

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

HMX is a high explosive chemical which does not occur naturally. Most of the HMX entering environmental media is from discharge of waste waters from manufacture and processing of the chemical into aquatic environments. Treatment and disposal of other HMX-containing wastes also contributes to the environmental concentrations of this chemical.

HMX is persistent in the environment, with little transport from water to other media. Volatilization, sorption, and bioconcentration are not expected to be important. The primary transformation process is photolysis, with a half-life of about 17 days in river water. Biodegradation may occur in waste water and in water enriched with nutrients under aerobic and anaerobic conditions, but is not expected to be significant in ambient waters.

Exposure of the general population to HMX, if it occurs at all, is expected to be low. If exposure does occur, it is most likely to arise from drinking or showering with HMX-contaminated water at or near processing facilities or hazardous waste sites.

HMX has been identified in at least 10 of the 1,416 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 1995). However, the number of sites evaluated for HMX is not known. The frequency of these sites within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

Although no data were located, it is unlikely that substantial quantities of HMX are released to air. The chemical is not volatile, but, based on detection of RDX on particulate emissions (Army 1984a), may adsorb to particulates generated during burning of HMX-containing materials. Concentrations of

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HMX released to air in this manner are expected to be low. HMX is not listed on the TRI database, so estimates of environmental release of this chemical are not available from this source.

5.2.2 Water

Releases of HMX to surface water may occur from discharge of waste waters from production and processing of the chemical. In the past, reported concentrations of HMX in manufacturing effluents ranged from 0.09 to 3.59 mg/L (Army 1983, 1984a). Based on these concentrations, it was estimated that the Holston facility discharged about 45-123 pounds per day of HMX into the Holston River (Army 1984a). Waste waters from LAP operations such as washdown, explosive melting, and reject warhead steam cleaning may also contain HMX (EPA 1988). However, based on data for RDX, waste water treatment may reduce HMX concentrations by one to two orders of magnitude (Army 1984a). No information on the current status of waste water treatment at facilities generating waste waters containing HMX was located.

5.2.3 Soil

HMX may be released to soil by industrial sources and from hazardous waste sites at which this chemical has been detected. Releases may be via deposition of airborne particles from manufacture or incineration, spills occurring during manufacture, transportation, or storage, or landfilling of explosive wastes or explosive-generated incineration ashes (Army 1984a; EPA 1988). No data regarding quantities of HMX released to soil by these processes were located.

5.3 ENVIRONMENTAL FATE**5.3.1 Transport and Partitioning**

HMX released to water or soil may volatilize into air or sorb onto soil and sediments. However, neither volatilization nor sorption are expected to be major removal mechanisms for HMX. The volatilization rate constant from aquatic systems was estimated at about 2.4×10^{-4} to $7.2 \times 10^{-4} \text{ day}^{-1}$, resulting in a volatilization half-life of about 3,000-1,000 days for HMX (Army 1984a). In aquatic environments, adsorption to suspended solids and partitioning to sediments may occur, but is not

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considered a major fate process (EPA 1988). Thus, HMX may be transported for a considerable distance in water.

Based on the calculated soil adsorption factor ($\log K_{oc}$ of 0.54), HMX is expected to have high mobility in soil. Results of laboratory studies indicate that HMX was present in leachate from various types of soils and is likely to migrate into groundwater (Army 1982b, 1984b). However, the extent of migration to groundwater is limited by the relatively low solubility of HMX in water (6.63 mg/L) (EPA 1988). Therefore, the migration of HMX through soil is expected to be slow, resulting in low concentrations in groundwater (EPA 1988). The highest migration rate was reported in coarse, loamy soil (Army 1984a). More recently, a study was conducted on the migration of HMX in soil obtained from the Milan Army Ammunition Plant in Milan, Tennessee (Checkai et al. 1993). Experiments involved leaching soil columns with synthetic rainwater for up to 243 days. HMX, at an average concentration of 0.4 mg/L, was detected in the leachate samples. No biodegradation products of HMX were detected. HMX had migrated the full soil-core length by 19.5 weeks.

Atmospheric transport of HMX may occur, based on persistence of munitions compounds in air (Army 1984a), but no data were located to support this hypothesis.

No data regarding the bioconcentration potential of HMX were located. Bioaccumulation of HMX is not expected to be significant, based on bioconcentration and elimination studies on RDX, an HMX analog, in several species (Army 1984a).

5.3.2 Transformation and Degradation

5.3.2.1 Air

No data were located on HMX transformations in the atmosphere.

5.3.2.2 Water

HMX is relatively stable in the aquatic environment. Neither hydrolysis nor oxidation of HMX in water are expected to be important removal processes (EPA 1988). Direct photolysis is probably the primary transformation pathway for HMX in aquatic systems. Photolysis rate constants reported for

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HMX were 0.19, 0.166, and 0.0099 day⁻¹ in pure water, Holston River water, and Louisiana Army Ammunition Plant (LAAP) lagoon water, respectively (Army 1983). The resulting photolytic half-lives for HMX were 1.4, 1.7, and 70 days, respectively. The major difference affecting the photolysis rate in these laboratory experiments appeared to be light attenuation by ultraviolet absorbing species in the lagoon water. The rate did not appear to be affected by co-substrates in solution. The observed stable end products of HMX photolysis were nitrate, nitrite, and formaldehyde. Since the nitrate and nitrite ions accounted for only 50% of the nitro groups per mole of HMX consumed, the authors proposed a photolysis mechanism, summarized in Figure 5-2, which includes dinitrogen oxide, ammonia, and formamide as additional end products. Modeling of Holston River and LAAP lagoon waters, including such factors as water flow, depth, and seasonal changes in rate constants, indicated that the average half-life of HMX would be 17 days in the Holston River and 7,900 days in the LAAP lagoon. Dilution served as the primary mechanism for reduction of HMX concentration, with photolysis contributing losses of 1-5%. The authors concluded that HMX may persist in the Holston River for a significant distance (more than 20 km) from the Holston plant.

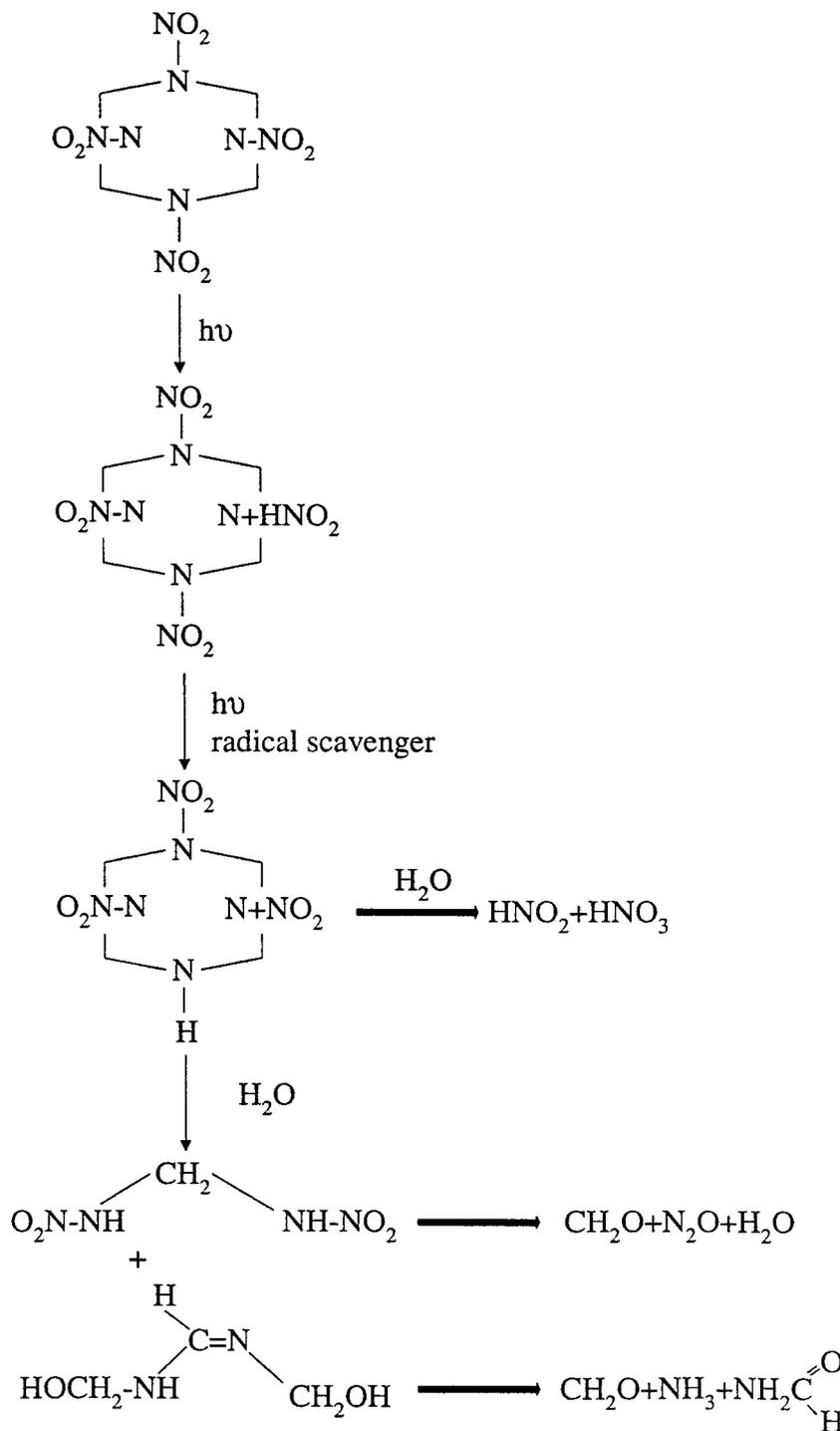
Biodegradation does not appear to be significant in ambient waters; however, some studies indicate that biodegradation may be an important removal process for HMX in manufacturing effluents and in waters containing organic nutrients. Aerobic and anaerobic biotransformation was reported in waste water and river water enriched with nutrients. The transformation products included mono- through tetra-nitroso derivatives of HMX, which eventually were metabolized to 1,1-dimethylhydrazine (Army 1983). Transformation was not significant in the Holston River water or the LAAP lagoon water. The authors postulated that the levels of organisms and nutrients in the water were too low to support the biotransformation of HMX (Army 1983). Other studies confirmed the anaerobic, but not aerobic, biotransformation of HMX in nutrient broth culture systems inoculated with sewage sludge (Army 1984d).

5.3.2.3 Sediment and Soil

No data were located regarding HMX transformation in soil or sediment. Based on data for RDX and HMX transformations in water, microbial degradation does not proceed rapidly and the chemical may be persistent in soil and sediments (Army 1984a).

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FIGURE 5-2. Proposed Mechanism for the Solar Photolysis of HMX in Water*



*Adapted from Army 1983

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

No monitoring data for HMX in ambient air were located.

5.4.2 Water

HMX has been detected in groundwater samples at the northern facility boundary of the Milan Army Ammunition Plant in Milan, Tennessee (EPA 1994). Concentrations of 0.53-821.0 µg/L HMX were detected in monitoring well groundwater samples. HMX has also been detected in surface waters receiving effluents from HMX manufacturing and processing facilities. HMX was detected at a concentration of 67 µg/L in the Holston River, one mile downstream of the last plant effluent (Army 1984a).

5.4.3 Sediment and Soil

At the Joliet Army Ammunition Plant located in Joliet, Illinois, HMX has been detected in soil samples at concentrations of 5-3,054 µg/g (Phillips et al. 1994). HMX, at a concentration of 13 µg/g, was detected by high-performance liquid chromatography (HPLC) in soil obtained from the Milan Army Ammunition Plant, Milan, Tennessee (Phillips et al. 1993). High levels could be present in limited areas as a result of releases from manufacture and processing as well as from waste disposal in landfills (Army 1984a).

5.4.4 Other Environmental Media

No data were located regarding HMX in foods or other environmental media.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Exposure of the general population to HMX is expected to be extremely low, but data are insufficient for exposure estimates. The chemical has only been detected in environmental media in the vicinity of

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manufacturing or processing facilities or hazardous waste sites. If exposure of the general population to HMX occurred, water would be the most likely source (Army 1989).

Workers in military facilities manufacturing or processing HMX may be exposed to the chemical. Plant personnel may handle HMX dissolved in various solvents (Army 1984a). The National Occupational Exposure Survey (NOES) estimated that six technicians for research and development laboratories were potentially exposed to HMX in the United States between 1981-1983 (Sieber et al. 1991). The NOES database does not contain data on the frequency, duration, concentration, or route of exposure of workers to chemicals.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Residents or workers near hazardous waste sites containing HMX wastes or manufacturing or processing facilities handling explosives are at greater risk of exposure to HMX than the general population.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of HMX is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of HMX.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of HMX are sufficiently well characterized to allow estimation of its environmental fate (see Table 3-2) (Army 1989; EPA 1988; HSDB 1995). On this basis, it does not appear that further research in this area is required.

Production, Import/Export, Use, Release, and Disposal. HMX is manufactured by only one facility in the United States (Army 1984a, 1989; EPA 1986). Current production volumes, both as a primary product and as a by-product in RDX, and import and export information are not available. Current amounts of this chemical consumed by each use were not located. Current information on the amounts of HMX released to the environment and disposed by various treatment methods are also not available. This information would be helpful in assessing potential exposure to workers and the general population.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1992, became available in May of 1994. This database will be updated yearly and should provide a list of industrial production facilities and emissions. However, HMX is currently not listed in the TRI database.

Environmental Fate. The environmental fate of HMX has been investigated in several studies (Army 1982b, 1983, 1984b, 1984d). The chemical is relatively unreactive and degrades slowly in environmental media. It is not likely that exposure to the general population is of concern. Nevertheless, because it appears to be persistent in aquatic and terrestrial environments and may migrate to groundwater (Army 1982b, 1984b), additional studies might be useful to assess the potential for transport of this chemical from hazardous waste sites. In addition, determining the effect of chlorination on HMX degradation rates would be useful in predicting potential exposure via drinking water.

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Bioavailability from Environmental Media. No studies were located regarding the bioavailability of HMX from environmental media. However, studies in rodents indicate that HMX is not well absorbed (<5%) in the gastrointestinal tract following exposure by gavage or in the diet (Army 1985g, 1986). Based on a log K_{oc} value of 0.54 (Army 1989), interactions between HMX and soil may decrease bioavailability to some extent, but this is not expected to be significant. Studies which investigate the bioavailability of HMX from environmental media would be useful in estimating exposure to persons who live near hazardous waste sites contaminated with HMX.

Food Chain Bioaccumulation. No data on bioconcentration of HMX by aquatic organisms were located. Based on data for RDX, food chain bioaccumulation is unlikely, but information on the bioconcentration potential of this chemical would be useful to confirm this assumption.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of HMX in contaminated media at hazardous waste sites are needed so that the information obtained on levels of HMX in the environment can be used in combination with the known body burden of HMX to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. Monitoring data were not located for HMX in ambient air or soil. The chemical has been detected in surface waters receiving effluents from HMX manufacturing and processing facilities. Since this chemical is not expected to be prevalent in the environment and exposure of the general population is not expected to be of concern, monitoring of ambient environmental media does not appear to be required. However, monitoring of environmental media (particularly tap water from surface water sources) in the vicinity of HMX manufacturing and processing facilities, and at hazardous waste sites at which HMX has been detected, would help determine potential sources and magnitude of exposure.

Exposure Levels in Humans. No data were located regarding exposure levels of HMX to humans. This information is necessary for assessing the need to conduct health studies on these populations. Since HMX does not appear to be well absorbed, analyzing blood or urine of workers potentially exposed to the chemical is unlikely to provide useful information unless the exposure levels are very large. Analysis of feces, although impractical for large scale monitoring, might provide documentation of oral exposure.

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Exposure Registries. No exposure registries for HMX were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

5.7.2 On-going Studies

Current research on the environmental fate of HMX involves studies of biological waste management including the anaerobic degradation of HMX and the effectiveness of white rot fungus in degrading HMX for bioremediation of contaminated soil and water (FEDRIP 1995).

