

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Otto Fuel II is a mixture of three component chemicals, propylene glycol dinitrate, 2-nitrodiphenylamine, and dibutyl sebacate. Otto Fuel II enters the environment as these three components, which partition to the different environmental media according to their individual chemical and physical properties. Otto Fuel II is primarily released to water in waste streams from Navy facilities that produce it or are involved in torpedo rework operations. There is also a possibility that it could be spilled on soil during transfer operations. The limited data located on the environmental fate of Otto Fuel II components indicate that propylene glycol dinitrate is removed from water primarily by volatilization. Propylene glycol dinitrate is the most water soluble of the three components, although its solubility is low and it is not expected to persist in water for more than a few days. Neither 2-nitrodiphenylamine nor dibutyl sebacate is volatile or soluble enough for the partitioning to air or water to be important fate processes. 2-Nitrodiphenylamine has been found in river sediment receiving waste water runoff from an army ammunition plant; this is considered the most likely fate for this chemical. The information on dibutyl sebacate is too limited to determine its transport and partitioning in the environment. However, it is known to be rapidly biodegraded by a wide range of microorganisms. Both propylene glycol dinitrate and 2-nitrodiphenylamine are photolyzed and photooxidized in water. It is likely that these substances are similarly broken down in the air. The data on biodegradation of propylene glycol dinitrate and 2-nitrodiphenylamine are mixed. Some experiments indicate these compounds are readily degraded and others indicate limited biodegradation. A bioconcentration factor has been calculated only for 2-nitrodiphenylamine. It indicates that this chemical does not bioconcentrate in aquatic organisms or biomagnify in the food chain. People working in occupations in which Otto Fuel II is manufactured or used, such as personnel involved in clean up operations or waste treatment facilities handling Otto Fuel II, are most likely to be exposed to the chemical and its components. Incomplete data on disposal practices and levels in the environment prevented a determination of the likelihood of exposure of people living or working near hazardous waste sites. General population exposure to Otto Fuel II is not expected to occur because of the limited manufacture and use of the compound, and the suggested low mobility of Otto Fuel II and its components in the environment. However, the general population may be significantly exposed to 2-nitrodiphenylamine or dibutyl sebacate as a result of their manufacture and use in a number of civilian products.

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Otto Fuel II has been detected at 2 of the 1,397 NPL sites that have been proposed for inclusion on the NPL (HazDat 1994). 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

There is no information on the release of Otto Fuel II, 2-nitrodiphenylamine, or dibutyl sebacate to air. Propylene glycol dinitrate could be released to air during torpedo maintenance procedures, manufacturing, transport, etc. However, since the vapor pressure of propylene glycol dinitrate is very low, these releases are not expected to be substantial. Azeotropic evaporation of propylene glycol dinitrate from Otto Fuel II manufacturing waste water may also release propylene glycol dinitrate into the air (Wyman et al. 1984). Experiments conducted using a photochemical smog chamber to simulate reactions that might occur in polluted atmospheres indicate that low levels of propylene glycol dinitrate (approximately 0.1 ppm or less) are generated when air containing 3 ppm propylene and 1.5 ppm nitrogen oxide compounds (NO or NO₂) are irradiated with high pressure xenon lamps (Akimoto et al. 1978, 1980). Further investigation showed that the production of propylene glycol dinitrate was a result of the reaction of photochemically generated nitrogen pentoxide (N₂O₅) (Akimoto et al. 1978, 1980) with atmospheric propylene (Akimoto et al. 1978; Hoshino et al. 1978). This suggests that photooxidation of atmospheres containing propylene and nitrogen oxide compounds may result in release of propylene glycol dinitrate to the atmosphere. However, the applicability of these laboratory experiments to actual events taking place in the atmosphere is uncertain since multiple factors that could affect such a reaction (e.g., presence of other compounds, concentrations of reactants, turbulence affecting the chance of collisions between potential reactants) are not present in the smog chamber.

5.2.2 Water

Propylene glycol dinitrate and 2-nitrodiphenylamine are released in waste water effluent streams from plants manufacturing and/or using the compounds to formulate special military propellants including Otto Fuel II (Army 1979, 1981 a). In 1979, only one facility, Radford Army Ammunition Plant in Radford, Virginia, was engaged in the manufacture of propellants containing 2-nitrodiphenylamine

FIGURE 5-1. FREQUENCY OF NPL SITES WITH OTTO FUEL II CONTAMINATION *



*Derived from HazDat 1994

FREQUENCY  2 SITES

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(Army 1979). At that time, the level of 2nitrodiphenylamine released in the waste stream from this plant was estimated to be 240-670 lbs/per month. Of this amount, about one-half to two-thirds was expected to be recovered as particulates from the effluent filters. Approximately 80-200 lbs/per month was estimated to be released to the New River, which receives the waste water effluent from the Radford Army Ammunition Plant. No information on current releases was located.

5.2.3 Soil

Otto Fuel II has been detected in soils (data on levels not available) from two of the 1,397 hazardous waste sites that have been proposed for inclusion on the NPL (HazDat 1994). Otto Fuel II accidentally spilled on soil during transfer operations could result in additional sites contaminated with this monopropellant.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Otto Fuel II has a relatively low vapor pressure (8.8×10^{-2} mm Hg at 25 °C) (Air Force 1985a). Its primary component, propylene glycol dinitrate, also has a low vapor pressure (9.8×10^{-2} mm Hg at 25 °C) (Crater 1929), which suggests that little evaporation of the compound occurs. In a biodegradation study, 80% loss of propylene glycol dinitrate was observed over a 30-day period. Since growth curves showed essentially static growth of the microbial culture and no breakdown products of biodegradation were detected, the loss could not be attributed to biodegradation. In subsequent experiments employing the commercial culture and including a trap to catch released gases, 61% of the propylene glycol dinitrate added to the culture media was recovered in the exhaust gas trap. As in the previous experiments, no metabolites of biodegradation were detected. It was concluded that the loss of propylene glycol dinitrate was due to formation of an azeotrope with water. The Henry's law constant for the azeotrope was estimated to be 3.3×10^2 mm Hg ($\approx 1 \times 10^{-2}$ atm m^3/mole) (Wyman et al. 1984). This value of Henry's law constant would account for the volatilization loss of propylene glycol dinitrate from water and indicates that volatilization may be an important fate process in water. The vapor pressures of the remaining two components of Otto Fuel II, 2-nitrodiphenylamine (1×10^{-5} mm Hg at 25 °C) and dibutyl sebacate (3 mm Hg at 180 °C) indicate that evaporation is not a significant fate process for these chemicals (Baughman and Perenich

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1988). However, no values for Henry's law constants were located that might corroborate the volatility characteristic predicted from the vapor pressure data alone.

Otto Fuel II and its component, dibutyl sebacate are insoluble in water (Air Force 1985a; HSDB 1994), and 2-Nitrodiphenylamine is insoluble to only slightly soluble (American Cyanamid 1982; Army 1979). Therefore, these two compounds are not expected to partition substantially to water and these compounds are unlikely to leach from soil to groundwater (Lyman et al. 1982). Propylene glycol dinitrate has a solubility of 1.3 g/L (ACGIH 1986) and is expected to partition substantially into water, However, since this chemical forms an azeotrope with water that readily volatilizes, it is not expected to persist in water for more than a few days.

2-Nitrodiphenylamine is sparingly soluble in water and was found to precipitate out of waste water effluent and sorb to sediment (Army 1979). The chemical has been detected in sediment in a river receiving runoff water from an army ammunition plant (Army 1979). An octanol-water partition coefficient of 3.07 has been calculated for 2-nitrodiphenylamine (Army 1979). The estimated value of octanol-water partition coefficient from EPA's Graphic Exposure and Modelling System (GEMS) (EPA 1986) is 21.7. Both of these values indicate that 2nitrodiphenylamine does not bioaccumulate in aquatic organisms and is not likely to biomagnify in the environment. No information on sorption to particles, sediments, or soils or on bioaccumulation for Otto Fuel II was located.

5.3.2 Transformation and Degradation

5.3.2.1 Air

No information on the transformation and degradation of Otto Fuel II or its components in air was located. However, experiments in aqueous media indicate that both propylene glycol dinitrate and 2-nitrodiphenylamine are subject to photolysis and photooxidation and that these processes are expected to occur in the air as well (Wyman et al. 1984).

5.3.2.2 Water

Decomposition of both the propylene glycol dinitrate and 2-nitrodiphenylamine components of Otto Fuel II was observed when a solution of the mixture was exposed to ultraviolet (UV) radiation

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(Wyman et al. 1984) under air and under nitrogen. When the tests were conducted in air, >96% of the propylene glycol dinitrate was decomposed in 42 hours compared to 57% in the dark controls. Decomposition of propylene glycol dinitrate was >89% in 72 hours under nitrogen compared to 9.5% in controls. Under both sets of test conditions, 2-nitrodiphenylamine was removed from the solution as determined by disappearance of its characteristic peak at 442 nm. However, no quantitative rate data on its decomposition were presented. ¹³C-Nuclear magnetic resonance (¹³C-NMR) detected lactic and pyruvic acids in the water-soluble portion of the photolyzed Otto Fuel II. It was concluded that UV photolysis of propylene glycol dinitrate produces aldehydes, nitrite esters, nitrogen dioxide, nitric oxide and nitrous acid. In the presence of oxidants (oxygen, ozone produced during photolysis), the aldehydes possibly oxidize to lactic acid and pyruvic acid (Wyman et al. 1984). The importance of photolysis of propylene glycol dinitrate by sunlight can not be ascertained from the study of Wyman et al. (1984) since short wavelength UV lights (wavelengths <290 nm) were not filtered out from the light source. The observed photolysis may have occurred as a result of interaction with these short wavelength UV light that are not available in sunlight (available wavelengths in sunlight are >290 nm).

Limited data suggest that Otto Fuel II may hydrolyze under basic conditions. Incubation of an Otto Fuel II-water mixture with calcium hydroxide and with sodium hydroxide resulted in a loss of propylene glycol dinitrate from the solution (Kessick et al. 1978). Sixty percent of the propylene glycol dinitrate was lost within 4 hours when calcium oxide was added, and no propylene glycol dinitrate could be measured following 15 minutes of incubation with sodium hydroxide. The significance of this for the actual environmental fate of propylene glycol dinitrate is not known since the high pH involved (10.8 or higher) is rarely found in the environment. In addition, work of other investigators suggests that the loss of the propylene glycol dinitrate in these experiments could have been due to volatilization of the propylene glycol dinitrate-water azeotrope (Wyman et al. 1984).

There is conflicting evidence for the microbial breakdown of propylene glycol dinitrate. Experiments using batch and continuous culture methods with an inoculum of fresh activated sewage sludge from a domestic sewage treatment plant revealed evidence of biodegradation of the compound (Army 1981a). Loss of propylene glycol dinitrate from the cultures was observed and propylene glycol mononitrate was identified as a metabolite of the compound. Loss of propylene glycol mononitrate was also observed in this series of experiments. These data indicate that biodegradation occurs by sequential cleavage of the nitrate groups resulting in formation of propylene glycol. A companion study showed

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that propylene glycol was also rapidly biodegraded (Army 1981b). In contrast, studies performed with pure cultures of *Pseudomonas aeruginosa*, microorganisms from sewage sludge, and a commercial culture of mixed microorganisms specifically designed to degrade recalcitrant substances in waste water from treatment plants indicated that propylene glycol dinitrate was not readily biodegraded by microorganisms (Wyman et al. 1984). On addition of an inoculum of the culture into the Otto Fuel II solution, an initial increase in cells of 1-2 logs was observed over the first 24 hours followed by constant cell counts for the remainder of the 30-day study period. The initial increase in cells was likely due to degradation of the dibutyl sebacate plasticizer since this chemical has been shown to be readily degraded by environmental bacteria and fungi (Klausmeier 1986; Klausmeier and Jones 1960; Klausmeier and Osmon 1976; Osmon et al. 1972; Stahl and Pessen 1953). However, since this component of Otto Fuel II was not specifically monitored, the increased growth cannot be unequivocally attributed to degradation of the dibutyl sebacate. Propylene glycol dinitrate and 2-nitrodiphenylamine were not considered to be biodegraded as no metabolites were detected. Experiments with mixed bacterial cultures from municipal sewage, acclimated to Otto Fuel II by preexposure to the compound, did not degrade propylene glycol dinitrate (Kessick et al. 1978). In addition, biochemical oxygen demand (BOD) over a 5-day period did not change substantially when Otto Fuel II was used as the sole carbon source. These data indicate that Otto Fuel II is not readily degraded by microorganisms. Experiments monitoring BOD in the presence of glucose (as the carbon source) and increasing concentrations of Otto Fuel II (as measured by propylene glycol dinitrate) showed decreased BOD with increasing Otto Fuel II concentration, suggesting that Otto Fuel II was toxic to the microbial culture. The authors considered propylene glycol dinitrate to be the toxic component, although no data were presented to support this assumption. 2-Nitrodiphenylamine and dibutyl sebacate were not monitored in this study.

5.3.2.3 Sediment and Soil

No data on the biotransformation and degradation of Otto Fuel II and two of its components, propylene glycol dinitrate and dibutyl sebacate, were located. 2-Nitrodiphenylamine has been reported to be degraded by mixed cultures of microorganisms when it is available as the sole carbon source (Kessick et al. 1978). However, no data were located to support this or to indicate the importance of biodegradation on the environmental fate of 2-nitrodiphenylamine.

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5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Grab samples of air in four U.S. Navy torpedo facilities (Naval Weapons Station, Charleston, South Carolina; Naval Weapons Station, Yorktown, Virginia; Naval Submarine Support Facility, New London, Connecticut; and Naval Torpedo Station, Keyport, Washington) had levels ranging from 0 to 0.22 ppm propylene glycol dinitrate (detection limit not reported) (Horvath et al. 1981). No data on levels of 2-nitrodiphenylamine or dibutyl sebacate were located.

5.4.2 Water

Dibutyl sebacate was detected in one sample of finished water from an advanced waste treatment plant in Lake Tahoe, California. The concentration of the dibutyl sebacate was not reported. Since dibutyl sebacate is a commonly used plasticizer, it is likely that the dibutyl sebacate found in the water was not due to Otto Fuel II contamination (EPA 1984a, 1984b).

Levels of 2-nitrodiphenylamine ranging from 1 to 14 ppm (mean of 3.5 ppm) have been found in the New River, which receives effluent water from the Radford Army Ammunition Plant in Radford, Virginia (Army 1979).

No data on concentrations of propylene glycol dinitrate in water were located.

5.4.3 Sediment and Soil

Levels of 0.5-12.2 ppm (mean of 1.5 ppm) 2-nitrodiphenylamine were found in the sediments of the New River (Army 1976). The New River receives effluent waste water from the Radford Army Ammunition Plant.

5.4.4 Other Environmental Media

Limited data were located regarding levels of dibutyl sebacate in food. Samples of hard and processed cheese, liver pate, and black pudding purchased from supermarkets in the United Kingdom contained

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levels of dibutyl sebacate ranging from 2.3 to 137 mg/kg (Castle et al. 1988). The lowest levels were found in the hard cheese, and the highest levels were in the processed cheese and meat products packaged in plastic tubs. The diethyl sebacate in these samples was assumed to have migrated from the plastic wrap used to store the foods and known to contain dibutyl sebacate as a plasticizer. The plastic containers contained from 3.5% to 4.1% diethyl sebacate that had been added as a plasticizer when the containers were manufactured. A sample of leaf lettuce taken from a private garden in Finland contained 0.5 ug 2-nitrodiphenylamine/kg fresh weight of lettuce (Wickstrom et al. 1986). However, the source of the 2-nitrodiphenylamine was probably reaction of polyaromatic hydrocarbons with nitro compounds in the air and not Otto Fuel II contamination. These possible sources of dibutyl sebacate and 2-nitrodiphenylamine contamination should be considered when looking for evidence of Otto Fuel II contamination in environmental samples. No information on the concentrations of propylene glycol dinitrate in other environmental media were located.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

There were insufficient data to reliably assess the potential for general population exposure to Otto Fuel II and its components. However, given the limited manufacture and use of the compound, general population exposure is expected to be limited to persons in the immediate vicinity of waste water effluents containing Otto Fuel II or its components.

Workers employed in occupations in which Otto Fuel II is used (e.g., torpedo maintenance workers) may be exposed to airborne propylene glycol dinitrate. A survey of four Navy torpedo facilities suggested that, in some instances, the air concentrations might exceed the threshold limit value (TLV) of 0.2 ppm in effect at the time the measurements were taken (Horvath et al. 1981). Concentrations ranged from 0.0 to 0.22 ppm (one sample exceeded the TLV). However, 88% of the air samples taken from the facilities had levels of 0.1 ppm or less, and 50% were ≤ 0.05 ppm. Alveolar breath analysis was conducted on two workers employed in Navy torpedo facilities (Horvath et al. 1981). Propylene glycol dinitrate was monitored as an indicator of exposure to Otto Fuel II. A level of 0.001 ppm was measured in the breath of one of the workers 5 minutes after exposure to air concentrations ranging from 0.01 to 0.026 ppm ceased. No propylene glycol dinitrate was detected 15 minutes after exposure ceased. In the second worker, concentrations of 0.0008 and 0.0004 ppm were measured in the expired air 5 and 15 minutes, respectively, after exposure to 0.015-0.222 ppm.

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The National Occupational Exposure Survey (NOES) conducted by NIOSH during 1981-1983 to estimate worker exposure to chemicals in different professions did not include any estimate for Otto Fuel II or propylene glycol dinitrate (NOES 1991). However, this survey estimated that 4,856 workers employed in special contracted trades, miscellaneous manufacturing industries, and personal services were potentially exposed to dibutyl sebacate (NOES 1991). Professions included roofers, laundering and dry cleaning machine operators, assemblers, construction laborers, and hand packers and packagers. None of the exposed persons appeared to be employed in facilities or professions in which Otto Fuel II was manufactured or used. These data are not considered relevant to an assessment of occupational exposure to Otto Fuel II.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The only populations that appear to be potentially exposed to higher levels of Otto Fuel II and its components are people who manufacture Otto Fuel II and/or are involved in torpedo refueling and maintenance operations.

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 Otto Fuel II and its components is available. Where adequate information is not available, ATSDR, in conjunction with 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 Otto Fuel II and its components.

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 or eliminate 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 may be proposed.

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5.7.1 Identification of Data Needs

Physical and Chemical Properties. Several important physical properties of Otto Fuel II and its three components, propylene glycol dinitrate, 2-nitrodiphenylamine, and dibutyl sebacate, have yet to be characterized. These include their octanol-water and organic carbon partition coefficients and Henry's law constants. These data are important in estimating the fate of released Otto Fuel II in the environment and determining the potential for human exposure.

Production, Import/Export, Use, and Release and Disposal. Data were located that described the production of 2-nitrodiphenylamine and dibutyl sebacate (Army 1979; HSDB 1994). Dibutyl sebacate is currently manufactured in the United States (HSDB 1994; SRI 1991; Thomas Publishing 1990a), but no information on the current production of 2-nitrodiphenylamine was located. No information was located discussing the production of either Otto Fuel II or its major component, propylene glycol dinitrate. Import/export data on Otto Fuel II and its components were also missing. Only proposed methods of disposal were found (Army 1979; Dietrich et al. 1985; Kessick et al. 1978; Smith et al. 1983), and no information was located on methods of disposal commonly and/or currently used. These data are necessary to determine the likelihood of human exposure to Otto Fuel II and its components.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1988, became available in May of 1990. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. The environmental fate of Otto Fuel II and its components is largely unknown. Otto Fuel II and its components are not extremely volatile or soluble; however, propylene glycol dinitrate does form a volatile azeotrope with water (Wyman et al. 1984). This makes evaporation of propylene glycol dinitrate an important fate process. 2-Nitrodiphenylamine may precipitate from water or sorb to particulates (Army 1979). Dibutyl sebacate is rapidly biodegraded, but the data on biodegradation of propylene glycol dinitrate and 2-nitrodiphenylamine are equivocal. Both of these chemicals are photolyzed by UV light (Wyman et al. 1984). However, the importance of photolysis of propylene glycol dinitrate as a result of interaction with sunlight has not been

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ascertained. More information on the environmental fate of the mixture and its components is needed to fully assess the risk of exposure to populations living near facilities where they may be released.

Bioavailability from Environmental Media. Experiments in animals have shown that propylene glycol dinitrate is absorbed by inhalation, oral, and dermal routes (Andersen and Mehl 1979; Army 1979; Clark and Litchfield 1969; Jones et al. 1972; Mattsson et al. 1981; Smith 1953; Stewart et al. 1974). 2-Nitrodiphenylamine and dibutyl sebacate are also absorbed following ingestion (Andersen and Mehl 1979; Army 1979; Clark and Litchfield 1969; Jones et al. 1972; Smith 1953). The potential for absorption of 2-nitrodiphenylamine and dibutyl sebacate following inhalation or dermal contact could not be determined from the data located. No further information on bioavailability is needed for dibutyl sebacate because the compound is not toxic. However, propylene glycol dinitrate is toxic, and the potential toxicity of 2-nitrodiphenylamine is undetermined. Therefore, more data on the bioavailability of these compounds from air, water, soil, and food are needed to assess fully the risk posed by these Otto Fuel II components.

Food Chain Bioaccumulation. An estimated bioaccumulation factor for 2-nitrodiphenylamine based on calculations indicates that this chemical does not bioconcentrate (Army 1979). No data were located for the remaining two components of Otto Fuel II. More information on the bioconcentration potential of these chemicals, including experimental data, is needed to determine the risk of biomagnification in the food chain.

Exposure Levels in Environmental Media. Very little information was located on the levels of Otto Fuel II and its components in environmental media (Army 1976, 1979; Castle et al. 1988; EPA 1984a, 1984b; Horvath et al. 1981; Wickstrom et al. 1986). Most of the data that were located did not concern levels of components originating from Otto Fuel II contamination (Castle et al. 1988; EPA 1984a, 1984b; Wickstrom et al. 1986). This information would be useful in determining the risk to populations living or working in the vicinity of facilities releasing Otto Fuel II to water and soil. Reliable monitoring data for the levels of Otto Fuel II in contaminated media at hazardous waste sites are needed so that the information obtained can be used in combination with the known body burden of Otto Fuel II to assess the potential risk of adverse health effects in populations living the vicinity of hazardous waste sites.

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Exposure Levels in Humans. Limited data were located on exposure levels in humans working in facilities where Otto Fuel II is used. These data indicate that workers employed in occupations where Otto Fuel II is used are exposed to sub-ppm levels of Otto Fuel II (Horvath et al. 1981). Alveolar breath samples of two exposed workers had levels of propylene glycol dinitrate of less than 1 ppb. Additional monitoring studies in occupationally exposed workers would be useful for better defining human exposure to Otto Fuel II. This information is necessary for assessing the need to conduct health studies on these populations.

Exposure Registries. No exposure registries for Otto Fuel II or its components were located. This substance is not currently one of the substances 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 the exposure to this substance.

5.7.2 Ongoing Studies

No ongoing studies were located regarding the potential for human exposure to Otto Fuel II and its components.