX/kg body weight caused central nervous system disturbances in the Northern Bobwhite.<sup>15</sup>

Thus, the limited evidence available for CL-20 indicates that the species higher in the food chain that would be evaluated in advanced site-specific ecological risk assessments are less susceptible to CL-20 than to RDX.

There are no studies on the toxicity of CL-20 in mammalian species, including humans. In contrast, the Environmental Protection Agency (EPA) has established a reference dose (RfD) of 0.003 mg RDX/kg body weight/day for oral exposure based on the results of toxicity studies on rats.<sup>44</sup> The RfD is an estimate of a daily oral dose that is not likely to cause harmful effects in the human population, including sensitive subgroups such as children, during a lifetime of exposure.

EPA has also classified RDX as a possible human carcinogen, based on liver tumors in mice exposed to relatively high doses (7 mg RDX/kg body weight per day) for 2 years.<sup>44</sup>



### 3 Evaluation of Exposure Scenarios

Figures 3-1 through 3-4 illustrate four generic scenarios that serve as the framework for discussing the relative risks of CL-20 and RDX in this report. The figures do not depict a specific range, but together they provide good representation of range conditions across the continental United States. Each figure illustrates one of the four most likely exposure pathways on ranges:

- Direct contact of ecological receptors with munitions constituents in soil/sediment in a desert environment (Figure 3-1)
- Direct contact of ecological receptors with munitions constituents in soil in a continental climate (Figure 3-2)
- Exposure of ecological receptors to munitions constituents in surface water in a coastal temperate or tropical climate (Figure 3-3)
- Exposure of human receptors to munitions constituents in drinking water from a shallow aquifer (Figure 3-4)

Subsections 3-1 through 3-4, below, discuss the relative risks of CL-20 and RDX for each of the scenarios with the overall underlying assumption that CL-20 might be used and released to the environment in quantities similar to the historical and current use of RDX.

#### 3.1 Direct Contact with Soil/Sediment in a Desert Environment

Figure 3-1 is based on the Barry M. Goldwater Range (Arizona) and the National Training Center (California). These ranges are characterized by arid soils, deep groundwater tables, subtropical desert climate, and the potential for wildlife exposures through contact with soil and the dry sediment of ephemeral streams and dry lake beds both on- and off-range. The high ambient temperatures and the dry, aerobic, unsaturated conditions of the soil and sediments in this environment are likely to be common in locations where CL-20 may be used.

Little biodegradation is expected for either of these compounds under the dry, aerobic conditions of the surface soil and sediments in this environment.

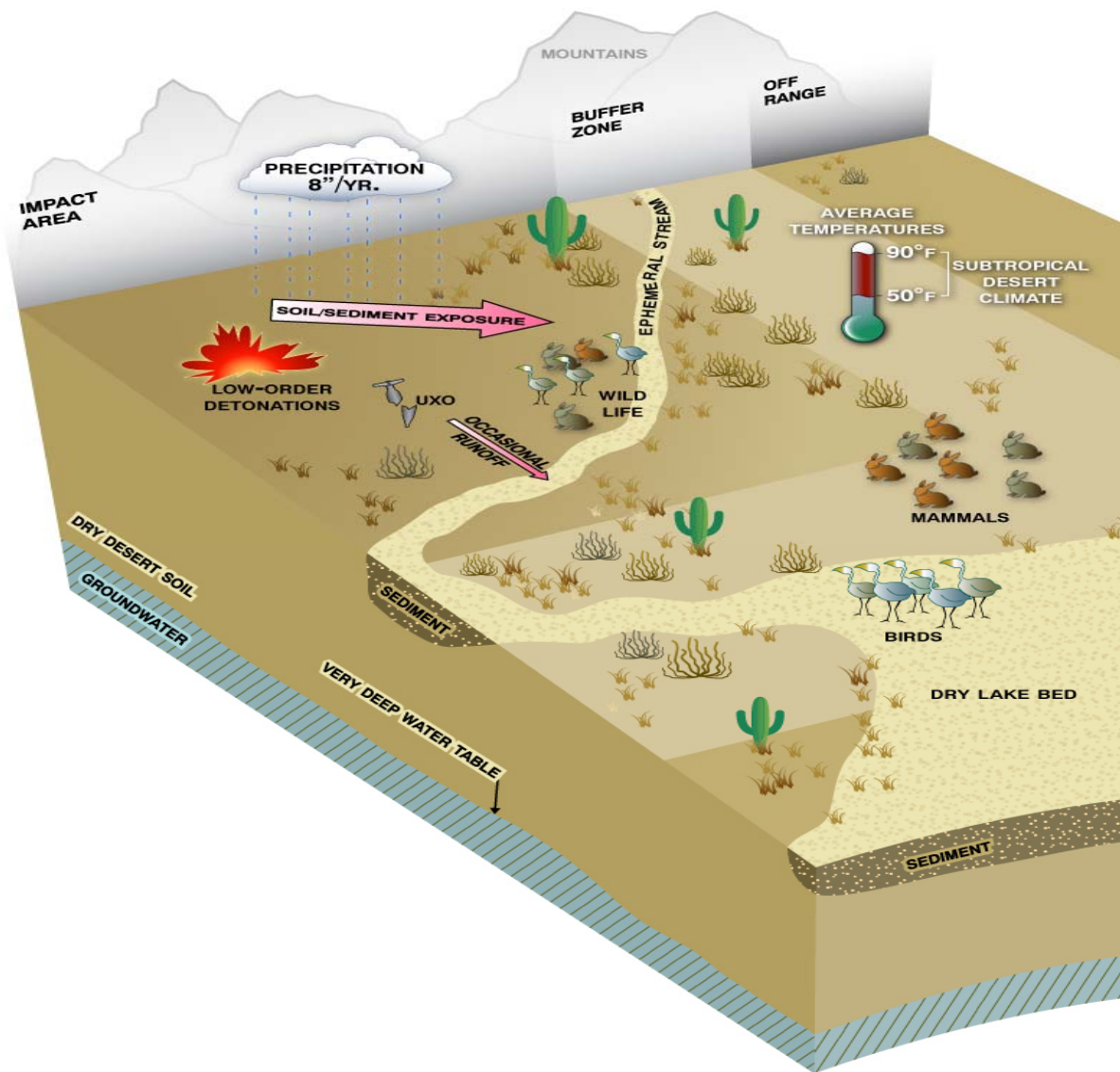
The occasional rainfall expected in these environments will carry some of the CL-20 and RDX in the dry surface soil virtually unimpeded through the subsurface soil and in runoff to the sediments of nearby dry lake beds. The lower solubility of CL-20 compared with RDX may be accentuated by the high temperatures expected in the desert, so that rainfall may reduce surface soil concentrations of CL-20 at a lower rate compared with RDX. On the other hand, intense sunlight at the surface may degrade CL-20 by photolysis quicker than it degrades RDX. However, differences in the effects of rainfall and photolysis on the surface soil concentrations of CL-20 and RDX will probably be negligible.

Thus, significant concentrations of both CL-20 and RDX can be expected to persist for long periods in the surface soil of a desert environment.

As noted above, CL-20 is much more toxic than RDX to earthworms, potworms and microarthropods (including insects), and probably to other invertebrates that live in moist or wet soils. However, earthworms and potworms are not likely to be found in the dry soils of the desert. Soil invertebrates in the desert are likely to be highly adapted to life in these dry soils. None of the studies examined specifically address the toxicities or tissue concentrations of CL-

20 and RDX in desert-dwelling soil invertebrates under the arid conditions typical of their natural habitats.

On the other hand, oral exposure to CL-20 appears to be substantially less toxic to birds than oral exposure to RDX.<sup>7,15,22</sup> The lower toxicity of CL-20 to these animals means that there will likely be lower risks to wildlife compared with RDX.



#### Scenario 1:

##### Active Range

##### Subtropical Desert Climate

- Very Low Precipitation
- Very Dry Soil
- Ephemeral Streams

##### Very Deep Groundwater Table

##### Soil Invertebrate: Primarily Insects

##### Birds, Mammals Potentially Exposed

- Direct Contact with Soil/Sediment
- On- & Off-Range Exposure Areas

##### Models:

- Barry Goldwater Range (AZ)
- National Training Center (CA)

Figure 3-1. Soil/Sediment Exposure for On-/Off-Range Ecological Receptors (in a Desert Environment)

### **3.2 Direct Contact with Soil in a Continental Climate**

Figure 3-2 is based on Hardwood Range (Wisconsin). This range is characterized by silty over loamy soils, shallow depth to groundwater, continental climate, and potential for direct on-base soil exposures to wildlife living in marshy and forest areas. In this report, this example represents a “closed range,” where wildlife may be exposed to residues that remain in the soil.

The considerable rainfall and snowmelts that characterize this environment can be expected to carry significant amounts of both CL-20 and RDX through the surface to the subsurface soil. Both CL-20 and RDX are expected to biodegrade substantially in the surface soil, and will biodegrade rapidly in the subsurface soil, especially if the subsurface is anaerobic or contains significant amounts of reducing materials (such as iron or manganese compounds). Thus, the concentrations of CL-20 and RDX in the soil can be expected to attenuate at a relatively rapid rate, and neither CL-20 nor RDX will persist for long periods in the soil in this environment.

CL-20 will be much more toxic than RDX to earthworms and probably also to other invertebrates living in the soil. Greater toxicity to soil invertebrates means that a screening-level ecological risk assessment is more likely to trigger an advanced site-specific ecological assessment.

However, the toxicity of CL-20 appears to be much lower than that of RDX to both plants and birds. The lower toxicity of CL-20 to birds, in particular, means that there will likely be lower risks to wildlife compared with RDX. Thus, an advanced site-specific risk assessment for CL-20 is more likely to support a no-further-action decision in this scenario, compared with RDX.

### **3.3 Exposure to Surface Water in a Coastal Temperate or Tropical Climate**

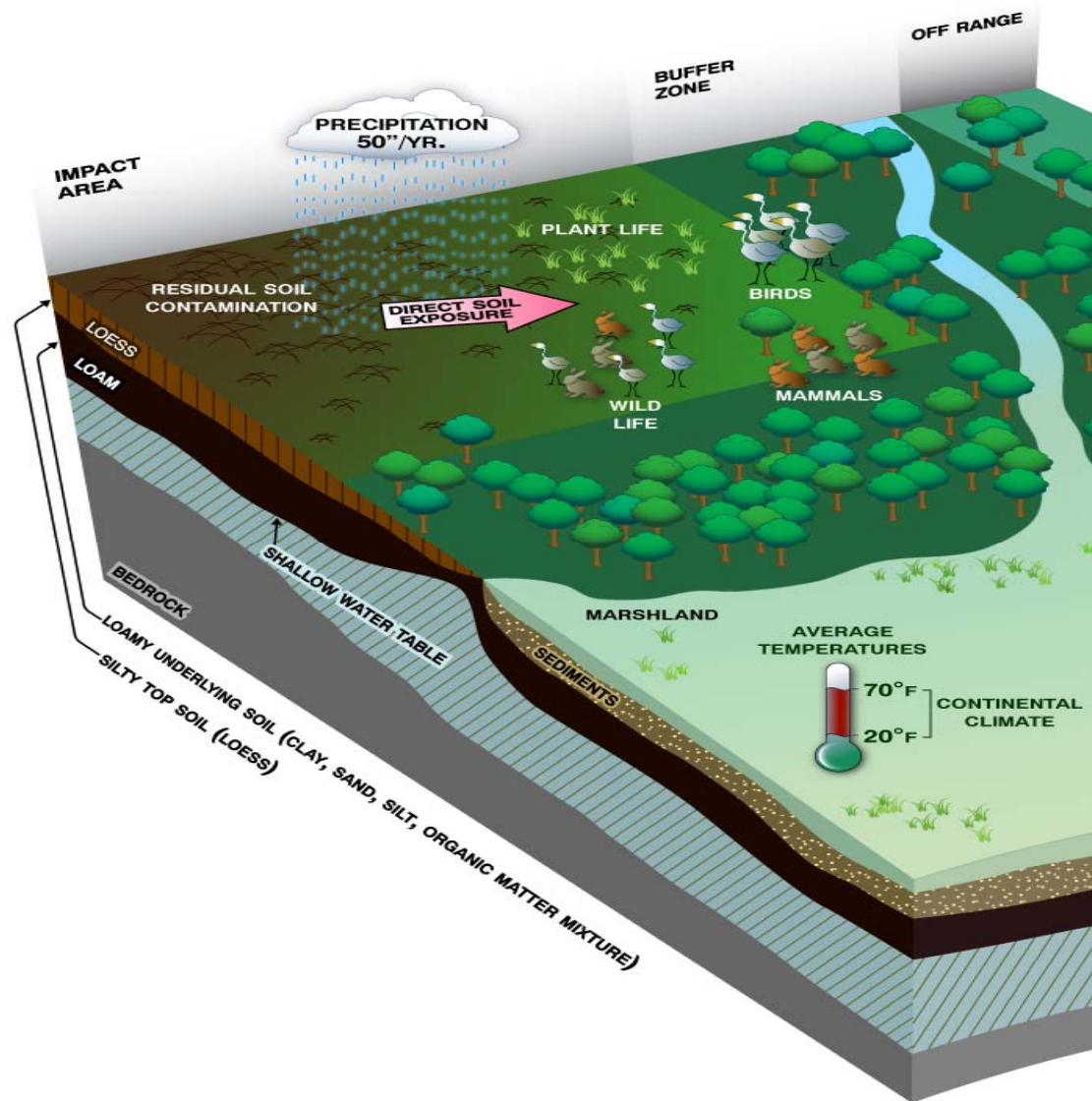
Figure 3-3 is based on Dare County (North Carolina) and Avon Park (Florida) ranges. These ranges are characterized by poorly drained soils that are mucky and peat-rich or porous and sandy, shallow depth to groundwater, temperate or tropical climates, and the potential for off-base exposures to wildlife and aquatic life in marshes and swamplands.

The considerable precipitation that characterizes these environments can be expected to carry significant amounts of both CL-20 and RDX through the subsurface soil to the groundwater and in runoff to the surface water. Some of the constituents entering groundwater may be discharged secondarily into downgradient sediments and surface water.

Both CL-20 and RDX, at concentrations on the order of 20 mg/kg soil, are likely to biodegrade substantially in the surface soil and will biodegrade rapidly in the subsurface soil, groundwater and sediments, especially if the subsurface is anaerobic or contains significant amounts of reducing materials (such as iron or manganese compounds). Thus, the concentrations of CL-20 and RDX in the soil can be expected to attenuate at a relatively rapid rate, and neither CL-20 nor RDX will persist for long periods in the soil in these environments. As noted above, the degradation rates of both CL-20 and RDX are likely to decrease as their concentrations increase in the soil.

However, the concentrations and extent of the surface water contamination may be lower for CL-20 than for RDX for several reasons. First, the lower solubility of CL-20 will reduce the maximum CL-20 concentrations that can be expected in rainwater runoff, groundwater, and wetlands. In addition, the high affinity of CL-20 for some types of organic matter may retard the migration of CL-20 through the rich organic soils, sediments, and groundwater matrices expected in these environments. By comparison, the organic matter content of these matrices will have no

effect on the migration of RDX. Further, sunlight can be expected to degrade CL-20 much more rapidly than RDX in the shallow surface waters that characterize this scenario.



#### Scenario 2:

Closed Range

Continental Climate

- Substantial Precipitation
- Marshy, Forested Areas

Poorly-Drained Soils

- Topsoil: Silt Deposits (Loess)
- Subsurface Soil: Clay-Sand-Silt-Organic Matter Mixture (Loam)
- Groundwater: Shallow Table, Slow Flow

Soil Invertebrates and Microorganisms

- Diverse
- Plentiful

Birds, Mammals, Plants Potentially Exposed

- Direct Contact with Soil
- On-Range Exposure Areas

Models:

- Hardwood Range (WI)

Figure 3-2. Soil Exposure for On-Range Ecological Receptors (on a Closed Range)



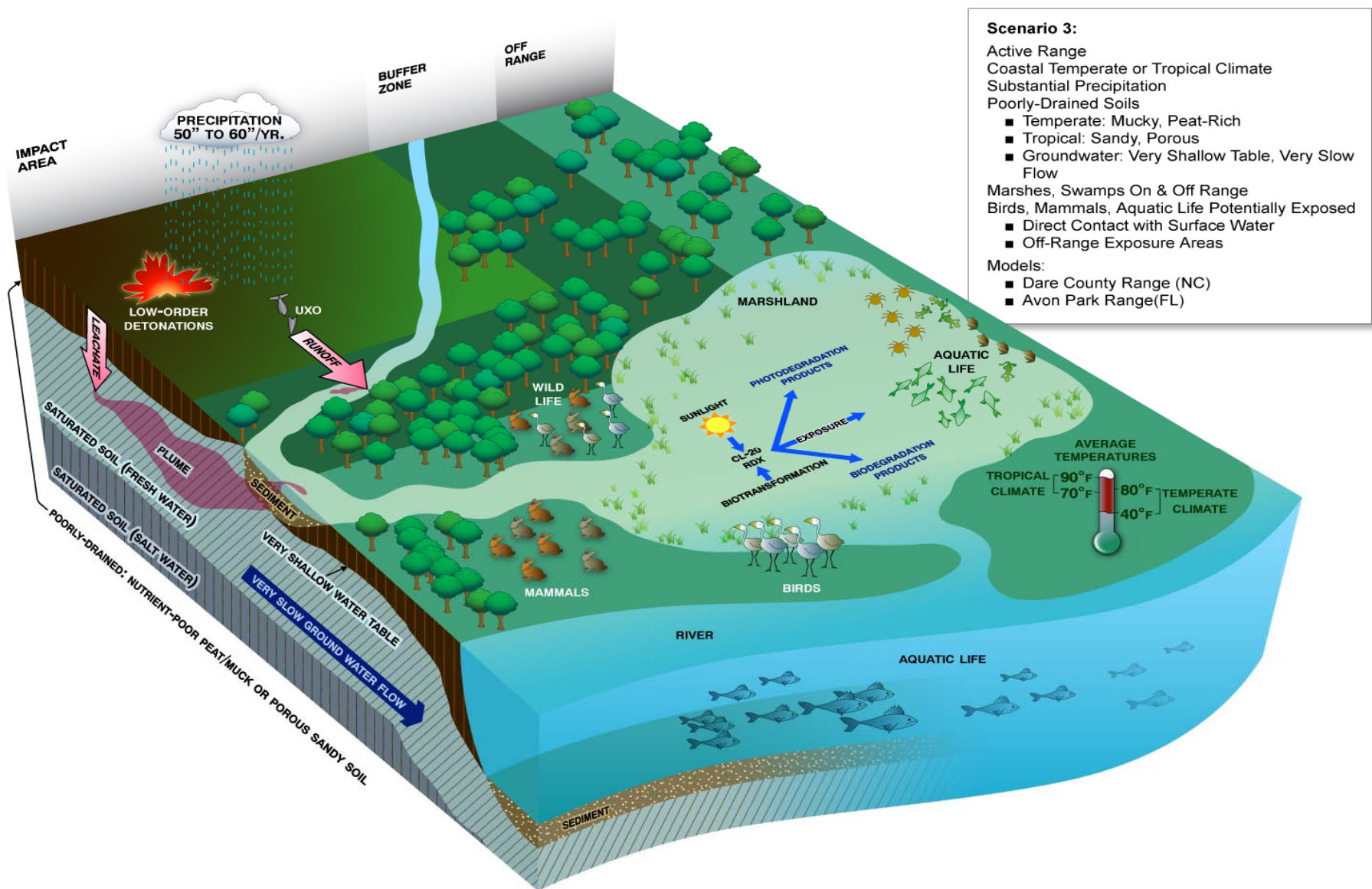


Figure 3-3. Surface Water Exposure for Off-Range Ecological Receptors (in a Coastal Environment)

On the other hand, CL-20 may be more toxic than RDX to aquatic invertebrates and fish in the surface water. Greater toxicity means that lower concentrations of CL-20 may threaten aquatic organisms, compared with RDX.

On balance, the lower concentrations and reduced extent of CL-20 contamination that can be expected in the surface water, coupled with the potentially greater toxicity of CL-20 to aquatic life, suggests that, all other factors being equal, the threat posed by CL-20 may be equivalent to that of RDX in this exposure scenario.

### 3.4 Exposure to Drinking Water from a Shallow Aquifer

Figure 3-4 is based on the Massachusetts Military Reservation Range (Cape Cod, Massachusetts). This range is characterized by porous soils, shallow depth to groundwater (aquifer), temperate climate, and the potential for off-range drinking-water exposures.

The considerable rainfall and snowmelts that characterize this environment can be expected to carry significant amounts of both CL-20 and RDX essentially unimpeded through the surface soil to the shallow groundwater. Both of these constituents will migrate rapidly through the groundwater toward off-site drinking-water wells. The movement of CL-20 through the environment will probably be indistinguishable from that of RDX in this scenario.

Unfortunately, there is no toxicity data available in the current literature for CL-20 in humans or other mammals. Thus, although exposures to CL-20 and RDX are equally likely in this scenario, there is no basis for differentiating the human-health risks that may be associated with exposures to these chemicals.

## 4 Regulatory Issues

There are no chemical-specific human-health or ecological regulatory standards or guidance values for CL-20 (Table 4-1). Such standards and values have not been established because CL-20 is a relatively new compound, its toxicity to humans or other mammals has not yet been studied, toxicity studies on other animals are limited, and widespread or persistent environmental contamination with CL-20 is unknown. However, continuing research on the toxicity and environmental degradation of CL-20 could be used to help develop standards or guidelines for soils and groundwater if CL-20 production is scaled up substantially in the future.

**Table 4-1. Current Risk-Based Concentrations, Preliminary Remedial Goals, and Health Advisory Levels for Selected Constituents**

Compound	EPA Region III RBCs/Region IX PRGs for Soil <sup>1</sup> (mg/kg)		EPA Region III Ecological Risk Values (Chronic)		EPA Water RBCs/PRGs/HALs for Water	
	Residential (mg/kg)	Industrial (mg/kg)	Water (mg/L)	Sediment (mg/kg)	RBC/PRG <sup>1,2</sup> (mg/L)	HAL (mg/L)
CL-20	NA	NA	NA	NA	NA	NA
RDX	5.8 4.4	26 16	0.36	0.013	0.00061 0.00061	0.002
HMX	3,900 3,100	51,000 31,000	0.15	NA	1.8 1.8	0.400
TNT	21 16	95 57	0.10	0.092	0.0022 0.0022	0.002

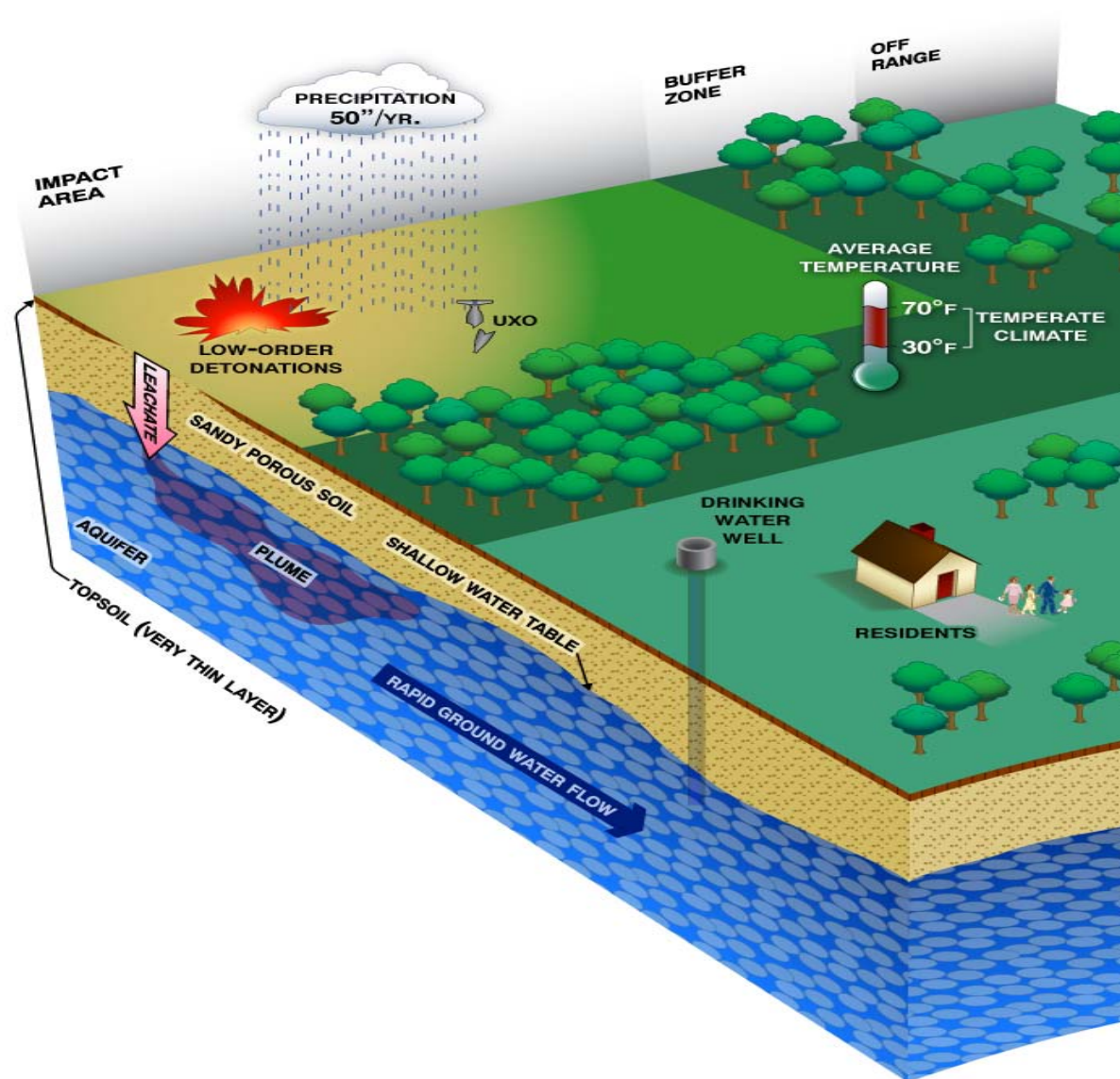
1: EPA Region III RBC value (2005) is listed first, followed by Region IX values (2004).

2: Tap water PRGs are the same as the federal Maximum Contaminant Level (MCL) when a contaminant has an MCL.

NA = not available

HAL = EPA Lifetime Health Advisory Limit





#### Scenario 4:

Active Range

Temperate Climate

Substantial Precipitation

Rapidly Drained Soils

- Soil: Very Porous, Sandy, Gravelly
- Groundwater: Shallow Table, Rapid Flow, Aquifer

People Potentially Exposed

- Drinking Water
- Off-Range Residents

Model:

- Massachusetts Military Reservation (MMR)

Figure 3-4. Drinking-Water Exposure for Off-Range Humans (from a Shallow Aquifer)

In contrast, long-standing guidelines are available from EPA for RDX, HMX, and TNT (Table 4-1). These guidelines are advisory only, rather than legally enforceable standards. However, they help to provide a context for identifying some of the likely regulatory issues that may arise for CL-20 in the future because CL-20 is related to RDX and HMX in composition, structure, and physicochemical properties and shares with RDX many of the same intermediates and end products of environmental degradation.

As indicated in Table 4-1, several EPA regional offices have developed risk-based concentrations (RBCs), preliminary remediation goals (PRGs) or ecological-risk–screening values for some energetic chemicals in soil, sediment, and water. The most commonly cited are EPA Region III’s RBCs and EPA Region IX’s PRGs. In addition, EPA has developed Health Advisory Limits (HALs) for RDX, HMX, and TNT in drinking water.

The PRGs for a contaminant in drinking water are typically the same as the federal Maximum Contaminant Level (MCL) for the contaminant, which are legally enforceable drinking-water standards. There are no federal MCLs for the four energetic chemicals listed in Table 4-1. However, RDX and TNT are included in the EPA Unregulated Contaminant Monitoring Rule, suggesting that enforceable standards may be promulgated for these substances in the future.

The ecological-risk–screening values for surface waters and the drinking-water RBCs, PRGs, and HALs for the energetic chemicals listed in Table 4-1 are all lower than the corresponding solubility limits of these chemicals (Table 2-1). These findings indicate that even though an energetic chemical may have extremely low solubility, it may still be soluble enough to pose a threat to human health or the environment.

RBCs, PRGs, and ecological-risk–screening levels for soil, sediment, and water, like those presented in Table 4-1, are typically derived based on conservative, generic exposure assumptions and are meant to be used in the preliminary or screening-level risk assessment of a site or an area. They cannot usually serve as a credible or technically defensible basis for deciding to remediate a site or as final remediation goals for the site. However, the toxicity data available in the current scientific literature for soil invertebrates and aquatic species, as discussed in Section 2, indicate that ecological-risk–screening levels that may be developed in the future for CL-20 may be substantially more stringent than those for RDX. The lack of toxicity data for CL-20 in humans and other mammals precludes similar speculation about soil and drinking-water guidelines that might someday be developed to screen sites for their potential to threaten human health.

## **5 Programmatic Risks**

All acquisition strategies must include an identification of and management strategy for the ESOH risks associated with the product. PMs are required to prevent ESOH hazards where possible and to manage ESOH hazards where they cannot be avoided to reduce the overall risk associated with an acquisition effort.<sup>43</sup> The following conclusions, based on the current scientific literature, should assist PMs in identifying the ESOH risks associated with the use of CL-20 in munitions.

The information available from the current scientific literature suggests that CL-20 and RDX will display similar fate and transport characteristics in a wide variety of potential exposure scenarios.

Clearly, CL-20 is substantially more toxic than RDX to soil invertebrates. The toxicity of a chemical to soil invertebrates typically serves as the basis for developing risk-screening concentrations for the

chemical in terrestrial ecosystems. The concentrations of the chemical measured in soil samples from a site are compared with these risk-screening concentrations to decide whether a no-further-action decision is appropriate or a more advanced site-specific risk assessment is warranted to better characterize the ecological risks associated with the chemical. Although soil invertebrates are common surrogates or indicators in screening-level ecological risk assessments, they are unlikely to drive regulatory action by themselves.

There is limited evidence in the current literature suggesting that CL-20 may be substantially more toxic to aquatic animal life, including aquatic invertebrates and fish, but much less toxic than RDX to plants, birds, and perhaps other wildlife as well. Thus the weight of the current evidence suggests that substituting CL-20 for RDX in munitions would decrease the risks to terrestrial ecosystems, but may increase the risks to aquatic ecosystems.

Considering the information available for comparing CL-20 and RDX, a decision to substitute CL-20 for RDX would yield three issues, based on the limited toxicity data available for CL-20. These issues should be considered by the PMs when evaluating CL-20 for use in munitions.

- A lack of any toxicity data for CL-20 in humans or other mammals results in major barriers to assessing the human and ecological risks of CL-20. Human-health risks associated with CL-20 cannot be assessed until toxicity studies of CL-20 relevant to human-health risk are performed in mammalian species. An assessment of ecological risks associated with CL-20 will necessarily be incomplete and inadequate until mammalian toxicity studies are completed to provide the data necessary for assessing risk to sensitive and critical ecological mammalian species.
- Second, toxicity data for CL-20 in non-mammalian species higher in the food chain than soil invertebrates are limited to a single bird species and a single fish species, and there is no toxicity data for CL-20 in amphibians and reptiles. This limitation in the available data, like the lack of toxicity data in mammalian species, presents a major barrier to assessing the ecological risks of CL-20.
- Third, the scarcity of the toxicity data on species higher than soil invertebrates in the food chain means that there is a chance that continuing toxicology research will show CL-20 to pose a substantially greater threat than RDX to human health or one or more important ecological receptor.

PMs should consider the following programmatic risks associated with these issues:

- Potential costs for having to perform toxicology studies
- Potential production delays while data are gathered and evaluated
- Potential establishment of risk-based standards or enforceable drinking-water standards for CL-20
- Unanticipated cleanup costs
- Potential for CL-20 to be withdrawn from the market because of newly discovered toxicity (to production workers or human or ecological receptors on or near a range)

On the other hand, the similarity of CL-20 and RDX in their physicochemical properties and fate and transport characteristics suggests that, like RDX, CL-20 will not accumulate in the environment to concentrations that might threaten the environment even after decades of use in Scenarios 1-3

(Figures 3-1 to 3-3). This view assumes that CL-20 would be used in quantities similar to the historical and current use of RDX.

However, in Scenario 4 (Figure 3-4), given the similarities of CL-20 and RDX, there is a likely potential for CL-20 to accumulate in soil and contaminate groundwater, and for people to be exposed to CL-20 in drinking water. This means that the programmatic risks listed above are most probable in Scenario 4. Therefore, overall programmatic risks could be reduced substantially by avoiding the use of munitions containing CL-20 at test and training ranges represented by Scenario 4.

## 6 References

- <sup>1</sup>Agency for Toxic Substances and Disease Registry (ATSDR) (1995a). *Toxicological Profile for RDX*. Agency for Toxic Substances and Diseases Registry, June.
- <sup>2</sup>ATSDR (1995b). *Toxicological Profile for 2,4,6-Trinitrotoluene*. Agency for Toxic Substances and Diseases Registry, June.
- <sup>3</sup>ATSDR (1996). *ToxFAQs for 2,4,6-Trinitrotoluene (TNT)*. Agency for Toxic Substances and Diseases Registry, 30 September.
- <sup>4</sup>ATSDR (1997). *Toxicology Profile for HMX*. Agency for Toxic Substances and Diseases Registry, September.
- <sup>5</sup>ATSDR (1999). *Toxicology Profile for Formaldehyde*. Agency for Toxic Substances and Diseases Registry, July.
- <sup>6</sup>Balakrishnan, V.K., F. Monteil-Rivera, M.A. Gautier, and J. Hawari (2004). *Sorption and Stability of the Polycyclic Nitramine Explosive CL-20 in Soil*. J. Environ. Qual. **33**:1362-1368.
- <sup>7</sup>Bardai, G., G.I. Sunahara, P.A. Spear, M. Martel, P. Gong, and J. Hawari (2005). *Effects of Dietary Administration of CL-20 on Japanese Quail Coturnix coturnix japonica*. Arch. Environ. Contam. Toxicol. **49**: 215-222.
- <sup>8</sup>Best, E.P., K.N. Geter, H.E. Tatem, and B.K. Lane (2006). *Effects, Transfer, and Fate of RDX from Aged Soil in Plants and Worms*. Chemosphere **62**: 616-25.
- <sup>9</sup>Bhushan, B., A. Halasz, J.C. Spain and J. Hawari (2004). *Initial Reaction(s) in Biotransformation of CL-20 is Catalyzed by Salicylate 1-Monooxygenase from Pseudomonas sp. Strain ATCC 29352*. Appl. Environ. Microbiol. **70**: 4040-4047.
- <sup>10</sup>Boyer, I., J.K. Miller, R.E. Watson, J. DeSesso, and C.M. Vogel (2007). *Evaluation of the Relative Risk of China Lake 20 (CL-20) Based on Current Toxicity, Fate and Transport, and other Technical Information (Draft Final)*. Noblis Technical Report.
- <sup>11</sup>Brannon, J.M., P. Deliman, C. Ruiz, C. Price, M. Qasim, J.A. Gerald, and S. Yost (1999). *Conceptual Model and Process Descriptor Formulations for Fate and Transport of UXO*. U.S. Army Corps of Engineers, Waterways Experiment Station, Technical Report IRRP-99-1, February 1999.
- <sup>12</sup>Cataldo, D.A., S.D. Harvey, and R.J. Fellows (1993). *The Environmental Behavior and Chemical Fate of Energetic Compounds (TNT, RDX, Tetryl) in Soil and Plant Systems*. Prepared by Pacific Northwest Laboratory (PNL), Richland, WA under DOE contract DE 93-019614.

- <sup>13</sup>Crocker, F.H., K.T. Thompson, J.E. Szecsody, and H.L. Fredrickson (2005). *Biotic and Abiotic Degradation of CL-20 and RDX in Soils*. J. Environ. Qual. **34**: 2208-2216.
- <sup>14</sup>Dodard, S.G., G.I. Sunahara, R.G. Kuperman, M. Sarrazin, P. Gong, G. Ampleman, S. Thiboutot, and J. Hawari (2005). *Survival and Reproduction of Enchytraeid Worms, Oligochaeta, in Different Soil Types Amended with Energetic Cyclic Nitramines*. Environ. Toxicol. Chem. **24**: 2579-2587.
- <sup>15</sup>Gogal, R.M., M.S. Johnson, C.T. Larsen, M.R. Prater, R.B. Duncan, D.L. Ward, and S.D. Holladay (2003). *Dietary Oral Exposure to 1,3,5-Trinitro-1,3,5-Triazine in the Northern Bobwhite (Colinus virginianus)*. Environ. Toxicol. Chem. **22**: 381-387.
- <sup>16</sup>Gong, P., G.I. Sunahara, S. Rocheleau, S.G. Dodard, P.Y. Robidoux, and J. Hawari (2004). *Preliminary Ecotoxicological Characterization of a New Energetic Substance, CL-20*. Chemosphere **56**: 653-658.
- <sup>17</sup>Harvey, S.D., R.J. Fellows, D.A. Cataldo, and R.M. Bean (1991). *Environmental Chemistry: Fate of the Explosive Hexahydro-1,3,5-Triazine (RDX) in Soil and Bioaccumulation in Bush Bean Hydroponic Plants*. Env. Tox. Chem. **10**: 845-855.
- <sup>18</sup>Hawari, J., F. Monteil-Rivera, V. Balakrishnan, M. Bhatt, B. Bhushan, D. Fournier, C. Groom, A. Halasz, G. Sunahara, P.Y. Robidoux and S. Rocheleau (2003). *Environmental Fate and Transport of a New Energetic Material, CL-20*. Annual Technical Report CP-1256 submitted to the U.S. DoD Strategic Environmental Research and Development Program by the Biotechnology Research Institute, National Research Council of Canada, Montreal, Canada.
- <sup>19</sup>Hawari, J., S. Deschamps, C. Beaulieu, L. Paquet and A. Halasz (2004). *Photodegradation of CL-20: Insights into the Mechanisms of Initial Reactions and Environmental Fate*. Water Res. **38**: 4055-4064.
- <sup>20</sup>Hoffman, D.M. (2003). *Voids and Density Distributions in 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-Hexaazaisowurtzitane (CL-20) Prepared Under Various Conditions*. Propellants, Explosives, Pyrotechnics **28**: 194-200.
- <sup>21</sup>HSDB. Hazardous Substances Data Bank, National Library of Medicine, Bethesda, MD., available at <http://toxnet.nlm.nih.gov>, February 14, 2007.
- <sup>22</sup>Huff, G.R., W.E. Huff, J.M. Balog, N.C. Rath, N.B. Anthony, and K.E. Nestor (2005). *Stress Response Differences and Disease Susceptibility Reflected by Heterophil to Lymphocyte Ratio in Turkeys Selected for Increased Body Weight*. Poult. Sci. **84**: 709-717.
- <sup>23</sup>IPCS (2004). *Glyoxal*. Concise Qualitative Assessment Document 53, International Programme for Chemical Safety, World Health Organization.
- <sup>24</sup>Jenkins, T.F., C. Bartolini, and T.A. Ranney (2003). *Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in Moist, Unsaturated Soil*. Technical Report ERDC/CRREL TR-03-7, U.S. Army Corps of Engineers, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH.
- <sup>25</sup>Kuperman, R. (2003). *Development of Ecological Toxicity and Biomagnification Data for Explosives Contaminants in Soil*. Final Technical Report CU-1221, Prepared for the U.S. DoD Strategic Environmental Research and Development Program (SERDP) by the U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD.

- <sup>26</sup>Kuperman, R.G., R.T. Checkai, M. Simini, C.T. Phillips, J.E. Kolakowski, C.W. Kurnas, and G.I. Sunahara (2003). *Survival and Reproduction of Enchytraeid crypticus (Oligochaeta, Enchytraeidae) in a Natural Sandy Loam Soil Amended with the Nitro-Heterocyclic Explosives RDX and HMX*. *Pedobiologia* **47**: 651-656.
- <sup>27</sup>Kuperman, R.G., R.T. Checkai, M. Simini, C.T. Phillips, J.S. Anthony, J.E. Kolakowski, and E.A. Davis (2006). *Toxicity of Emerging Energetic Soil Contaminant CL-20 to Potworm Enchytraeus crypticus in Freshly Amended or Weathered and Aged Treatments*. *Chemosphere* **62**: 1282-1293.
- <sup>28</sup>Kuperman, R.G., R.T. Checkai, and M. Simini (2006). Environmental Fate and Transport of a New Energetic Material CL-20. U.S. Army Edgewood Chemical Biological Center, SERDP Report ER-1254, February 2006.
- <sup>29</sup>Lynch, J.C. (2002). *Dissolution Kinetics of High Explosive Compounds (TNT, RDX, HMX)*. U.S. Army Engineer Research and Development Center Technical Report ERDC/EL TR-02-23, September 2002.
- <sup>30</sup>The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals. (1996). Twelfth Edition, Published by Merck Research Laboratories, Merck & Company, Inc. Editor: Budavari, S.
- <sup>31</sup>Monteil-Rivera, F., L. Paquet, S. Deschamps, V.K. Balakrishnan, C. Beaulieu, and J. Hawari (2004). *Physico-Chemical Measurements of CL-20 for Environmental Applications: Comparison with RDX and HMX*. *J. Chrom. A*. **1025**: 125-132.
- <sup>32</sup>Mukhi, S., X. Pan, G.P. Cobb, and R. Patino (2005). *Toxicity of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine to Larval Zebrafish (Danio rerio)*. *Chemosphere* **61**: 178-185.
- <sup>33</sup>Robidoux, P.Y., G.I. Sunahara, K. Savard, Y. Berthelot, S. Dodard, M. Martel, P. Gong, and J. Hawari (2004). *Acute and Chronic Toxicity of the new Explosive CL-20 to the Earthworm (Eisenia andrei) Exposed to Amended Natural Soils*. *Environ. Toxicol. Chem.* **23**: 1026-1034.
- <sup>34</sup>Rocheleau, S., R.G. Kuperman, M. Martel, L. Paquet, G. Bardai, S. Wong, M. Sarrazin, S. Dodard, P. Gong, J. Hawari, R.T. Checkai, and G.I. Sunahara (2006). *Phytotoxicity of Nitroaromatic Energetic Compounds Freshly Amended or Weathered and Aged in Sandy Loam Soil*. *Chemosphere* **62**: 545-558.
- <sup>35</sup>Rosen, G., and G.R. Lotufo (2005). *Toxicity and Fate of Two Munitions Constituents in Spiked Sediment Exposures with the Marine Amphipod Eohautorius estuarius*. *Environ. Toxicol. Chem.* **24**: 2887-97.
- <sup>36</sup>Rosenblatt, D.H., E.P. Burrows, W.R. Mitchell and D.L. Palmer (1991). In: *The Handbook of Environmental Chemistry*, Vol. 3, Part G, Hutzinger, O. ed., Springer-Verlag Berlin Heidelberg, p. 195.
- <sup>37</sup>Szecsody, J.E., D.C. Girvin, B.J. Devary B.J. and J.A. Campbell (2004). *Sorption and Oxidative Degradation of the Explosive CL-20 During Transport in Subsurface Sediments*. *Chemosphere* **56**: 593-610.
- <sup>38</sup>Szecsody, J.E., R.E. Riley, B.J. Devary, D.C. Girvin, T. Resch, J.A. Campbell, H.L. Fredrickson, K.T. Thompson, F.H. Crocker, M.M. Qasim, A.P. Gamerdinger, and L.A. Lemond (2005). *Factors*

*Effecting the Fate and Transport of CL-20 in the Vadose Zone and Groundwater*. Final Technical Report CP/ER-1255 (PNNL-15245), Prepared for the U.S. DoD Strategic Environmental Research and Development Program (SERDP) by the Pacific Northwest National Laboratory (PNL), Richland, WA.

- <sup>39</sup>Thompson, K.T., F.H. Crocker, and H.L. Fredrickson (2005). *Mineralization of the Cyclic Nitramine Explosive Hexahydro-1,3,5-Trinitro-1,3,5-Triazine by Gordonina and Williamsia spp.* Appl. Environ Microbiol. **71**: 8265-8272.
- <sup>40</sup>Townsend, D.M., and T.E. Myers. (1996). *Recent Developments in Formulating Model Descriptors for Subsurface Transformation and Sorption of TNT, RDX, and HMX*. U.S. Army Corps of Engineers Waterways Experiment Station Technical Report IRRP-96-1, February.
- <sup>41</sup>Trott, S., S.F. Nishino, J. Hawari, and J.C. Spain (2003). *Biodegradation of the Nitramine Explosive CL-20*. Appl. Environ. Microbiol. **69**: 1871-1874.
- <sup>42</sup>U.S. Army (1984). *Database Assessment of the Health and Environmental Effects of Munition Production Waste Products*. Document no. AD-A145 417, U.S. Army Medical Research and Development Command, Fort Detrick (authored by M.G. Ryon et al.).
- <sup>43</sup>U.S. Department of Defense (2003). *Department of Defense Instruction Number 5000.2—Operation of the Defense Acquisition System*. USD(AT&L), May 12.
- <sup>44</sup>U.S. EPA (2006). *Integrated Risk Information System (IRIS)*. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Cincinnati, OH.
- <sup>45</sup>Winfield, L.E., J.H. Rodgers, and S.J. D'Surney (2004). *The Responses of Selected Terrestrial Plants to Short (<12 Days) and Long Term (2, 4, and 6 Weeks) Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX) Exposure, Part I: Growth and Developmental Effects*. Ecotoxicology **13**: 335-347.
- <sup>46</sup>Yoon, J.M., D. Van Aken, and J.L. Schnoor (2006). *Leaching of Contaminated Leaves Following Uptake and Phytoremediation of RDX, HMX, and TNT by Poplar*. Int. J. Phytoremediation **8**: 81-94.