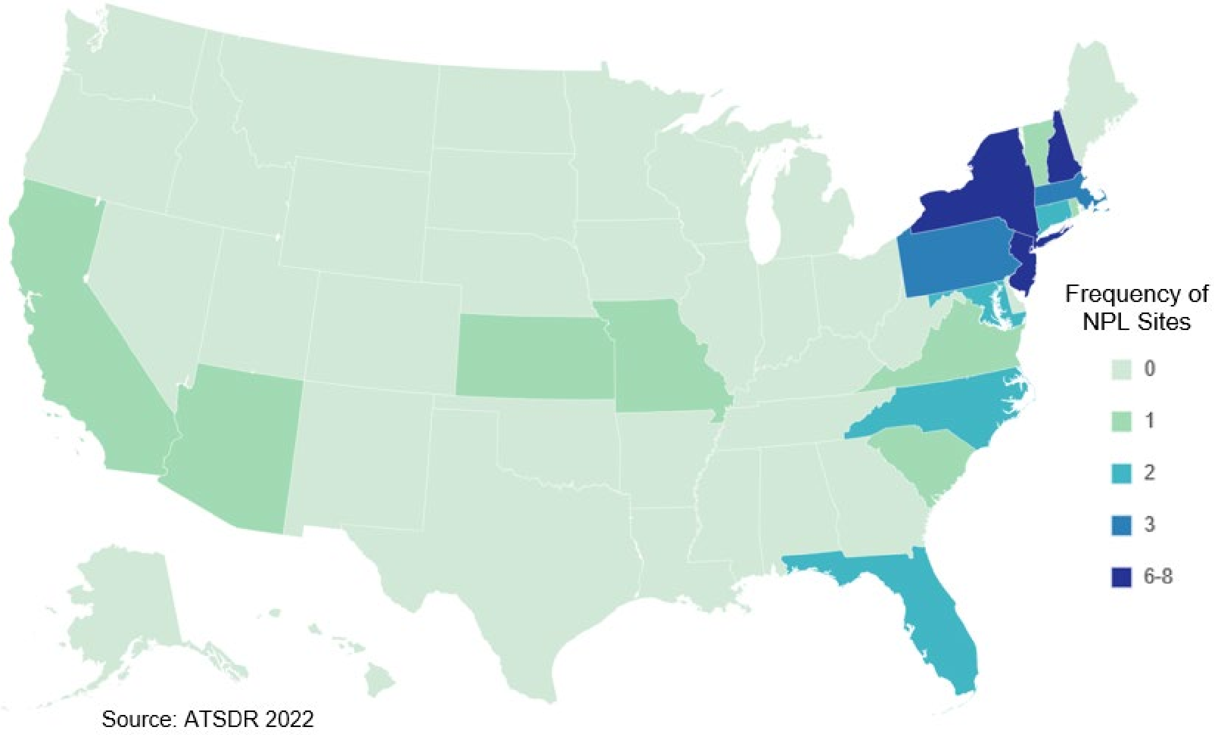
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

MTBE has been identified in at least 45 of the 1,868 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2022). However, the number of sites in which MTBE has been evaluated is not known. The number of sites with MTBE in each state is shown in Figure 5-1. Of these sites, 44 are located within the United States, and 1 is located in the Virgin Islands (not shown).

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



Source: ATSDR 2022

- Since MTBE is no longer used as an oxygenate in gasoline in the United States, exposure is significantly lower today as compared to previous decades.

- MTBE was still manufactured within the United States as recently as 2020 (primarily for export to other countries); it is unclear if MTBE is still being produced in the United States for export to other nations (no reported production volume since December 2020 and no exports reported since 2019).

- The general population may be exposed to MTBE via inhalation of ambient air, ingestion of drinking water, and dermal exposure from contaminated water.
- Exposure to MTBE from indoor air by vapor intrusion can occur if the residence is near a contaminated aquifer.
- MTBE possesses high mobility in soil and leaches into groundwater.
- MTBE volatilizes from surface water and surface soils.
- MTBE is slow to degrade in the environment.
- MTBE does not bioconcentrate in aquatic or terrestrial organisms.

During the 1970s, EPA moved to phase out leaded gasolines and to reduce the levels of air pollution from pre- or post-combustion vehicular emissions. This conversion to unleaded fuels tended to reduce the octane ratings. Additives such as benzene or toluene increase octane levels, but these aromatic VOCs can lead to serious air pollution problems due to their known toxic properties. Various highly oxygenated blending agents, including several ethers and alcohols, can boost the octane of unleaded gasoline and, since they are less toxic, can mitigate many of the air pollution concerns. MTBE is one such product that was used in Reformulated Gasoline (RFG). Some states started requiring the seasonal use of RFGs in the 1970s, and this became a requirement for many parts of the country under provisions of the 1990 Clean Air Act. These requirements led to a rapid expansion in the production and use of MTBE starting in the mid-to-late 1980s as part of the oxyfuel program, with peak usage in the late 1990s. As MTBE possesses high mobility in soil and was being detected in groundwater, concern grew over the continued use of it as an additive to gasoline and many states began restricting or banning its use entirely. In 2005, Congress passed the Energy Policy Act that removed the oxygenate requirement for RFG and added a requirement for renewable blends of RFG (USC 2005). Consequently, ethanol replaced MTBE in gasoline and MTBE use as a gasoline additive in the United States has essentially been eliminated. In 1980, commercial production in the United States was only 19,000 barrels (around 5 million pounds or 2.2 million kg) per day; its domestic use peaked in 1999 at 260,000 barrels per day (EIA 2018). MTBE is still used as an oxygenate in fuels in other countries and the United States still exported substantial quantities of MTBE or gasoline blends containing MTBE to other nations, especially Mexico, as recently as 2020 (EIA 2018, 2022).

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Typical production processes use feedstocks like isobutylene, often in combination with methanol, in adiabatic fixed reactors (Winterberg et al. 2012). The isobutylene and methanol react in the presence of ion-exchange resin catalysts at medium pressures and temperatures. Highly volatile byproducts are removed through distillation, and methanol is reclaimed using water washing or molecular sieves. In a variant of this basic technology called reaction distillation, the catalysis and distillation steps take place simultaneously (Shanley 1990). There are numerous variants in these manufacturing processes, the details of which are protected under patents or license agreements (Lorenzetti 1994; Rhodes et al. 1991).

Until the late 1980s, isobutylene and other feedstocks could be readily obtained from existing refinery operations. With minor investments, these refineries added MTBE production with yields in the range of 8,000–20,000 barrels per day. As demand for MTBE increased, large specialized production facilities were built. These larger specialized plants accounted for the vast majority of domestic production when MTBE was used domestically as a gasoline additive (Lorenzetti 1994).

Nearly all the MTBE produced in the United States was used as octane boosters and oxygenating agents in reformulated gasoline, and these uses are the only ones for which reliable production figures are readily available. Starting in the mid-to-late 1980s, MTBE production increased rapidly. According to data submitted to the Chemical Data Reporting (CDR) database, U.S. production of MTBE was 4,774,345,888 pounds (2.16×10^6 metric tons) in 2011 (EPA 2022a). In 2012, 2014, and 2015, the national aggregated production volume was estimated to be 1,000,000,000–5,000,000,000 pounds (4.53×10^5–2.27×10^6 metric tons). In 2013, the estimated production volume range was 5,000,000,000–10,000,000,000 pounds (2.27×10^6–4.53×10^7 metric tons) (EPA 2022a). There were 18 companies that reported manufacturing or importing MTBE in the United States in 2016 (EPA 2022a).

Table 5-1 lists the facilities in each state that manufactured or processed MTBE in 2021, the intended use, and the range of maximum amounts of MTBE that are stored on site. The data from the Toxics Release Inventory (TRI) listed in Table 5-1 should be used with caution, however, since only certain types of facilities were required to report (EPA 1995b). This is not an exhaustive list.

Table 5-1. Facilities that Produce, Process, or Use Methyl *tert*-Butyl Ether (MTBE)

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	1	10,000	99,999	6
AR	3	100	99,999	2, 3, 9, 12
AZ	1	10,000	99,999	10
CA	6	0	99,999	10
CO	2	100,000	999,999	10
HI	1	1,000	9,999	9
IA	4	1,000	999,999	7, 8, 9, 10, 12
ID	1	0	0	0
IL	3	10,000	999,999	1, 5, 10, 12
IN	4	10,000	999,999	7, 9, 10, 12
KS	3	1,000	99,999	6, 12, 14
KY	2	0	0	0
LA	5	0	999,999	1, 3, 4, 5, 6, 12, 13, 14
MA	1	10,000	99,999	10
ME	1	0	99	9
MI	4	10,000	999,999	1, 5, 8, 10, 12
MN	1	100,000	999,999	7, 12
MO	6	1,000	999,999	7, 9, 10, 12
MP	1	100,000	999,999	1, 5, 9
MS	6	100,000	999,999	9
MT	3	10,000	99,999	9
NC	5	10,000	99,999	6, 9, 12
NE	1	10,000	99,999	9, 12
NH	3	0	0	0
NJ	5	1,000	99,999	2, 3, 4, 9, 10, 12
NY	4	0	0	0
OH	4	1,000	99,999	7, 9, 12
OK	1	10,000	99,999	12
OR	3	10,000	99,999	10, 12
PA	1	0	0	0
PR	2	100,000	49,999,999	9
SC	5	100	99,999	10, 12
TN	3	10,000	999,999	7, 9, 10, 11, 12
TX	20	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14
UT	1	10,000	99,999	9, 12
VA	3	1,000	999,999	9, 10
VI	2	10,000	9,999,999	1, 5, 7, 9, 14

Table 5-1. Facilities that Produce, Process, or Use Methyl *tert*-Butyl Ether (MTBE)

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
WA	2	10,000	99,999	9, 14
WI	3	10,000	999,999	7, 9, 10, 12

[a]Post office state abbreviations used.
[b]Amounts on site reported by facilities in each state.
[c]Activities/uses:

1. Produce
2. Import
3. Used Processing
4. Sale/Distribution
5. Byproduct
6. Reactant
7. Formulation Component
8. Article Component
9. Repackaging
10. Chemical Processing Aid
11. Manufacture Aid
12. Ancillary
13. Manufacture Impurity
14. Process Impurity

Source: TRI21 2022 (Data are from 2021)

Table 5-2 shows U.S. plant MTBE production data as supplied by the U.S. Energy Information Administration (EIA 2022) from 2005 to 2020, with the last reported production volume of 1,599 thousands of barrels occurring in December 2020. Therefore, it is unclear if MTBE is still being produced in the United States for export to other nations.

5.2.2 Import/Export

Virtually all MTBE produced domestically in the United States is now exported to other nations, primarily Mexico, Chile, and Venezuela (EIA 2019, 2022). The monthly U.S. exports of MTBE from 2004 to 2019 are illustrated in Table 5-3. A review of the data from the EIA has shown no updated information since September of 2019; therefore, it is not clear if MTBE is still being exported from the United States. The EIA has likewise not shown any U.S. plant production of MTBE since December of 2020.

5.2.3 Use

Nearly all MTBE produced in the United States was produced for use in reformulated gasolines as part of the oxyfuel program. MTBE has been used as a non-surgical pharmaceutical treatment to dissolve gallstones in cases in which surgical treatments are considered too risky (e.g., elderly patients) (Angle 1991; Bergman et al. 1994; Edison et al. 1993; Gilbert and Calabrese 1992; Kim et al. 2015). This treatment was first used in 1986, declined in usage with development of minimally invasive laparoscopic procedures, and (as of 2015) is no longer approved in the United States due to concerns over MTBE

Table 5-2. U.S. Production of Methyl *tert*-Butyl Ether (MTBE) (Thousands of Barrels)

Year	January	February	March	April	May	June	July	August	September	October	November	December
2005	3,944	3,436	4,137	4,248	4,371	4,522	4,226	4,682	3,096	3,333	3,530	3,849
2006	3,732	2,520	3,050	2,909	2,752	2,561	3,103	3,022	2,479	1,575	1,482	1,503
2007	1,687	1,733	2,170	1,893	1,939	1,615	2,003	1,861	1,897	1,533	1,639	1,736
2008	1,731	1,419	1,595	1,613	1,639	1,501	1,671	1,549	563	1,539	1,236	1,263
2009	1,388	1,353	1,526	1,485	1,578	1,561	1,566	1,620	1,386	938	808	900
2010	570	596	1,073	970	1,185	1,287	1,300	1,371	1,241	1,227	1,351	1,328
2011	1,118	949	1,452	1,391	1,137	1,217	1,342	1,351	1,336	1,303	1,298	1,469
2012	1,111	951	1,008	1,402	1,453	1,398	1,410	1,395	1,320	1,304	1,496	1,056
2013	1,329	961	1,332	1,448	1,697	1,625	1,591	1,768	1,398	1,438	1,616	1,565
2014	1,023	957	1,135	1,315	1,481	1,210	1,263	819	1,110	1,135	1,093	1,215
2015	997	520	823	1,368	1,634	1,549	1,570	1,313	1,378	1,582	971	1,257
2016	1,300	1,196	1,649	1,623	1,611	1,475	1,475	1,412	1,493	1,440	1,400	1,268
2017	1,519	1,130	1,137	1,404	1,223	1,543	1,673	1,400	969	1,492	1,571	1,624
2018	1,632	1,359	1,372	1,654	1,823	1,690	1,637	1,658	1,627	1,827	1,662	1,723
2019	1,500	1,493	1,730	1,767	1,720	1,917	1,859	1,822	1,679	1,806	1,552	1,261
2020	1,487	1,122	1,169	1,176	1,281	1,709	1,842	1,565	1,369	1,683	1,885	1,599

Source: EIA 2022

Table 5-3. U.S. Exports of Methyl *tert*-Butyl Ether (MTBE) (Thousands of Barrels)

Year	January	February	March	April	May	June	July	August	September	October	November	December
2004	482	617	680	556	783	513	831	757	605	404	481	734
2005	1,000	417	549	898	984	1,312	906	1,424	1,079	888	969	1,007
2006	1,080	716	1,049	2,779	2,035	2,599	2,690	3,253	1,883	1,822	1,104	1,303
2007	1,021	1,713	2,346	1,310	2,833	1,216	1,569	1,842	1,696	1,682	1,550	1,685
2008	1,087	1,471	1,553	1,351	1,528	1,573	1,524	1,981	882	1,794	1,509	964
2009	1,184	1,293	2,067	1,298	1,773	1,860	1,639	2,096	1,789	1,209	498	647
2010	935	421	897	999	856	876	1,277	1,718	1,317	1,196	1,060	1,482
2011	1,026	638	1,537	1,089	1,218	862	1,111	1,811	820	1,333	1,087	1,453
2012	1,514	1,279	790	1,319	1,757	1,682	1,300	1,608	1,649	1,235	1,254	1,080
2013	624	1,770	1,403	1,233	1,371	1,443	1,878	1,528	1,499	1,368	1,285	1,770
2014	985	789	1,159	1,106	1,391	1,411	1,284	1,237	1,129	1,253	1,136	1,179
2015	962	548	436	1,160	1,180	1,496	1,444	1,539	1,181	1,212	1,205	1,028
2016	1,362	895	1,308	1,773	1,694	1,277	1,382	1,223	1,246	1,379	1,245	817
2017	1,376	1,130	1,124	915	679	1,485	1,072	1,130	1,500	1,124	1,276	1,362
2018	1,501	810	1,116	1,136	917	958	1,184	1,193	1,491	1,324	1,294	1,206
2019	874	699	1,420	906	1,218	1,377	1,618	1,361	1,353			

Source: EIA 2022

toxicity (Aetna 2020; Kim et al. 2015). In countries that still utilize MTBE dissolution (e.g., South Korea), safer alternative dissolution agents are being developed (You et al. 2019). MTBE can also be used in other petroleum related applications. It can be cracked (broken down) to produce isobutene and methanol, resulting in high purity (>99.8%) isobutene (Winterberg et al. 2012). It can also be used in chemical reactions such as the production of methacrolein and methacrylic acid (Winterberg et al. 2012).

5.2.4 Disposal

Since most MTBE is used as a component in reformulated gasoline, provisions for its disposal are generally subsidiary to regulations for disposing of gasolines or similar volatile or semi-volatile organic compounds such as benzene or toluene. MTBE is likely to be encountered in waste sites or NPL sites where blended gasoline has been disposed of, or at NPL sites around pipelines, large tank batteries, or refineries and other facilities involved in the manufacture of reformulated fuels. Once dissolved in water, MTBE can readily leach into groundwater supplies. MTBE from past disposal in dumps and waste sites or from spills, leakage from underground storage tanks (USTs), or other releases to the environment are recognized as a pollutant to groundwater supplies (EPA 2022b). Chapter 7 contains an overview of regulations and guidelines regarding disposal practices for MTBE. No information was located on the quantities of MTBE disposed of by each disposal method, or on trends in disposal amounts or practices. Enhanced biodegradation of MTBE can be accomplished using degrading bacterial consortiums, which can then be used to clean up contaminated soils or water (Li et al. 2014). Bioremediation methods have been used to remove MTBE from aqueous solution such as gasoline-contaminated waters using continuous up-flow packed-bed biofilm reactors (Alfonso-Gordillo et al. 2016; Bianchi et al. 2009).

5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005a). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ ≥10 full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005a).

5.3.1 Air

Estimated releases of 230,947 pounds (~104.8 metric tons) of MTBE to the atmosphere from 127 domestic manufacturing and processing facilities in 2021, accounted for about 89% of the estimated total environmental releases from facilities required to report to the TRI (TRI21 2022). These releases are summarized in Table 5-4.

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Methyl *tert*-Butyl Ether (MTBE)[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AL	1	20,667	0	0	0	0	20,667	0	20,667
AR	3	743	0	0	0	0	743	0	743
AZ	1	437	0	0	0	0	437	0	437
CA	6	1,837	0	0	0	0	1,837	0	1,837
CO	2	6,200	5	0	0	0	6,200	5	6,205
HI	1	402	0	0	0	0	402	0	402
IA	4	10,323	10	0	0	0	10,333	0	10,333
ID	1	0	0	0	0	0	0	0	0
IL	3	716	0	0	156	0	716	156	872
IN	4	5,842	0	0	0	0	5,842	0	5,842
KS	3	3,270	0	10,183	255	0	3,270	10,438	13,708
KY	2	0	0	0	0	0	0	0	0
LA	5	3,900	79	0	0	0	3,979	0	3,979
MA	1	216	0	0	0	0	216	0	216
ME	1	2	0	0	0	0	2	0	2
MI	4	212	0	0	0	0	212	0	212
MN	1	312	4	0	0	0	316	0	316
MO	6	4,880	3,500	0	0	723	8,380	723	9,103
MP	1	803	0	0	0	0	803	0	803
MS	6	2,026	0	0	0	0	2,026	0	2,026
MT	3	52	0	0	0	0	52	0	52
NC	5	3,572	0	0	0	336	3,572	336	3,908

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Methyl *tert*-Butyl Ether (MTBE)[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
NE	1	680	0	0	959	0	680	959	1,639
NH	3	0	0	0	0	0	0	0	0
NJ	5	381	0	0	0	0	381	0	381
NY	4	0	0	0	0	0	0	0	0
OH	4	154	0	0	0	0	154	0	154
OK	1	4	0	0	0	0	4	0	4
OR	3	2,480	5	0	0	0	2,480	5	2,485
PA	1	0	0	0	0	0	0	0	0
PR	2	1,928	0	0	0	0	1,928	0	1,928
SC	5	1,805	0	0	0	0	1,805	0	1,805
TN	3	5,534	0	0	0	0	5,534	0	5,534
TX	20	141,107	85	11,763	30	70	152,955	100	153,055
UT	1	0	0	0	0	2	0	2	2
VA	3	1,100	0	0	0	0	1,100	0	1,100
VI	2	1,099	0	0	0	0	1,099	0	1,099
WA	2	86	3	0	0	0	89	0	89
WI	3	8,177	5	0	0	0	8,177	5	8,182
Total	127	230,947	3,696	21,946	1,401	1,131	246,391	12,729	259,120

[a] The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b] Data in TRI are maximum amounts released by each facility.
[c] Post office state abbreviations are used.
[d] Number of reporting facilities.
[e] The sum of fugitive and point source releases are included in releases to air by a given facility.
[f] Surface water discharges, wastewater treatment (metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g] Class I wells, Class II-V wells, and underground injection.
[h] Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i] Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.
[j] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k] Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI21 2022 (Data are from 2021)

Although MTBE was listed as a hazardous air pollutant under the 1990 Clean Air Act Amendments, it was also an EPA-approved alternative for use in reformulated gasoline (EPA 1994). When it was being used as a gasoline additive in the United States, the most common types of releases to the air 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). A risk assessment conducted by the European Union Chemicals Bureau estimated that emissions from the exhaust of various types of automobiles commonly used in Europe ranged from approximately 7 to 250 kg of MTBE emitted per metric ton of gasoline used (ECB 2002). According to the National Emissions Inventory (NEI) database, which includes air emissions sources of both criteria and hazardous air pollutants, 462,295 pounds of MTBE were emitted to the atmosphere from point and non-point sources in 2017 (EPA 2017). This is down 33% from the 691,760 pounds of MTBE reported in 2014 (EPA 2014).

5.3.2 Water

Estimated releases of 3,696 pounds (~1.7 metric tons) of MTBE to surface water from 127 domestic manufacturing and processing facilities in 2021, accounted for 1.4% of the estimated total environmental releases from facilities required to report to the TRI (TRI21 2022). This estimate includes releases to wastewater treatment and publicly owned treatment works (POTWs). These releases are summarized in Table 5-4.

Most releases of MTBE to surface water would likely result from leaks or spills. On March 9, 2015, a collision between a bulk carrier and a tanker named the Carla Maersk occurred in the Houston Ship Channel near Morgan Point, Texas, resulting in the estimated release of 2,100 barrels of MTBE into the Galveston Bay (NTSB 2016).

Since MTBE has a fairly high degree of solubility in water, precipitation 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 wastewater 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 mmHg and Henry's Law constant of 5.87×10^{-4} atm-m^3/mole, however, MTBE would be expected to volatilize rapidly from surface water or soil surfaces (EPA 1994).

A source of groundwater contamination is from leaking USTs. As of March 2005, there were >660,000 USTs that were in use and about 1.6 million UST no longer in use according to the EPA Underground Storage Tank program. States identified about 449,000 tank releases (leaks) and about

416,000 initiated cleanups, with almost 324,000 of those cleanups completed. There is no information on the number of USTs that may contain MTBE (EPA 2022b).

5.3.3 Soil

Estimated releases of 1,401 pounds (~1.6 metric tons) of MTBE to soil from 127 domestic manufacturing and processing facilities in 2021, accounted for about 0.5% of the estimated total environmental releases from facilities required to report to the TRI (TRI21 2022). An additional 21,946 pounds (~26.9 metric tons) accounted for about 8.5% of the total environmental emissions, were released via underground injection (TRI21 2022). These releases are summarized in Table 5-4.

Emissions to surface soils can occur following an accidental spill of MTBE or MTBE-containing gasoline as well as atmospheric deposition. Leaks from storage tanks would frequently release MTBE to subsurface soils when it was being used as a gasoline additive; however, amounts released from these sources have not been quantified.

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

If released to the atmosphere, MTBE is expected to exist entirely in the vapor phase where it can be transported to the earth by wet and dry deposition. Based upon a vapor pressure of 245 mm Hg at 25°C (Budavari 1989) and Henry's Law constant of $5.87\text{x}10^{-4}$ atm-m^3/mol (Hine and Mookerjee 1975), MTBE is expected to volatilize rapidly if released to soil or water surfaces. However, the soil-adsorption coefficient (K_{oc}) of MTBE indicates that it possesses high mobility in soil, and MTBE that is not volatilized is likely to leach into lower soil horizons and contaminate groundwater. MTBE released from USTs has been shown to move rapidly in the soil column and contaminate groundwater; this has been verified in large monitoring studies (WQP 2022). The actual rate of volatilization of MTBE from surface water is dependent upon the environmental conditions of the surrounding air and water body such as the flow rate, wind velocity, temperature, and depth of the water body. Pankow et al. (1996) estimated the rate of volatilization of MTBE under various environmental conditions by varying these factors and using a two-layer model to calculate the mass transport parameters that were used to estimate the half-life. Volatilization half-lives ranged from several minutes at very shallow depths, ambient temperature, and high wind speeds to >80 days at a water depth of 32 feet, temperature of 5°C, and low flow velocities and wind speed. The study authors noted that MTBE and benzene, toluene, ethylbenzene, and xylene (BTEX) have similar estimated volatilization rates in deep slow-moving water bodies (e.g., lakes), but compounds such as benzene volatilize significantly faster in shallow, fast-moving water bodies due to its greater Henry's Law constant.

Few experimental measurements of the bioconcentration factor (BCF) in aquatic organisms (e.g., fish) are available for MTBE. In one study that used a flow-through water system with exposures carried out over a 4-week period, the highest measured BCF value measured in carp was 1.5 (Fujiwara et al. 1984). Using the EPA's EPI Suite^{TM} software (EPA 2012), an estimated BCF value of 3 was derived using its log K_{ow} and a regression derived equation (Meylan et al. 1999). These data indicate that MTBE is unlikely to bioconcentrate in aquatic organisms. It is also true that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

5.4.2 Transformation and Degradation

Air. If released to the atmosphere, MTBE is expected to undergo degradation through reaction with photochemically generated 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 nonpolluted rural air (EPA 1994). An estimated hydroxyl radical rate constant of 2.2×10^{-12} cm^3/molecule-second was calculated using a structure-based estimation method (Meylan and Howard 1993). This corresponds to an atmospheric half-life of about 2.4 days assuming a hydroxyl radical concentration of 1.5×10^6 hydroxyl radicals per cm^3 of air. MTBE does not absorb light in the environmental ultraviolet (UV) spectrum (λ >290 nm); therefore, direct photolysis is not expected to be an important environmental fate process.

There are two main decomposition pathways depending on whether the methyl group or the *tert*-butyl group is attacked by hydroxyl radicals. 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. 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 NOx. Under conditions typical of polluted urban air (Japar et al. 1990), decomposition products were shown to include 2-methoxyl-2-methyl propanol, acetone, acetaldehyde, and peroxyacetyl nitrate (PAN). Other laboratory studies also indicate that decomposition products include formaldehyde (Tuazon et al. 1991) and methyl acetate (Smith et al. 1991; Tuazon et al. 1991). 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).

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 (Shanley 1990). This can make it difficult to relate laboratory studies or modeling predictions to actual monitoring observations.

Water. In surface waters, MTBE shows little tendency to degrade due to hydrolysis or other abiotic processes. Due to its high volatility, it will usually be removed from surface waters very rapidly. It is also resistant to biodegradation (EPA 1994) and not readily biodegradable in screening-level tests. MTBE present at 100 mg/L achieved 0% of its theoretical oxygen demand over the course of a 4-week incubation period using an activated sludge inoculum in a Japanese Ministry of International Trade and Industry (MITI) test (Organisation for Economic Cooperation and Development [OECD] 301C) (CITI 2022). These results were consistent with two closed bottle studies (OECD 301D) in which MTBE achieved 0–1.8 % of its theoretical oxygen demand after 28 days using 2 mg/L of test substance exposed to a sewage inoculum (ECB 2002).

In groundwater, the persistence of MTBE would be more prominent since volatilization to the air is reduced or eliminated and MTBE is resistant to most types of bacterial biodegradation (Yeh and Novak 1991). Finneran and Lovley (2001) investigated the biodegradation of MTBE in petroleum contaminated aquifer sediments maintained under anaerobic conditions. It was shown that MTBE degradation was enhanced by the addition of humic material in sediments containing Fe(III), which acts as an electron acceptor in iron-reducing microorganisms; however, little degradation was observed in sediments lacking humic substances and Fe(III) (Finneran and Lovley 2001). In an aerobic co-substrate study conducted with gasoline-impacted and -nonimpacted groundwater and aquifer material, MTBE had maximum degradation rates of 0.36/day and 0.24/day, respectively. However, the co-substrate, ethyl *tert*-butyl ether, was preferentially biodegraded (Nicholls et al. 2020).

The behavior of a plume of MTBE mixed with gasoline and other organic hydrocarbons such as the BTEX series in contact with water in an aquifer can become very complicated. A key factor is the percentage of MTBE in the original fuel mixture. Over time, higher percentages of MTBE in reformulated gasoline were used in the United States, with the percentage being at 7% in 1979 and increasing to 11% and 15%, respectively in 1981 and 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 by increasing BTEX water solubilities (Mihelcic 1990; Poulsen et al. 1992). These impacts will be minor when the levels of MTBE in a reformulated gasoline mixture are <10% by volume but become greater as the levels of MTBE increase. 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.

Sediment and Soil. There is limited information available on degradation processes in soils or sediments. Results from field or laboratory microcosm studies suggest considerable persistence in deeper soil layers or in sediments since MTBE 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. Li et al. (2014) used mixed microbial cultures to identify and isolate various strains of bacterium that could use MTBE as a sole carbon source. Other investigators studied the aerobic biodegradation of MTBE in a microbial consortium using a continuous up-flow packed-bed biofilm reactor (Alfonso-Gordillo et al. 2016). While MTBE was shown to be toxic to the microbes at high loading rates, lower levels of MTBE could be degraded in the bioreactor with a theoretical chemical oxygen demand of up to 90%.

Kuder et al. (2005) utilized a novel approach using compound-specific stable isotope analysis (CSIA) to study the anaerobic biodegradation mechanisms of MTBE in enrichment cultures and field studies. Following the isotopic fractionation allows for a better understanding of the degradation of MTBE in gasoline plumes since following the concentration of MTBE's main metabolite, *tert*-butyl alcohol, is confounded in plumes since it is often a constituent in gasoline anyway. Martienssen et al. (2006) studied the degradation of MTBE in a contaminated groundwater plume located in Leuna (eastern Germany). They determined that degradation occurred primarily under microaerobic conditions with little or no degradation under anoxic conditions.

5.5 LEVELS 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. Concentrations of MTBE in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on MTBE levels monitored or estimated 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.

Table 5-5 shows the lowest limit of detections that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-6.

Table 5-5. Lowest Limit of Detection Based on Standards[a]

Media	Detection limit	Reference
Air[b]	0.009 ppbv	EPA 2018a
Drinking water	0.006 ppb	USGS 2016
Surface water and groundwater	0.006 ppb	USGS 2016
Soil[c]	1.7–2.6 μg/kg	USGS 2019
Sediment[c]	1.7–2.6 μg/kg	USGS 2019
Human blood	0.0006 μg/L	Hashemi et al. 2021
Human urine	0.006 μg/L	Hashemi et al. 2021

[a] Detection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.
[b] Detection limit depends on sampling time and volume.
[c] Reporting limit of the method.

Table 5-6. Summary of Environmental Levels of Methyl *tert*-Butyl Ether (MTBE)

Media	Low	High[a]	For more information and references
Outdoor air (ppbv)	<LOD	131.6	Section 5.5.1
Indoor air (ppbv)	<LOD	<LOD	Section 5.5.1
Surface water (ppb)	<LOD	0.226	Section 5.5.2
Ground water (ppb)	<LOD	23,000	Section 5.5.2
Drinking water (ppb)	<LOD	40,000	Section 5.5.2
Food (ppb)	No data	No data	
Soil (ppb)	<LOD	2–3	Section 5.5.3

[a] Highest mean daily value obtained when MTBE was still being used as a gasoline additive in the United States.

LOD = limit of detection

Detections of MTBE in air, water, and soil at NPL sites are summarized in Table 5-7.

Table 5-7. Methyl *tert*-Butyl Ether (MTBE) Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median[a]	Geometric mean[a]	Geometric standard deviation[a]	Number of quantitative measurements	NPL sites
Water (ppb)	38.0	26.5	11.1	31	23
Soil (ppb)	No data	No data	No data	No data	No data
Air (ppbv)	1.92	2.54	6.39	8	5

[a] Concentrations found in ATSDR site documents from 1981 to 2022 for 1,868 NPL sites (ATSDR 2022). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

MTBE is a pollutant monitored in the national Air Quality System (AQS) database, which contains ambient air pollution data collected by EPA, state, local, and tribal air pollution control agencies from monitors throughout the country. To illustrate the differences in ambient levels in the atmosphere of the United States over time, daily monitoring data from 2000, 2005, 2010, 2018, and 2021 were downloaded from the AQS website. Table 5-8 shows the average daily mean 24-hour percentile distributions of MTBE concentrations measured during these years at all the sites nationwide that tested for MTBE. As expected, the trend shows a rapid decrease in atmospheric levels following the phase-out of MTBE usage in gasoline after the 2005 Energy Policy Act.

Table 5-8. Percentile Distribution of Daily Mean Methyl *tert*-Butyl Ether (MTBE) Concentrations (ppbv) Measured in Ambient Air at Locations Across the United States[a]

Year	Total number of observations	10th	50th	75th	95th	Maximum
2000	5,873	0.177	0.502	0.851	1.94	18.6
2005	10,508	0.023	0.070	0.138	0.374	131.2
2010	7,555	0.003	0.003	0.004	0.008	0.890
2018	7,851	0.002	0.003	0.005	0.154	26.89
2021	8,401	0.000	0.000	0.001	0.007	0.340

[a]Values were originally reported in parts per billion carbon (ppbC) and converted to ppbv.

Source: U.S. Environmental Protection Agency (EPA) Air Quality System (AQS) annual summaries (EPA 2022c)

The Michigan Department of Environmental Quality monitored air samples at nine locations around the city of Detroit to gather air quality data in 2001–2002 (Michigan DEQ 2005). MTBE was detected in 72 out of 480 samples with a maximum concentration of 2.11 μg/m^3 (0.584 ppbv). Outdoor MTBE levels were measured in New York City, New York and Los Angeles, California (Sax et al. 2004). Median levels in the winter and summer months in New York were 10.0 and 10.9 μg/m^3 (2.77 and 3.02 ppbv), respectively. In Los Angeles, the median levels were 16.0 and 13.0 μg/m^3 (4.43 and 3.60 ppbv) in the winter and fall, respectively.

MTBE was not detected in a study in southeast Louisiana conducted in 2013–2015 of the indoor air of 99 homes, the median and range of the method detection limit were reported as 0.57 and 0.16–1.10 μg/m^3, respectively (Wickliffe et al. 2020). A research initiative by the Health Effects Institute (HEI) measured indoor, outdoor, and personal exposure concentrations of pollutants between the summer of 1999 and the spring of 2001 that included measurements obtained from 100 homes in Los Angeles, California; Houston, Texas; and Elizabeth, New Jersey (HEI 2005). The mean concentration of MTBE in indoor air samples was 11.8 μg/m^3 (3.27 ppbv) with 93% of all samples (N=553) at or above the detection limits. Hun et al. (2011) also analyzed indoor air data collected from the HEI and determined that homes with attached garages had higher indoor air levels as compared with homes that did not have attached garages, presumably due to automobile exhaust that infiltrated the residences. The mean MTBE level in garages of residences located in Boston, Massachusetts was reported as 131 μg/m^3 (36.3 ppbv), whereas the mean MTBE ambient outdoor level was 1.2 μg/m^3 (0.33 ppbv) (Dodson et al. 2008). Indoor air levels in randomly sampled homes located in Ottawa, Canada during the winter of 2002–2003 ranged from

0.025 to 3.32 μg/m^3 (0.0069–0.920 ppbv) and the detection frequency was 9% (Zhu et al. 2005). MTBE was detected in indoor air of homes that heat with fuel oil at a mean concentration of 11.8 μg/m^3 (3.27 ppbv) in air sampling conducted by the New York State Department of Health (NYSDOH) from 1997 to 2003 (NYSDOH 2006).

MTBE in water is expected to rapidly volatilize; thus, there is potential for inhalation exposure during showering and bathing. ATSDR's three-compartment Shower and Household-Use Exposure (SHOWER) model predicts air concentrations in the shower stall, bathroom, and main house throughout the day by estimating the contribution from showering or bathing and the contribution from other water sources in the house, such as the dishwasher, clothes washer, and faucets. This information, along with human activity patterns, is used to calculate a daily TWA exposure concentration via inhalation exposure and from dermal uptake from skin contact. ATSDR's SHOWER model is available by sending a request to showermodel@cdc.gov.

Vapor intrusion may be a potential source of MTBE exposure, though indoor and ambient sources may also contribute to indoor air levels. EPA's compilation of four studies of background indoor air concentrations found a 9–70% detection rate for MTBE in 502 U.S. resident samples between 1990 and 2005 (EPA 2011). The background medians ranged from 0.025 to 3.5 μg/m^3, 95th percentiles ranged from 71 to 72 μg/m^3, and maximum values ranged from 3.3 to 470 μg/m^3. ATSDR compared detected MTBE concentrations from 20 vapor intrusion sites to ATSDR vapor intrusion comparison values from air, soil gas, or groundwater in a review of 148 public health assessments published between 1994 and 2010 (Burk and Zarus 2013). The AM/PM Gas Station site in Belmont California was the only site to exceed an ATSDR vapor intrusion comparison value for MTBE with groundwater concentrations up to 190,000 ppb (ATSDR 2005). The soil gas concentrations were all less than the comparison value at the site. Remedial actions that occurred at the site could decrease the potential for exposures in the future. The site was not considered a public health hazard. Ma et al. (2017) developed a numerical model that used groundwater monitoring data from the EPA Underground Storage Tank program to estimate the potential vapor intrusion into buildings depending upon the characteristics of the buildings, soils, and MTBE level in groundwater. Their findings indicated that indoor air concentrations can exceed the EPA indoor air screening level for MTBE for highly contaminated groundwater plumes. Sanders and Hers (2006) analyzed indoor air in buildings potentially affected by contaminated groundwater due to a leaking underground gasoline storage tank in Stafford Township, New Jersey. Groundwater levels of MTBE ranged from 0.370 to 590 mg/L at five sampling locations. Indoor air was sampled on the main floor, in the basement, and under the foundation slab. In the location with the highest groundwater MTBE level, the indoor air concentrations were reported as 130 and 52.0 μg/m^3 (36.0 and 14.4 ppbv) in the basement and main floor, respectively. The vapor concentration of MTBE 2 m below the slab was 18,000 μg/m^3 (~5,000 ppbv).

5.5.2 Water

During the mid-1980s, New Jersey 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 (NJDEP 1994). During this period, at least 30 wells serving six different community drinking 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, it was as high as 40,000 ppb. When MTBE levels of ≥100 ppb were detected, there were also detections of such gasoline constituents such as benzene, toluene, xylene, or other hydrocarbons. 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 have contained MTBE levels >70 ppb (NJDEP 1994). MTBE was monitored as part of the Unregulated Contaminant Monitoring Rule (UCMR-1) program to collect data for contaminants suspected to be present in drinking water, but that do not have health-based standards set under the Safe Drinking Water Act (SDWA). Between 2001 and 2005, MTBE was detected above its minimum reporting level (5 ppb) in 26 out of 34,131 samples of drinking water obtained from public water systems (PWSs) (EPA 2005b). It was detected above its minimum reporting level in 19 out of 3,877 PWSs that reported results. The maximum observed level was reported as 49 ppb and the mean of all positive detects was 15.2 ppb. A national water quality study was done for contaminants including MTBE over the period of 1991–2010 (USGS 2014). For 40 aquifers that used for drinking water, the percentage containing MTBE at ≥0.2 μg/L ranged from 0 to 21.37%, with an average of 2.62%. For 17 shallow groundwater aquifers beneath agricultural land, the average detection was 0.89% (range 0–13.33%) and for 22 shallow groundwater aquifers beneath urban land, an average 12.09% (range 0–60.53%) MTBE detection rate was reported (USGS 2014). Flanagan et al. (2017) monitored MTBE concentrations in private wells located in the state of New Hampshire from 2005 to 2015. Of 195 wells sampled in 2015, 10.3% had levels greater than the reporting level of 0.2 μg/L (ppb) as compared to 26.7% of the wells in 2005. Maximum concentrations in the wells sampled ranged from 4.47 to 151 μg/L (ppb) in 2005 and declined over the next decade. The maximum concentration range in 2015 was reported as 0.2–4.55 μg/L (ppb). There appeared to be a correlation with frequency of detection and population density. For example, in 2015, wells in areas of higher population densities had a 15.5% detection frequency, whereas wells in areas of low population density the detection frequency was about a third of that value (5.1%).

MTBE may also contaminate drinking water by leaching out of cross-linked polyethylene (PEX) constructed water pipes (some PEX products may utilize the catalyst *tert*-butyl peroxide, and MTBE is a breakdown product of this). Holder et al. (2019) showed that degassing of pipes was found to be an efficient strategy for reducing MTBE migration into water. MTBE was detected at levels ranging from 1.45 to 11.7 μg/L (ppb) in water samples obtained from six apartment houses with epoxy-lined drinking water pipes in Helsinki, Finland (Rajasarkka et al. 2016).

To assess drinking water contamination after the 2018 Camp Fire in California, water samples were collected from 136 homes in the burn area around Paradise, California. MTBE was detected in one home at 0.67 μg/L (Solomon et al. 2021). MTBE was not detected as a biproduct of pyrolysis of polyvinyl chloride (PVC), cross-linked polyethylene (PEX), or high-density polyethylene (HDPE) in laboratory experiments (Draper et al. 2022).

The United States Geological Survey (USGS 1995) summarized VOC data on MTBE derived from a series of studies in its National Water-Quality Assessment (NAWQA) Program. NAWQA data were presented 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; however, only 3% of the urban wells showed MTBE concentrations that exceeded 20 ppb. The highest concentration of MTBE detected in a groundwater sample was 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. The USGS data suggest that when MTBE was used as a gasoline additive, urban areas with a long history of reformulated gasoline usage in USTs had more frequent and higher levels of groundwater contamination from MTBE as compared to other areas (USGS 1995).

MTBE was found at 0.03 μg/L in 1 of 50 domestic well groundwater samples located in the Marcellus Shale region (four counties in Pennsylvania, two counties in New York) collected in 2017; all other wells contained <0.01 μg/L (McMahon et al. 2019). A groundwater assessment conducted by the USGS from 1985 to 2001 analyzed 55 VOCs, including MTBE, from approximately 2,400 domestic and 1,100 public wells (USGS 2006). MTBE was the third most frequently detected VOC in the assessment. The median concentration of MTBE was reported as 0.20 μg/L (ppb) (n=2,422). In a subset of samples from 1,687 wells that were analyzed using a lower assessment level (0.02 μg/L [ppb]), MTBE was detected in

7.1% of the wells. USGS (2016) analyzed 262 groundwater samples and 14 surface water samples in 2013 collected from 25 USGS projects nationwide and determined that MTBE was detected in 7% of the samples, with a concentration range of 0.016–0.226 µg/L (ppb). In a systematic assessment of occurrence for 85 VOCs in raw (untreated) groundwater used for public supply across the United States, MTBE was the second most commonly detected VOC (8.4% of area, 11% of wells) (Bexfield et al. 2022). Samples were collected from 2013 through 2019 from 1,537 public-supply wells in aquifers, representing 78% of the volume pumped for public drinking water supply (Bexfield et al. 2022).

In groundwater, studies of NPL and UST program remediation sites can provide highly site-specific indications of MTBE levels in groundwater. UST sites with MTBE groundwater contamination may potentially affect a larger total population since older gasoline stations are ubiquitous. Detections of MTBE triggered by reports of offensive odors in groundwater are common. Reported odor thresholds for MTBE in water range from 15 to 680 µg/L (ppb) (Angle 1991; EPA 1997; Gilbert and Calabrese 1992). 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).

5.5.3 Sediment and Soil

The USGS conducted an environmental monitoring study at a U.S. Army ammonium perchlorate destruction facility located in Chambersburg, Pennsylvania in 2016 (USGS 2019). MTBE was identified at levels above the detection limit of 1.7–2.6 µg/kg in 50% of samples; however, exact quantitative levels were not identified. MTBE was detected at a concentration of 18,000 µg/kg in soil (depth of 3 m) contaminated by a leaking underground gasoline storage tank in Stafford Township, New Jersey (Sanders and Hers 2006).

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 that 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).

5.5.4 Other Media

A laboratory study conducted on fish (Fujiwara et al. 1984) does not suggest any tendencies for bioconcentration, biomagnification, or bioaccumulation of MTBE that would present human health threats.

MTBE has been detected in milk samples purchased in Las Vegas, Nevada in January and February 2002 (Hiatt and Pia 2004). Maximum concentrations in whole milk, 2% milk, and 1% milk were 0.03, 0.02, and 0.03 ng/mL, respectively, with a minimum detection limit of 0.01 ng/mL.

5.6 GENERAL POPULATION 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. The Fourth National Report on Human Exposures to Environmental Chemicals (CDC 2019) summarizes blood levels of MTBE for the U.S. population categorized by age, sex, and race. Table 5-9 shows these levels for survey years 2001–2008 and Table 5-10 provides these data for survey years 2011–2016 (MTBE levels were not measured in survey years 2009–2010). MTBE was still being used in gasoline for many of the years depicted in Table 5-8, but this use was generally discontinued after 2005. The decrease in blood MTBE levels after 2005 indicate that the general population was largely exposed to this substance due to its use as a fuel additive; current exposure levels are much lower than in previous decades. Silva et al. (2019) analyzed NHANES data prior to the discontinued use of MTBE and afterwards. They determined that the unweighted proportion of the individuals with MTBE blood levels above the limit of detection (LOD) for years 2001–2002 was 93%; this dropped to 25.4% of the population for the period 2011–2012. Prior to discontinuation of MTBE as a fuel additive, the general population was exposed via inhalation and dermal exposure during fueling operations, inhalation of ambient air including automobile exhaust, and oral exposure from drinking water. Cattaneo et al. 2021 studied exposure to 51 individuals living and working in the Milan metropolitan area from November 2014 to March 2015. MTBE was detected in the respiratory zone of 67% of individuals with exposure levels of 0.3–2.5 $\mu g/m^3$ and a median of 0.8 $\mu g/m^3$. Current routes of exposure may arise from oral ingestion of drinking water, inhalation of ambient air, and possible dermal and inhalation exposure during showering activities of water containing MTBE. Vapor intrusion of MTBE into buildings and residences from contaminated groundwater may result in indoor air inhalation exposure. Since MTBE has been

Table 5-9. Geometric Mean and Selected Percentiles of Methyl-*tert*-Butyl Ether (MTBE) Whole Blood Concentrations (in pg/mL) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) (2001–2008)

	Survey years[a]	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Total	2001–2002	16.4 (4.77–56.7)	27.7 (7.29–64.9)	73.8 (35.5–127)	132 (64.0–278)	188 (109–339)	672
	2003–2004	11.0 (5.98–20.1)	10.0 (4.60–25.1)	45.0 (16.0–98.0)	110 (70.0–180)	170 (110–340)	1,307
	2005–2006	6.16 (2.94–12.9)	4.60 (1.80–15.0)	20.0 (5.20–73.0)	75.0 (22.0–140)	110 (49.0–250)	3,080
	2007–2008	*[b]	<LOD	<LOD	3.50 (2.00–7.83)	7.27 (3.40–22.3)	2,964
Age group							
12–19 years	2005–2006	5.85 (2.61–13.1)	4.20 (1.40–18.0)	18.0 (4.60–75.0)	70.0 (18.0–140)	110 (62.0–180)	911
	2007–2008	*	<LOD	<LOD	3.74 (1.90–8.47)	8.43 (3.10–19.0)	476
20–59 years	2001–2002	16.4 (4.77–56.7)	27.7 (7.29–64.9)	73.8 (35.5–127)	132 (64.0–278)	188 (109–339)	672
	2003–2004	11.0 (5.98–20.1)	10.0 (4.60–25.1)	45.0 (16.0–98.0)	110 (70.0–180)	170 (110–340)	1,307
	2005–2006	6.26 (3.05–12.9)	4.80 (2.00–14.0)	20.0 (5.50–70.0)	71.0 (21.0–150)	110 (46.0–250)	1,512
	2007–2008	*	<LOD	<LOD	3.16 (1.90–5.10)	5.10 (2.87–19.0)	1,597
≥60 years	2005–2006	6.00 (2.67–13.5)	3.80 (1.60–14.0)	22.0 (4.00–94.0)	22.0 (4.00–94.0)	120 (55.0–290)	657
	2007–2008	*	<LOD	1.80 (<LOD–3.10)	1.80 (<LOD–3.10)	14.0 (5.25–28.0)	891
Sex							
Males	2001–2002	16.9 (4.96–57.7)	27.9 (6.82–64.6)	75.0 (35.5–131)	132 (54.9–307)	167 (109–417)	334
	2003–2004	12.2 (6.29–23.6)	11.0 (4.80–29.0)	55.0 (18.0–110)	130 (79.0–200)	200 (110–470)	641
	2005–2006	6.24 (3.07–12.7)	4.60 (1.90–15.0)	20.0 (5.90–69.0)	73.0 (25.0–120)	110 (52.0–230)	1,462
	2007–2008	*	<LOD	1.40 (<LOD–2.21)	3.40 (1.93–8.40)	7.27 (3.00–26.0)	1,481
Females	2001–2002	16.0 (4.12–61.8)	26.6 (5.93–74.6)	72.7 (32.6–132)	142 (73.5–255)	194 (92.3–336)	338
	2003–2004	9.88 (5.62–17.4)	8.90 (4.30–23.0)	38.0 (14.0–85.0)	94.0 (58.0–160)	140 (90.0–250)	666
	2005–2006	6.08 (2.81–13.1)	4.50 (1.70–14.0)	19.0 (4.90–79.0)	76.0 (20.0–160)	110 (48.0–250)	1,618
	2007–2008	*	<LOD	<LOD	3.50 (1.90–8.40)	7.30 (3.60–16.5)	1,483
Race/ethnicity							
Mexican Americans	2001–2002	23.3 (4.96–110)	33.4 (2.92–187)	91.3 (26.1–255)	225 (80.6–339)	273 (182–358)	166
	2003–2004	11.6 (5.35–25.3)	12.0 (3.80–29.0)	32.0 (14.0–80.0)	80.0 (38.0–190)	160 (74.0–220)	245
	2005–2006	7.61 (2.99–19.3)	5.40 (2.00–33.0)	30.0 (4.60–90.0)	67.0 (26.0–190)	100 (45.0–330)	735
	2007–2008	*	<LOD	1.71 (<LOD–2.90)	4.10 (2.19–9.60)	8.80 (5.20–11.5)	559

Table 5-9. Geometric Mean and Selected Percentiles of Methyl-*tert*-Butyl Ether (MTBE) Whole Blood Concentrations (in pg/mL) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) (2001–2008)

	Survey years[a]	Geometric mean (95% CI)	Selected percentiles (95% CI)				Sample size
			50th	75th	90th	95th	
Non-Hispanic blacks	2001–2002	14.9 (6.11–36.4)	26.4 (3.11–55.6)	52.6 (30.0–86.8)	87.4 (38.6–155)	120 (70.0–155)	119
	2003–2004	9.63 (4.83–19.2)	10.0 (3.50–28.0)	32.8 (11.0–85.0)	77.0 (36.0–160)	140 (61.0–210)	285
	2005–2006	9.14 (3.16–26.5)	5.70 (1.80–50.0)	48.0 (5.00–150)	120 (46.0–280)	180 (88.0–460)	820
	2007–2008	*	<LOD	1.90 (<LOD–3.80)	3.50 (2.40–7.27)	5.80 (3.50–15.3)	587
Non-Hispanic whites	2001–2002	16.0 (4.13–62.4)	27.9 (4.71–74.6)	72.7 (33.3–132)	132 (59.6–249)	165 (92.8–366)	333
	2003–2004	11.5 (5.51–23.8)	11.0 (4.00–33.5)	59.0 (14.0–120)	120 (73.0–230)	180 (110–430)	673
	2005–2006	5.55 (2.47–12.5)	4.00 (<LOD–15.0)	16.0 (4.30–75.0)	70.0 (15.0–150)	110 (40.0–250)	1,291
	2007–2008	*	<LOD	<LOD	3.30 (1.42–12.0)	7.10 (2.59–31.0)	1,349

[a] The limit of detection for survey years 2001–2002, 2003–2004, 2005–2006, and 2007–2008 were 0.232, 2.0, 1.4, and 1.4 pg/mL, respectively.
[b] Not calculated; proportion of results below limit of detection was too high to provide a valid result (*).

CI = confidence interval; LOD = limit of detection

Source: CDC 2019

Table 5-10. Geometric Mean and Selected Percentiles of Methyl-*tert*-Butyl Ether (MTBE) Whole Blood Concentrations (in pg/mL) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) (2011–2016)

	Survey years[a]	Geometric mean (95% CI)	Selected percentiles (95% CI) 50th	75th	90th	95th	Sample size
Total	2011–2012	*[b]	<LOD	1.62 (<LOD–2.11)	3.50 (2.98–4.12)	4.63 (4.05–5.63)	2,509
	2013–2014	*	<LOD	<LOD	< LOD	<LOD	3,027
	2015–2016	*	<LOD	<LOD	< LOD	<LOD	2,858
Age group							
12–19 years	2011–2012	*	<LOD	<LOD	3.21 (2.53–3.49)	3.83 (3.38–4.43)	455
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	555
	2015–2016	*	<LOD	<LOD	<LOD	<LOD	502
≥20 years	2011–2012	*	<LOD	1.70 (<LOD–2.14)	3.60 (3.07–4.15)	4.77 (4.12–5.96)	2,054
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	2,472
	2015–2016	*	<LOD	<LOD	<LOD	<LOD	2,356
Sex							
Males	2011–2012	*	<LOD	1.77 (<LOD–2.18)	3.62 (3.15–4.28)	4.85 (4.15–5.96)	1,286
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	1,458
	2015–2016	*	<LOD	<LOD	<LOD	<LOD	1,407
Females	2011–2012	*	<LOD	1.49 (<LOD–2.11)	4.49 (3.72–5.55)	4.49 (3.72–5.55)	1,286
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	1,458
	2015–2016	*	<LOD	<LOD	<LOD	10.0 (<LOD–12.0)	1,407
Race/ethnicity							
Mexican Americans	2011–2012	*	<LOD	1.94 (<LOD–2.50)	3.66 (2.70–4.33)	4.66 (3.05–17.6)	271
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	494
	2015–2016	*	<LOD	<LOD	<LOD	10.0 (<LOD–18.0)	499
Non-Hispanic blacks	2011–2012	*	<LOD	<LOD	2.42 (1.90–2.96)	3.55 (2.89–4.31)	639
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	571
	2015–2016	*	<LOD	<LOD	<LOD	10.0 (<LOD–13.0)	574

Table 5-10. Geometric Mean and Selected Percentiles of Methyl-*tert*-Butyl Ether (MTBE) Whole Blood Concentrations (in pg/mL) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) (2011–2016)

	Survey years[a]	Geometric mean (95% CI)	Selected percentiles (95% CI) 50th	75th	90th	95th	Sample size
Non-Hispanic whites	2011–2012	*	<LOD	1.77 (<LOD–2.37)	3.71 (3.15–4.41)	4.80 (4.10–5.96)	891
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	1,208
	2015–2016	*	<LOD	<LOD	<LOD	<LOD	941
All Hispanics	2011–2012	*	<LOD	1.80 (<LOD–2.23)	3.24 (2.51–4.01)	4.21 (3.25–6.09)	548
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	792
	2015–2016	*	<LOD	<LOD	<LOD	10.0 (<LOD–14.0)	885
Asians	2011–2012	*	<LOD	<LOD	2.33 (1.41–3.89)	3.89 (2.01–6.85)	356
	2013–2014	*	<LOD	<LOD	<LOD	<LOD	353
	2015–2016	*	<LOD	<LOD	<LOD	<LOD	339

[a] The limit of detection for survey years 2011–2012, 2013–2014, and 2015–2016 were 1.40, 10.0, and 10.0 pg/mL, respectively.
[b] Not calculated: proportion of results below limit of detection was too high to provide a valid result (*).

CI = confidence interval; LOD = limit of detection

Source: CDC 2019

detected at NPL sites (see Section 5.1), populations living near hazardous waste sites may be exposed. MTBE is readily absorbed by oral and inhalation routes; however, it is reported to have low absorption dermally (EPA 2003b; Prah et al. 2004).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Although it is no longer used as a gasoline additive in the United States, MTBE was still manufactured and exported to other nations that still use it as an oxygenate in fuels; however, this practice may have been discontinued at the end of 2020 as the most recent statistics from the EIA (2022) show no MTBE production since December 2020 and no exports of MTBE since the end of 2019. Workers employed in industries that manufactured, formulated, store, or transported MTBE, and workers involved in the disposal of MTBE-containing wastes, are expected to have greater exposures than the general population. In occupational settings, inhalation and dermal exposure with subsequent absorption through intact skin are the most important routes of exposure. Persons residing near facilities that manufacture or blend MTBE into fuels for export will likely have greater exposure than the general population. Andreoli et al. (2015) studied a population of children in Sicily residing near a gasoline refinery and an additional group residing approximately 70 km away from the refinery to assess exposure to BTEX and MTBE. Levels of urinary MTBE and other compounds consistent with gasoline exposure were significantly higher at two sampling times (morning and evening) for the group residing near the refinery as compared to the group 70 km away. The geometric mean urinary MTBE levels for the children living close to the refinery were 0.79 μg/L (evening) and 0.82 μg/L (morning). The geometric mean urinary MTBE levels for the population living far-removed from the refinery were 0.56 μg/L (evening) and 0.59 μg/L (morning). It is possible that similar trends will exist in the United States for populations in close proximity to MTBE manufacturing facilities.

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 byproducts. The Alaskan study was conducted after January 1993, at which time the use of MTBE as an anti-pollutant oxygenating agent had been suspended regionally. MTBE was still in use as an octane booster in high-octane (premium) grades of gasoline, but this would have been at levels (≤1% 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 <1 ppmv. In Stamford, Connecticut, where MTBE was still being used as an anti-pollutant additive, the mean workplace concentration at automotive repair centers was 0.4 mg/m^3 (0.11 ppmv), with a range of 0.11–43.41 mg/m^3 (0.03–12.04 ppmv).