

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Methyl mercaptan is a naturally occurring gaseous compound produced as a result of microbial degradation and present in trace amounts in natural gas. It is likely to volatilize from soil and water and be photooxidized in the atmosphere. Methyl mercaptan is probably mobile in soils, and it is not likely to bioaccumulate.

Human exposure to trace amounts of methyl mercaptan probably occurs from all environmental media. However, since this compound has an extremely unpleasant odor and the odor threshold is quite low, it is unlikely that significant human exposure to methyl mercaptan will occur, except possibly in the vicinity of sewage treatment plants or industrial facilities or in the workplace.

The EPA has identified 1,177 NPL sites. Methyl mercaptan has been found at 2 of the sites evaluated for the presence of 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 occurrence at these sites within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

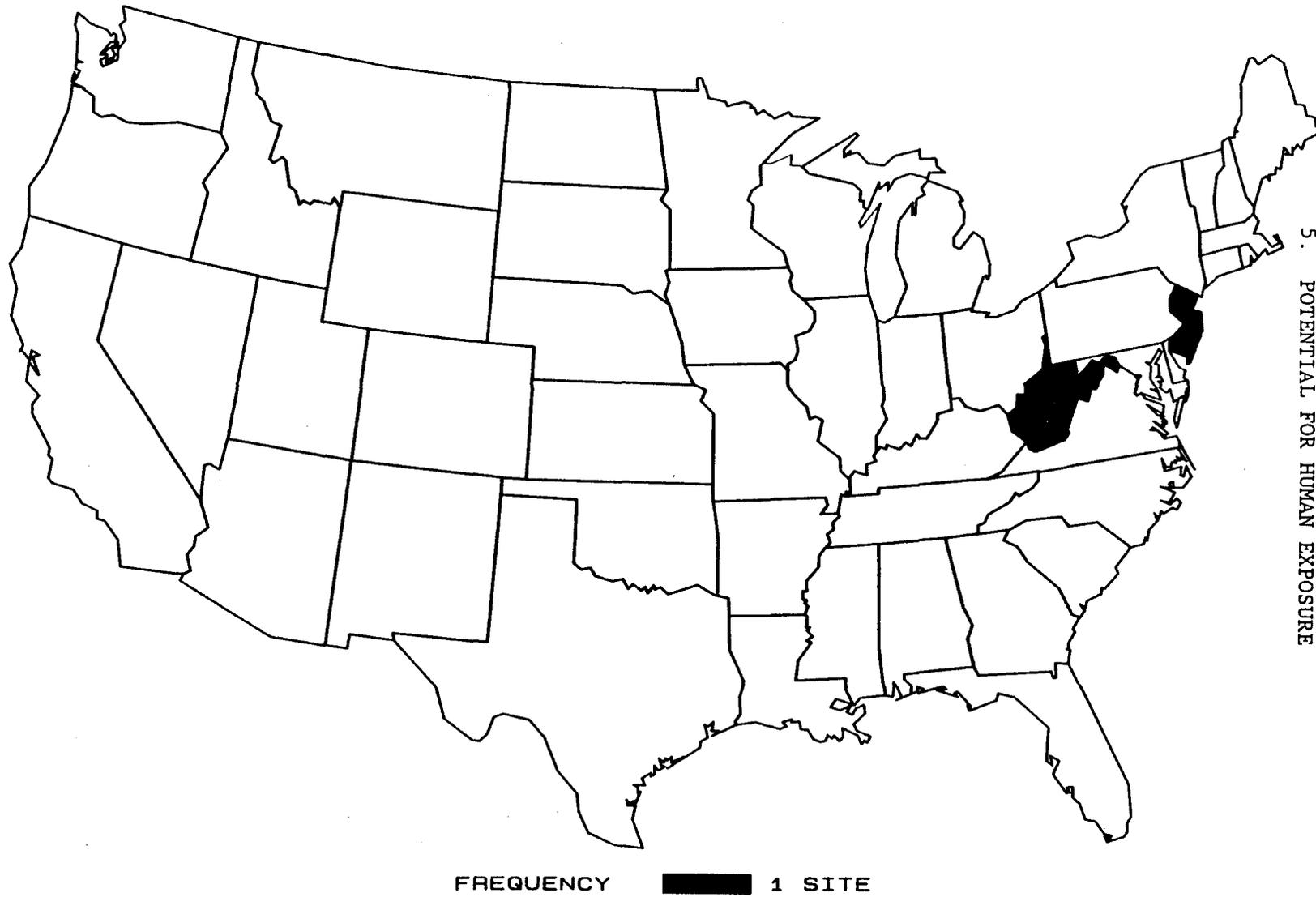
Releases of methyl mercaptan may occur from industrial sources. However, manufacturers, users, and processors of methyl mercaptan are not required to report quantities of this substance released to environmental media, since methyl mercaptan is not on the SARA Section 313 Toxic Chemical List. Therefore, releases of methyl mercaptan during normal operations are not reported in the Toxics Release Inventory (TRI 1989).

5.2.1 Air

Methyl mercaptan is released to the atmosphere from both natural and anthropogenic sources. Natural sources include vegetation, animal wastes, microbial degradation, and natural gas (Adams et al. 1979; Farwell et al. 1979; Graedel 1978; Reid 1958). Estimation of average methyl mercaptan emission from a saline marsh in North Carolina was 6.56 g sulfur/m²/year (Adams et al. 1979). No other quantitative data regarding emissions from natural sources were located.

Potential industrial emission sources include wood pulp, oil shale, and petroleum-processing plants and sewage treatment plants (EPA 1987b; Graedel 1978; Reid 1958; Sklarew et al. 1984). Releases may also occur from hydrolysis or combustion of wool (Junk and Ford 1980; Reid 1958). A survey of about 2,950 industrial facilities in North Carolina reported fugitive and stack emissions of methyl mercaptan totalling 239,594 pounds/year (McCune 1990).

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



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* Derived from View 1989

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5.2.2 Water

No data were located regarding the amount of methyl mercaptan released to water. However, this compound was identified in both the influent and the effluent of a wastewater treatment plant. It is likely that methyl mercaptan is formed in the water by chemical reaction or microbiological fermentation, rather than being released from industrial or municipal sources (Reid 1958; Van Langenhove et al. 1985). Data from the Contract Laboratory Program (CLP) Statistical Database indicate that methyl mercaptan was not detected in surface water or groundwater at about 400 hazardous waste sites (CLPSD 1986).

5.2.3 Soil

Methyl mercaptan occurs naturally in many soils and may be adsorbed to the soil from the atmosphere (Smith et al. 1973). No data were located regarding land releases of methyl mercaptan from industrial sources. Land disposal restrictions have been proposed for methyl mercaptan (EPA 1989c).

Methyl mercaptan was detected in two soil samples at a geometric mean concentration in positive samples of 83 $\mu\text{g}/\text{kg}$, at 1 of 455 hazardous waste sites (CLPSD 1986). It is important to note that the CLP Statistical Database includes data from both NPL and non-NPL sites. Since methyl mercaptan may occur naturally in soils, occurrence at a hazardous waste site does not necessarily indicate a release to the environment from the site.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Methyl mercaptan is a gas with a vapor pressure of 1.97 atm at 25°C (EPA 1983). A small fraction of atmospheric methyl mercaptan may dissolve into water vapor (such as clouds and rain drops). A Henry's law constant (H) estimates the tendency of a chemical to partition between its gas phase and water. A value for H has not been experimentally measured, but it may be estimated by dividing the vapor pressure of methyl mercaptan by its water solubility at the same temperature (Mabey et al. 1982). In this case, an estimated value for H is $3.85 \times 10^{-3} \text{ atm}\cdot\text{m}^3/\text{mole}$ (EPA 1983). The magnitude of this value suggests that only a small fraction of gaseous methyl mercaptan would dissolve in water and that most would remain in the air.

Gaseous methyl mercaptan may also partition to soils. Sorption capacities of six-air-dry soil samples ranged from 2.4 to 32.1 mg CH_3SH per g of soil (Smith et al. 1973). The range for most soils was 2.2-21.4 mg/g of soil. These authors concluded that soil may be a sink for gaseous organosulfur compounds. No information was located on the fate of sorbed methyl mercaptan.

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Methyl mercaptan is very soluble in water. Its solubility at 20°C is approximately 23.3 g/L (EPA 1983). The magnitude of the estimated Henry's law constant ($3.85 \times 10^{-3} \text{ atm-m}^3/\text{mole}$) indicates that a large fraction of the dissolved methyl mercaptan will volatilize from solution, depending on temperature, relative humidity, air currents, and the extent of mixing of the solution.

Methyl mercaptan may not be bioconcentrated significantly in water; however, no information was located on this topic. An octanol/water partition coefficient (K_{ow}) estimates the partitioning of a chemical between octanol and water. Octanol is believed to best imitate the fatty structures in plants and living animal tissues. Based on its solubility in water (Hassett et al. 1983), the K_{ow} of methyl mercaptan can be calculated as approximately 19. This low value suggests that methyl mercaptan will not partition to fat tissues significantly. A bioconcentration factor (BCF) relates the concentration of chemical in aquatic plants or animals to the concentration of the chemical in the medium in which they live. Based on the empirical regressions of Kenaga (1980) using soil sorption parameters, an estimated BCF for methyl mercaptan is about 1-2. This low BCF indicates that bioconcentration is not a significant fate mechanism for volatile methyl mercaptan released into the environment. However, no experimentally-measured BCFs for methyl mercaptan were located to corroborate these predicted values.

Methyl mercaptan in water may have very little tendency to be adsorbed by soils and sediments. The extent of adsorption of sparingly water-soluble compounds is often highly correlated with the organic-carbon content of the adsorbent (Hassett et al. 1983). When adsorption is expressed as a function of organic-carbon content, an organic carbon/water partition coefficient (K_{oc}) is generated, and may be used to rank the relative mobility of the chemical in soil-water systems. Based on its solubility in water, an estimated K_{oc} for methyl mercaptan can be calculated as 17, using the empirical regression of Hassett et al. (1983). This low value indicates that methyl mercaptan is very highly mobile in soil as compared with other compounds listed by Roy and Griffin (1985). However, methyl mercaptan is not a sparingly soluble chemical in water. Methyl mercaptan is also a weak acid that dissociates in water, yielding an anion. The adsorption of ionic chemicals cannot be predicted by K_{oc} concepts. The dissociation constants (pKa) of mercaptans in general are on the order of 11.4 (Reid 1958; Yabroff 1940). Consequently, the relative proportion of methyl mercaptan as an ion is probably insignificant in environmentally-relevant waters where the pH is less than 9. Therefore, the estimated K_{oc} value of 17 may be a reasonable indicator of how this chemical partitions between water and soil. No corroborative information was located.

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5.3.2 Transformation and Degradation

5.3.2.1 Air

The major fate of atmospheric methyl mercaptan is photooxidation. Methyl mercaptan may be transformed by photon-photolytic oxidation, yielding hydrogen, sulfur dioxide, dimethyl disulfide, and other polysulfides (Haines et al. 1956; Sheraton and Murray 1981). Methyl mercaptan may also be oxidized by tropospheric oxygen radicals, yielding dimethyl disulfide and other sulfide compounds (Nip et al. 1981). The rate constant for this reaction at ambient temperatures (about 25°C) has been measured to be approximately $1.77\text{--}1.90 \times 10^{-12}$ cm³/molecule-set (Nip et al. 1981; Slagle et al. 1976). If the mean concentration of ground-state oxygen radicals is about 5×10^{-4} molecules/cm³ (Cupitt 1980), then the atmospheric half-life of methyl mercaptan is on the order of 4 months.

Methyl mercaptan may be more rapidly transformed by interacting with atmospheric hydroxyl radicals. The measured rate constant for this reaction at ambient temperatures ranges from 2.1 to 9.04×10^{-11} cm³/molecule-see (Atkinson et al. 1977; Cox and Sheppard 1980; Hynes and Wine 1987; Mac Leod et al. 1984; Wine et al. 1984). Given that the concentration of tropospheric hydroxyl radicals varies from 3×10^5 to about 1×10^7 molecules/cm³ (Mac Leod et al. 1984), it follows that the atmospheric half-life of methyl mercaptan is on the order of 0.2-30 hours. Consequently, it appears that gaseous methyl mercaptan is labile in the troposphere. Transformation products include sulfur dioxide, methylsulfenic acid (CH₃SOH), and methyl sulfide radicals (Hatakeyama and Akimoto 1983). Several other reaction products have been predicted but not confirmed.

Experimental data have also demonstrated that methyl mercaptan is labile in polluted air where nitrogen oxide (NO_x) concentrations are higher (Balla and Heicklen 1985; Sickles and Wright 1979). Nitrogen oxides catalyze the photooxidative transformations of methyl mercaptan. Reaction products under these conditions include sulfur dioxide, nitric acid, formaldehyde, methyl nitrate, methanesulfonic acid, inorganic sulfate (Grosjean 1984), dimethyl disulfide, and nitric oxide (Balla and Heicklen 1985).

Reaction with the nitrate radical (NO₃) may be the dominant atmospheric loss process for methyl mercaptan under certain conditions (Dlugokencky and Howard 1988; Mac Leod et al. 1986). The rate constant for the reaction of atmospheric methyl mercaptan with NO₃ was recently determined (Dlugokencky and Howard 1988; Mac Leod et al. 1986). Based on a rate constant of about 1×10^{-12} cm³/molecule-set and a NO₃ concentration of 2.4×10^8 molecule/cm³, Mac Leod et al. (1986) calculated an atmospheric lifetime of 1.2 hours for methyl mercaptan, less than the estimated atmospheric lifetime (8.4 hours) based on reaction with the OH radical.

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5.3.2.2 Water

Very little is known about nonbiologically-mediated transformations of methyl mercaptan in water. It seems likely that methyl mercaptan will photooxidize and oxidize in water, but no information was located.

5.3.2.3 soil

Methyl mercaptan may be degraded by methanogenic bacteria in soil, but there is little information available. Methyl mercaptan in solution was metabolized to methane and carbon dioxide when in contact with anaerobic freshwater sediments and sewage sludge (Zinder and Brock 1978). No other information on transformation or degradation in soil was located.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Methyl mercaptan was detected in ambient air at 4 ppb ($8.2 \mu\text{g}/\text{m}^3$) and in a primary school in Japan at 2.8 ppb ($5.7 \mu\text{g}/\text{m}^3$) (Okita 1970). No other studies were located regarding atmospheric concentrations of methyl mercaptan.

5.4.2 Water

Groundwater and surface water monitoring studies do not generally include methyl mercaptan. This compound was not detected in a screen of about 1,800 community and private wells in Wisconsin (Krill and Sonzogni 1986). No other studies regarding water concentrations of methyl mercaptan were located.

5.4.3 Soil

Although methyl mercaptan is produced by microbial degradation in soils, is adsorbed from the atmosphere by soil, and is volatilized from soil (Adams et al. 1979; Farwell et al. 1979; Reid 1958; Smith et al. 1973), no quantitative data on the concentration of methyl mercaptan in ambient soils were located.

5.4.4 Other Environmental Media

Methyl mercaptan has been identified as a volatile component of roasted filberts and Beaufort cheese (Dumont and Adda 1978; Kinlin et al. 1972). Trace amounts are present in the roots and leaves of some plants, in natural gas and, as a result of digestive and metabolic processes, in urine and feces (Reid 1958). Methyl mercaptan is also found in commercially extractable quantities in the "sour gas" of west Texas (Reid 1958).

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5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Since methyl mercaptan is a naturally occurring substance present in foods and sometimes formed during digestive and metabolic processes, the general population will most likely be exposed to trace amounts of this compound. However, the available data are inadequate to estimate the extent of exposure of the general population to either natural or anthropogenic sources of methyl mercaptan.

Inhalation exposure in occupational settings is probably the most significant human exposure scenario for methyl mercaptan. Santodonato et al. (1985) estimated that about 19,000 workers were potentially exposed to methyl mercaptan in the 1970s. The estimate of workers potentially exposed to methyl mercaptan increased from 357 in the early 1970s to about 6,200 in the early 1980s (NOES 1989; NOHS 1989). 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. Most occupational exposures are likely to occur in sewage treatment plants and pulp mills, rather than in methyl mercaptan production or consumptive use facilities. Mean methyl mercaptan concentrations in workplace air ranged from 0.070 to 0.263 ppm in sewage plants and from 0.021 to 3.70 ppm in pulp mills in Finland (Kangas and Ryosa 1988; Kangas et al. 1984) and from 0.55 to 1.06 ppm at a lockgate on a Japanese river (Okita 1970). No other data on workplace air concentrations were located.

Since methyl mercaptan has a penetrating and extremely unpleasant odor and the odor threshold in air is quite low (1.6 ppb) (Amoore and Hautala 1983), it is unlikely that humans would willingly tolerate exposure to concentrations much above the odor threshold for any substantial time period. However, humans in occupational settings may rapidly succumb to extremely high levels of methyl mercaptan, as in the case of the worker who died after emptying tanks of methyl mercaptan (see Chapter 2).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers in sewage treatment plants, pulp mills, chemical plants, and other industrial or agricultural settings where chemical or microbiological formation of methyl mercaptan is significant would have potentially high exposure to this compound. People living in the immediate vicinity of these facilities as well as in the vicinity of hazardous waste sites also have higher exposure potential than does 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

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health effects of methyl mercaptan 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 methyl mercaptan.

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. The dissociation constant of methyl mercaptan in water is not known precisely (Reid et al. 1958; Yabroff 1940) and this measurement would be useful in predicting the environmental fate and transport of this compound. A laboratory verification of the estimated Henry's law constant for methyl mercaptan (Hassett et al. 1983) would provide a more accurate measurement of air-water partitioning.

Production, Import/Export, Use, and Disposal. No data were located with regard to past or present production, use, release, or disposal of methyl mercaptan. Since most human exposure to methyl mercaptan is not associated with production, use, or disposal, but rather with sewage treatment, wood pulping, or oil processing facilities (EPA 1987b; Graedel 1978; Reid 1958; Sklarew et al. 1984), additional data on its production and use will probably not significantly affect estimates of human exposure to this compound. However, data on methyl mercaptan releases from those facilities where the chemical is produced inadvertently (sewage treatment, wood pulping, etc.) would be useful in evaluating the potential for human exposures.

Environmental Fate. Small amounts of methyl mercaptan may partition from air to water or soil (EPA 1983; Smith et al. 1973). Based on measured physical properties, methyl mercaptan is likely to volatilize from water to air (EPA 1983), but has little tendency to adsorb to soils (Hassett et al. 1983). Methyl mercaptan is likely to be mobile in environmental media (Hassett et al. 1983). Additional research on the soil sorption of gaseous methyl mercaptan may be helpful in describing the transport of the gas phase in the vadose zone. The reaction mechanisms of methyl mercaptan transformations in the atmosphere are fairly-well understood (Atkinson et al. 1977; Balla and Heickler 1985; Cox and Sheppard 1980; Dlugokencky and Howard 1988; Haines et al. 1956; Hynes and Wine 1987; MacLeod et al. 1986; Nip et al. 1981; Sheraton and Murray 1981; Slagle et al. 1976), but the environmental fates of some of the transformation products are not well known. Very little is known about the fate of methyl mercaptan in water. It would be helpful to collect data on oxidation, hydrolysis, photodegradation, and

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biodegradation in surface water and groundwater. Research on the biodegradation and abiotic transformation of methyl mercaptan in soils would also be useful.

Bioavailability from Environmental Media. Methyl mercaptan is soluble in water and may have very little tendency to be adsorbed to soils or sediments (EPA 1983; Hassett et al. 1983). Therefore, it will be bioavailable from natural waters. However, there are no data on the potential absorption of methyl mercaptan via the oral or dermal routes. These data would be useful in assessing the potential effects of recreational use of natural waters contaminated with methyl mercaptan. Information on the absorption of inhaled methyl mercaptan released to air would also be useful in assessing its bioavailability from that medium.

Food Chain Bioaccumulation. There are no data on the bioconcentration of methyl mercaptan by aquatic organisms, or data on the bioaccumulation of methyl mercaptan in the food chain. However, this lack of data may not be a major limitation, because the food chain bioaccumulation of methyl mercaptan is unlikely owing to its high volatility and water solubility (EPA 1983; Hassett et al. 1983).

Exposure Levels in Environmental Media. There are few studies measuring concentrations of methyl mercaptan in any environmental media (Krill and Sonzogni 1986; Okitu 1970). Since levels in ambient air, water, and soil are unknown, monitoring studies would confirm the presence or absence of this compound in these media. Data on ambient air levels at hazardous waste sites and estimates of human intake would be particularly useful.

Exposure Levels in Humans. Exposures of humans to natural sources of methyl mercaptan are difficult to estimate. Measurements of methyl mercaptan in workplace air would be useful in estimating occupational exposures. Because methyl mercaptan is always present in human tissue independent of exposure, these levels cannot be used as a measure or indication of exposure without confirmatory data on exogenous levels of methyl mercaptan.

Exposure Registries. No exposure registries for methyl mercaptan 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.

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5.7.2 On-going Studies

Remedial investigations and feasibility studies conducted at the 2 NPL sites known to be contaminated with methyl mercaptan will add more information to the available database on exposure levels in environmental media and exposure levels in humans. No other information was located on any on-going studies on the fate, transport, or potential for human exposure to methyl mercaptan.