

## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Stoddard solvent is a mixture of hydrocarbons derived by refining crude oil; its environmental fate is dependent on the physical and chemical properties of the individual components. The hydrocarbon chain length ranges from C<sub>7</sub> to C<sub>12</sub>, although a form of Stoddard solvent called 140 flash contains C<sub>5</sub> and C<sub>6</sub> hydrocarbons as well. These hydrocarbons consist primarily of linear and branched alkanes (also called paraffins) (30-50% of the total mixture), cycloalkanes (30-40%), and aromatics (10-20%).

Stoddard solvent may be released to the environment during its use as a solvent in dry cleaning plants or as an industrial degreasing agent. It may also enter water or soil as a result of spills during use or transportation or from leaking shipping and storage containers such as 55-gallon drums. The lower molecular weight alkanes and aromatics may volatilize and undergo photodegradation in the atmosphere, while higher-molecular-weight alkanes and cycloalkanes tend to be sorbed to organic matter in soil or water. Lower-molecular-weight alkanes may also be sorbed to organic matter if volatilization is not rapid. The higher-molecular-weight aromatic components may dissolve in surface waters, or they may desorb from soil particles and leach into the groundwater. Biodegradation is expected to be the primary fate process for Stoddard solvent in soil and water, except that fraction which has volatilized. The rate of biodegradation is dependent on the ambient temperature, the presence of a sufficient number of microorganisms capable of metabolizing these hydrocarbons, and the concentration of Stoddard solvent in or on the soil or water. If biodegradation occurs under anoxic conditions, then the availability of Fe(III) may influence the biodegradation of aromatics (Lovley et al. 1994).

Exposure of the general population to Stoddard solvent may result primarily from inhalation or dermal contact when it is used for such commercial purposes as dry cleaning, degreasing in machine shops, and in paints. Individuals living in areas where Stoddard solvent may have contaminated the soil may be exposed if it has entered their homes through volatilization from the soil, has been transported in flowing groundwater, or if they play or otherwise come in direct contact with contaminated soil.

Inhalation of the volatile components of Stoddard solvent is likely to be the main route of occupational exposure for individuals employed in dry cleaning plants where it is used as a cleaning solvent,

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machine shops where it is used as a degreasing agent, and other industries where Stoddard solvent is used for a variety of purposes. Dermal exposure is also possible if machine parts that have been degreased in Stoddard solvent are not dry when handled or protective clothing is not worn. Stoddard solvent has been identified in at least 7 of the 1,397 hazardous waste sites on the EPA National Priorities List (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

Stoddard solvent may be released to the atmosphere in the exhaust emissions of dry cleaning plants. Emissions from one plant were determined to be 2,100 ppm (measured as propane) (EPA 1980). Fugitive emissions from other industrial or domestic uses (such as incompletely sealed or punctured barrels) may contribute to levels of Stoddard solvent in the environment, including contributions to general levels of volatile organic carbon. In addition, surface water contamination may occur as a result of direct spills of Stoddard solvent onto surface waters, runoff from spills to soil with subsequent transmission to nearby water sources, or from improper disposal, such as pouring Stoddard solvent down drains. Accidental spills of Stoddard solvent to various media are reported to the Emergency Response Notification System (ERNS) maintained by EPA. Total spill data for Stoddard solvent are:

<u>Year</u>	<u>Media</u>	<u>Quantity spilled in pounds</u>	<u>Kilograms</u>
1991	Land	2,020	918.2
	Water	8,580	3,900
1992	Land	33	15
	Water	0	0

No spills were reported to air, groundwater, at facilities, or for other types of releases. In addition, no spills of Stoddard solvent were reported in 1993 (ERNS 1993).

Releases of Stoddard solvent are not required to be reported under SARA Section 313; consequently, there are no data for this compound in the 1990 Toxics Release Inventory (TRI90 1992). There are



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seven NPL sites where Stoddard solvent is present in waste materials or containers. It is unknown whether there have been releases to the environment from these sites (HAZDAT 1994).

### 5.2.1 Air

No information was located on releases of Stoddard solvent to the atmosphere.

### 5.2.2 Water

Stoddard solvent may be released to surface waters as a result of spills, in runoff from industrial facilities where it is used as a solvent, or from the intentional disposal of excess solvent down drains. Stoddard solvent is not listed in the Contract Laboratory Program Statistical Database (CLPSD) of chemicals detected in groundwater and surface water samples taken only at NPL sites. Stoddard solvent itself, as a hydrocarbon mixture, is not included as a target chemical at NPL sites, but some components of the Stoddard solvent mixture such as alkanes, substituted benzenes, and naphthalenes have been detected in groundwater and surface water samples (CLPSD 1989). However, the presence of these compounds does not necessarily imply contamination by Stoddard solvent.

### 5.2.3 Soil

Stoddard solvent is not listed in the CLPSD of chemicals detected in soil samples taken only at NPL sites; however, while Stoddard solvent, as a hydrocarbon mixture, is not included as a target chemical, some components such as alkanes, substituted benzenes, and naphthalenes have been detected in soil samples (CLPSD 1989). However, the presence of these compounds does not necessarily imply contamination by Stoddard solvent.

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### 5.3 ENVIRONMENTAL FATE

#### 5.3.1 Transport and Partitioning

The transport and partitioning of Stoddard solvent is dependent on the environmental fate of its hydrocarbon components. Based on Mackay's equilibrium partitioning model using low concentrations (below maximum aqueous solubility) of Stoddard solvent, sorption to organic matter in soil or water is a major partitioning process for all hydrocarbon classes (alkanes, cycloalkanes, and aromatics) with partitioning to the soil-vapor phase being relatively unimportant. At low concentrations, the aromatic constituents of Stoddard solvent, particularly the alkyl benzenes, are more water soluble than alkanes and cycloalkanes and may dissolve in infiltrating water with a minimum of volatilization. As such, the model indicates, they may be transported through soil into the underlying groundwater, although sorption to soil organic matter will retard this leaching process. For saturated deep soils that contain no oxygen and little organic matter, the model predicts that some (20%) aromatic hydrocarbons will not undergo biodegradation, but will be dissolved in the soil-water phase, and subsequently will be transported to underlying groundwater (Air Force 1989b).

If a release of Stoddard solvent exceeds the sorptive capacity of the soil, the equilibrium partitioning model is no longer applicable. Large quantities of Stoddard solvent may move through the soil with gravity as bulk fluid and enter the groundwater. At the soil/groundwater interface, the soluble components can dissolve in the water, while insoluble components with specific gravities of less than 1 will float on top of the water table and move horizontally along the soil/water interface (Air Force 1989a). In addition, horizontal movement of Stoddard solvent through the soil, particularly through cracks and fissures in the soil material, is possible if the concentration is large enough to exceed the sorptive capacity of the soil or if the release has occurred below the surface of the soil (for example from a leaking underground storage tank).

Alkanes are likely to be sorbed to organic matter in the soil and are, therefore, unlikely to be dissolved in water moving through soil. However, some of these compounds may volatilize more quickly than they will bind to organic matter. Most aliphatic hydrocarbons have low water solubilities, but those with higher water solubilities are likely to be dissolved in water and may be transported through soil more rapidly, although the extent may be reduced by sorption to organic matter or volatilization (Air Force 1989a).

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Laboratory studies have shown that mineral spirits are sorbed by fresh snow with a mean sorption ratio of 1.5 g mineral spirits/g snow. This would indicate that if a spill occurred on a snow-covered site, not only would sorption to soil be decreased if the ground were frozen, but drainage from the site would be decreased due to snow sorption (Marte and Nadeau 1994). When the snow melted, the solvent would be expected to be transported in the same way as the melted snow.

No information was found on the bioaccumulation potential of Stoddard solvent in either aquatic or terrestrial ecosystems. However, the potential for bioaccumulation of Stoddard solvent in either ecosystem is dependent on the bioaccumulation potential of the individual hydrocarbon components. In general, lower molecular weight alkanes do not tend to bioaccumulate, aromatics may have a moderate tendency to bioaccumulate, and the higher molecular weight alkanes, such as cycloalkanes, tend to bioaccumulate (Air Force 1989a). However, these bioaccumulation tendencies may not be true for all compounds within a class. Water-soluble aliphatics and aromatics may be expected to have low bioconcentration factors based on their octanol-water partition coefficients (Menzer 1991). Although no information is available on the bioconcentration of Stoddard solvent directly, aquatic organisms have been found to bioconcentrate some of the hydrocarbons found in fuel oils, many of which are also found in Stoddard solvent. Mussels exposed to fuel oil no. 2 were found to have significantly increased concentrations of alkanes, cycloalkanes, and aromatics in their tissue on the first day of exposure although by day 5 after removal from exposure, the n-alkanes were barely detectable and by day 21, concentrations of a mixture of alkanes and cycloalkanes had decreased to 30% of the day 1 concentrations. Aromatic hydrocarbons decreased more slowly, to about 35% of the day 1 value at 21 days. The half-life of naphthalenes substituted at C-2 and C-3 were 0.9 and 1.5 days, respectively (Farrington et al. 1982).

### 5.3.2 Transformation and Degradation

#### 5.3.2.1 Air

Volatilization from soil and surface waters with subsequent rapid photooxidation in the atmosphere is expected to be an important fate process for several constituents of Stoddard solvent based on its vapor pressure of 3.0 mmHg (at 20°C) and also, by analogy, based on the environmental fate of jet fuel 4 (JP-4), which contains similar classes of hydrocarbons (Air Force 1989a). This is particularly true for the alkane constituents of Stoddard solvent with low water solubilities. Low ambient temperatures

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tend to reduce the volatilization process. Other less volatile constituents of Stoddard solvent, such as alkylbenzenes, are more likely to be affected by processes such as sorption or biodegradation.

### 5.3.2.2 Water

The C<sub>5</sub>-C<sub>9</sub> hydrocarbon components of Stoddard solvent released to surface waters are primarily lost by evaporation to the atmosphere. Higher-molecular-weight hydrocarbon components are most likely to undergo biodegradation. Microorganisms capable of degrading these hydrocarbons have been found in surface waters (Air Force 1989a). In aquatic environments, C<sub>10</sub>-C<sub>25</sub> *n*-alkanes are degraded by microorganisms, although biodegradation decreases as the hydrocarbons become more complex (Edgerton 1987). Cometabolism by bacterial species may occur, but the transformation is generally slow and its rate does not increase over time (Alexander 1994).

In aqueous environments, photooxidation of trisubstituted benzenes and naphthalenes may be quite rapid, while alkanes, benzenes, and monosubstituted benzenes are relatively resistant to photooxidation (Air Force 1989a).

### 5.3.2.3 Soil

Stoddard solvent released to soil surfaces will undergo “weathering” over time that will result in changes in the concentrations of the constituent hydrocarbons. A high percentage of low-molecularweight hydrocarbons (such as C<sub>5</sub>-C<sub>9</sub> alkanes and aromatics), if not sorbed, are likely to evaporate from soil rather than be biodegraded (Air Force 1989a). Loss of higher-molecular-weight aliphatic and aromatic constituents of Stoddard solvent will occur by both slow evaporation and by biodegradation. Soil microorganisms may degrade certain components of Stoddard solvent, with the rate of biodegradation being fast for low-molecular-weight aromatics. Biodegradation is often slower for aliphatic hydrocarbons that are branched or cyclic or that contain 10 or more carbons. The length of time required to achieve total degradation of Stoddard solvent may be substantial as demonstrated by the degradation of another petroleum distillate, fuel oil no. 2, which was degraded by 86-90% after 1 year (Raymond et al. 1975, 1976). Sometimes, a small residual fraction may persist for many years.

Oxygen is used as an electron acceptor for microbial respiration and is a direct reactant in oxic hydrocarbon oxidation (Lovley et al. 1994). In contaminated ground waters, oxygen may be added to

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enhance biodegradation. Anoxic conditions can occur after contamination of ground water. Water-soluble aromatic hydrocarbons can be degraded under anoxic conditions, although the rate of degradation will be slower than under aerobic conditions (Lovley et al. 1994).

Fe(III) oxides can act as electron acceptors during the biodegradation of aromatic hydrocarbons in shallow aquifers; however, these Fe(III) oxides are frequently not bioavailable to microorganisms. The addition of organic ligands, which bind Fe(III) and thus increase the bioavailability of Fe(III), has been reported to increase the rate of biodegradation of aromatic hydrocarbons (including benzene) under anoxic conditions (Lovley et al. 1994). Thus, the use of Fe(III) ligands might be valuable in the bioremediation of hydrocarbon-contaminated, anoxic aquifers (Lovley et al. 1994). However, the effects on the biodegradation of Stoddard solvent or its constituents, such as alkylbenzene, are not known.

Stoddard solvent, applied to soil at a toxic concentration of 100 gallons per acre, reduced the number of soil microorganisms by more than half (Persidsky and Wilde 1956), indicating that in areas contaminated with high concentrations of Stoddard solvent, biodegradation rates may be decreased.

In order to determine the potential hazard to operators of landfill sites where solvents may be disposed, the evaporation of white spirits (Stoddard solvent) from a simulated landfill site (using pulverized domestic waste) was studied. Evaporation of Stoddard solvent from the landfill was compared with its evaporation from a holding lagoon (using a liquid pool of the solvent). The volatile components of Stoddard solvent initially evaporated rapidly from both sites, although the rate of evaporation was much greater from the waste site. After 6 hours, the loss of solvent from the waste was still twice that from the pool of liquid, suggesting that land application may pose a greater initial hazard to site operators from fumes than would disposal by lagooning; however, other disposal methods, such as incineration, are preferred (Jones and McGugan 1977).

### 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

#### 5.4.1 Air

Stoddard solvent per se is not monitored in air; its volatile components, such as low-molecular-weight alkanes and aromatics, are more likely to be detected as individual compounds in the air.

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Stoddard solvent, used in industrial paints for dump trucks, was present in the paint booth at concentrations between 7.0 and 12.0 ppm (41.2-70.7 mg/m<sup>3</sup>) as determined by personal sampling apparatus; however, this was considerably below the threshold limit value (time-weighted average) of 100 ppm for occupational safety (Bradley and Bodsworth 1983).

The use of hazardous wastes as fuel for industrial and commercial boilers may result in significant population exposures to hazardous air emissions, particularly when compared with disposal in incinerators regulated under the Resource Conservation and Recovery Act (RCRA) which must achieve a removal efficiency of at least 99.99%. Using EPA's population exposure and air dispersion models, the potential population exposure was measured for five combustion scenarios (one commercial incinerator and four boilers with varying capacities and destruction efficiencies) using Stoddard solvent and the trimethylbenzene component of Stoddard solvent as potential industrial waste streams. Modeling results showed that the greatest exposure to emissions and the highest emission concentrations were generated by a 15-million British thermal unit (Btu) boiler operating at 97.0% destruction capacity. Under this scenario, the highest concentrations of Stoddard solvent and trimethylbenzene to which people would be exposed were 103 µg /m<sup>3</sup> and 15.4 µg/m<sup>3</sup>, respectively. By comparison, a 75million Btu incinerator operating at 99.99% destruction and removal efficiency would expose people to concentrations several orders of magnitude less (exact number unspecified) (Coyle and Potenta 1983).

### 5.4.2 Water

No information was located on levels of the Stoddard solvent as a hydrocarbon mixture monitored in surface or groundwater. Although some hydrocarbon components of Stoddard solvent have been detected in water samples, it is not evident whether the source was a release of Stoddard solvent or some other hydrocarbon mixture or compound.

### 5.4.3 Soil

No monitoring studies for Stoddard solvent as a hydrocarbon mixture in soil were located. Although some hydrocarbon components of Stoddard solvent have been detected in soil samples, it is not evident whether the source was a release of Stoddard solvent or some other hydrocarbon mixture or compound.

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### 5.4.4 Other Environmental Media

No monitoring studies for Stoddard solvent in other environmental media were located.

### 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

According to the National Occupational Exposure Survey conducted from 1981 to 1983 by NIOSH, 1,922,235 employees (including 230,356 females) in 404 plants were potentially exposed to Stoddard solvent in the workplace (NOES 1992). Most exposure was for persons employed as cleaners or janitors. It is expected that workers who use Stoddard solvent as a degreasing agent or who work in dry cleaning establishments or print shops where it is used as a solvent may have significant exposure potential.

Transport of Stoddard solvent through soil and into groundwater may result in general population exposure through the ingestion of contaminated drinking water or through inhalation or dermal exposure during showering or bathing. Inhalation exposure may also result from the volatilization of Stoddard solvent components from contaminated soil, including the diffusion of volatile components through soil and into the basements of buildings (Air Force 1989b).

Use of Stoddard solvent in dry cleaning may result in the occupational exposure of workers in these establishments, either through inhalation or dermal exposure (Air Force 1989b). The use of Stoddard solvent (mineral spirits) in commercial paints may result in inhalation exposure, particularly if the paint is applied with a sprayer (Fidler et al. 1987), as well as dermal exposures if protective clothing is not worn (Air Force 1989b).

### 5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

No studies were-located regarding populations with potentially high exposures; however, it is possible that persons living or working near facilities that use Stoddard solvent may receive exposure to the more volatile components.

Use of Stoddard solvent for painting and in printing inks increases the likelihood of exposure by painters and others who work in areas where Stoddard solvent is used. In addition, people who use

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commercial products such as degreasers and paints which contain Stoddard solvent may also be exposed by inhaling solvent vapors or by dermal contact with the product. Use of a respirator and good ventilation can reduce exposure to the solvent vapors and protective clothing will help prevent dermal contact.

### 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 Stoddard solvent 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 Stoddard solvent.

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.

#### 5.7.1 Identification of Data Needs

**Physical and Chemical Properties.** More information on the exact identity and properties of each of the various formulations that are called Stoddard solvent would make it easier to distinguish the toxicity and environmental effects caused by Stoddard solvent and to trace its fate based on levels of distinguishing components, if any. Identification of components or ratios between different components that may be used to distinguish Stoddard solvent from other hydrocarbon mixtures in waste streams or other applications would be useful. See Table 3-3 for more information on possible formulations of Stoddard solvent.

**Production, Import/Export, Use, and Release and Disposal.** Data on the potential for human exposure are limited (Air Force 1989b; NOES 1992). Further information on current uses, production

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volumes, and releases of Stoddard solvent from industrial uses or as a result of its disposal would be helpful in assessing the potential risk of exposure to this compound.

**Environmental Fate.** Stoddard solvent partitions to the various environmental compartments according to the physical/chemical properties of its individual components. Major fate processes include volatilization of low molecular weight alkanes and aromatics with photooxidation in the atmosphere, sorption to soil and water organic matter for cycloalkanes and longer chain alkanes, and dissolution of aromatic hydrocarbon constituents in water (Air Force 1989b). Biodegradation in soils may be significant for the aliphatic and aromatic hydrocarbon components of Stoddard solvent that are not primarily lost by evaporation (Air Force 1989a). The behavior of Stoddard solvent upon release to the environment has not been well characterized. Limited information is available on the environmental fate of the three hydrocarbon classes (linear and branched alkanes, cycloalkanes, and aromatics) that comprise Stoddard solvent, although further study on the interactions of these classes, particularly over time, would be useful in assessing the persistence and degradation of Stoddard solvent in the environment. More data would be helpful on the use of Fe(III) ligands to increase biodegradation of Stoddard solvent or its components under anoxic conditions in contaminated aquifers. In addition, fate information regarding sorption to organic material in soil and water, derived from the use of an equilibrium partitioning model, should be experimentally verified.

**Bioavailability from Environmental Media.** Since the factors characterizing the absorption of Stoddard solvent are not known for humans or animals, the bioavailability is also unknown. There are no data on whether Stoddard solvent released to soil or water will be absorbed by humans or animals through contact with contaminated media. It is expected that the alkylbenzene components of Stoddard solvent, being more water soluble than the alkanes and cycloalkanes, will be more readily available for adsorption from contaminated waters. In addition, there are also no data to indicate whether plants grown on contaminated soil or fish living in contaminated water are likely to absorb Stoddard solvent or its constituents and thus enter the food chain. More data on possible rates and extent of absorption through the inhalation, oral, and dermal routes would be useful in determining bioavailability from environmental media.

**Food Chain Bioaccumulation.** No information was found on the bioaccumulation potential of Stoddard solvent in either terrestrial or aquatic ecosystems; however, the individual components making up the mixture may bioaccumulate depending on their individual properties. In general,

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polycyclic aromatic compounds may have the greatest tendency to bioaccumulate (Air Force 1989a). Because these compounds account for such a small percentage of the mixture, bioaccumulation is not expected to be a major exposure pathway for humans (Air Force 1989b). Research on the biomagnification of Stoddard solvent would not be useful because it is not available to the food chain as a mixture. It is possible that research on the biomagnification of some Stoddard solvent components for which there is sparse data would be useful.

**Exposure Levels in Environmental Media.** There are very limited exposure data for air concentrations of Stoddard solvent in areas where it is used as an industrial paint solvent (Bradley and Bodsworth 1983). More data on levels in air resulting from other uses or storage or disposal would be useful. Data on levels in contaminated surface water, groundwater, and soil are needed to assess the potential risk from these likely sources of exposure.

**Exposure Levels in Humans.** Since characteristic ratios of the components of Stoddard solvent have not yet been determined, monitoring information based on these ratios in the workplace or for the general population is not available. Monitoring surveys that examine levels of Stoddard solvent in the workplace and for the populations living or working in the vicinity of manufacturing or industrial use sites, or near disposal, dump, or leakage sites would be useful in determining approximate levels of exposure for these populations, although there may be difficulties in distinguishing exposure to Stoddard solvent versus other hydrocarbon mixtures, e.g., fuel oils or naphthas. Such distinctions may be based on ratios of hydrocarbon components and determination of actual use of Stoddard solvent.

**Exposure Registries.** No exposure registries for Stoddard solvent 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 the exposure to this substance.

### 5.7.2 On-going Studies

No on-going studies were located.