

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

MTBE is generated solely through manufacturing processes and is released to the environment by human activities. Until the 1970s when a shift to unleaded gasolines attracted interest in relatively non-polluting high octane additives, MTBE production was extremely limited. As recently as 1980, commercial output in the United States was only 19,000 barrels (around 5 million pounds or 2.2 million kg) per day; it has since climbed to around 250,000 barrels (about 64.8 million pounds or 29.4 million kg) per day (Lorenzetti 1994). When production was low, the risks for human exposure were minimal outside certain occupational settings. Exposures to MTBE at high levels would usually be expected only in the case of accidents or spills, especially in enclosed spaces. But the current widespread use of MTBE in reformulated gasoline significantly increases the possibility of the general public being exposed to MTBE at low levels. Opportunities for exposure will closely parallel those for other organic hydrocarbon gasoline additives such as benzene or toluene. In addition to inhalation risks while fueling motor vehicles and direct exposures from vehicle emissions, MTBE will be emitted to the ambient air, primarily from precombustion volatilization. This can then lead to low-level background exposure potentials over a large geographical area.

While these atmospheric pathways are of most concern for the general population, more localized risks can arise when MTBE becomes a groundwater contaminant. Groundwater contamination risks exist around major production sites, pipelines, large tank batteries, transfer terminals, and active or abandoned waste disposal sites; in addition, gasoline leaks from up to 20% of the nation's 1.4 million underground storage tanks (USTs) can lead to exposures to MTBE through contaminated groundwater. Groundwater sampling programs are beginning to document numerous cases of MTBE contamination, especially in shallow groundwater aquifers; contamination is often related to spills or releases from USTs (Schorr 1994; USGS 1995).

According to much of the existing literature, MTBE poses no severe human health threats at the exposure levels anticipated for the general population. However, MTBE does produce an extremely offensive odor. When included in a liquid mixture, its odor detection threshold is in the neighborhood of 680 µg/L, which is much lower than the 4,700 µg/L threshold for other common volatile organic compounds (VOCs) like benzene (Angle 1991; Gilbert and Calabrese 1992). In many cases, the smell of MTBE in well water has

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been an early indicator of groundwater contamination from even more dangerous VOCs released from leaking USTs (Angle 1991).

MTBE has been identified in at least 12 of the 1,430 current or former EPA National Priorities List (NPL) hazardous waste sites (HazDat 1996). However, the number of sites evaluated for MTBE is not known. The frequency of these sites can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

Environmental releases of MTBE may occur at industrial sites involved in the manufacture of MTBE or in the blending of MTBE with gasoline; during the storage, distribution and transfer of MTBE-blended gasoline, and from spills or leaks or fugitive emissions at automobile service stations (EPA 1994c). The major source for quantitative estimates of releases to environmental media for MTBE is the Toxics Release Inventory (TRI).

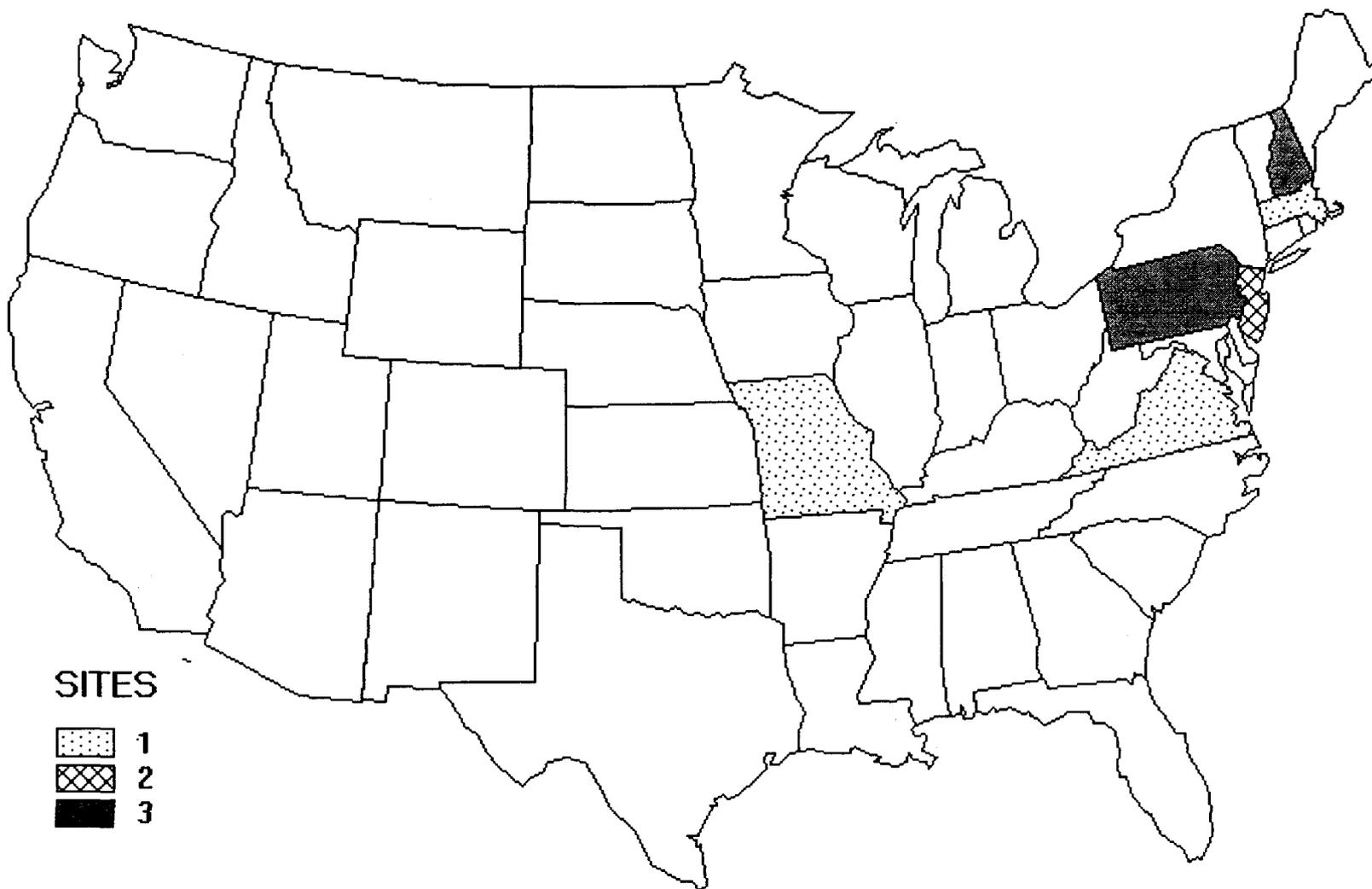
Releases of MTBE are required to be reported under SARA Section 313; consequently data are available for this compound starting with the 1993 survey period in the TRI (EPA 1995a). According to the TRI, a total of 3,163,305 pounds (1,434,865 kg) was released to some environmental media in 1993 (TRI93 1995). This total figure includes 9,405 pounds (4,266 kg) released through the Underground Injection Control program. In addition, an estimated 92,030 pounds (41,744 kg) were released by manufacturing and processing facilities to publicly owned treatment works (POTWs), and an estimated 859,424 pounds (389,832 kg) were transferred off-site (TRI93 1995).

MTBE has been identified in at least 12 of the 1,430 NPL current or former NPL hazardous waste sites (HazDat 1996). According to HazDat (1996) MTBE has been detected only in groundwater. MTBE has been found in groundwater samples at all 12 NPL sites with MTBE contamination (HazDat 1996).

5.2.1 Air

Although MTBE was listed as a hazardous air pollutant under the 1990 Clean Air Act Amendments, it is also an EPA-approved alternative for use in reformulated gasoline (EPA 1994c). While its notoriety as a gasoline additive has led to some regional case studies (LaGrone 1991), information on MTBE is not available allowing comprehensive estimates of releases to the air. Since MTBE is a VOC, it has been included under emissions inventories for some industrial facilities (LaGrone 1991).

Figure 5-1. Frequency of NPL Sites with Methyl *tert*-Butyl Ether (MTBE) Contamination



SITES

-  1
-  2
-  3

Derived from HazDat 1996

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Major markets for MTBE were very limited until MTBE and ethanol became the two favored ingredients for use in reformulated gasolines in the late 1980s. It is therefore reasonable to assume an increasing trend in releases of MTBE to the atmosphere in the 1990s. However, the limited availability of data makes it difficult to make any quantitative assessment of trends in releases to the air.

Most releases would be from the MTBE included in reformulated gasoline. The most common types of releases would involve refueling operations at fuel terminals or service stations and emissions from automobile exhaust or background levels in the ambient air encountered during commuting (Lioy et al. 1994). Since these emissions are not from stationary sources, broad-based monitoring and record-keeping is minimal, precluding precise estimates of these releases.

Many types of human exposure will involve transient events related to adding fuel to automobiles or igniting reformulated fuels in a car engine under “cold” start-up conditions. With the switch to unleaded fuels, manufacturers have encountered challenges in maintaining adequate levels of what is called the Front End Octane Number (FEON). When first starting an engine, especially if the weather conditions are extremely cold, the initial combustion reactions focus on those components of the fuel that can boil below 100 °C. In reformulated gasolines, such components will include MTBE, other VOC additives, and the most volatile components of the gasoline itself (Piel 1988). This can increase the levels of transient exposure and is a major reason that cars burning reformulated fuels give off objectionable odors until the engines have warmed up. This phenomenon, which could clearly be exacerbated under extremely cold climate conditions, is a factor in the ongoing controversy over MTBE exposure in states with extremely cold winters (Illman 1993; Piel 1988).

According to the TRI, releases of 3,095,069 pounds (1,403,914 kg) of MTBE to the atmosphere from 34 manufacturing or processing facilities in 1993 accounted for about 97.8% of the total environmental releases (TRI93 1995). These releases are summarized in Table 5-1. The data from the TRI listed in Table 5-1 should be used with caution, however, since only certain types of facilities are required to report (EPA 1995a). This is not a comprehensive list.

MTBE has not been identified in air samples collected at any of the 12 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1996).

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Methyl tert-Butyl Ether

| State ^b | Number of facilities | Range of reported amounts released in pounds per year ^a | | | | | | |
|--------------------|----------------------|--|---------|-------|-----------------------|--------------------------------|---------------|-------------------------|
| | | Air | Water | Land | Underground injection | Total environment ^c | POTW transfer | Off-site waste transfer |
| AK | 1 | 2424 | 0 | 0 | 0 | 2424 | 0 | 0 |
| AL | 2 | 5-10658 | 0 | 0 | 0 | 5-10658 | 0 | 0 |
| CA | 15 | 3-42000 | 0-8800 | 0-81 | 0 | 3-50881 | 0-55000 | 0-644 |
| CO | 2 | 12069-15000 | 33-880 | 0 | 0 | 12102-15880 | 0 | 0 |
| DE | 1 | 5390 | 520 | 5 | 0 | 5915 | 0 | 30 |
| FL | 1 | 1719 | 0 | 0 | 0 | 1719 | 0 | 100 |
| GA | 1 | 1450 | 250 | 0 | 0 | 1700 | 0 | 250 |
| IL | 4 | 0-35000 | 0 | 0 | 0 | 0-35000 | 0 | 0 |
| IN | 6 | 255-13800 | 0 | 0 | 0 | 255-13800 | 0-1200 | 0-28000 |
| KY | 2 | 2417-14058 | 0-1112 | 0 | 0 | 2417-15170 | 0 | 62-123 |
| LA | 11 | 60-68100 | 0-50 | 0-52 | 0 | 60-68150 | 0 | 0-1 |
| MI | 10 | 0-49250 | 0 | 0 | 0 | 0-49250 | 0 | 0-363500 |
| MN | 2 | 250-2580 | 0 | 0 | 0 | 250-2580 | 0 | 0 |
| MS | 1 | 63700 | 0 | 0 | 0 | 63700 | 0 | 3 |
| MT | 1 | 6600 | 0 | 0 | 0 | 6600 | 0 | 0 |
| NJ | 9 | 51-76500 | 0-2300 | 0 | 0 | 51-76510 | 0-1000 | 0-38520 |
| NM | 2 | 3250-17782 | 0 | 0-5 | 0 | 3255-17782 | 0 | 0 |
| NY | 1 | 1300 | 0 | 0 | 0 | 1300 | 0 | 0 |
| OH | 1 | 5114 | 0 | 0 | 0 | 5114 | 0 | 0 |
| OK | 2 | 90-14097 | 0-46 | 0 | 0 | 90-14143 | 0 | 0 |
| PA | 7 | 780-42300 | 0-5 | 0 | 0 | 785-42300 | 0-33000 | 0 |
| PR | 1 | 159237 | 0 | 0 | 0 | 159237 | 0 | 0 |
| SC | 2 | 540 | 0 | 0 | 0 | 540 | 0 | 0 |
| TN | 4 | 250-4212 | 0 | 0 | 0 | 250-4212 | 0 | 0-3031 |
| TX | 36 | 0-557925 | 0-44000 | 0-113 | 0-8772 | 0-557925 | 0-1370 | 0-71236 |
| UT | 2 | 1505-1590 | 0 | 0 | 0 | 1505-1590 | 0 | 0 |
| VA | 1 | 8200 | 0 | 0 | 0 | 8200 | 0 | 265 |
| VI | 1 | 2770 | 0 | 0 | 0 | 2770 | 0 | 0 |

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Methyl tert-Butyl Ether (MTBE) (continued)

| State ^b | Number of facilities | Range of reported amounts released in pounds per year ^a | | | | | | |
|--------------------|----------------------|--|-------|------|-----------------------|--------------------------------|---------------|-------------------------|
| | | Air | Water | Land | Underground injection | Total environment ^c | POTW transfer | Off-site waste transfer |
| WA | 1 | 5800 | 0 | 0 | 0 | 5800 | 0 | 0 |
| WI | 4 | 255-16186 | 0 | 0 | 0 | 255-16186 | 0-26 | 0-191247 |
| WY | 3 | 5-29555 | 0 | 0 | 0 | 5-29555 | 0 | 0 |

Source: TRI93 1995

^a Data in TRI are maximum amounts released by each facility.

^b Post office state abbreviations used

^c The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

POTW = publicly owned treatment works

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5.2.2 Water

MTBE is not a priority pollutant under the Clean Water Act and has not been a target analyte in ordinary surface water quality monitoring and assessment programs or the focus of much attention in discharge permitting. Therefore, very limited data are available on releases of MTBE to surface waters. Most releases to surface water would likely result from leaks or spills. Since MTBE has a fairly high degree of solubility in water (42,000 mg/L as used in Mackay et al. 1993), rain scouring could also transfer MTBE from the atmosphere to surface waters (USGS 1995). Wet weather runoff will often wind up being diverted into storm drains or waste water treatment facilities in urban areas or industrial facilities, where the MTBE may then be introduced to receiving waters. Given its high vapor pressure of 245 mm Hg and Henry's Law Constant of around $5.87 \times 10^{-4} \text{ atm}\cdot\text{m}^3/\text{mole}$ (see Chapter 3, Table 3-2), however, MTBE would be expected to volatilize rapidly from surface water or soil surfaces (EPA 1994c).

According to the TRI, releases of 58,509 pounds (26,539 kg) of MTBE to surface water from 22 manufacturing or processing facilities in 1993 accounted for about 1.8% of the total environmental releases (TRI93 1995). An additional 92,030 pounds (41,744 kg) of MTBE were introduced as influents to POTWs (TRI93 1995). While much of this input to municipal waste water treatment works would be expected to volatilize to the air, perhaps up to 10% might be released to surface water in treated effluents (van Luin and Teurlinckx 1987). These releases are summarized in Table 5-1. The data from the TRI listed in Table 5-1 should be used with caution, however, since only certain types of facilities are required to report (EPA 1995a). This is not a comprehensive list.

While no comprehensive quantitative estimates of MTBE releases to groundwater seem possible, the chemical has been reported in groundwater at all 12 NPL sites where MTBE contamination is documented in the HazDat database (HazDat 1996). Another source of groundwater contamination is from leaking USTs. There are around 1.4 million small underground storage facilities regulated under the EPA Underground Storage Tank (UST) program. Up to 20% of these facilities may either be leaking now or can be expected to start leaking in the near future (Mihelcic 1990). Since the UST program requirements for upgrading storage tank construction only began to take effect by the late 1980s some leaking tanks would have contained reformulated fuels containing MTBE. Since the focus of remediation efforts under the UST program is on such known carcinogens as benzene, detection of MTBE contamination often takes place qualitatively due to its offensive odor (Angle 1991). The odor threshold of MTBE is in the range of 0.32-0.47 mg/m³ (1.15-1.70 ppm) in air (EPA 1994a), which corresponds to a level that would volatilize

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from a concentration of around 680 ppb ($\mu\text{g/L}$) in water (Angle 1991); MTBE levels in either media are much lower than for other common VOCs such as benzene.

5.2.3 Soil

No quantitative estimates of releases to soils or sediments could be identified. Releases around production facilities, pipelines, or transfer terminals are possible from spills. The organic carbon partitioning coefficient (K_{oc}) for MTBE is around 11.2, a low value indicating little tendency to sorb to soil particles and suggesting a considerable mobility, with the leaching of the chemical into groundwater considered likely (EPA 1994c; Swann et al. 1983) (see Table 3-2). In estuaries and harbors, aquatic sediments may become sinks, at least on a seasonal basis, for MTBE introduced from a combination of spills, runoff, or automobile emissions (Bianchi et al. 1991).

According to the TRI, releases of 320 pounds (145 kg) of MTBE to the land from 10 manufacturing or processing facilities in 1993 accounted for less than 1% of the total environmental releases (TRI93 1995). These releases are summarized in Table 5-1. The TRI data listed in Table 5-1 should be used with caution, however, since only certain types of facilities are required to report (EPA 1995a). This is not a comprehensive list.

The limited availability of data makes it difficult to assess releases of MTBE to soils or sediments. MTBE has not been identified in soil or sediment samples collected at any of the 12 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1996).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Based on equilibrium fugacity models, the high vapor pressure of MTBE leads to partitioning to the atmosphere (Mackay et al. 1993) for MTBE releases to surface waters or soil surfaces. In model systems, half-lives (first-order kinetics) in moving water are estimated in the neighborhood of 4.1 hours (HSDB 1995, noting estimates based on a method presented in Lyman et al. 1982). Under dynamic systems where there might be substantial ongoing loadings to air, soils, sediment, or water, the partitioning to the air compartment is slightly less pronounced (Mackay et al. 1993). When introduced into subsurface soils or to groundwater, MTBE may be fairly persistent since volatilization to the atmosphere is reduced or

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eliminated. Especially where MTBE is introduced as part of a gasoline mixture from leaking USTs, its relatively high water solubility combined with little tendency to sorb to soil particles can be expected to encourage migration to local groundwater supplies (EPA 1994c).

Based on analogy with other ethers, the potential for bioconcentration appears to be very minor, and standard references will often not even attempt to estimate bioconcentration factors (BCFs) for such chemicals (Mackay et al. 1993). The only case in the literature presenting an empirical estimate on a BCF for MTBE is a Japanese study using the Japanese carp. Using a flow-through water system with exposures carried out over a 4-week period, the highest measured BCF for whole tissue was 1.5 (Fujiwara et al. 1984). Following the end of exposure, tissue levels rapidly declined. A BCF of 3 was estimated from octanoYwater partition coefficients for the fathead minnow (ASTER 1995; Veith and Kosian 1983). Based on these results, the bioconcentration potential for MTBE can be rated as quite insignificant.

5.3.2 Transformation and Degradation

MTBE is expected to be undergo destruction once released into the atmosphere from reactions with hydroxyl radicals. Photolytic decay processes do not seem to play a role in its degradation since MTBE does not absorb light in range above 210 nm (EPA 1994c). If introduced into surface soils, MTBE would rapidly re-volatilize to the atmosphere. When introduced into subsurface soil layers, which would be common in seepage from leaking USTs, MTBE may be fairly persistent since it shows very limited tendency for either abiotic or biotic degradation processes. When released to surface waters, MTBE would also tend to re-volatilize rapidly to the air. While MTBE has a reasonably high water solubility (up to 42,000 mg/L as used in Mackay et al. 1993), it shows little tendency to degrade from hydrolysis and has little tendency to sorb to suspended particulates, soils, or sediments. In groundwater, MTBE can be fairly persistent since it shows limited susceptibility to either anaerobic or aerobic biodegradation (EPA 1994c).

5.3.2.1 Air

MTBE is not expected to persist in the atmosphere because of its fairly rapid reactions with hydroxyl radicals. Based on available laboratory studies, a total atmospheric lifetime for MTBE of approximately 4 days has been estimated (Cox and Goldstone 1982; Smith et al. 1991; Wallington et al. 1988). In other studies, atmospheric half-lives of approximately 3 days are reported in polluted urban air and around 6.1 days in non-polluted rural air (EPA 1994c).

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There are two main decomposition pathways depending on whether the methyl group or the *tert*-butyl group is attacked. The pathway involving OH radical decomposition on the methyl group results in such final products as acetone and *tert*-butyl formate. While acetone would be relatively resistant to further OH radical degradation, there is very little research on the reactivity of the *tert*-butyl formate degradation products, with available research suggesting atmospheric residence times of up to 15 days (Cox and Goldstone 1982). This would make the *tert*-butyl formate much more persistent in the atmosphere than the original MTBE. There is very limited information available on the toxicology and human health impacts of *tert*-butyl formate. The pathway involving decomposition of the *tert*-butyl group can become extremely complex, with the final products being dependent on the levels of other free radicals and such pollutants as NO_x. The initial decomposition is not sensitive to photolysis since MTBE does not absorb radiation in the spectrum above 200-210 nm (EPA 1994c; Schuchmann and von Sonntag 1973); however, OH radical decomposition is critical to the initial reactions. Photolysis reactions can play a much greater role in the subsequent breakdown of the *tert*-butyl group. Under conditions typical of polluted urban air (Japar et al. 1990), decomposition products can include 2-methoxyl-2-methyl propanol, acetone, acetaldehyde, and peroxyacetyl nitrate (PAN). Other laboratory studies also indicate that the decomposition products include formaldehyde (Tuazon et al. 1991), and methyl acetate (Smith et al. 1991; Tuazon et al. 1991). The decomposition products actually formed are often highly dependent on the presence of other types of air pollutants. Studies in highly polluted urban airsheds such as Mexico City have documented statistically significant increases in the ambient levels of formaldehyde following efforts to encourage greater use of reformulated gasolines such as MTBE (Bravo et al. 1991). Alternative oxygenated fuel additives such as ethanol, however, also produce aldehydes as combustion products (Shanley 1990).

Several of the decomposition products stemming from the *tert*-butyl group breakdown pathway are products that can be produced from non-oxygenated unleaded gasolines or from reformulated products using such alternative oxygenating agents as ethanol. This can make it hard to relate laboratory studies or modeling predictions to actual monitoring observations. For instance, analyses of time series data in both Mexico City, Mexico, and Denver, Colorado, have been interpreted as confirmation for the position that the use of MTBE in gasolines can contribute, especially when used with other reformulated gasoline agents, to increases in the levels of such air pollutants as formaldehyde (Humberto et al. 1991; Illman 1993).

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5.3.2.2 Water

In surface waters, MTBE shows little tendency to degrade due to hydrolysis or other abiotic processes. It is also resistant to biodegradation (EPA 1994c). Due to its high volatility, will usually be removed from surface waters very rapidly.

In groundwater, the persistence of MTBE would be accentuated since volatilization to the air is reduced or eliminated and this ether is apparently refractory to most types of bacterial biodegradation (Yeh and Novak 1991). Since large plants devoted almost exclusively to the manufacture of MTBE are a relatively recent phenomenon, most spills around older refineries, pipelines, and transshipment terminals would result in a complex mixture of different organic hydrocarbons in groundwater pollution incidents.

Contamination at larger facilities involving reformulated fuels would involve mixtures, and contamination to groundwater from leaking USTs will almost invariably involve blended hydrocarbon mixtures.

The behavior of a plume of MTBE mixed with gasoline and other organic hydrocarbons such as the BTEX series (benzene, toluene, ethylbenzene, and xylene) in contact with water in an aquifer can become very complicated. A key factor is the percentage of MTBE in the original fuel mixture. Since 1979, EPA has allowed progressively higher percentages of MTBE in reformulated gasolines, the percentage has risen from 7% in 1979 to 11% in 1981, and then to 15% in 1988 (Lorenzetti 1994). Below levels of about 5%, the pollution chemistry of a reformulated gasoline plume mixing with fresh groundwater will be driven mostly by the effects from the BTEX components. At higher MTBE levels, however, studies based on theoretical considerations and modeling exercises suggest that MTBE may increase the partitioning of the BTEX toxics into groundwater (Mihelcic 1990; Poulsen et al. 1992). These impacts will be minor when the levels of MTBE in a reformulated gasoline mixture are less than 10% (by volume), with BTEX solubilities in water increasing by 10% or less. At higher MTBE mixture ratios, however, increases in the MTBE mixture percentage can increase the BTEX water solubilities to a higher degree. For instance, a reformulated gasoline mixture containing 0.1% MTBE by volume could increase BTEX water solubilities by only around 1%; a 10% MTBE mixture could result in a 100% increase in BTEX water solubilities (Mihelcic 1990). The MTBE co-solvent can also change the sorption/desorption characteristics of other hydrocarbons, thus increasing their mobility.

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5.3.2.3 Sediment and Soil

There is very limited information available on degradation processes in soils or sediments. On analogy with water media, there would be limited tendency for destruction from hydrolysis or other abiotic processes. Results from field or laboratory microcosm studies suggest considerable persistence in deeper soil layers or in sediments since this ether appears to be highly refractory to microbial decomposition (Jensen and Arvin 1990; Yeh and Novak 1991). For instance, microcosm studies using several soil types and bacterial flora showed no significant biodegradation in experiments carried out over a 250-day period, with most losses due to sorption to organic matter or volatilization (Yeh and Novak 1991). Soils in these microcosm studies were taken from agricultural sites showing moderate acidity (pH 5-6) and a wide range in organic matter content.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to MTBE depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on MTBE levels monitored in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

5.4.1 Air

No information could be identified summarizing levels of MTBE in the ambient air based on a national monitoring database. One regional ambient study from the Houston Regional Monitoring Network (LaGrone 1991) included MTBE in a suite of VOC target analytes to be monitored. This part of Texas contains the Houston Ship Channel and includes some of the nation's largest MTBE manufacturing facilities, many in close proximity to residential neighborhoods. Data collections on every sixth day were obtained over a period from September 8, 1987, through September 18, 1988, following the EPA National Sampling Day protocols. Monitoring results for the Harris and Chambers county area showed total yearly MTBE emissions of 285 tons, with a mean ambient air concentration for MTBE less than the detection limit of 0.2 ppb (0.0007 mg/m³). This study used good quality control features and concluded that occupational and residential exposure potentials in this area with a heavy concentration of MTBE production and processing facilities were likely to be lower than in urban areas in other parts of the United States. The EPA has estimated that annual mean MTBE concentrations in ambient air in the United States during the late 1980s were less than 0.2 ppb (EPA 1994c).

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No information was identified on typical levels for indoor residential air spaces. There are a number of studies where data were collected around auto service or filling stations that would bear on exposures in special locations for the general population as well as for occupational groups that work at these automobile service facilities. Levels from several urban locations suggested that MTBE levels around such auto service facilities would be less than 1 ppm (Hartle 1993). These special microenvironments can help assess a broad range of exposure risks, but often involve short-term exposures or large variations in potential dosages that complicate the interpretation of the data; such data do not provide a basis for estimating typical ambient air levels (Huber 1994).

5.4.2 Water

Until recently, MTBE has not ordinarily been included as a parameter in most surface water or groundwater monitoring programs. Especially for surface waters, very limited information could be identified in the literature for the United States on ambient levels. Studies in England's Southampton Harbor, with conditions that may find parallels in other countries in temperate climates where there is extensive use of reformulated gasoline (Bianchi et al. 1991), found MTBE could accumulate in sediments in the pollutant sink environment of the harbor area. The sediment was then a major source of MTBE reintroduction to the surface waters. For an 18-month period of record, ambient water concentrations of MTBE were observed with a range of 15-81 ng/L (ppt).

In groundwater, studies of NPL and UST program remediation sites can provide highly site specific indications of MTBE levels in groundwater. UST sites showing MTBE groundwater contamination may potentially involve a larger total population since older gasoline stations are ubiquitous. Apparently, detections of MTBE triggered by reports of offensive odors in groundwater are becoming ever more common. A value of 680 µg/L (ppb) is a common odor threshold for MTBE dissolved in water (Angle 1991). Since the odor thresholds of much more dangerous chemicals like benzene are considerably higher (4,700 µg/L [ppb] for benzene), odor detections of MTBE are viewed as a type of early warning indicator of potentially more serious groundwater problems (Angle 1991).

In addition to these highly site-specific sources of information related to groundwater, some states have assembled significant amounts of water-well data that include testing for MTBE. Since the mid-1980s, New Jersey has conducted some screening analysis for public drinking water supplies that included MTBE tests as well as analyses from public and private wells as part of spill investigations or testing related to leaking USTs (Schorr 1994). From 1989 to 1983, at least 30 wells serving 6 different community drinking

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water systems, and at least 150 private wells had documented detectable amounts of MTBE. In cases involving a petroleum product spill or leakage, MTBE levels tended to be very high, in one case as high as 40,000 ppb. In all cases where MTBE levels of 100 ppb or higher were detected, there were also detections of such gasoline constituents as benzene, toluene, xylene, or other hydrocarbons. The highest incidence of MTBE detections involved non-public wells, where 10% of the wells sampled showed MTBE levels of 70 ppb or higher. Extrapolating the available samples to all private wells and public wellheads in New Jersey led to the estimate that 0.5-1 % of the state's drinking water wells might show MTBE levels greater than 70 ppb (Schorr 1994).

The United States Geological Survey (USGS 1995) has also summarized VOC data on MTBE derived from a series of studies in its National Water-Quality Assessment (NAWQA) Program. Many of the NAWQA studies include a groundwater component. At present, the NAWQA data are available from 211 shallow wells in 8 urban areas and 524 shallow wells in 20 agricultural areas. MTBE was detected in 27% of the urban wells, but in only 1.3% of the rural wells. Only 3% of the urban wells showed MTBE concentrations that exceeded 20 ppb. One well showed a level of around 23,000 ppb. Certain parts of the country with longer histories in the use of reformulated gasolines showed a higher incidence of MTBE detections. For instance, 79% of the test wells in the Denver, Colorado, area showed detectable traces of MTBE, and 37% of wells in New England showed detectable levels (detection limit, 0.2 ppb). While the shallow wells targeted for analysis in the NAWQA studies would seldom be part of the aquifers used in public drinking water systems, the USGS suggests that urban areas with a long history of reformulated gasoline usage may face increased risks of groundwater contamination from MTBE (USGS 1995).

5.4.3 Sediment and Soil

No quantitative information from the United States documenting levels of MTBE in soils or sediments was found. The documented instances of MTBE contamination of shallow groundwater supplies demonstrate the likelihood of MTBE contamination of soils, especially when related to leaks from USTs that contained reformulated gasoline. However, since programs to remediate soil or groundwater contamination from underground tanks have generally focussed on clean-up standards for gasoline products in general or specific toxicants such as benzene, the EPA and state UST programs do not usually yield much monitoring evidence on MTBE.

Studies in England's Southampton Harbor, with conditions that may find parallels in other countries in temperate climates where there is extensive use of reformulated gasoline (Bianchi et al. 1991), found

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MTBE could accumulate in sediments in the pollutant sink environment of the harbor area. The sediment was then a major source of MTBE re-introduction to the surface waters. For an 18-month period of record, concentrations from sediment interstitial water samples were reported with a range of 14-20,645 ng/kg (ppt) (Bianchi et al. 1991).

5.4.4 Other Environmental Media

Analogies with the behavior of other highly volatile solvents and ethers, results from a QSAR analysis based on fathead minnow data (ASTER 1995), and results of a confirmatory laboratory BCF for a fish (Fujiwara et al. 1984; HSDB 1995), do not suggest any tendencies for bioconcentration, biomagnification, or bioaccumulation of MTBE that would present human health threats.

Where chemicals have a tendency to bioconcentrate, biomagnify, or bioaccumulate, they may show up in fish consumption advisories issued by the states. Examination of EPA's Fish Consumption Advisory Database (EPA 1995b) showed that no advisories had been issued for MTBE through September 1994.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

MTBE can be emitted to any or all environmental media (air, surface water, groundwater, and soil) depending on the source of the release, formulation mixture, and prevailing environmental conditions. Little information was identified that would allow estimation of current levels of daily intake or exposure to MTBE. General population exposure to MTBE may occur through three routes: inhalation, dermal contact, and ingestion of contaminated groundwater. The major route of exposure to MTBE for the general population is through inhalation of contaminated ambient air, particularly during regular visits to gasoline refueling stations or after major spills or accidents at manufacturing, distribution, or storage facilities. During normal manufacturing, distribution, and storage operations, however, very low levels of MTBE are generally detected in ambient air. A regional survey for a 2-county area along the Houston Ship Channel, where a large number of MTBE production facilities are located, reported average ambient air concentration levels at less than 0.2 ppb (LaGrone 1991).

A second route of exposure is by dermal contact with MTBE-containing gasolines during regular visits to refueling stations or when tilling lawn mowers, chain-saws, or other gasoline-powered equipment. The oral route of exposure may include consumption of drinking water contaminated with MTBE. Leaking

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USTs or spills at manufacturing, distribution, or storage sites can all be sources of contamination to local groundwater supplies.

A study of two types of microenvironments with the potential for MTBE general population exposure provides useful estimates of air concentrations experienced by many urban commuters (Lioy et al. 1994). Air samples from commuter-car interior areas showed a geometric mean for MTBE of $21 \mu\text{g}/\text{m}^3$ (0.006 ppm) with a range from $4 \mu\text{g}/\text{m}^3$ (0.001 ppm) to $580 \mu\text{g}/\text{m}^3$ (0.16 ppm). Air sampling of gasoline refueling station microenvironments involved both the air at the refueling pumps (measured over the hood of the car) and pre- and postsampling of the interior cabins. The refueling station air samples ranged in concentrations from 0.01 to 14 ppm ($40\text{--}49,000 \mu\text{g}/\text{m}^3$) and clearly offered higher short-term exposure levels than the interior cabin air. Elevated levels of MTBE have been detected in human blood samples by the Centers for Disease Control and Prevention (CDC) in residents of Alaska exposed to MTBE; many of these individuals reported various symptoms related to wintertime use of MTBE-enhanced fuels (CDC 1993a; Illman 1993). Based on those observed effects, the EPA granted Fairbanks a waiver on the required use of MTBE in oxygenated fuels. However, since low-level exposures to MTBE have not been considered particularly harmful, this ether is not normally included in ambient air sampling studies.

Workers employed in industries that manufacture, formulate, store, or transport MTBE, and workers involved in the disposal of MTBE-containing wastes, may be exposed to the highest concentrations of MTBE. In occupational settings, inhalation and dermal exposure with subsequent absorption through intact skin are the most important routes of exposure. Inhalation of MTBE depends on its volatility, the percentage of MTBE in the mixture used, and the physical setting in which it is released. Industrial hygiene assessments carried out in the mid-1980s on workspace air concentrations associated with truck drivers or truck terminal operators have documented concentrations of MTBE ranging from less than 1 ppm to 139 ppm (Gilbert and Calabrese 1992). Estimates have also been made for workplace concentrations for gasoline truck drivers and gasoline service station attendants, with short-duration exposures ranging from $1.4 \text{ mg}/\text{m}^3$ (0.4 ppm), where trucks with vapor recovery systems are used, to $\leq 96 \text{ mg}/\text{m}^3$ (26.6 ppm), where vapor recovery systems are not used (Gilbert and Calabrese 1992). In research at several urban areas supported by the American Petroleum Institute, occupational exposures for service station attendants were well under a level of 1 ppm, even in cities where reformulated fuels contained up to 12% MTBE (API 1993; Hartle 1993). The highest of these levels falls well below the 100 ppm Workplace Environmental Exposure Limit recommended by the American Industrial Hygiene Association (see Chapter 7 below). The conversion factor of $1 \text{ ppm} = 3.61 \text{ mg}/\text{m}^3$ ($1 \text{ ppb} = 0.00361 \text{ mg}/\text{m}^3$) can be used for air concentrations of MTBE (Moolenaar et al. 1994).

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Two studies carried out by the National Institute for Occupational Safety and Health (NIOSH) at the request of the National Center for Environmental Health, Centers for Disease Control and Prevention, gathered case study measures of levels of MTBE in the air at a variety of workplaces in Stamford, Connecticut (NIOSH 1993a), and in Fairbanks, Alaska (NIOSH 1993b). Both studies focused on automobile repair centers where workers might be exposed to emissions or combustion by-products. The Alaskan study was conducted after January 1993, at which time the use of MTBE as an anti-pollutant oxygenating agent had been suspended. MTBE was still in use as an octane booster in high-octane (premium) grades of gasoline, but this would have been at levels (1% or less by weight) well below the levels associated with the use of MTBE as an anti-pollutant additive. The highest workplace concentrations found during the Alaskan studies were less than 1 ppm. In Stamford, Connecticut, where MTBE was being used as an anti-pollutant additive, workplace concentrations at automotive repair centers $\leq 12 \text{ mg/m}^3$ (3.3 ppm) were documented. In the Stamford study, blood samples were collected from commuters and people in workplace settings where higher MTBE exposures were likely. The blood samples were analyzed for MTBE, *tert*-butanol (the MTBE metabolite), and the gasoline VOC components benzene, toluene, and xylene (White et al. 1995). Although the blood levels of MTBE varied widely, statistical analysis indicates a tendency for workers in car repair facilities and workers who pump gasoline into cars to have considerably elevated blood MTBE levels, compared to average blood levels in commuters. The median blood level for MTBE among car repair workers was about $2 \text{ }\mu\text{g/L}$ (ppb); for gas pumping attendants the median was slightly over $10 \text{ }\mu\text{g/L}$ (ppb); while the median level for the commuter group was less than $0.3 \text{ }\mu\text{g/L}$ (ppb) (White et al. 1995).

The National Occupation Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimated that 5,996 workers (1,783 females, 4,213 males) employed at 614 facilities were potentially exposed to MTBE in the United States (NOES 1991). The occupational groups were in industries such as commercial testing laboratories, hospitals, medical laboratories, gasoline service stations, airport maintenance facilities, and paper mills. The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace (Sieber et al. 1991).

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5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals occupationally exposed to MTBE during its production, formulation, distribution, use, or disposal, people exposed to higher than background concentrations include those living near chemical manufacturing or processing sites where accidental releases or spills may occur, individuals living in the vicinity of leaking USTs, and individuals living near hazardous waste sites. While accidents or spills can pose special exposure threats for workers at petrochemical facilities, exposures are ordinarily limited by the closed and highly automated nature of MTBE manufacturing processes. The high degree of automation also limits the number of workers at risk (Gilbert and Calabrese 1992). In the event of major accidents or spills, residential populations close to such facilities could be exposed to high concentrations of MTBE in the air. In local areas where leachates from waste disposal sites or underground storage facilities might contaminate groundwater used for drinking and bathing purposes, there is the potential for lesser MTBE exposures by ingestion of contaminated drinking water, and by dermal contact with and inhalation of MTBE during bathing.

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 MTBE 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 MTBE.

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

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5.7.1 Identification of Data Needs

There is limited empirical monitoring data on typical levels of MTBE in all environmental media. Special statistically designed national surveys and more routine sampling are needed, especially focusing on such obvious exposure pathways as the ambient air or groundwater. In the 1990s the USGS began to include MTBE as a target analyte in groundwater sampling under its NAWQA Program (USGS 1995), and some states are developing useful databases on groundwater levels related to VOC tests on drinking water wells and investigations related to chemical and gasoline spills or leakages from USTs (Schorr 1994). There is limited monitoring information for other environmental media. Data are also limited for workplace settings; the few studies available provide some rough estimates of air concentrations, and of blood levels of people in workplace settings where higher levels of exposure are likely, or of population segments such as commuters (Huber 1994; Liroy et al. 1994; White et al. 1995). While the basic physical and chemical properties of MTBE are adequately known, the degradation processes in air can become very complicated in polluted urban settings. Degradation products such as *tert*-butyl formate (Cox and Goldstone 1982) appear to be more persistent than the original MTBE, and there is little information on the toxicity of this degradation product.

Physical and Chemical Properties. The chemical and physical information available for MTBE is generally adequate (EPA 1994c; Mackay et al. 1993). No major data needs have been identified in this area.

Production, Import/Export, Use, Release, and Disposal. Industry trade magazines currently give reasonably reliable figures for total domestic production (Lorenzetti 1994). Starting in 1992-1993, the U.S. government began tracking import, export, and production levels of MTBE (NTDB 1995; USITC 1995), but for earlier time periods, gross production figures are virtually the only available data. Since most MTBE is mixed into gasolines, there has been no systematic tracking of disposal of MTBE itself. Most releases to the environment involve venting to the atmosphere during the production process (TRI93 1995) although these releases may pose fewer human health risks than the types of unintentional releases resulting from the use of gasoline in workplaces or commuting, or from spills or leaks of gasoline that can contaminate groundwater supplies. These types of releases have higher probabilities of human exposures, but very limited information is available.

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

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TRI, which contains this information for 1993, became available in 1995 (TRI93 1995). The 1993 TRI made provisions for the inclusion of MTBE. This database will be updated yearly and can help provide a list of industrial production facilities and emissions.

Environmental Fate. There has been limited routine monitoring for MTBE for all environmental media; most information comes from waste remediation activities, rare regional investigations, or isolated case studies (Bianchi and Vamey 1989; Bianchi et al. 1991; Jensen and Arvin 1990; LaGrone 1991; Yeh and Novak 1991). Recently, the USGS has placed greater emphasis on including MTBE in the set of target analytes for groundwater sampling in its NAWQA Program (USGS 1995), and some states have useful databases on groundwater detections of MTBE (Schorr 1994). While such efforts will eventually provide a better picture of background conditions for such media as groundwater, there are very limited historical data before the early 1990s. Most conclusions on environmental fate, therefore, tend to depend heavily on the results of models (MacKay et al. 1993). The degradation processes in air can become very complicated in polluted urban settings. Degradation products such as *tert*-butyl formate (Cox and Goldstone 1982) appear to be more persistent than the original MTBE, and there is little information on the toxicity of this degradation product. Additional empirical data on fate and transport processes are needed, especially around production facilities or from sediments or groundwater supplies where MTBE may build up to appreciable concentration levels.

Bioavailability from Environmental Media. Based on its physical properties and results from species tested so far, it is unlikely that MTBE will bioconcentrate to any degree (Fujiwara et al. 1984; MacKay et al. 1993). There is no indication that MTBE is a concern in any raw or processed food items. MTBE is highly volatile and shows little tendency to sorb to soil particles. Therefore, except in situations related to recent spills or other large releases of pure MTBE or reformulated fuels containing MTBE, exposure routes involving dermal contact with the chemical or contaminated media such as soils are generally of minor concern. The main concerns involve inhalation of fumes in the air or volatilized from water or surface soils. The major opportunities for exposure likely involve inhalation of MTBE around automobile service or fueling facilities. While there are documented instances of shallow groundwater supplies contaminated with MTBE, the chemical's low odor threshold and extremely offensive smell make it unlikely that ingestion of drinking water is of much concern. Additional information on bioavailability is not viewed as a significant data need.

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Food Chain Bioaccumulation. While there is limited information on food chain bioaccumulation of MTBE, data for other similar non-chlorinated chemical solvents indicate no potential for bioaccumulation (Fujiwara et al. 1984; Gilbert and Calabrese 1992; MacKay et al. 1993). Toxicokinetics, metabolism, and excretion data similarly suggest no potential for bioaccumulation (Bioresearch Laboratories 1990a, 1990b, 1990c, 1990d; Brady et al. 1990; Gilbert and Calabrese 1992). Therefore, information in this area is not considered a major data need.

Exposure Levels in Environmental Media. While limited data preclude the estimation of exposure levels in such media as surface waters or surface soils, MTBE's high volatility and tendency to quickly migrate into groundwater suggests that further information for these media is not particularly needed. For air, there are a number of special studies around auto service and fueling facilities, but there is still debate on how to relate these findings to provide exposure levels for these specialized sites of concern to both the general population and various occupational groups (Huber 1994). Outside the areas around auto service or fueling facilities, there is a lack of data on ambient air levels and a lack of up-to-date information on exposure opportunities for different occupational groups (NIOSH 1993a, 1993b; White et al. 1995). Data on exposures from groundwater sources are also generally lacking (Angle 1991; USGS 1995).

Additional reliable monitoring data for the levels of MTBE in contaminated media at hazardous waste sites are needed so that the information obtained on levels of MTBE in the environment can be used in combination with the known body burden of MTBE to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. MTBE has not been commonly included in standard ambient monitoring programs for air, surface water, or groundwater (Angle 1991; LaGrone 1991). Therefore, the relatively small number of detections at NPL sites (HazDat 1996) does not necessarily mean that all NPL sites or candidate waste disposal sites have undergone extensive testing.

Exposure Levels in Humans. Outside certain occupational settings, the available information is inadequate to make reliable estimates of exposure levels in humans (Huber 1994; LaGrone 1991; NIOSH 1993a, 1993b). The few studies available provide some rough estimates of air concentrations, and of blood levels of people in workplace settings where higher levels of exposure are likely, or of population segments such as commuters (Huber 1994; Liroy et al. 1994; White et al. 1995). No information could be identified documenting levels detected in human adipose tissues, blood, urine, or breast milk. No information could be identified dealing with exposure levels in the vicinity of NPL sites. Thus, the determination of exposure levels in the general population and in people likely to be exposed at hazardous waste sites is needed.

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

5.7.2 Ongoing Studies

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the National Center for Environmental Health, Centers for Disease Control and Prevention, will be analyzing human blood samples for MTBE and other volatile organic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.

The USGS will continue to collect data on VOCs, including MTBE, as part of the groundwater investigations in many of its National Water-Quality Assessment projects (USGS 1995). The USGS also cooperates with states and other groups in special studies. A cooperative project involving the USGS and the U.S. Virgin Islands Water and Power Authority will implement a groundwater monitoring network on the islands of St. Croix and St. Thomas. MTBE will be included among the target analytes (FEDRIP 1995).