

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Pyridine is an organic liquid with an unpleasant odor; it is very soluble in water. It is released to the environment from industrial sources that manufacture and use it and as fugitive emissions from facilities such as coal gasification and oil shale processing. Pyridine may be removed from the atmosphere by photooxidation or wet deposition (precipitation). Pyridine in water is unlikely to volatilize appreciably, but may sorb to soils and sediments or biodegrade. Bioconcentration of pyridine in aquatic organisms is not likely to be important.

Pyridine has rarely been detected in ambient air, water, or soil, except in the vicinity of industrial sources. Several foods may contain pyridine, and ingestion of these foods is the most likely route of pyridine exposure for the general population. Occupational exposure to pyridine may be high. Populations living in the vicinity of hazardous waste sites where pyridine has been detected may also be exposed. The EPA has identified 1,177 NPL sites. Pyridine has been found at 4 of the sites evaluated for this chemical. However, we do not know how many of the 1,177 NPL sites have been evaluated for this chemical. As more sites are evaluated by the EPA, the number may change (View 1989). The frequency of these sites within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

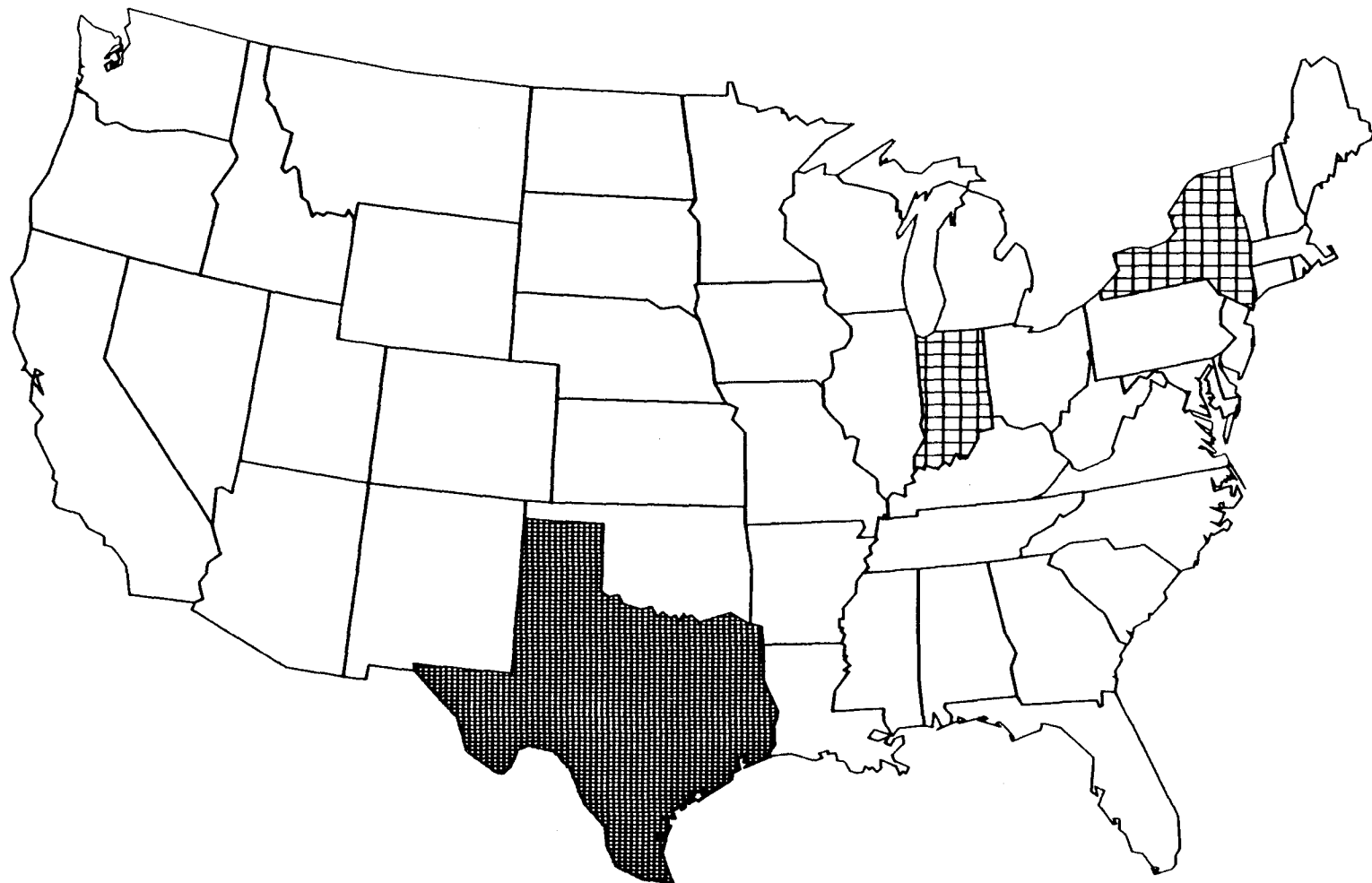
Manufacturers, processors, and users of pyridine are required to report quantities of releases of this substance to environmental media annually (EPA 1988a). According to the SARA Section 313 Toxics Release Inventory (TRI), an estimated total of 635,374 pounds of pyridine were released to the environment from manufacturing and processing facilities in the United States in 1987 (TRI 1989). The TRI data should be used with caution since the 1987 data represent first-time reporting by these facilities. Only certain types of facilities were required to report. This is not an exhaustive list. The 28 facilities reporting releases in 1987 are presented in Table 5-1.



Additional releases of pyridine may occur from oil shale processing and coke oven facilities, but these releases are not included in the TRI. Releases of pyridine relevant to specific media are discussed below.

5.2.1 Air

Pyridine is released to the atmosphere from facilities that manufacture and use this compound and from oil shale processing and coke oven facilities. Releases of an estimated 298,438 pounds of pyridine to air from domestic industrial sources were reported in 1987 (TRI 1989). Atmospheric emissions of pyridine from shale oil waste waters ranged from 0.44 to 30 $\mu\text{g/mL}$ of wastewater (Hawthorne and Sievers 1984).

FIGURE 5-1. FREQUENCY OF NPL SITES WITH PYRIDINE CONTAMINATION *



FREQUENCY  1 SITE  2 SITES

* Derived from View 1989

TABLE 5-1. Releases to the Environment from Facilities That Manufacture or Process Pyridine*

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW ^b transfer	Off-site transfer
Arkansas Eastman Company	Batesville, AR	4,400	0	570	0	4,970	No Data	0
Pfizer Inc. Groton Site	Groton, CT	0	0	0	0	0	0	250
Eli Lilly And Company Clinton Laboratories	Clinton, IN	3,250	0	250	250	3,750	0	0
Reilly Tar & Chemical Corporation	Indianapolis, IN	31,009	0	0	2	31,011	57,225	3,906
Air Products & Chemicals, Inc.	Wichita, KS	250	250	No Data	No Data	500	No Data	No Data
Union Carbide Corporation Industrial Chemicals	Hahnville, LA	884	No Data	0	0	884	0	0
Olin Corporation Lake Charles Plant	Lake Charles, LA	500	0	500	250	1,250	0	250
Dow Chemical Louisiana Division	Plaquemine, LA	0	0	1,900	0	1,900	0	0
The Upjohn Company Portage Site	Portage, MI	13,250	43,400	0	0	56,650	No Data	0
Burroughs Wellcome Co. Kollman	Greenville, NC	121,700	0	0	0	121,700	250	297,000
Hoffmann-La Roche Inc. Nepera, Inc.	Merrimack, NH	0	0	0	0	0	0	0
Eastman Kodak Company Kodak Park	Nutley, NJ	5,100	0	0	27,900	33,000	0	No Data
Olin Corporation	Harriman, NY	10,022	0	0	0	10,022	0	0
The Wool Bureau, Inc.	Rochester, NY	17,800	0	610	4	18,414	0	0
Du Pont Circleville Plant	Rochester, NY	19,890	0	0	0	19,890	12,610	0
Orsynex	Woodbury, NY	0	0	0	0	0	250	0
Bp Chemicals America, Inc.	Circleville, OH	28,760	0	50	No Data	28,810	No Data	33,150
American Cyanamid Company	Columbus, OH	1	0	0	0	1	0	20,000
New Boston Coke Corporation	Lima, OH	250	260,000	0	250	260,500	0	0
The Upjohn Company	Marietta, OH	250	0	0	0	250	0	0
Schering Industrial Development Corporation	New Boston, OH	163	No Data	0	0	163	0	0
Tennessee Eastman Company	Barceloneta, PR	500	0	0	0	500	0	0
Monsanto Company	Manati, PR	500	0	0	0	500	250	0
Ici Americas Inc. Bayport Site	Kingsport, TN	2,434	0	390	0	2,824	0	0
Dan River Inc. Chemical Products Division	Alvin, TX	0	0	0	0	0	0	0
Rhone-Poulenc Incorporated Ag Company	Pasadena, TX	21,958	0	0	0	21,958	139,295	0
Totals	Danville, VA	12,250	0	0	0	12,250	0	0
	Institute, WV	3,317	0	360	No Data	3,677	0	0
		298438	303650	4630	28656	635374	209880	354556

*Derived from TRI 1989

^bPOTW -- publicly-owned treatment works

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5.2.2 Water

Releases of pyridine to ambient waters have been reported. Industrial releases to surface water and groundwater (underground injection) reported in 1987 were estimated to be 4,630 pounds and 303,650 pounds, respectively (TRI 1989). In addition, 209,880 pounds of pyridine were disposed of in publicly owned treatment works (POTWs) in 1987 (TRI 1989). Some fraction of the quantity treated at POTWs is probably released to the environment. Pyridine was detected in one of two oil shale processing effluents at a concentration of 152 $\mu\text{g/L}$ (ppb), but not in coal gasification plant effluents (Pellizzari et al. 1979). It was also detected in effluents from coke-oven quenching operations at 11 mg/L (EPA 1982b) and detected, but not quantified, in four industrial effluents (Shackelford and Keith 1976). Pyridine was also found in oil-shale retort water in Australia at a concentration of about 5 mg/L (Dobson et al. 1985).

Data from the Contract Laboratory Program (CLP) Statistical Database indicate that none of the hazardous waste sites sampled were positive for pyridine in surface water or groundwater (Eckel 1990).

5.2.3 Soil

Pyridine releases to land from industrial sources totalled an estimated 28,656 pounds in 1987 (TRI 1989). Additional releases of pyridine to soil may occur from spillage of oil shale waste waters on land surfaces (Leenheer and Stuber 1981). No other information was located on pyridine releases to soil. Pyridine was not detected in soil samples from hazardous waste sites (Eckel 1990).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Pyridine exists in the atmosphere as a vapor. Its vapor pressure is approximately 0.027 atm (20.6 mmHg) at 25°C (Chao et al. 1983). Because of its high water solubility, a large fraction of vapor-phase pyridine released to the atmosphere would tend to dissolve in water vapor (such as clouds and rain drops). A Henry's law constant estimates the tendency of a chemical to partition between its vapor state and water. The Henry's law constant for pyridine was measured as $1.1 \times 10^{-5} \text{ atm}\cdot\text{m}^3\cdot\text{mole}^{-1}$ at 25°C for aqueous solutions (5 mg/L) (Hawthorne et al. 1985). The magnitude of this value indicates that much of the pyridine in the atmosphere is removed by wet deposition (precipitation).

Pyridine is highly soluble in water (Jori et al. 1983). The magnitude of Henry's law constant ($1.1 \times 10^{-5} \text{ atm}\cdot\text{m}^3\cdot\text{mole}^{-1}$ for aqueous solutions) suggests that pyridine in water will not volatilize into the atmosphere quickly. In addition, the equilibrium partitioning of pyridine between water and air was

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found to be influenced by the pH of the water; a decrease in pH resulted in less partitioning from solution (Hakuta et al. 1977). The rate of pyridine volatilization from water has not been experimentally measured.

Pyridine in water may partition to soils and sediments to an extent that depends on the pH of the water, and to a lesser extent, the organic-carbon content of the soil. Pyridine is a weak organic base in solution; its ionization constant is 5.23×10^{-6} at 20°C (Albert et al. 1948). Consequently, pyridine is predominantly in a cationic electrolyte form (pyridinium ion) in acidic solutions, whereas it is a neutral molecule in alkaline media.

The extent of pyridine adsorption by pure-clay minerals was greatest in the pH range of 4-5.5, whereas adsorption was negligible in alkaline solutions (pH greater than 7) (Baker and Luh 1971). The magnitude of pyridinium adsorption was correlated with the cation-exchange capacity of the clays. The rate of pyridinium desorption from the clays was slower than that of adsorption (Luh and Baker 1971).

Pyridine was weakly adsorbed by sandstone at 38°C (Donaldson et al. 1975), but these authors did not report any pH measurements. Pyridine adsorption by an alkaline soil was negligible (Felice et al 1984); Zachara et al. (1987) also found that pyridine adsorption was more significant in acidic soils because of salt formation.

The extent of adsorption of neutral organic molecules by soils is often correlated with the organic-carbon content of the soil (Hassett et al. 1983). When adsorption is expressed as a function of organic-carbon content, an organic carbon/water partition coefficient (K_{oc}) can be calculated and may be used to classify the relative mobility of the chemical in soil. Based on its octanol-water partition coefficient (Table 3-2), an estimated K_{oc} for pyridine is 7 (Roy and Griffin 1985). An experimentally derived K_{oc} of about 40 can be calculated from the adsorption data in Zachara et al. (1987). As compared with K_{oc} values listed for other compounds, these low K_{oc} values suggest that pyridine is very highly mobile in soil, whereas pyridine as pyridinium will be less mobile, particularly in acidic soils.

Pyridine may not partition to organisms in water. An octanol/water partition coefficient (K_{ow}) estimates the likelihood of a chemical to partition to organisms in an aquatic environment. Octanol is believed to best imitate the fatty structures in plants and animal tissues (Kenaga and Goring 1980). The K_{oc} of pyridine has been measured as 4 (Leo et al. 1971). This low value indicates that pyridine will not partition to fatty tissues in plants or animals.

A bioconcentration factor (BCF) relates the concentration of a chemical in the tissues of aquatic organisms to the concentration of the chemical in the media in which they live. BCFs for pyridine have not been experimentally measured, but they may be less than 5, based on the empirical regressions of

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Kenaga (1980) and Neely et al. (1974). These low BCFs suggest that pyridine is probably not bioconcentrated by aquatic plants and animals and therefore probably not biomagnified in terrestrial or aquatic food chains.

5.3.2 Transformation and Degradation

5.3.2.1 Air

Atmospheric pyridine may be slowly photodegraded by hydroxyl radicals in the troposphere. The rate constant for this reaction at 23°C has been measured as 5×10^{-13} cm³/molecule-s, and the estimated atmospheric life time of pyridine may range from 23 to 46 days, depending on the concentration of hydroxyl radicals (Atkinson et al. 1987). Reaction by-products were not studied. It appears that the rate of ozone-initiated decay of pyridine is too slow to be an important mechanism for removing pyridine from the atmosphere. The decay rate of pyridine by ground-state oxygen (O(³P)) has been measured as 1.7×10^{-13} cm³/molecule-s (Mani and Sauer 1968). If the mean concentration of ground-state oxygen radicals is 5×10^{-4} molecules/cm³ (Cupitt 1980), then the half-life of this reaction (2.6 years) may also be too slow to be important.

5.3.2.2 Water

Biodegradation may be the most important mechanism that can degrade pyridine in water. Pyridine may oxidize in water, but the reactions are very slow. The rate constant for pyridine oxidation by alkylperoxy radicals (RO₂) was estimated as approximately 0.67/M-s at 50°C (Mill et al. 1979). Because of the low concentration of these radicals in photolyzed natural waters, the half-life of this reaction may be on the order of decades. The rate constant for hydroxyl radical-initiated decay in water has been measured as 1.8×10^9 /M-s at 21°C, pH 7 (Dorfman and Adams 1973). radicals is 10^{-17} mole/L (Mill et al. If the mean concentration of hydroxyl 1979), the half-life of this reaction would be about 1.2 years. No information was located that suggests that pyridine hydrolyzes in water nor should it be anticipated from its chemical structure.

Most pyridine biodegradation studies have been concerned with transformations in soils and sewage sludges (see Section 5.3.3). In a study of pyridine biodegradation in unfiltered river water, the rate of removal depended on the initial concentration of pyridine, but in general, at lower concentrations (less than 20 mg/L), pyridine degradation was virtually complete in 8 days or less (Cassidy et al. 1988). No information concerning the microorganisms present in the water was given, but this study suggests that biodegradation may be a much more rapid mechanism for the removal of pyridine from the environment than are abiotic mechanisms.

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5.3.2.3 Soil

It is very likely that pyridine biodegrades in soils and sewage sludges, but the rate and extent of the process is uncertain. Pyridine has been found to biodegrade readily in laboratory-screening tests (Gerike and Fischer 1979, 1981; Ruffo et al. 1984). For example, about 94%-100% of the pyridine added to municipal wastewater biodegraded in 2-21 days, depending on the specific test procedure used. Other studies have reported that pyridine biodegraded in sewage water or sludge, but that the process was slow (Battersby and Wilson 1989; Cooper and Catchpole 1973; Ettinger et al. 1954; Gomolka and Gomolka 1978; Malaney 1960). For example, pyridine was found to be only partially degraded in dilute sewage sludge, and the process required a month before significant removal was detected (Battersby and Wilson 1989).

There is evidence that pyridine can be biodegraded in soil. A branching bacteria (Proactinomyces) that can utilize pyridine as a sole-source of carbon and nitrogen, and energy has been isolated (Moore 1949). Pyridine was biodegraded in an aqueous extract of a garden soil, but the process was slow (Naik et al. 1972). Complete degradation under aerobic conditions required 66-170 days, whereas 1-2 months were required under anaerobic conditions. However, in a soil incubated with low concentrations of pyridine, the compound was completely degraded in about 8 days (Sims and Sommers 1985). The half-life of the process was approximately 3 days.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Pyridine has not been detected in ambient outdoor air, except in the vicinity of industrial sources. Pyridine was not found in rural or urban air (Hawthorne and Sievers 1984; Shah and Heyerdahl 1988). However, pyridine was detected at a concentration of 13 $\mu\text{g}/\text{m}^3$ in air in the vicinity of an oil shale wastewater facility (Hawthorne and Sievers 1984; Shah and Heyerdahl 1988). Pyridine was also present in indoor air at the same oil shale facility at a concentration of 41 $\mu\text{g}/\text{m}^3$ (Hawthorne and Sievers 1984). The concentration of pyridine in indoor air contaminated with cigarette smoke may be as high as 16 $\mu\text{g}/\text{m}^3$ (Brunnemann et al. 1991).

Pyridine has been detected in workplace air at pyridine manufacturing plants and chemical plants using pyridine as an intermediate at time-weighted average (TWA) concentrations ranging from 0.02 to 3.2 mg/m^3 (EPA 1982b).

5.4.2 Water

Pyridine is rarely detected in ambient waters. It was present in surface water of the Cuyahoga River in Ohio (IJC 1983). The compound was not detected in groundwater samples in Wyoming (detection limit 0.1-0.5 ppb) (Pellizzari et al. 1979; Stuermer et al. 1982). However, it was detected in

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groundwater 15 months after completion of coal gasification activities at a Wyoming site at concentrations ranging from 0.82 to 53 ppb (Stuermer et al. 1982). Pyridine was detected in 2 of 17 drinking water concentrates (Lucas 1984).

5.4.3 Soil

No information was located on pyridine concentrations in ambient soils. Pyridine was detected in creosote-contaminated sediments in Puget Sound, Washington at a concentration of 0.22 µg/g (Krone et al. 1986).

5.4.4 Other Environmental Media

Pyridine may be present in foods from both natural and anthropogenic sources. Pyridine was detected among the natural volatile components of several foods, including fried chicken, Beaufort cheese, sukiyaki, fried bacon, and frozen mango (Dumont and Adda 1978; Ho et al. 1983; MacLeod and Snyder 1988; Shibamoto et al. 1981; Tang et al. 1983). The concentration was reported only for mango at 1.0 µg/g (MacLeod and Snyder 1988). Pyridine is approved by the Food and Drug administration (FDA) for use as a flavoring agent (Table 7-1) and, therefore, may be present in other foods as well. Pyridine has also been identified as a component of tobacco smoke (Curvall et al. 1984; Florin et al. 1980; Riebe et al. 1982) and is a coffee aroma constituent (Aeschbacher et al. 1989).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Humans may be exposed to pyridine by inhalation, ingestion, or dermal contact. However, in the United States the general population is most likely to be exposed to pyridine by the ingestion of foods naturally containing this compound or, possibly, by inhalation of tobacco smoke. EPA (1978) reported that total pyridine is estimated to be ingested in the United States at about 500 mg/year, per person, mainly from food. The presence of pyridine in expired air is not necessarily an indicator of exposure to this chemical since pyridine has been detected in the expired air (detection limits not specified) of nonsmoking subjects described as prediabetic (i.e., nine offspring of diabetic parents and five subjects having one diabetic parent and several diabetic relatives) (Krotoszynski and O'Neill 1982). Pyridine was not detected in the expired air of 20 nonsmoking control (nondiabetic) or 28 diabetic subjects.

The greatest potential for exposure to pyridine occurs in the workplace. Occupational exposures, usually by inhalation or dermal absorption, may occur during pyridine production or its use as a chemical intermediate or solvent (Santodonato et al. 1985). Additional exposures may occur at coke-oven and oil-shale processing facilities. Reported workplace TWA concentrations range from 0.02 to 3.2 mg/m³ (ppm) (EPA 1982b), but these data do not include cokeoven plants. It has been estimated that maximum long-term workplace exposures

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to pyridine will not exceed 3.2-16 mg/m³, except for possible brief exposures to higher concentrations (Santodonato et al. 1985). The National Institute for Occupational Health and Safety (NIOSH) estimated that the number of workers exposed to pyridine increased from about 29,000 during the early 1970s (NOHS 1990) to about 41,000 during the early 1980s (NOES 1990). These estimates also do not include workers at coke-oven plants. Neither the NOHS nor the NOES databases contain information on the frequency, concentration, or duration of exposure of workers to any of the chemicals listed therein. These surveys provide only estimates of the number of workers potentially exposed to chemicals in the workplace.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers in industrial facilities that manufacture, use, or produce fugitive emissions of pyridine have the highest potential for exposure to this compound. Other populations with potentially higher than average exposure are those living in the vicinity of these facilities or of hazardous waste sites at which pyridine has been identified.

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 pyridine 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 pyridine.

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. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Data Needs

Physical and Chemical Properties. Most of the physical/chemical properties required to predict the environmental fate and transport of pyridine have been measured. However, it appears that the volatility and sorption of pyridine from water varies considerably with the pH of the water (Baker and Luh 1971). Additional data on the effect of pH on the Henry's law constant, volatilization rate, and K_{oc} would be useful to predict more accurately the environmental fate of pyridine.

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Production, Import/Export, Use, and Disposal. Information is generally available regarding the production, use, and disposal of pyridine in commercial facilities (Harper et al. 1985; HSDB 1989). The production locations, major uses, and disposal methods have been identified, and land disposal of pyridine is restricted by EPA. However, current production, import, and disposal volumes were not located. Releases from manufacturing and use facilities are reported in the TRI, but fugitive emissions from cokeoven and oil-shale processing facilities have not been reported. These data would be useful in evaluating both occupational exposures and exposures of the populations living in the vicinity of these facilities.

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 1987, became available in May of 1989. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. The available data are insufficient to predict accurately the environmental fate of pyridine. Pyridine most likely partitions to soils and sediments and from the atmosphere to water vapor. Additional data regarding the K_{oc} of pyridine, especially in nonacidic environments, would be useful in confirming the likelihood of pyridine partitioning among environmental media.

Data on transport and degradation are limited. Data on the composition and fate of the products of the atmospheric photodegradation of pyridine would enhance our understanding of the atmospheric fate of this compound, and additional studies on the biodegradation of pyridine in water and soil would be helpful in evaluating the fate of pyridine in these media.

Bioavailability from Environmental Media. Pyridine is very soluble in water (Sax and Lewis 1987). Human and animal data indicate that it is well absorbed by the oral route (D'Souza et al. 1980). It is expected to be available when it is present in natural waters. Under acidic conditions, it will adsorb to soils and sediments to some degree (Baker and Luh 1971). However, ingestion of soil-bound pyridine is an unlikely route of exposure. Information on dermal absorption from water would be useful in assessing the potential effects of recreational use of natural waters contaminated with pyridine. Information on absorption of inhaled pyridine released to the air would also be useful in assessing its bioavailability from that medium.

Food Chain Bioaccumulation. Because of pyridine's low K_{ow} (Verschueren 1983) and high water solubility (Sax and Lewis 1987), it probably will not bioconcentrate in plants, aquatic organisms, or animals. However, no data on bioconcentration factors or biomagnification in terrestrial or aquatic food

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chains were located. Additional information on bioconcentration and biomagnification is needed to confirm the predicted limited importance of these processes in the environmental fate of pyridine.

Exposure Levels in Environmental Media. Although pyridine has been identified in air, water, and sediments, data regarding pyridine concentrations in environmental media are sparse. The available data are insufficient to evaluate the potential for human exposure to this compound; therefore, human intake levels of pyridine from environmental media have not been estimated. Additional monitoring data for this compound in all media in the vicinity of identified potential pollution sources and at hazardous waste sites would be useful in assessing the potential for human exposure. In addition, identification and monitoring of those foods to which pyridine is added as a flavoring agent would increase the accuracy of estimates of human intake by this route of exposure.

Exposure Levels in Humans. It would be useful to collect information on levels of exposure to pyridine in the environment that are associated with blood, urine, or tissue levels of pyridine and/or its metabolites in the exposed populations. Additional information relating those levels to the subsequent development of health effects would also be extremely useful.

Exposure Registries. No exposure registries for pyridine were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The compound 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 compound.

5.7.2 On-going Studies

Remedial investigations and feasibility studies conducted at the 4 NPL humans sites known to be contaminated with pyridine will add to the available database on exposure levels in environmental media, exposure levels in and exposure registries.

No other on-going studies were located regarding the environmental transport, or potential for human exposure to pyridine.

