

property. The monitoring wells range in depth from 20 to 25 feet bgs, and are sampled on a semiannual basis. No soil or groundwater sampling appears to have been conducted off-site. Therefore, the extent of contamination in both of the horizontal and vertical directions, does not seem to be delineated.

Sampling of the monitoring wells showed highest concentrations of contaminants in MW-1 (next to the gasoline USTs). Concentrations in MW-1 dropped significantly over the sampling period on record, with MTBE concentrations dropping from 210,000 ppb in 4/2006 to 54 ppb in 3/2011. Similarly, benzene concentrations dropped from 1,450 ppb to 55 ppb during the same time period. In contrast, concentrations of ethyl benzene and total xylenes did not change as significantly during the sampling period. For example, ethyl benzene concentration measured at 3,610 ppb in 4/2006 compared to 3,840 ppb in 3/2011. Total xylenes on the other hand, were measured at 18,600 ppb in 4/2006, compared to 12,300 ppb in 3/2011¹². This would seem to indicate that MTBE and benzene were quick to move with the groundwater and away from the site. This could be attributed to the transport properties of the different chemicals, with MTBE and benzene being more mobile and less likely to adsorb to soil media. Ethyl benzene and xylenes on the other hand have higher retardation coefficients compared to benzene and MTBE.

Modeling work conducted by the consultants (MTBE plumes) indicates that the MTBE plume likely moved off site. A potable well, located on the northwest end of the property did not show contamination over the period of sampling from 2006 to 2012.

4.3 TS#3 Getty West Windsor

This site is located at 3710 Route 1, Princeton, in Mercer County. General topography around the area is relatively flat, and land use near the gasoline station is mostly commercial and residential. Approximately 927 feet north of the service station is an "unnamed body of water" (*Tyree, 2006*). The Millstone River and Carnegie Lake are approximately 3,333 feet northeast, and 3,899 feet north of the service station respectively.

Geology and Hydrogeology: The site is located within the Lockatong Formation which consists of "black and gray siltstone and shale ranging from thin to thick layers" (*Tyree, 2006*). Based on soil borings collected at the site, consultants describe the subsurface matrix as "red brown silts and fine to coarse sands some clays to approximately 20-feet below ground surface (bgs). Red brown fractured shale was encountered to approximately 46-feet bgs. Competent bedrock was encountered from 46-feet to approximately 61-feet bgs." (*Tyree, 2006*).

Groundwater at the site is between 13 to 21 feet bgs, and flows to the east-southeast. The average hydraulic gradient is estimated at 0.0194ft/ft, the hydraulic conductivity (K) has been calculated to be 3.8 ft/day, and the groundwater velocity was calculated at 69.35 ft/year (0.19 ft/day) (*Tyree, 2006*).

Dissolved oxygen concentrations in the monitoring wells, measured in January 2006, were below 1 mg/l in all wells, and the pH ranged between 6.43 and 7.16.

¹² Bates stamp # SOVCON015058

Nearby receptors: A well records search with the Bureau of Water Allocation (BWA) identified 7 domestic, 2 irrigation, 3 industrial, and 3 public wells within a one mile radius of the site. A door-to-door canvas identified three potable domestic wells within a 1000 feet radius, all located hydraulically down gradient from the service station (Tyree, 2006).

Release History: In July of 2004, a product line test failed, resulting in the initiation of soil investigation activity at the site. Results indicated BTEX and MTBE contamination in exceedance of the state's Soil Cleanup Criteria (Criteria). In June and July of 2005, USTs and associated piping were removed from the site. Excavated soils, approximately 5,600 tons, removed from the area of the unleaded gasoline UST and the dispenser island, were taken offsite for thermal destruction. Soil analysis conducted in August of 2004 showed significant MTBE contamination in 7 out of 19 soil borings examined (concentrations ranging from 10 to 696 mg-MTBE/kg-soil, well above the State's Criteria of 3.1 mg/kg). In contrast, Benzene concentrations were above the State's Criteria of 1 mg/kg in 3 out 19 soil borings examined. Concentrations ranged between 2.77 to 4.78 mg-benzene/kg-soil.

Monitoring and Remediation: Between the end of 2004 and the beginning of 2006, twelve monitoring wells were installed onsite. All monitoring wells had relatively high concentrations of benzene and MTBE indicating the plume was not delineated, and was potentially moving offsite. Four additional monitoring wells were later installed on an adjacent property across the street and in the general down gradient direction from the contamination site. MTBE and TBA concentrations measured in those four wells were mostly below the State's GWQS (70 ppb). However, given that the wells are shallow, it is probable that the MTBE/TBA plume moved below the monitoring network (see *Ellis 2000; API 2000; Wilson et al 2005c; API, 2006*).

It should be noted that the maximum MTBE and TBA concentrations measured at the site are considerably high. For example, maximum MTBE concentration was measured in MW-5 (converted into an extraction well in early 2006) at 2,030,000 ppb (2,030 ppm) on 11/10/2004. The maximum TBA concentration for the site was measured in the same well (MW-5) at 333,000 ppb (on 5/12/2005). In contrast, the maximum benzene concentration was recorded in well MW-6 (converted to extraction well in early 2006) at 11,300 ppb, on 3/1/2005.

Remedial action has been taken at the site. Four groundwater extraction wells were installed, and by April 2010 an estimated 462,111 gallons of groundwater had been extracted (Tyree, 2010). Additionally, a soil vapor extraction system (SVE) was to be installed at the site to augment site remediation (Tyree, 2010).

4.4 TS#4 Exxon Livingston

The site is located at 38 East Mount Pleasant Avenue, Livingston, in Essex County. The gasoline station is in an area with commercial and residential property. The site slopes to the west along East Mount Pleasant Avenue. The surface water body nearest the site is Canoe Brook, located approximately 950 feet southwest of the site.

Geology and Hydrogeology: Subsurface activities at the site indicate that the overburden consists of “brown silt with fine sand up to an approximate depth of 30 feet below grade and brown fine to coarse sand with well-rounded coarse gravel up to an approximate depth of 40 feet below grade” (*Kleinfelder 2010*). This is characteristic of the Pleistocene glaciation in the area. The consultants also note that: “the sand and gravels tend to sit within the buried valleys of the bedrock topographic surface and act as groundwater recharge areas when present near the current land surface” (*Kleinfelder 2010*).

At the site, bedrock was encountered at depths somewhere between 20 and 45 feet bgs. The bedrock is described as being part of the Towaco formation, and “consists of reddish brown to brownish purple, fine to medium grained sandstone, siltstone, and silty mudstone. These deposits are generally located within upward fining sequences one to three meters thick. The sandstones of this formation are commonly cross-laminated, and the siltstones are commonly planar laminated or bioturbated. Locally, beds in the Towaco formation strike north 45 degrees and dip 7 to 12 degrees to the northwest in Essex County. Both vertical and horizontal fractures are common within this formation (Drake et al., 1996)” (*Kleinfelder 2010*).

Groundwater in the overburden is encountered at depths of 30 to 40 feet bgs, and moves predominately to the west. The hydraulic conductivity was calculated to be 3.805 ft/day based on testing done in June 2003. The hydraulic gradient was estimated between 0.02 and 0.07 ft/ft (based on wells MW-1 to MW-5, measured three different times between September 2009 and June 2010).

In the bedrock, the hydraulic head is “highly variable and ranges from approximately 30 to 112 feet below grade” (*Kleinfelder 2010*). Based on aquifer testing done in January 2007 on two bedrock wells (MW-5D and MW-11D) the flow of water in the bedrock aquifer was concluded to be “predominately along strike to the southwest” (*Kleinfelder 2010*). The hydraulic conductivity in the fractures was calculated at 0.9378 ft/day, and in the bedrock matrix at 9.678×10^{-6} ft/day.

Nearby receptors: The closest commercial supply well is approximately 800 ft down gradient (southwest) of the site. During sampling events in October 2009 and April 2010, MTBE was detected at concentrations of 0.13 and 0.19 ppb respectively. No BTEX were detected in the well.

Release History: The site contains three fiberglass gasoline USTs (8,000, 10,000 and 12,000-gallons) which were installed in 1986 (*Kleinfelder 2010*). Site investigation activity was initiated after the accidental discharge (“drive-off”) of an estimated one-gallon of regular gasoline to the pavement and the pea gravel beneath the dispenser island in May 2001. In February 2002, approximately 0.09 feet of liquid phase hydrocarbon (LPH) was detected in one of three monitoring wells (MW-1) installed at the time. In March 2003, LPH was detected in two additional monitoring wells (0.17 feet in MW-4, and 0.1 feet of LPH in MW-6). The maximum LPH was detected at 0.48ft in monitoring well MW-4 in February 2004. By March 2004, “five 1,000-gallon gasoline USTs that were previously abandoned-in-place were identified and removed from the site” (*Kleinfelder, 2010*). Between June 2002 and April 2004, approximately 20 gallons of LPH were extracted from the site as part of interim remedial activities.

Monitoring and Remediation: The monitoring systems includes 14 overburden and 14 bedrock monitoring wells. The consultant's report indicates that remediation involves groundwater pump and treat (GW P&T) and soil vapor extraction (SVE), and the monitoring network is relatively large. Onsite, there are 8 extraction wells (MW-1 to MW-8) 3 bedrock monitoring wells (MW-5D, MW-5D2R and MW-5D3) and "active GWP&T and SVE remedial systems." Additionally, 16 monitoring wells (MW-9, MW-9D, MW-10D, MW-10R, MW-11D, MW-11R, MW-12D, MW-13, MW-14S, MW-14D, MW-15S, MW-15D, MW-16D, MW-16D2, MW-17D and MW-17D2) are located offsite on nearby properties. The SVE system was started in July of 2004, and the GWP&T system was started in November of the same year.

4.5 TS#5 Sunoco Bloomfield

The site is at 72 Bloomfield Avenue and 17th street in Bloomfield, Essex County, and has operated as a petroleum retail station since 1947.

Geology and Hydrogeology: The general area in the vicinity of the site is characterized by overburden on top of bedrock. The bedrock, of the Passaic formation, is "overlain by approximately 50 to 100 feet of unconsolidated glacial/fluvial deposits, consisting of silt, clay, and sand" (*GES, 2006*). At the site, split-spoon sampling and drill cuttings indicate the overburden consists of brown sand to depth of five to ten feet overlying at least 15 feet of compact silt. Soil borings for the installation of monitoring wells extended only to a depth of 25 feet bgs, and depth to bedrock was not evaluated.

The average hydraulic conductivity for the site was calculated at 0.168 ft/day (5.93×10^{-5} cm/sec). The groundwater flow, based on the sampling event in November 2005, was to the northeast at an average hydraulic gradient of 0.015 ft/ft (*GES, 2006*).

Nearby Receptors: A search of the records of the NJDEP Bureau of Water Allocation indicates the presence of twelve wells (one domestic, seven commercial, and four industrial) within a one-mile radius of the site. The domestic well is upgradient (approximately 700 ft southwest) of the site. All identified wells are in bedrock, with depth of 110 feet or more.

Release History: In January 1992, soil contamination was discovered during the removal of a 1000-gallon UST from the site. Consequently, approximately 28 tons of soil was excavated and removed from the site (*GES, 2006*). Groundwater sampling was started in 1992.

The monitoring network includes 9 on-site, and 9 off-site monitoring wells, sampled semi-annually.

Remediation activity: groundwater extraction and SVE, were started in May and June of 2005 respectively (*GES 2006*). By early 2006 approximately 26,114 gallons of groundwater were recovered. In their 2006 report, the consultants note that the remediation system does not address contamination off-site noting: "It is acknowledged that the VOC concentrations in groundwater at offsite MW-9 are not addressed by the existing remedial system" (*GES, 2006*).

4.6 TS# 6 Hess Maple

The site is located at 2815 Route 73 and Regent Avenue, Maple Shade in Burlington County. It is located in the Inner Coastal Plain. Some 450 feet west of the Site is a “deciduous wooded wetland” which surrounds the South Branch Pennsauken Creek. The Creek, the surface water body nearest to the Site, is approximately 600 feet to the west.

Geology and Hydrogeology: The site slopes gently to the southwest, and based on site investigation activity, groundwater flows to the west-southwest, and the average hydraulic gradient is 0.012 ft/ft.

The consultant’s report (*Envirotrack, 2012*) describes the local geology as consisting of Upper Cretaceous Age sedimentary rocks, adding that: “Unconsolidated Pleistocene and recent deposits form a thin, discontinuous cover over the bedrock surface. Bedrock geology underlying the Site is the Woodbury Formation which consists of unconsolidated clay, sand, and silt” (*Envirotrack, 2012*; emphasis added).

Release History: According to the consultant’s report (*Envirotrack, 2012*), contamination at the site was first noted in December 1989, “during closure activities of three 8,000-gallon steel underground storage tanks.” At the time, both “impacted soil and LNAPL were observed”. In May 1990, three 10,000-gallon fiberglass USTs were installed. Not long after, in August 1996, “Hess ceased retail operations at the site” and divested the property to ARFA. However, in October 1999 and April 2000, elevated concentrations of MTBE were reported in the monitoring wells in near the UST field. As a result, the NJDEP ordered ARFA to conduct a 7-day investigation into the source of the increased concentrations. Based on LNAPL characterization, the investigation concluded that a discharge likely occurred between September 1999 and August 2000 (*Envirotrack, 2012*).

The consultant’s report however, indicates the presence of a significant amount of LNAPL at the site over the span of many years:

“The maximum horizontal extent of the LNAPL body was 92 feet long in the direction of groundwater flow and 52 feet wide perpendicular to the direction of groundwater flow on December 19, 2000. As of August 18, 2011, the horizontal extent of the LNAPL body was 50 feet long in the direction of groundwater flow and 45 feet wide perpendicular to the direction of groundwater flow. The vertical extent of the LNAPL body has ranged from 14.25 feet below the top of casing (MW2 on November 27, 1992) to 8.07 feet below the top of casing (MW5 on April 30, 1993). The thickness of the LNAPL body has ranged from 0.01 feet (MW2 on December 19, 2000) to 2.80 feet (TW-N on December 19, 2000). During the August 18, 2011 groundwater gauging and sampling event, LNAPL was detected in TW-N at a thickness of 0.21 feet, TW-E at a thickness of 0.25 feet, TW-W at a thickness of 0.25 feet, and TW-S at a thickness of 0.12 feet.” (*Envirotrack, 2012*)

The 2012 consultant report indicates the presence of LNAPL in 4 out of 27 monitoring wells. On February 1, 2012, samples of groundwater and LNAPL were collected from tank field well TW-W and sent to Torkelson Geochemistry for analysis. Torkelson “reported that the TW-W extract LNAPL/groundwater sample appears to be a mixture of extremely weathered gasoline and a smaller amount of severely weathered middle distillate, either diesel fuel or fuel oil” (*Envirotrack, 2012*). However, “the age and the

octane rating of the LNAPL sample submitted to the lab could not be estimated” (*Envirotrack, 2012*).

As of the most recent consultant’s report: “[a]quifer testing has not been completed” and “LNAPL mobility, recoverability or treatability tests have not been completed” (*Envirotrack, 2012*).

Monitoring and remediation: The monitoring wells appear to be shallow for the most part, with depth to 25 feet. Offsite wells include monitoring wells MW-18 through MW-22 in the downgradient direction.

Remediation efforts include groundwater extraction, which was conducted between November 1990 and December 1995 from four monitoring wells (MW1, MW2, MW3, and MW5). During that time period, an estimated “537,000 gallons of combined LNAPL and groundwater” were recovered (*Envirotrack, 2012*). In 1998, groundwater extraction was restarted (wells MW2 and MW5) and continued through November 2002. During this second phase, an estimated 36,000 gallons of “combined LNAPL and groundwater” were recovered. More recently, extraction was started again in March 2011 (wells TW-N, TW-E, TW-W, and TW-S), and continues as of the date of the most recent consultant report (*Envirotrack, 2012*). Additionally, “Total-Phase Extraction¹³ (TPE) remediation events began in May 2011” targeting monitoring well MW11, as an additional remediation measure.

4.7 TS#7 Gulf Waldwick

The site, an active Gulf Service Station, is located at 49 Franklin Turnpike Waldwick, Bergen County. It is surrounded by a mixture of residential and commercial properties. The site is situated within the Piedmont Physiographic Province.

Several surface water bodies are located within a half-mile radius of the site, and those include:

- Cole Pond (1,350 feet south, sidegradient to site)
- Hohokus Brook (1,600 feet south, sidegradient to site)
- Smokis Vall Brook (1,950 feet west, sidegradient to site)

Geology and Hydrogeology: The local geology is described as consisting of “reddish-brown pebble conglomerate, pebbly sandstone, and sandstone in upward-fining sequences three feet to six feet thick. Clasts are sub-angular to sub-rounded quartz and quartzite in the sandstone matrix” (*Brilliant Lewis, 2009*).

Kleinfelder (2007) described the site geology at different depths below ground surface (bgs) as:

- From 0 to 20 feet bgs: “brown silty sand, some gravel and clay.”
- From 20 to 50 feet bgs: “reddish brown medium to coarse sand, minor gravel.”
- From 50 to 70 feet bgs: “brownish red medium sand/silt, minor gravel.”
- From 80 to 120 feet bgs: “red medium grained sandstone.”

The aquifer is unconfined, and groundwater tends to occur at a depth of 9 to 12 feet bgs (*Brilliant Lewis,*

¹³ Although not clear from the consultant’s report, TPE appears to be dual phase extraction.

2009).

Hydrogeology: Groundwater flow velocity was calculated to be 1.7 ft/yr, based on the shallow zone (0-25 ft bgs). The hydraulic conductivity (K) was calculated to be 0.018 ft/day (for 0 – 25 ft bgs), and 0.35ft /day for groundwater at depth 30 to 40 ft bgs. Groundwater flow direction was estimated to be to the southwest (Kleinfelder, 2007).

For well MW-4D (Nov. 2005): Storativity (S) = 1.242 square ft/day; Transmissivity (T) = 0.2327;
Conductivity (K) = 0.018 ft/day

For well MW-16 (February 2006): Storativity (S) = 16.91 square ft/day; Transmissivity (T) = 0.01499;
Conductivity (K) = 0.242 ft/day

For well CRD-125 (July 2006) K= 0.35ft/day

Nearby Receptors: Within a one-mile radius, seven public CWS wells were identified, though none of the wells are within the half-mile radius. The closest public CWS wells are (Kleinfelder, 2007):

- Waldwick Water Department's Well 2, located approximately 2,700 feet west/northwest, sidegradient.
- Ridgewood Water Department's Andover Well, located approximately 2,900 feet south/southwest, downgradient.
- Hohokus Water Department's Wells 5 and 6, located approximately 3,280 and 4,300 feet respectively, and south/southeast, sidegradient of the site.

Release History: Contamination at the site appears to be the result of multiple release events as explained below:

- In July 1996, a “release of an unknown quantity of product was identified during tank and line testing” (Brilliant Lewis, 2009). As a result, limited excavation was conducted with approximately 200 cubic yards of impacted soil being removed from the site. During that time, “an abandoned dispenser, associated product piping, and a previously unknown 550-gallon heating oil UST were also decommissioned.” (Brilliant Lewis, 2009). Nine monitoring wells were installed.
- In February 1998, while conducting tank gauging activities, it was discovered that a fiberglass UST (on the eastern edge of the UST field) was cracked. The amount of gasoline released could not be identified. In response, “10 enhanced fluid recover (EFR) events” and “15 multiphase recovery (MPR) events” were conducted. One additional monitoring well was installed.

- In September 1998, another release was reported to NJDEP after “initial tank readings indicated that 985 gallons of gasoline had potentially been released and subsequent stick readings were inconsistent” (*Brilliant Lewis, 2009*). As a result, multiple MPR events were completed between 1999 and 2002.

In September 2002, three single walled fiberglass USTs were removed and replaced with three new double walled fiberglass USTs. At the time “802 tons of soil/pea gravel was removed” from the site and transported for disposal. Between 2003 and 2008 several MPR events were conducted, and eleven monitoring wells were installed. Also, during 2008 (between January and October) ten multiphase extraction/air sparging (MPR/AS) events were conducted (8 hours each). These events were carried out using well MW-16 for air sparging and wells MW-4D and MW-5 for extraction (*Brilliant Lewis, 2009*). In total, it was estimated that 13.6 pounds of vapor phase hydrocarbons were recovered, and 21,112 gallons of groundwater was removed in 2008.

In communication from the State in November 2004, NJDEP noted that the extent of groundwater contamination at the site had not been delineated, noting:

“Delineation of the groundwater contamination is not complete, as results from the Burger King property monitoring well samples still show contamination above the Department’s GWQS. Therefore additional delineation is required down gradient of the site” (*Kleinfelder 2005*)

Monitoring and remediation: The site includes a relatively large monitoring network, mostly located within the shallow zone:

On-site:

- In the shallow zone: Seven monitoring wells (MW-1 through MW-5, MW-8, and RW-1).
- In the intermediate zone: two wells (MW-4D and MW-16).
- In the deep zone: one well (BW-1).

Off-site, and adjacent to the site:

- In the shallow zone: Five wells (MW-10 through MW-14).
- In the intermediate zone: One well (MW-17).
- In the deep zone: One well (BW-2).

Off-site, on properties not adjacent to the site:

- Eleven wells¹⁴ are located on nearby business properties, including Waldwick Shopping Center, a bank, and Kaplan Cleaners.

Three additional wells (MW-6, MW-7 and MW-9), depicted on a site plan previously submitted to NJDEP (in 2006), are reported to be sealed and located onsite, but have not been located on the property by the more recent consultants (*Brilliant Lewis*). Off-site, Monitoring well MW-15 also has not been located on the grounds.

Based on results from more recent sampling record (*Brilliant Lewis, 2009*), the consultant concluded that delineation of the contamination was still not completed, and additional monitoring wells would need to be installed: “The installation of additional wells is necessary to complete characterization and delineation of groundwater. [Cumberland Farms Inc.] (CFI) proposes to install five off-site monitoring wells.” Two of the proposed wells would be deep, with screen lengths in the range of 75-95 and 105-125 feet bgs.

4.8 TS#8 Shell Ridgewood

The site is located at 657 Franklin Turnpike, Ridgewood, in Bergen County. It is currently an active Shell Service Station. The property covers approximately 32,700 square feet and sits at about 107 feet above mean sea level.

Geology and Hydrogeology: Geology in the area consists of unconsolidated material on top of bedrock. Stratified glacial sediments cover a depth of 25 to 30 feet, and consist of “coarse to fine sand with variable percentages of clay, silt, gravel, and cobbles” (*Handex, 1988*). Underneath the glacial sediments is 8 to 10 feet of “regolith; extremely weathered pieces of bedrock ranging in size from gravel to boulders in a clayey-silt matrix” (*Handex, 1988*).

Groundwater is encountered at 20 to 25 feet, and generally moves to the south/southeast. The hydraulic gradient was estimated at 0.006 ft/ft.

Competent bedrock, fine-grained sandstone of the Brunswick formation underlies the regolith.

Release History: The exact history of the release(s) at the site is not clear. However, according to consultant’s report site investigation was initiated in 1987 after “two municipal wells in the area of the service station had been taken off line due to residents complaining of odors in their tap water on June 23, 1987” (*Handex, 1988*). In July 1987, the MTBE concentration in one of the wells, Twinney, measured at 145 µg/L, whereas in the other well, Walthery, MTBE measured at 84 µg/L in the same month. In August 1996, a third municipal well, Paramus, was shut down because of contamination (*Sovereign, 2010*). Concentrations of MTBE in the three wells fluctuated significantly as can be seen from Table 4.3 below which lists the lowest and the highest MTBE concentrations measured in the three wells, over the time period in which they were sampled.

¹⁴ Those wells include CFS-37, CBS-50, CRD-125, KCMW-1through KCMW-7, and KCMW-8D.

Table 4.3: Range of measured MTBE concentrations in the three municipal wells within a half-mile radius of the Shell Ridgeway Site.

Well Name	Period sampled	Lowest MTBE measured		Highest MTBE measured	
		Concentration (µg/L)	Date	Concentration (µg/L)	Date
Twinney	11/21/83-6/28/00	0.49	6/28/00	197	2/24/98
Walthery	7/5/83-3/10/98	2.2	7/17/90	485	8/5/96
Paramus	8/8/83-9/7/99	0.6	5/28/99	689	9/9/96

Monitoring and Remediation: As a result of discovering MTBE contamination in the municipal wells, 20 shallow and 10 deep monitoring wells were installed in 1987 at the site. Shallow wells extended to a maximum depth of approximately 39 feet below surface, whereas the bedrock wells extended to a maximum of 96 feet (*Handex, 1988*). Separate phase product was discovered in wells W-1 and W-4 with thickness up to 6.25 inches in August 1987 (*Handex, 1988*). Initial site investigation concluded that by November 1987, the MTBE plume had migrated over 500 feet downgradient from the site. Furthermore, “elevated levels of MTBE in the Walthery well and monitoring well D-1 (in bedrock) indicated that contaminants had migrated from the water table aquifer to the bedrock aquifer” (*Handex, 1988*).

In September 1990, a pump and treat system was started, and in June 1992, free product was detected in well 4 at a thickness of 1.9 feet.

In February 1995 a line-leak was reported in a 1,000-gallon, 89-octane regular gasoline tank. As a result, two additional monitoring wells were installed, and in October 1995 “recovery wells were redeveloped via surge/bail”. In August 1996, a soil vapor extraction (SVE) system was started.

In June 1998, there was a reported “Leaking flex connector discovered underneath the middle pump island”, and in September 2002 ORC (oxygen release compound) was injected at the site, followed in February 2004 with upgrades to the pump and treat system and the SVE system, with three additional SVE wells installed. The Pump & Treat system was shut down in January 2009, and the SVE system was eventually shut down in May 2009.

Over the years the monitoring network extended to some 60 wells onsite and offsite (see *Sovereign 2010b*), with wells added on over time. The extent of the MTBE plume exceeded that of benzene as can be seen from the monitoring record in wells 27, 33, 37, 53, 55, and others.

4.9 TS#9 Points BP

The site is located at 109 Delsea Drive, Sewell in Gloucester County. It is an active gasoline service station, and has operated as such for “over 50 years” (*ELM, 2012*). The site lies within the Coastal Plain Physiographic province.

The property sits on a topographical mound, and the area generally slopes to the northwest (*ELM, 2012*). The surrounding property is mostly commercial. Immediately to the south of the site is an “active home heating oil distribution facility” which is associated with a residential unit (*Brilliant, 2011*). The residential unit is located west of the site. Also nearby are an auto dealership (to the north), a dry cleaner (to the northeast) and an abandoned Exxon service station located to the east of the site.

Nearby Receptors: To the north and northeast of the site, beyond the commercial property, is an “extensive wooded area with wetlands”. Immediately downgradient of the site is a “detention basin” on the property with the auto dealership (Adorin Auto) (*Brilliant, 2011*). This property appears to be identified as “Dylans RV Center (Dylans) in a different consultant report (*ELM, 2012*), and the detention basin is described as a “storm water detention basin.” To the west of the site is another commercial property, Tortorice Contractors, which also includes a storm water detention basin.

To the northwest, and beyond the Tortorice property is a “forested wetland, drainage features, and surface water bodies” (*ELM, 2012*). The ditches and drainage features (which contribute to Monongahela Brook) and which form drainage channels in the wooded area are believed to be remnants of agricultural cultivation dating to a period between the 1930’s through the 1960’s (based on aerial photography of the area from that time period; *ELM, 2012*).

Geology and Hydrogeology: the subsurface soils at the site are described as “tan to grey, sandy silts to silty sands with clay and intermittent gravel lenses” (*Brilliant, 2011*).

Groundwater flow is to the north, northwest direction (*ELM, 2012*). Groundwater occurs at a depth of approximately 25 feet below ground surface. However, closer to the nearby surface water body (a man made drainage ditch, and a forested wetland approximately 500 feet downgradient of the site), groundwater occurs at depths of 1 to 6 feet below the surface (in monitoring wells MW-17 and MW-27); “Groundwater intersects the channel bottom of the ditch and provides baseflow in the waterway under non-storm conditions” (*ELM, 2012*).

Release History: the record seems to indicate that the first report of contamination at the site occurred in October 1995, during soil investigation activities related to the sale of the site. Subsequently, in 1996, during station upgrades and the removal of three gasoline USTs, “petroleum odors were noted in the soil” and another case number was issued (*Brilliant, 2011*). In April 1998, liquid phase hydrocarbon (LPH) was found at the water table at the site. Since then, LPH has repeatedly been detected (in different monitoring wells, and at different times, with thickness up to 6.89ft) during sampling events. Based on consultant’s report (*ELM, 2012*): “Remedial activities initiated in April 2000 have removed thousands of gallons of LPH to date.”

Monitoring and Remediation: Based on *ELM (2012)*, investigation activities have been ongoing at the site since 1995. However, as noted earlier, LPH has been measured repeatedly in numerous monitoring wells over time.

Between 2007 and 2009 free product was removed from the site using “hand bailing”. Since 2009 however, Multi-Phase Recovery (MPR) events were used instead to extract vapors and liquid from the “pea gravel within the tank field and pipe trenches” (*Brilliant, 2011*). The MPR events have involved wells MW-2, MW-3, MW-4, MW-5, and MW-12. Between September 2009 and April 2011, 10 MPR events were carried out, with a total of 4,129 pounds of vapor, and 5,386 gallons of water extracted from the wells.

In August 2009, an additional monitoring well (MW-24) was installed offsite, and in the downgradient direction, on residential property. The well depth extended to 20 feet below surface. Remediation also involved the use of oxygen release compound enhance natural degradation processes (*ELM, 2012*).

As of May 2011, two onsite wells (MW-5 and MW-12) contained measurable amounts of LPH. A letter from NJDEP to ARFA Enterprises (dated February 2011) notes several deficiencies in the containment and stabilization of contamination (presence of liquid phase hydrocarbon in several monitoring wells at the site), as well a lack of delineation of the extent of contamination at the site, including in the horizontal and vertical directions, and the extent of the free and residual product in the subsurface (*Brilliant, 2011*).

The ecological evaluation report by ELM (*2012*) notes that: “Source control is on-going and has not been fully achieved.” The consultants also noted that contamination detected in surface water samples and sediment samples from the nearby ditch/drainage features is the result of discharge of contaminated groundwater from the site. ELM (*2012*) concluded: “The principle exposure pathway for contaminants associated with the gas station property to contact sensitive receptors is through groundwater discharge to the unnamed tributary” and “Discharge of contaminated groundwater to the unnamed tributary (ESA-3) represents a complete exposure pathway between Site contaminants and environmentally sensitive receptors” (*ELM, 2012*).

4.10 TS# 10 HP Delta

The H.P. Delta, also known as Rob’s Service Station is located at 439 Lake Avenue Woodbridge, in Middlesex County. The property has an active gasoline station, as well as an auto repair service station (*Louis Berger, 2010*). The majority of the property in the surrounding area is residential, but the property near the intersection of Lake Avenue and Lancaster Road is mainly commercial.

The site is approximately 80 feet above mean sea level (msl) and gently slopes to the southwest. Drainage from the site follows a west-southwest direction, towards Pumpkin Patch Brook, which is approximately 0.3 miles from the site (*Louis Berger, 2010*).

It is noted that the area this site is in receives an average of 44 inches in precipitation, with the heaviest amounts normally falling in the summer months (*Louis Berger, 2010*).

Geology and Hydrogeology: The geology around the site is described as being “classified as Haledon Urban Land Complex with 0-8 percent slopes. The Haledon is described as coarse loamy basal till originally derived from basalt. Urban land is characterized by surfaces covered by pavement, concrete, buildings, and other structures underlain by disturbed and natural soil material” (*Louis Berger, 2010*). The

till is reported to be Rahway Till, some 20 feet thick near the site, and described as consisting of “reddish-brown clayey, silty sand to clayey, sandy silt” (*Louis Berger, 2010*).

The underlying bedrock is the Passaic Formation. The Passaic Formation “consists of reddish-brown to brownish-purple to grayish-red siltstone and shale that strikes northeast and dips approximately 11° northwest in the area of the site.” The fractured bedrock is reported to occur at approximately 17 to 22 feet below ground surface (bgs) (*Louis Berger, 2010*).

Groundwater in the overburden occurs at depths of 10 to 18 feet below the surface, and tends to flow in a southwesterly direction, towards Pumpkin Patch Brook. Based on sampling done in October and December 2009, as well as in March 2010 groundwater flow in the overburden was reported to be to the west.

Fractured bedrock appears to occur at a depth of 17 to 22 feet bgs. Based on sampling done in three bedrock wells in October 2009, groundwater flow in the bedrock was reported to be to the south, whereas based on the sampling event done in December 2009, flow was reported to be to the southeast. A third sampling event done in March 2010 indicated groundwater flow in the bedrock was to the south (*Louis Berger, 2010*).

The local aquifer is classified as Class II-A, with groundwater that can be consumed untreated. The supply wells “tapping this aquifer have highly variable yields reported to average 19 gmp” (*Louis Berger, 2010*). Groundwater flow in the aquifer is affected by local pumping conditions as explained in the consultant’s report:

“Under natural conditions, the regional groundwater within the underlying bedrock of the Passaic Formation would be expected to flow northeast, toward the Rahway River, as this is a regional groundwater discharge feature... However, the pumping of groundwater supply wells in the area could locally affect the groundwater flow. The bedrock of the Passaic Formation is generally considered non-porous; however, the bedrock is typically fractured along bedding planes and contains variably-spaced joints, which tend to produce a relatively high secondary permeability. These structural elements tend to create anisotropic flow conditions when influenced by well pumping” (*Louis Berger, 2010*).

Nearby receptors: There are many domestic and irrigation wells within a one-mile radius of the site, but no public supply wells. A memo sent from the Office of Wellfield Remediation to the Office of Community Relations (NJDEP) dated April 28, 2009 (*Louis Berger, 2010*), notes the contamination of multiple nearby residential wells with MTBE and benzene. The memo notes that sampling done by the NJDEP and the Woodbridge Township Health Department in 2007-2009 indicated that a total of sixteen private well and one irrigation well had detections of MTBE, benzene, and trichloroethane at concentrations above the Safe Drinking Water Standards. The “levels of MTBE rang[ed] from 70 ppb to 12,000 ppb” (*Louis Berger, 2010*). The wells were reported to be mostly shallow, less than 30 feet in depth. The contaminated wells were sealed and “a public water line was installed to supply the affected residences.” However, “it is suspected that many residences in the area are still utilizing private wells” (*Louis Berger, 2010*).

Release History: The property associated with the site is owned by Mr. R. Mellecci, who was the sole

owner and operator of the gasoline service station until 1988. At that time (1988), Mr. Mellecci leased the retail gasoline operation to H.P. Delta, and continued to operate the auto repair business (*Louis Berger, 2010*). Though no record appears to have been filed, it is believed that as part of the lease transaction, the older USTs associated with the gasoline retail operation were replaced with the tanks currently at the site, sometime in 1988 (*Louis Berger, 2010*).

The first record of a release occurred in December 2004 when “a turbine spill containment sump on the regular gasoline UST was found to be filled with product” (*Louis Berger, 2010*). In the summer of 2006 the “Woodbridge Township Health Department conducts a groundwater investigation after contamination was detected in nearby residential potable well to the south and west of the Site” (*Louis Berger, 2010*). Testing showed that 13 residences had GWQS exceedances for MTBE, TBA, and BTEX.

In February 2007, the NJDEP rejects a Site Investigation Report submitted on behalf of H.P. Delta (by MIG Environmental) because it “did not meet minimum standards for review.” Consequently, NJDEP conducted “publicly-funded remediation activities at the site” in the summer of 2007. Remediation included pump and treat, as well as soil vapor extraction.

In total, there are 10 shallow monitoring wells, and three bedrock wells (to a depth of approximately 60 to 64 feet). Groundwater sampling of the monitoring wells done in October and December 2009 indicated no contamination (benzene, TBA or MTBE) above the State’s GWQS (1, 70, and 100 $\mu\text{g/L}$ respectively). However, a sampling event conducted in March 2010, two weeks after the remediation system was shut down (pump & treat and SVE) shows exceedances for all three contaminants in MW01. Benzene, MTBE and TBA concentrations in MW01 (a bedrock well, offsite and to the west of the Site) in March 2010 were 4.4, 120 and 740 $\mu\text{g/L}$ respectively (*Louis Berger, 2010*).

4.11 Summary

Based on information gathered at the trial sites, it is clear that MTBE has impacted the underlying aquifers at each of the ten sites, and has impacted drinking water supplies at several of them. Remediation (primarily groundwater extraction and or soil vapor extraction employed at some of the sites) can remove some of the contaminant mass near the release source. However, contamination mass not captured by remediation is free to travel with groundwater and is likely to impact other nearby receptors as it travels away from the source.

Without significant biodegradation, MTBE attenuation in groundwater is generally poor (see Chapter 6 for details). To my knowledge, there was no documented evidence of biodegradation of MTBE or TBA at any of the ten Trial Sites in New Jersey. Without biodegradation or remediation, MTBE (and TBA) mass will persist and continue to move with the groundwater to impact large volumes of water for many years to come.

5 Fate and Transport of MTBE in Groundwater

In the United States today, there are thousands of public drinking water wells (and many more private wells) in the vicinity of MTBE plumes from leaking underground storage tanks¹⁵ (LUSTs) (see Figures 2.2, 2.3 and 2.5). These "... LUST sources can persist for decades and ... it can take tens to hundreds of years for groundwater to flow from source areas to a [community water supply] CWS well" (*Johnson et al., 2000*). Knowledge of the hydrogeologic processes governing MTBE fate and transport is therefore key to assessing past, present, and potential MTBE impacts on groundwater.

5.1 Chemical and Physical Characteristics of MTBE in Groundwater

MTBE is a problematic groundwater contaminant because it is both a health concern and has an objectionable taste and odor at very low concentrations; it is highly mobile, migrating at nearly the same speed as the groundwater itself; extremely soluble leading to high source concentrations at release sites; and very persistent, giving it time to spread and contaminate large volumes of groundwater.

As of 2003, 42 states had, or were expected to have, MTBE action levels, cleanup levels, or drinking water standards (*NEIWPCC, 2003*). Minute amounts of MTBE-containing gasoline can pollute large volumes of water to the point where that water is no longer usable. "Very small releases of MTBE (even small overfills seeping into cracks in the pavement) have the potential to adversely impact groundwater" (*Stanley, 1998*). To put it in perspective, just 1 tablespoon of MTBE can render more than 586,000 gallons (2,220,000 liters) of water undrinkable (at 5 µg/l). Thus, the MTBE in reformulated gasoline¹⁶ in a 16-gallon (60.6 liters) tank of a car has the potential to render more than 230 million gallons (870 million liters) of water undrinkable.

In effect, small volumes of gasoline can result in contamination of large volumes of water with MTBE. Examples of case studies, documented by the State of Maine, where small surface gasoline spills resulted in substantial contamination of groundwater wells are provided in the report by the Northeast States for Coordinated Air Use Management (*NESCAUM, 1999*). In one example the report states:

"In December 1997, a car accident in the town of Standish, ME, spilled 8 to 10 gallons of gasoline that contaminated 24 area wells with MTBE. Eleven wells were contaminated above the State's 35µg/L (ppb [parts per billion]) state drinking water standard for MTBE. Two of the wells were

¹⁵ Most LUST sites are leaking underground fuel (gasoline) tanks (LUFTs). For the purposes of this document, LUST and LUFT are generally interchangeable. The term LUST is commonly used in California because of the California State Water Resources Control Board Underground Storage Tank Program.

¹⁶ RFG contained approximately 11% MTBE by volume in gasoline sold in California prior to the bans effective on January 1, 2004

contaminated at levels of MTBE exceeding 1,000 µg/L, with the highest level reaching 6,500 µg/L in the well nearest the accident site. When the State discovered the contaminated wells in May 1998, it located and removed 79 cubic yards of contaminated soil. The contamination extended to the top of the underlying bedrock at a depth of nine feet below the surface. The degree of soil contamination at the bedrock surface was 100 to 230 µg/L of gasoline (total hydrocarbons).”

MTBE is normally a chemically stable compound that does not biodegrade readily in either aerobic or anaerobic environments (*Jensen and Arvin, 1990; Suflita and Mormile, 1993; Mormile et al., 1994; Yeh and Novak, 1994; Kay-Shoemaker and Watwood, 1996; Pasteris et al., 2002; Hohener et al., 2003; Prenafeta-Boldu et al., 2004; Kim and Engesser, 2004; McClay et al., 2007; Henderson et al., 2008; Waul et al., 2008*). A detailed discussion of the microbial degradation of MTBE is presented in the following sections.

The fate and transport properties of MTBE in groundwater are often compared to those of BTEX components of gasoline (Benzene, Toluene, Ethyl-benzene, and Xylenes). Although conventional (non-oxygenated) gasoline can contain as many as 180 chemicals (*Cline et al., 1991*), the BTEX compounds make up a relatively large percentage of gasoline (*Hartley and Englande, 1992*). Further, prior to the widespread use of MTBE, the BTEX compounds were generally considered the most water-soluble compounds contained in gasoline. Hence, the BTEX compounds typically have been the groundwater contaminants of concern: “The components of highest aqueous concentration are the constituents of primary concern for regulation of gasoline releases to groundwater, i.e., benzene, toluene, ethyl-benzene and xylenes (BTEX)” (*Cline et al., 1991*).

However, compared to many other common groundwater contaminants including, among others, BTEX, MTBE is more highly soluble and will therefore tend to create high concentration plumes in groundwater. MTBE solubility¹⁷ (expressed as a concentration in water) from gasoline (at approximately 11% by volume) is about 350 times higher than benzene, 100 times higher than BTEX, 40 times higher than perchloroethylene (PCE) (*Imhoff et al., 1995*), and 6 times higher than trichloroethylene (TCE) (*Russell et al., 1992*) (see Figure 5.1). The resulting MTBE concentrations in groundwater can be 10’s to 100’s of times greater than those of benzene. Furthermore, MTBE is highly mobile in groundwater. The rate of transport of a contaminant in groundwater can be attenuated by sorption to soil and sediments. The octanol/water partitioning coefficient (K_{ow}) of MTBE, which is indicative of its ability to adsorb to soil organic matter, is one order of magnitude less than that of BTEX. As such, MTBE has been observed to move in groundwater at about the same rate as the conservative (nonsorbing) tracer chloride (*Barker et al., 1990*).

Of the BTEX compounds, benzene is the most toxic, most soluble, and most mobile. The fate of MTBE is often compared to that of benzene. However, benzene constitutes less than 1% of the volume of gasoline, whereas MTBE can account for up to 15% by volume of gasoline.

¹⁷ MTBE and Benzene solubilities computed for MTBE 87 octane gasoline from EPA website <http://www.epa.gov/athens/learn2model/part-two/onsite/es.htm>. Last accessed 6/24/10.

At the same time, the fuel-water partitioning coefficient for MTBE (350) is 22 times higher than that of benzene (15.5) (Cline et al., 1991) meaning that it is much more likely to partition out of gasoline into water as compared to benzene. The ability to adsorb to soil organic matter is slightly higher for benzene, compared to MTBE (ITRC, 2005), allowing MTBE to move at rates closer to those of natural groundwater flow. Most importantly, research has shown that benzene degrades readily under aerobic conditions (USEPA, 2005), whereas MTBE requires long acclimation times, if it degrades at all (see following section). Under anaerobic conditions, benzene biodegradation is slower and less reliable (NRC, 2000). Were benzene biodegradation to be limited to anaerobic conditions, the outlook for benzene natural attenuation would not be as optimistic.

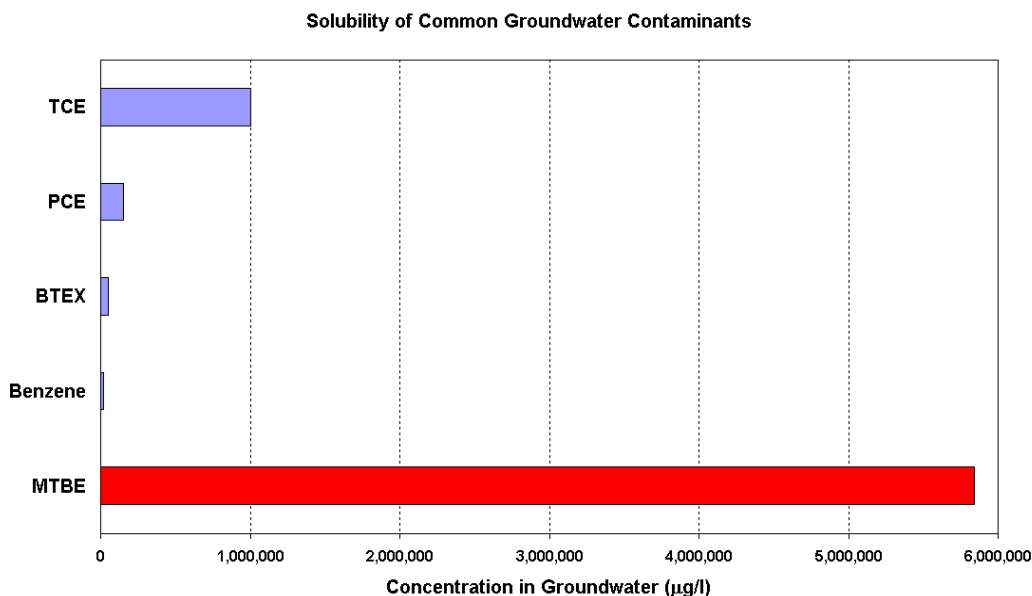


Figure 5.1. Solubility expressed as an equilibrium concentration in groundwater for MTBE from gasoline (10.4% mass fraction), benzene (0.7% mass fraction) from gasoline, Total BTEX (9.8% mass fraction), PCE and TCE demonstrating the potential for reformulated gasoline with MTBE to create relatively high-concentration MTBE plumes as compared to many other contaminants.

5.2 Resistance of MTBE to Biodegradation under Natural Groundwater Conditions

Several characteristics of MTBE biodegradation, documented through observations from experimentation and research carried out for many years now, point to the poor biodegradability of MTBE under natural conditions. For example, early studies on MTBE biodegradability were mostly negative, and by 1998 most published reports on MTBE biodegradation referred to the compound as recalcitrant or resistant to biodegradation. “If a research investigation determines that a compound does not degrade, a half-life is not reported and the compound is simply classified as recalcitrant. MTBE is generally reported as recalcitrant and there are no widely accepted estimates of the half-life.” (USGS Fact Sheet FS-203-96; Squillace et al., 1998).

The resistance of MTBE to biodegradation has been linked to two aspects in particular in its molecular structure (see Figure 5.2): the tertiary carbon structure and the ether linkage (C-O-C) (Sufliata and Mormile

1993; Salanitro 1995; Fayolle et al., 2001, Muller et al., 2007). The ether linkage is common to many natural (e.g. lignin) and xenobiotic (e.g., agrochemicals and detergents) compounds (White et al., 1996). It has been recognized as a “major barrier to biodegradation” since the mid 1960’s. Yet, after three decades of research and new discoveries of organisms and pathways that can break down chemicals containing the ether bond, a review of many of these studies concluded:

“The ether linkage is the single most common and unifying structural feature which confers to both biological and xenobiotic compounds a high degree of resistance to biological mineralization.” (White et al., 1996).

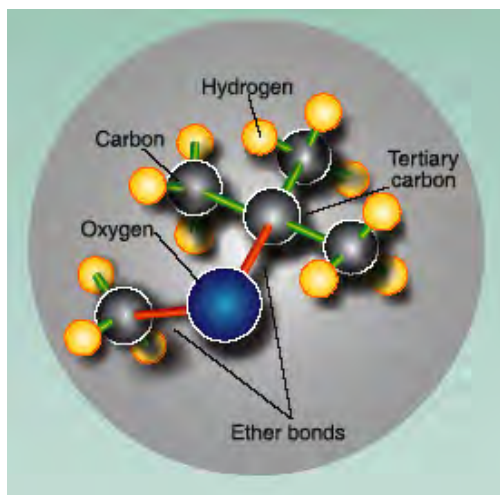


Figure 5.2: Molecular structure of MTBE (from Zogorski et al., 2006).

In recent years, some studies have shown successful biodegradation under certain laboratory conditions, while others have claimed biodegradation under natural field conditions. Meanwhile, however, the results of numerous other scientific studies confirmed MTBE’s resistance to biodegradation, especially in comparison to the BTEX components of gasoline. MTBE either did not biodegrade within the time limit of the study, or it was biodegraded poorly, or under specific conditions, generally not found in natural groundwater sediments. For example, some studies (Jensen and Arvin, 1990; Salanitro et al., 1994; Cowan and Park 1996; Mo et al., 1997; Hanson et al., 1999; Pruden et al., 2001; Francois et al., 2002; Zaitsev et al., 2007) have been conducted with microbial cultures derived from activated sludge (material, or flocs, containing high concentrations of diverse groups of organisms, mostly bacteria, but also fungi and protozoa, produced during the secondary treatment process of wastewater, i.e. sewage treatment). In other words, the results of such studies cannot be applied directly to groundwater environments that lack the population numbers and activity of microorganisms commonly found in activated sludge. Moreover, and as will be explained in the following sections, many studies which showed evidence of MTBE biodegradation were conducted with surface water sediments (lakes, rivers, estuaries, etc...) and not aquifer sediments.

After nearly two decades of research on MTBE biodegradation, the consensus remains that MTBE is not an easily biodegradable compound (McKelvie et al., 2007; Youngster et al., 2008; Waul et al., 2008; Malandain et al., 2010), and convincing proof of degradation under natural groundwater conditions (without engineered intervention) is scarce. Research is ongoing into the mechanisms involved in microbial breakdown of the compound, enzyme induction and regulation, reasons for long acclimation periods when

biodegradation does occur, slow growth rates of microorganisms, as well as the nature and prevalence of organisms capable of biodegradation, among other issues.

The following is a detailed discussion of the available literature on the biodegradability of MTBE. It should be noted that in the presence of naturally occurring oxygen in groundwater, other gasoline constituents of concern, particularly benzene, toluene, ethyl benzene and the xylenes (BTEX) would be biodegraded preferentially (compared to MTBE), resulting in depletion of oxygen (*USEPA, 2005*). Consequently, “most MTBE plumes are anaerobic” (*USEPA, 2005*). As such, in considering the biodegradation potential of MTBE in aquifers, under natural non-engineered conditions, anaerobic conditions are of particular significance for the natural attenuation of MTBE. And while dissolved oxygen concentrations as low as 0.1 mg/l may be enough for aerobic BTEX biodegradation, aerobic MTBE biodegradation appears inhibited at concentrations less than 1.0 mg/l (*Wilson, 2003*) or 2 mg/l (*Wei and Finneran 2009*). Studies conducted under aerobic conditions therefore, are necessary for understanding the potential for engineered remediation of MTBE plumes where high dissolved oxygen concentrations can be maintained.

5.2.1 Anaerobic Biodegradation of MTBE

In the absence of oxygen, bacteria may use other naturally occurring chemicals to carry out biodegradation reactions (anaerobic biodegradation). Such chemicals, referred to as electron acceptors, include nitrate (NO_3^-), Manganese (Mn(IV)), Iron (Fe (III)), sulfate (SO_4^-), and carbon dioxide (CO_2). Because the “electron acceptor” becomes “reduced” as part of the reaction, the conditions under which such reactions occur are referred to as reducing, e.g. nitrate reducing, sulfate reducing, iron reducing, etc.... When carbon dioxide is used as the electron acceptor, methane is produced, and the reaction conditions are generally referred to as methanogenic.

The different electron acceptors are used preferentially by bacteria. For example, for the BTEX group, *USEPA (2005)* explains:

“Bacterial communities acclimate readily to degrade BTEX compounds using oxygen and nitrate as electron acceptors. Depletion of oxygen and nitrate should be expected at almost every gasoline spill. Bacterial communities also acclimate readily to degrade sulfate. Depletion of sulfate should be expected at most sites as well. Bacterial communities require from months to years to acclimate to ferment BTEX compounds to methane”.

In comparison, a close look at MTBE anaerobic biodegradation studies reveals contradictory results, as well as the fact that there is little evidence to indicate that such processes have been documented in aquifer sediments. Some of the studies that did show evidence of biodegradation under anaerobic conditions have been conducted with surface water sediments, and not aquifer sediments, as discussed later. Furthermore, biodegradation was not always established, even after very long acclimation periods.

Summary of Anaerobic Biodegradation Studies: One of the earlier studies (*Mormile et al. 1994*) reported no biodegradation of MTBE in aquifer sediments, under nitrate reducing conditions, in 85 days of incubation, and no biodegradation under sulfate reducing conditions in 244 days of incubation. Similarly,

Borden et al. (1997) reported no MTBE biodegradation in aquifer sediments in 263 days incubation under low oxygen, nitrate rich conditions. *Suflita and Mormile (1993)* showed no biodegradation in aquifer sediments under anaerobic/methanogenic conditions in 250 days of incubation. Similarly, *Church et al. (1999)* found no evidence of MTBE biodegradation under anaerobic conditions in aquifer sediments from 4 different sites in 120 days. *Finneran and Lovley, (2001)* reported no biodegradation in aquifer sediments in 275 days, under sulfate reducing conditions when incubated without amendments (natural conditions). The aquifer sediments degraded MTBE only after the addition of iron and humic substances, leading the authors to conclude: “the aquifer sediments evaluated in this study also had little intrinsic potential to degrade MTBE” (*Finneran and Lovley, 2001*).

On the other hand, research conducted by USGS scientists (*Bradley et al., 2001a; Bradley et al., 2001b*) on surface sediments from different sources (lakes and streams) showed varying degrees of biodegradation of MTBE, depending on source, incubation and redox conditions, under nitrate reducing, sulfate reducing, iron reducing, manganese reducing, and methanogenic conditions. Meanwhile, *Somsamak et al. (2001)* showed biodegradation of MTBE under sulfate reducing conditions in one out of two microcosms, with estuarine sediments, after more than 3 years of incubation. However, in the same study, the sediments taken from Arthur Kill estuarine inlet (located between Staten Island, New York and New Jersey) showed no evidence of MTBE biodegradation under nitrate reducing, iron reducing, or methanogenic conditions in three years of incubation. In another study, *Finneran and Lovley (2001)* showed biodegradation of MTBE under iron reducing conditions in sediments from the Potomac River after an acclimation period of 250 to 300 days. *Somsamak et al. (2005)* showed biodegradation of MTBE in only 1 out of 3 microcosms with estuarine sediments under anaerobic/methanogenic conditions, after an acclimation period of 390 days.

In a recent study (*Waul et al., 2008*), experiments were conducted on the anaerobic biodegradation of MTBE both in batch, and continuous bioreactor settings, and under various electron acceptor conditions, including nitrate, sulfate and iron (Fe(III)) reducing conditions, as well as methanogenic conditions. Several sources of inocula, presumably rich in anaerobic bacteria, including sludge and contaminated soil from a petroleum refinery that handles MTBE, were used “such that the best conditions existed for the detection of anaerobic MTBE degradation.” The batch experiments were incubated for periods ranging from 2 months to 2.5 years, whereas the bioreactors were operated for periods of 2 months and 3.5 years. The researchers (*Waul et al., 2008*) reported no MTBE biodegradation in the bioreactors under any of the redox conditions specified. In the batch experiments meanwhile, no degradation was reported under any of the redox conditions, except for the Fe(III) reducing conditions where a 30 to 60% conversion of MTBE to TBA was observed. Those batch experiments were not buffered and *Waul et al., (2008)* concluded that: “The use of complexed Fe(III) created an initial low pH of 1-2 in these batches due to its acidic nature, therefore the removal may be due to acid hydrolysis rather than biological processes.” The degradation of MTBE to TBA through hydrolysis under acidic conditions has been reported previously (*O’Reilly et al., 2001; Zwank et al., 2005; Fischer et al., 2007*).

Wei and Finneran (2009) were the first to establish a stable liquid anaerobic culture derived from sediments from petroleum-contaminated groundwater from a gasoline station site in California. Enrichments were prepared by the addition of the electron acceptors anthraquinone-2,6-disulfonate (AQDS), fumarate, nitrate and sulfate. The samples enriched with either AQDS, fumarate, or sulfate degraded MTBE after “significant lag periods for each of the electron acceptors tested, ranging from 240 to 315 days prior to complete degradation”. In each case, “TBA was produced as a result of MTBE degradation, but was not itself degraded under any of the conditions tested”. Interestingly, *Wei and Finneran (2009)* reported no MTBE biodegradation in the “nitrate-amended enrichments”. Furthermore, it appeared that the added amendments (AQDS, fumarate or sulfate) were necessary for the cultures to grow on MTBE; incubations without amendments were not able to grow on MTBE.

The researchers (*Wei and Finneran 2009*) tried to identify individual pure anaerobic microorganisms responsible for MTBE biodegradation, but were not able to. Analysis of the microbial community “indicated that the dominant populations in the MTBE-degrading cultures are not closely related to known species, suggesting that anaerobic microorganisms growing on MTBE are in fact *novel*” [emphasis as published]. Similarly, *Youngster et al., (2010)* tried unsuccessfully to isolate pure cultures degrading MTBE, enriched from surface water sediments, noting that: “[c]haracterization of the MTBE-utilizing enrichment cultures was hampered by their very slow growth.....the low population density contributes to the difficulty in sustaining anaerobic MTBE-degrading activity in cultures over successive transfers and dilutions.” The authors (*Youngster et al., 2010*) also speculated that interactions between more than one species of organisms “may be required for appreciable anaerobic MTBE degradation to occur.”

It should be noted that from a theoretical standpoint, the oxidation of MTBE under the different electron accepting conditions is thermodynamically feasible (*Schmidt et al., 2004*). However, the thermodynamic feasibility of a reaction does not account for kinetic limitations and the ability of microorganisms to break down and metabolize organic chemicals, or even the presence of degrading microorganisms. As evidenced by the results of years of research so far on MTBE biodegradation, the presence of electron acceptors is not necessarily enough for biodegradation to proceed.

In summarizing findings from research studies on MTBE biodegradation, *USEPA (2005)* cautioned: “Although these studies prove that anaerobic biodegradation of MTBE in sediments is possible, they do not indicate that anaerobic biodegradation in aquifer sediments is common or pervasive.” Similarly, *Somsamak et al., (2005)* cautioned: “Considering that anaerobic MTBE degradation is very rare, the enzyme system involved in attack may not be widely distributed”. *Stupp (2007)* also concluded “[a]ccording to field observations in groundwater, MTBE is hardly microbiologically degradable by pure natural processes alone.” Hence it would be imprudent to entrust such poorly understood activity with plume attenuation at appreciable rates.

Biodegradation in Aquifer Sediments Compared to Surface Water Sediments: The results of MTBE degradation in surface water sediments, as compared to aquifer sediments, need to be considered in the

context of the different environments (for example, microbial abundance, biodiversity), and how that influences microbial activity. For example, a study by *Kazumi and Capone (1994)* on microbial population and activity in the Upper Glacial Aquifer on Long Island (using glucose, a simple sugar), concluded: “bacterial activity and abundance estimates [in the Upper Glacial Aquifer] are similar to values found in other aquifer environments, but are 10- to 1000-fold lower than values in soil or surface sediment of marine and estuarine systems” (*Kazumi and Capone 1994*). Consequently, for a chemical that is more difficult to biodegrade (e.g. MTBE as compared to glucose), the disparity in response between the two environments (surface versus aquifer sediments) would be expected to be more pronounced because of the nature, and numbers of organisms available in each environment.

In fact, a review by *Kieft and Phelps (1997)* noted that: “microbiological activities in uncontaminated subsurface habitats proceed at rates that are orders of magnitude slower than those encountered in nearly every other portion of the biosphere”. Based on the work of *Kieft and Phelps (1997)*, a more recent review of “Microbial Biodiversity in Groundwater Ecosystems” by *Griebler and Lueders (2008)* noted that: “in general, differences in microbial activities between subsurface and surface environments can reach up to 10 orders of magnitude (*Kieft and Phelps, 1997*)”. *Griebler and Lueders (2008)* also noted that published reports “support the idea that indigenous groundwater microbial communities are distinct from those found in surface environments.” As such, results of biodegradation experiments conducted in the laboratory with samples from surface water, or sludge from wastewater treatment plants, cannot be directly extrapolated to subsurface environments without further evidence from aquifer studies, particularly when it is an anthropogenic chemical like MTBE, that is not easily degradable.

5.2.2 Abiotic degradation and apparent biodegradation under methanogenic conditions

There are some reports of anaerobic degradation of MTBE in aquifer sediments that were conducted under methanogenic conditions in what is referred to as an “anaerobic glove box” (*Wilson et al., 2000; Kolhatkar et al., 2002; Wilson et al., 2005b*). An “anaerobic glove box” refers to incubation under an “anaerobic mixed gas” consisting of carbon dioxide, nitrogen, and up to 5% by volume Hydrogen (*Bradley et al., 2006*). Recently, USGS scientists (*Bradley, Landmeyer, and Chapelle in Bradley et al., 2006*), the same group that conducted the surface water sediment experiments showing MTBE biodegradation under different electron accepting conditions (*Bradley et al., 2001a; Bradley et al., 2001b; Bradley et al., 2001c*), showed that under conditions similar to those enforced in an anaerobic glove box, specifically relatively high hydrogen concentrations, which is also typical of methanogenic aquifer conditions, the transformation of MTBE to TBA is likely chemically (abiotic), and not microbially mediated. Interestingly, in their own work previously (*Bradley et al., 1999*) with surface sediments under methanogenic conditions, incubated with Helium gas instead of in an anaerobic glove box, no biodegradation of MTBE was observed in sediments from 2 different sites in 105 days of incubation.

In the field, fermentative microorganisms produce hydrogen as they decompose organic matter under

anaerobic conditions (*Chapelle et al., 1996*). Methanogenic conditions are characterized by hydrogen concentrations in the range of 5 to 15 nM (*Chapelle et al., 1996*). In their work, *Bradley et al. (2006)* showed that abiotic transformation of MTBE to TBA occurs at hydrogen concentrations above 5nM. The experiments included comparisons of MTBE transformation in “live” (non-autoclaved) microcosms to microcosms repeatedly autoclaved (heat sterilized) to kill or suppress microbial activity. The autoclaved samples included microcosms with hydrogen (not flushed), and microcosms flushed with nitrogen to remove the hydrogen (flushed). The results showed that MTBE transformation in the “live” microcosms was almost identical to that in the autoclaved microcosms not flushed (containing hydrogen). In comparison, the samples that were autoclaved, but flushed with nitrogen to eliminate hydrogen, showed no transformation. In other words, in the absence of hydrogen, there was no transformation of MTBE, leading *Bradley et al. (2006)* to conclude that at hydrogen concentrations greater than 5nM (typical of methanogenic conditions), abiotic reduction, and not biological degradation, of MTBE to TBA is likely the primary transformation pathway.

The results by *Bradley et al. (2006)* suggest that under natural aquifer conditions, biologically produced hydrogen can facilitate MTBE reduction to TBA and methane, without the reaction being microbially mediated. This is also particularly important since it is common practice to add hydrogen gas to the headspace of laboratory microcosms incubated under anaerobic conditions (*Bradley et al., 2006*). Given that the anaerobic biodegradation of MTBE has yet to be connected to specific microorganisms, or clear enzymatic pathways, this puts into question published literature on anaerobic MTBE biodegradation under methanogenic conditions. It produces doubt on whether MTBE transformation to TBA under high hydrogen concentration conditions is mediated by microorganisms or is simply a chemical reaction catalyzed by other elements within the sediment matrix. Importantly, under such conditions TBA is likely to be a dead end product. TBA biodegradation under anaerobic conditions has not been well documented in field studies (*USEPA, 2005*).

5.2.3 Aerobic biodegradation

In one of the earliest laboratory studies, *Jensen and Arvin (1990)* used 4 sources of inocula rich in microbial cultures (soil, sandy aquifer material, and two types of activated sludge), to examine the biodegradability of typical gasoline aromatics (BTEX and naphthalene) as well as MTBE. The aromatics were completely degraded within 3 to 13 days, but no MTBE biodegradation was observed in 60 days.

Probably the first study to demonstrate successful mineralization (transformation to carbon dioxide and water) of MTBE under laboratory conditions was published by *Salanitro et al. (1994)*. In this study, three types of activated sludge (municipal, refinery, and chemical plant bioreactors) were used in multiple inoculations to enrich for a microbial culture that degrades MTBE. After 2 months, the chemical plant activated sludge developed an MTBE-degrading culture. The bacterial culture however was found to have a low growth rate and a low cell yield. *Cowan and Park (1996)* also developed a mixed microbial culture that degraded MTBE using inoculum from activated sludge from a petroleum-refinery wastewater treatment

plant. Rates of MTBE biodegradation were higher at 30°C (86°F) compared to 20°C (68°F) (*Park and Cowan, 1997*). The rate of biodegradation was also found to be dependent on oxygen concentrations, with rates dropping significantly at dissolved oxygen concentrations below 2.1 milligrams per liter (mg/l). Several other studies (*Borden et al., 1997; Bradley et al., 1999; Salanitro et al. 2000; Feris et al., 2004; Chen et al., 2007*) have also noted the process of biodegradation was dependent on oxygen.

However, in many other cases, MTBE was reported to be resistant to biodegradation in the presence of oxygen. For example, in a controlled laboratory experiment, *Pasteris et al. (2002)* noted that out of a mixture of 13 fuel compounds, MTBE was the only one to persist in groundwater through 70 days of monitoring. In another study (*Ruiz-Aguilar et al., 2002*), no evidence of MTBE biodegradation was observed in aquifer material collected from 4 different sites, during 100 days of incubation (both under aerobic and anaerobic conditions). *Da Silva and Alvarez (2002)* also reported no biodegradation of MTBE in biologically active columns in a period of 110 days. Similarly, *Dakhel et al. (2003)* reported that MTBE persisted for longer than 6 months with no evidence of biodegradation.

5.2.4 Engineered Bioremediation

Given that “most MTBE plumes are anaerobic” (*USEPA, 2005*), and that the biodegradation of MTBE is more likely to proceed at appreciable rates under aerobic conditions, several field studies have been conducted on the efficacy of “oxygenation” as a remediation option (for example *Salanitro et al., 2000; Wilson et al., 2002; Landmeyer et al., 2003; and Smith et al., 2005*). In this case, several site-specific conditions will influence process performance. For example, *Landmeyer and Bradley (2003)* showed that the addition of oxygen release compounds did not result in changes in the dissolved oxygen or MTBE concentrations in the source zone, but did result in measurable reduction in MTBE concentrations 200 m down-gradient from the source of contamination. This difference in response at the two locations was attributed to difference in the hydrologic, geochemical and microbiological characteristics of the two zones of contamination, including redox conditions, and the nature of the microorganisms present at the two locations.

At the contaminated site in Port Hueneme, California, *Salanitro et al. (2000)* conducted a pilot test to study the effect of oxygen injection alone, as compared to oxygen injection, combined with bioaugmentation (addition of proprietary MTBE degrading microorganisms) on the removal of MTBE in situ. Results indicated that the bioaugmented plot performed better (lag time approximately 30 days), compared to the oxygen only plot (lag time 186 to 261 days). A follow-up study published recently (*Lesser et al., 2010*) compared the activity of MTBE degradation in different cores from the site. The authors (*Lesser et al., 2010*) noted that: “cores from the bioaugmented regions had the highest frequency of MTBE biodegradation to nondetect levels among their sections suggesting a direct effect of the inoculum and its distribution when it was implanted”. *Smith et al. (2005)* conducted a similar experiment at Port Hueneme. The addition of oxygen alone in one plot was compared to the addition of oxygen combined with bioaugmentation with the UC Davis MTBE degrading bacterial strain PM1. Similar results were observed

with less lag time in the bioaugmented plot. In both studies oxygen delivery was problematic at depths greater than approximately 15 feet, limiting its applicability to shallow contamination. At the same time, the large network of wells necessary to create a “biobarrier” can limit the applicability of such a process because of the need for site access for installation, operation and maintenance. Other site-specific conditions would have to be considered. For example, heterogeneity and low permeability sediments, as well as large fluctuations in groundwater levels may complicate treatment. As *Wilson et al. (2002)* concluded: “We believe a wide range of methods are available to create aerobic conditions [in situ]; what is needed is an assessment of the efficacy of each method for a range of hydrogeologic and geochemical conditions and continued work to understand the prevalence and reliability of native MTBE-degrading microbes.”

When the contaminated water is deep underground, ex-situ treatment may be necessary. Ex-situ treatment involves pumping groundwater, and treating it above ground. More recently *Tornatore et al., (2005; 2006)* reported on the use of granular activated carbon (GAC) beds to seed native MTBE degraders. By providing oxygen and nutrients, bacteria in the groundwater, capable of MTBE biodegradation, created a biofilm that is capable of treating MTBE and TBA. This project, in Los Angeles County, is particularly unique because the treated water is allowed to be re-injected in the subsurface, rather than be disposed of off-site. This approach, possible because the degrading microorganisms are native to the aquifer, serves to preserve the water source. Re-injection of oxygenated water may also stimulate in-situ biodegradation.

5.3 Factors Affecting Biodegradation

Based on the scientific literature, several factors appear to be necessary for MTBE biodegradation to occur in the subsurface, assuming the presence of native MTBE degraders. These factors include pre-acclimation to MTBE, the presence of sufficient oxygen, as well as other site-specific conditions, such as redox conditions, pH, and temperature.

5.3.1 Difficulty obtaining a degrading microbial culture: While evidence from some sites indicates that natural MTBE degraders are present and can be stimulated with the addition of oxygen (*Salanitro et al 2000; Wilson et al., 2002; Smith et al., 2005*), many researchers have noted that MTBE degrading microorganisms are not prevalent even at contaminated sites exposed to MTBE for long periods of times. “Generally it has proved difficult to isolate strains from enrichment cultures using MTBE as a sole carbon and energy source. Attempts for more than 15 years were of limited success” (*Muller et al., 2008*).

Unlike BTEX degrading microorganisms, microorganisms that biodegrade MTBE aerobically do not appear to be prevalent at contaminated sites. “Fuel oxygenates such as methyl and ethyl tert-butyl ether (MTBE and ETBE, respectively) are degraded only by a limited number of bacterial strains” (*Rohwerder et al., 2006*). Many of the aerobic microorganisms that have been identified as MTBE degraders were cultured from activated sludge (from sewage treatment plants) (*Salanitro et al., 1994; Cowan and Park*

1996; Mo *et al.*, 1997; Hanson *et al.*, 1999; Pruden *et al.*, 2001; Francois *et al.*, 2002; Zaitsev *et al.*, 2007). A study by Pruden *et al.* (2001) indicated that the group of organisms identified in MTBE biodegradation may be dominant in activated sludge, but may not be present in uncontaminated aquifers. Furthermore, microorganisms that degrade MTBE anaerobically have not been isolated. Youngster *et al.*, (2010) noted that: “[t]o date, very little is known about the anaerobic MTBE degradation process and none of the responsible organisms have been identified or isolated as yet”.

Spinnler *et al.* (2001a), for example, reported that no MTBE degrading microorganisms were found in samples collected from 2 contaminated sites, one in the Northeast, and one in Northern California. Spinnler *et al.* (2001b) stated: “Microorganisms capable of degrading MTBE are not so ubiquitous as BTEX degraders. ... few soils collected from MTBE contaminated sites showed any MTBE-degrading activity when stimulated with oxygen.” Salanitro *et al.* (1998) made similar observations. They found that 8 out of 10 soil and groundwater samples collected from different contaminated sites from around the country, had no MTBE-degrading microorganisms. Activated sludge from 4 refineries (out of 5 tested), also had no MTBE degrading capability. Salanitro *et al.* (1998) concluded: “Our survey results ... on the presence of ether-degraders in soil and ground water show that these populations are too low and/or grow too slowly to effectively attenuate observed levels of MTBE in aquifer plumes.” Lesser *et al.*, (2010) noted differences in degradation activity at the Port Hueneme site within small distances: “significant changes in activity level were observed over 0.3-m [~ 1 foot] vertical distances in the same location.”

Kane *et al.* (2001) examined aquifer sediments from 7 MTBE contaminated LUFT sites in Northern California, noting that only 3 out of 7 showed evidence of MTBE biodegradation. Similarly, Moreels *et al.* (2004) examined the potential for MTBE biodegradation, under aerobic conditions, in soils collected from seven different locations in Belgium. Five of the samples were collected from sites contaminated with gasoline, while two were topsoil samples. MTBE was degraded in samples from only one of the sites, with a lag-phase of up to 270 days. In contrast, benzene was degraded rapidly in all samples from all sites.

More recently, Babe *et al.*, (2007) examined the capacity of native microorganisms to biodegrade MTBE and other oxygenates in soil and groundwater samples from 14 different locations in Europe and the United States. All samples came from “fuel oxygenate contaminated sites”. Optimum growth conditions were provided with samples incubated under aerobic conditions (with oxygen in “large excess” of the theoretical demand) at 30°C, and with yeast extract added as a supplement to improve microbial growth. Results showed “either no or very low capacities for MTBE biodegradation” in nine out of the fourteen (64%) site samples. Out of the samples collected from the USA (seven out of the fourteen) only 2 sites showed efficient biodegradation. Three sites showed no biodegradation, while two others showed a low capacity to degrade MTBE (9% MTBE degraded in 345 days in one soil sample, and 21% MTBE biodegraded in 277 days in an aquifer sample from another location) Babe *et al.*, (2007).

Based on observations from the published literature on the difficulty in establishing MTBE biodegradation under natural anaerobic aquifer conditions, the difficulty isolating anaerobic microorganisms degrading

MTBE, the apparent contradictory results from surface sediments (some positive others negative), and the relative abundance of studies with degrading microorganisms isolated from activated sludge, combined with the apparent absence of aerobic MTBE degrading organisms from many contaminated sites it may be these observations can be explained partly by the specificity of organisms that can degrade MTBE. In his book “Biodegradation and Bioremediation” *Alexander (1994)* explains:

“It also is now clear that microorganisms acting on certain pollutants are absent from particular sites. A compound that is metabolized by many species will likely encounter one or several species in all microbial communities that can transform it. On the other hand, certain synthetic compounds are apparently transformed by very few species, and it is thus likely that not a single one of the very few species with the requisite enzymes may be present in a particular site. This view is in line with the frequent observation that some organic compounds are mineralized or otherwise metabolized in samples from one but not another environment and that active organisms can only be isolated from some environments.”

5.3.2 Acclimation: Also referred to as adaptation, or lag time, is the time needed for microorganisms to display measurable biodegradation. Acclimation is important in understanding when and under what conditions biodegradation will proceed. *Becker et al., (2006)* explain: “current understanding of the events that lead to microbial community adaptation to pollutants is extremely limited. This lack of understanding means that we are unable to predict when or where adaptive events will occur.”

Under ideal (e.g., controlled laboratory/oxygenated) conditions, time lags for MTBE biodegradation of 200 days (*Mosteller et al., 1997*), 260 days (*Salanitro et al., 2000*), and up to one year (*Eweis et al., 1997*) have been reported. Such observations suggest that the lag times in natural aquifers, typically under oxygen and nutrient limited conditions, will likely be even longer, maybe years (*USEPA, 2005*). The reasons for a long acclimation period remain unclear, but even assuming MTBE biodegradation does occur, a lengthy time lag will allow the leading edge of MTBE contamination to advance without any attenuation by biodegradation. From experience with a field experiment on MTBE biodegradation in the Borden Aquifer in Canada, *Schirmer et al. (2003)* concluded:

“It is possible that the lag periods reflect slow growth of a population originating from a very small number of cells, so that much time elapses before detectable MTBE loss. An alternate explanation of these findings is that fortuitous genetic change (perhaps mutation) plus selective pressure (MTBE as the only available organic substrate) has led to an MTBE-degrading capacity. If so, though useful when or if it occurs, this phenomenon would be impossible to predict. Natural attenuation of a MTBE plume as a result of such occurrences could never be relied on.”

5.3.3 Oxygen: In some cases, low oxygen concentrations have been associated with reduced or inhibited MTBE biodegradation (*Scow et al., 2000; Landmeyer et al., 2001*), and the addition of oxygen has been shown to stimulate MTBE biodegradation (*Salanitro et al., 2000 and Wilson et al., 2002*). At a site in South Carolina (discussed earlier in this document), *Landmeyer and Bradley (2003)* found that the addition of oxygen release compounds (to increase dissolved oxygen concentration in groundwater) did not result in changes in the dissolved oxygen or MTBE concentrations in the source zone. It did, however,

result in a measurable reduction in MTBE concentrations 200 m down-gradient from the source of contamination. This result (difference in response) at the two locations (source zone versus down-gradient) was attributed to differences in the hydrologic, geochemical and microbiological characteristics of the two zones of contamination.

Simply put, the presence, or introduction of oxygen, is not necessarily enough to induce MTBE biodegradation. In many cases, MTBE was reported to be persistent even in the presence of oxygen (*Pasteris et al., 2002; Da Silva and Alvarez 2002; Dakhel et al. 2003; Moreels et al., 2004; Babe et al, 2007*). In fact, a recent analysis (*Squillace et al., 2007 and Carter et al., 2008*) of data from 3,500 water samples collected between 1985 and 2002 from almost 100 different aquifer studies over the U.S., shows that MTBE detections in groundwater seem to be more highly associated with oxic groundwater, as compared to anoxic groundwater. Oxic groundwater was defined as having a dissolved oxygen (DO) concentration greater than 0.5 mg/L, while anoxic groundwater had a DO of less than or equal to 0.5 mg/L (*Squillace et al., 2007*). It should be noted that: “**Young ground water** usually has a larger dissolved oxygen concentration compared to **old ground water**” (*Zogorski et al., 2006, emphasis as published*). Young ground water was defined as “water recharged after 1955”. In other words, the association between MTBE detections and groundwater type (i.e., oxic versus anoxic) could have more to do with the relatively recent introduction of MTBE into the environment (young groundwater), and less to do with its biodegradation potential.

5.3.4 Other Factors: In some cases researchers have found that MTBE biodegradation is inhibited in the presence of more easily degradable compounds, such as the BTEX group (*Church et al., 2000; Deeb et al., 2001; Auffret et al., 2009*), or alkane compounds (*Johnson and Hyman, 2006*). The pH may also play a role; *Pruden et al. (2001)* reported an optimum pH range of 7.4 to 7.6, with rapid deterioration of MTBE removal efficiency outside of the pH range of 7.3 to 8.0. *Muller et al., (2008)* on the other hand, reported growth of a pure MTBE degrading strain within a pH range of 5.5 to 8.0, but no growth at pH below 5.0, and above 9.0. *Eweis et al. (1997)* reported similar results. At the same time, temperature can be a factor in biodegradation rates. For example, while *Park and Cowan (1997)* reported higher rates of MTBE biodegradation at 30°C compared to 20°C (in laboratory microcosms under aerobic conditions), *Bradley and Landmeyer (2006)* reported optimum biodegradation at 24°C with significant decrease in biodegradation potential at temperatures below, or above 24°C, under similar laboratory conditions. At the lower temperatures (as low as 4°C) biodegradation was significantly reduced, but not completely inhibited (*Bradley and Landmeyer, 2006*).

Another important factor is what appears to be the slow growth rates associated with MTBE degrading organisms. *Muller et al., (2007)* suggested that a relatively high threshold concentration might be necessary to drive growth on MTBE. For the most part, organisms that have been shown to grow on MTBE are relatively slow growing, with low cell yield (*Salanitro et al., 1994; Mo et al., 1997; Hanson et al., 1999; Fortin and Deshusses, 1999; Pruden et al., 2001; Zaitsev et al., 2007; Vosahlikova-Kolarova et al., 2008;*

Youngster et al., 2010). Rates of biodegradation are inherently tied to growth rates. *USEPA (2005)* explains:

“Typical strains of bacteria growing aerobically on petroleum hydrocarbons can divide and double their numbers every two to five hours at room temperature. As a consequence, laboratory enrichment cultures will grow up and remove the hydrocarbons in a few days. On the other hand, cultures of bacteria using MTBE as a growth substrate require several days to several weeks to double their numbers. Their growth rate is from one-tenth to one-hundredth of the growth rate of bacteria that degrade conventional petroleum hydrocarbons. Their very slow growth rate has an important effect on the time required for a culture to grow to densities that will entirely consume MTBE.”

Some studies have suggested that some amendments may be necessary to support MTBE biodegradation; for example cobalt (*Rohwerder et al., 2006*), or humic substances (*Wei and Finneran, 2009*). Other factors influencing MTBE biodegradation remain unclear. For example, in some laboratory studies, the biodegradation of MTBE was observed to cease, after it had progressed for some time, and at relatively high concentrations (*Mo et al., 1997; Borden et al., 1997; Schirmer et al., 1999*). In those studies, researchers could not identify a clear cause for the cessation of microbial activity.

5.4 Examples from field studies

Evidence of MTBE biodegradation in aquifers under natural conditions (in the absence of engineered remediation) remains scarce. Below is a summary of a few examples from field studies that are of particular interest because of their history or site-specific conditions that might influence MTBE fate.

Canadian Forces Base, Borden Ontario: A field experiment at this site in 1988, resulted in the controlled release of gasoline containing MTBE in the shallow aquifer. Monitoring over a period of 476 days showed MTBE to be recalcitrant, moving at the same rate as a conservative tracer (*Barker et al., 1990*). The researchers then re-sampled groundwater from the site in 1995-96, nearly 7 years from the time the plume had last been sampled (*Schirmer and Baker, 1998*). With limited sampling on a grid much coarser than that of the original experiment, they could not account for all of the MTBE mass that was originally injected. They indicated that this apparent mass loss may have been the result of biodegradation. However, because of the large time span between the sampling events and the lack of documentation of other processes that could be responsible for mass disappearance, the case for biodegradation remains weak. Other processes, such as diffusion into the underlying aquitard (which the plume had migrated close to), transient fluctuations of the hydraulic gradient causing plume migration into unanticipated locations and greater mixing, and relatively extreme precipitation events could have affected plume movement and concentrations. In fact *Schirmer and Barker (1998)* stated:

“While we are confident that MTBE mass has been lost, we cannot yet confirm biodegradation as the process.” In reference to the same study site, *Schmidt et al. (2004)* remarked: “even at a site with injection of a defined amount of the gasoline oxygenate methyl tert-butyl ether (MTBE) into groundwater, well-known hydrogeology, and a dense network of sampling wells, it was not possible to unequivocally determine MTBE biodegradation after a period of eight years”.

Former UST area near Beaufort, South Carolina: The importance of oxygen in MTBE biodegradation was further emphasized with several studies conducted at a site in South Carolina (*Landmeyer et al., 1997, Landmeyer et al., 1998, and Landmeyer et al., 2001*) where a plume of MTBE extends approximately 230 m (755 feet) down-gradient from a UST area, to where groundwater discharges into a concrete-lined ditch (surface water). Gasoline was detected in the shallow aquifer in 1991, “although the UST had most likely leaked since the mid-1980s” (*Landmeyer et al., 1998*). The study published in 1998, approximately 10 years after the release, examined the biodegradation of MTBE in microcosms containing sediments from the contaminated aquifer. The experiments were conducted using radio labeled MTBE. In a 7-month period, less than 3% of the radiolabeled MTBE was recovered as radiolabeled CO₂ (evidence of limited biological transformation to CO₂). Biodegradation was deemed insignificant as a natural attenuation mechanism in the contaminated aquifer. In a later study (*Landmeyer et al., 2001*), MTBE biodegradation was documented in samples from a microbial biofilm growing in the concrete-lined ditch (zone exposed to oxygen) where groundwater discharges into surface water. In other words, the conditions in the aquifer itself did not favor natural biodegradation, and biodegradation only occurred when water became oxygenated at the discharge surface.

Deer Park, New York: At this site, the release of gasoline was first detected in 1990, at a time when MTBE was used as an octane enhancer at lower concentrations. *Thuma et al. (2001)* reported that the BTEX plume extended approximately 700 feet, whereas the MTBE plume extended to about 8000 ft. Initial remediation at the site included excavation of the impacted soil and dual phase extraction (*Wilson and Kolhatkar 2002*). Based on the 2002 report the site was continuing to be remediated with air sparging and soil vapor extraction.

Kolhatkar et al. (2001) looked at MTBE concentrations in monitoring wells in the methanogenic zone of the plume, and “calculated” an MTBE attenuation rate, from which a rate of apparent biodegradation was further estimated. *Kolhatkar et al. (2001)* concluded: “[T]he ground water data in this flow path seem to suggest that MTBE is being naturally biodegraded in the methanogenic ground water. Laboratory microcosm experiments have been set up to further evaluate this possibility” However, the results of these laboratory experiments as reported later by *USEPA (2005)* were in fact negative.

Thuma et al. (2001) developed a model for the site to simulate fate and transport in the plume and investigate future remedial options, including monitored natural attenuation. The model assumed a biodegradation rate of 5.2/year (estimated value from *Kolhatkar et al., 2001*) in the “methanogenic” zone of the plume. The model did not seem to incorporate the effects of remediation processes already on site (air sparging and soil vapor extraction). *Thuma et al. (2001)* concluded: “The predicted model concentrations generally correlate well with field data in the upgradient half of the plume, however, further downgradient the model predicts higher concentrations than have been observed in the downgradient monitoring wells. We think this may be indicative of a methanogenic biodegradation zone extending further downgradient than assumed, or occurrence of MTBE biodegradation downgradient of the

methanogenic zone, but at a slower rate, or the importance of sorption retardation in attenuating MTBE”. However, in a follow up analysis, *Wilson and Kolhatkar (2002)* attributed the observed attenuation at the site, in the distal part of the plume, “almost entirely to the contribution of dispersion.” No tangible evidence of biodegradation was established, and the model did not match the field data well. Moreover, laboratory microcosms taken from the site showed no evidence of biodegradation (*USEPA, 2005*).

Hampton Bays, New York: The plume at Hampton Bays was discovered when 54,000 µg/L MTBE and other gasoline chemicals were detected in a well installed by Suffolk County Department of Health Services (SCDHS) as part of a pesticide monitoring program (*EAR, 2005*). An investigation of the site revealed the source of contamination to be a gasoline retailer, approximately 1000 feet up-gradient, with MTBE concentrations near the source of 450,000 µg/L (*EAR, 2005*). The MTBE plume discharged into Tiana Bay approximately 2,200 feet from the source. “Concerns for potential impact to the benthic biota of Tiana Bay, from the discharging contaminated groundwater, caused NYSDEC to undertake several interim remedial measures (IRM’s).” (*EAR, 2005*). The remedial measures included several treatment techniques, including Bio-GAC¹⁸ for above ground water treatment.

To assess the potential for biodegradation in the plume, samples were collected and analyzed for evidence of isotopic fractionation. After three rounds of sampling, over the span of approximately one year, the results of the isotopic fractionation study concluded that: “[T]he isotope data and contaminant concentration data for the most recent sampling round indicated that dilution and dispersion are likely the most dominant attenuation mechanisms for MTBE removal within the aquifer” (*Finneran, 2004, in EAR, 2005*). The isotopic signal for $\delta^{13}\text{C}\%$ MTBE, in three rounds of sampling, ranged between -30.9 and -29.1, which is within the range of -27.5% and -33% reported for MTBE in gasoline (*USEPA, 2005*), indicating no apparent enrichment. The lack of evidence of any significant biodegradation under either aerobic (dissolved oxygen concentrations up to 4 mg/L at leading edge of the plume), or anaerobic conditions at this site, were further confirmed in a recently published report (*McKelvie et al., 2007*): “biodegradation of MTBE is not a significant process at this site under either aerobic or anaerobic conditions”. In a more recent study (*Landmeyer et al., 2010*), the potential for biodegradation of MTBE (and TBA and TAME) in the hyporheic zone at Tiana Bay (where the plume discharges) was examined. The hyporheic zone, as described by *Landmeyer et al., (2010)*, is “the highly variable zone” in surface water bodies “where surface water flows through parts of the bed and bank material and thus can interact with discharging groundwater”. The authors also described the hyporheic zone as “a location of increased biological abundance and diversity”. Although laboratory controlled studies showed the potential for MTBE

¹⁸ A BIO-GAC differs from a conventional granular activated carbon (GAC) bed, which is designed to remove chemicals from water through adsorption (physical removal), in that a Bio-GAC will allow microorganisms to grow on the surfaces of the granules removing chemicals biologically, once the adsorption capacity of the bed is reached. In one of the Bio-GAC systems 1,350 gallons of Bio-Remedy biomass® □ (Shell Global Solutions patented MTBE degrading microorganisms), were added to the activated carbon beds to help remove MTBE.

biodegradation in samples from the hyporheic zone¹⁹, the authors concluded that “the primary mechanisms of natural attenuation observed in the hyporheic zone were dilution and dispersion”, with only 0.5% of attenuation attributed to “apparent biodegradation” in Tiana Bay (*Landmeyer et al., 2010*). The study which examined MTBE attenuation in the hyporheic zone at three other surface water bodies in Long Island, New York, reached similar conclusions for the other sites stating: “the attenuation observed in the hyporheic zone occurred primarily by physical processes such as mixing of groundwater and surface water” which is “in contrast to immeasurable attenuation in the shallow aquifer during contaminant transport between 0.1 and 1.5 miles” (*Landmeyer et al., 2010*).

Leuna, Eastern Germany: At an old refinery site dating over 20 years, releases of MTBE-containing gasoline resulted in widespread contamination, where the MTBE plume extends to about 1700 m (1.05 mile), and is several hundred meters wide. *Martienssen et al. (2006)* reported that MTBE biodegradation appears to be occurring under “microaerobic conditions”. While BTEX and other hydrocarbons appear to be degraded anaerobically, “there was no evidence for anaerobic MTBE degradation” (*Martienssen et al., 2006*). Samples from the site could not degrade MTBE anaerobically (*Waul et al., 2008*) whereas pure bacterial cultures isolated from the site were strictly aerobes (*Lechner et al., 2007*). Researchers (*Martienssen et al., 2006*) postulated that conditions at the Leuna site, such as unconfined aquifer, close to ground surface, result in oxygen replenishment following rainfall events and related groundwater rise, leading to areas with elevated oxygen concentration, (microaerobic conditions) that favor aerobic biodegradation. The researcher (*Martienssen et al., 2006*) concluded: “Since the oxygen supply is limited, natural attenuation of MTBE requires large reaction zones.”

In a recent publication (*Jechalke et al., 2010*), researchers used contaminated groundwater “from a well located downstream from the refinery” to examine the potential for biofilm formation and biodegradation of benzene and MTBE in aerated ponds. Two different “geotextiles” were used as support material for the biofilm in the aerated ponds: polypropylene fibers, and a natural coconut fiber. In the experiment that lasted 14 months, benzene was removed in both beds (from 20 mg/l in the inflow to about 1 µg/l in the outflow with 1% of the removal being attributed to volatilization). In contrast, “MTBE biodegradation was by far not as effective as benzene biodegradation” (*Jechalke et al., 2010*). Approximately 48-53% of MTBE removal²⁰ in the first 6 months was attributed to volatilization, although removal in the coconut fiber bed increased to 67% after that, presumably due to biodegradation. Laboratory microcosm experiments were set up using material from both types of beds (approximately 8 months after startup of pond experiments) to examine/confirm biodegradation. Samples from the coconut fiber bed were able to degrade MTBE, though “no biodegradation was observed for polypropylene after 100 days of incubation” (*Jechalke et al., 2010*). It should be noted that despite the presence of “microaerobic conditions” at the Leuna site (as reported above by *Martienssen et al., 2006*), *Jechalke et al., (2010)* noted that: “the inflowing groundwater is anoxic, and

¹⁹ Approximately 24% and 20% MTBE was degraded under aerobic and anaerobic conditions respectively, in 83 days of laboratory incubation.

²⁰ Based on an initial MTBE concentration of about 4mg/l.

major parts of the basins showed minimum oxygen concentrations between 0.0 and 1.0 mg/L.”

Meanwhile, at another site in Dusseldorf, Germany, *Rosell et al. (2005)* found no evidence of significant natural attenuation of MTBE (no measurable mass loss) over a two-year monitoring period. TBA concentrations at the site, at a level similar to that of MTBE, were attributed to its presence in the contamination source (gasoline spill). TBA was found to be recalcitrant in the mostly anaerobic (dissolved oxygen concentrations less than 1.1 mg/l) groundwater at the site.

5.5 Proxy Indicators of MTBE Biodegradation at Field Sites

Establishing clear evidence of MTBE biodegradation in the field is difficult. Microcosm studies which are typically used to document the presence of degrading microorganisms in field samples, can be "expensive, time consuming, and often yield equivocal results". (*USEPA, 2005*). Other evidence includes depletion of electron acceptors such as oxygen, nitrate, sulfate, etc. However, because MTBE is usually present as part of gasoline, the depletion of electron acceptors could be due to the consumption of BTEX (other gasoline components), and not necessarily MTBE. Sometimes, the detection of a degradation product can offer evidence of biodegradation. In the case of MTBE, TBA is "the primary degradation product of MTBE" (*USEPA, 2005*). However, and as explained in the following section, TBA is a fuel oxygenate that might have been added to gasoline intentionally. It is also a co-product of MTBE, and is often found as an impurity in the MTBE added to gasoline.

Recently, "isotopic fractionation" has been employed as a tool to infer MTBE biodegradation at contaminated sites. However, as discussed later, the application of this method to document MTBE biodegradation at contaminated sites is a relatively new, and still evolving field of research. While biodegradation in laboratory microcosms has been shown to result in isotopic fractionation, other physical and chemical processes at play in contaminated sites, and that can also affect isotopic fractionation, had been largely ignored until recently.

5.5.1 TBA at MTBE contaminated sites

At many sites, field data indicate that the frequency of occurrence of TBA and the range of concentrations are at a scale similar to that of MTBE (*Kolhatkar et al., 2000; Shih et al., 2004; Wilson et al., 2005a*). For example, *Shih et al. (2004)* found that for 868 randomly selected LUFT sites in the greater Los Angeles area, MTBE was detected at 82.7% of sites, comparable to benzene at 82.5% of sites, while TBA was detected at 61.1% of sites. At the sites studied, TBA was found to have the greatest site maximum concentration, followed by MTBE, suggesting high source concentrations. TBA concentrations ranged from 6 µg/l to 4,400,000 µg/l. On the other hand, MTBE concentrations ranged from 0.46 µg/l to 16,000,000 µg/l. As part of the study (*Shih et al., 2004*), 500 sites were considered for plume length analysis, a measure of the potential for contaminants to affect drinking water sources. MTBE was found to have the greatest plume length followed by TBA.

TBA is potentially more toxic than MTBE. In California, the notification level (previously known as the

action level) for TBA is 12 µg/l based on evidence of potential carcinogenic properties (OEHHA, 1999). Because of its properties (high mobility, low volatility, recalcitrance under natural field conditions) TBA can be the regulatory driver for remediation considerations at contaminated sites (Shih *et al.*, 2004), and is expected to add to the cost of treatment of MTBE contaminated drinking water (AMWA, 2005; AWWA, 2005). Yet, testing for TBA at contaminated sites is a relatively new practice (Wilson *et al.*, 2005a) and is not required in most states. In 2003 only 11 out of the 50 states required sampling and analysis for TBA in groundwater at gasoline contaminated LUFT sites (this compared to 31 states that required testing for MTBE) (NEIWPCC, 2003). Hence, the level to which TBA has spread in groundwater at gasoline contaminated sites remains largely unknown.

While TBA can be a product of MTBE degradation (Salanitro *et al.*, 1994; Kane *et al.*, 2001; Vainberg *et al.*, 2006; Skinner *et al.*, 2008; Wei and Finneran 2009; Youngster *et al.*, 2010), or reduction (Bradley *et al.*, 2006), as discussed earlier, it is also a co-product of MTBE and is found as an impurity in the MTBE added to gasoline (Eweis *et al.*, 2007). The TBA content in MTBE varies widely, and can be as high as 10% (Kramer and Douthit, 2000). Because TBA is completely miscible with water (no solubility limit), even trace amounts of TBA in gasoline can result in large aqueous TBA concentrations, e.g., hundreds of mg/l (Zwank *et al.*, 2002, DeVaul *et al.*, 2003), when MTBE oxygenated gasoline comes in contact with water. As such, it is difficult to determine the source of TBA at MTBE contaminate sites. The USEPA (2005) cautions:

“TBA accumulation by itself is not convincing evidence of MTBE biodegradation. This makes it particularly difficult to use conventional monitoring data to document biodegradation of MTBE at field scale, or to extract rate constants for attenuation that can be used in predictions of future behavior of plumes.”

High TBA concentrations, relative to MTBE concentrations, at contaminated sites can be a result of the differences in the physical/chemical properties of the two chemicals and how that influences their fate in the subsurface, especially in the presence of remediation activity on site. TBA is more water-soluble than MTBE, and has a comparatively higher solubility out of gasoline (compared to MTBE). At the same time, TBA is much less volatile than MTBE (see Table 5.1 and Figure 5.3). Since most gasoline releases occur above groundwater, significant mass of contaminants can reside in the unsaturated zone, on its way to groundwater. Fluctuations in the water table can further “smear” the contaminants in the unsaturated zone. Above the water table, contaminants are subject to volatilization to the atmosphere, as well as dissolution and transport to the groundwater through precipitation (rain) events:

“If there are strong seasonal effects on the recharge of precipitation to ground water, these effects may be reflected in the measured concentrations of MTBE in monitoring wells. As the water table moves up and down in response to recharge, the water may wet more or less of the gasoline in the smear zone, resulting in higher or lower concentrations of MTBE in the well. If a plume is vertically heterogeneous, the screened interval of a monitoring well may sample different vertical regions in the same plume as the water table shifts.” (USEPA, 2005).

For example, Beckenbach *et al.* (2002) noted that seasonal precipitation (infiltration) and water table

fluctuations significantly influence MTBE groundwater concentrations relative to BTEX concentrations. That is expected because of the high solubility and recalcitrance of MTBE relative to BTEX. Similarly, TBA groundwater concentrations would be expected to be influenced by infiltration and changes in groundwater level. The often reported organic carbon partitioning coefficient K_{oc} for TBA of 37 is similar to that of benzene and much greater than that of MTBE (Table 5.1 and Figure 5.3; *ITRC, 2005*; *Kavanaugh and Stocking in USEPA Blue Ribbon Panel <http://www.epa.gov/aaaac/mtbe/mtbeethan.pdf>*). However, Schmidt et al. (2004) computed a K_{oc} for TBA of 2.6, more in line with other alcohols. For this value of K_{oc} , sorption of TBA would tend to be negligible in most aquifers.

Table 5.1. Properties of TBA, MTBE, benzene, toluene, and p-xylene.

Compound	Solubility (mg/l)	Vapor Pressure (mm mercury)	Henry's Law (dimensionless)	K_{fw}	K_{oc}
TBA	Miscible ^a	40-42 ^a	$4.8 \times 10^{-4} - 5.9 \times 10^{-4}$ ^a	0.15-0.33	2.6, 37
MTBE	43,000-54,000 ^a	245-256 ^a	0.023 – 0.123 ^a	15.5	11
Benzene	1,780 ^a	76.0-95.2 ^a	0.22 ^a	350	36 - 141
p-Xylene	589 ^b	8.9 ^b	0.283 ^b	4350	159

^aAPI, 2000

^bEweis et al., 1998

K_{fw} from Zwank et al., 2002.

K_{oc} for TBA of 37, MTBE and benzene from ITRC (2005).

K_{oc} for TBA of 2.6 from Schmidt et al. (2004).

K_{oc} for p-xylene based on mixed isomers: http://www.epa.gov/oppsrrd1/REDs/xylene_red.pdf.

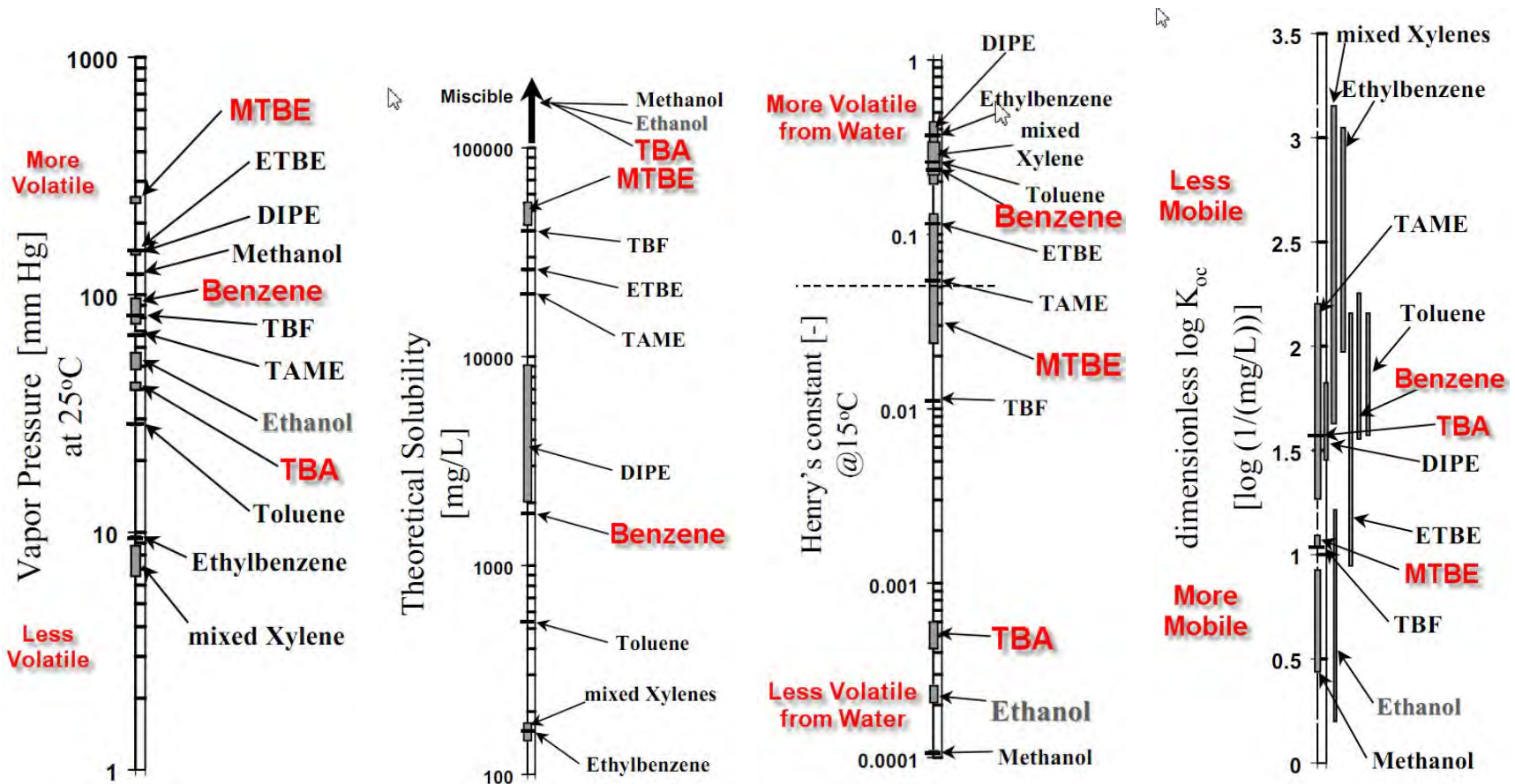


Figure 5.3. Physical/chemical properties related to the fate and transport of selected oxygenated gasoline constituents including MTBE, TBA and benzene. The physical/chemical properties of MTBE and TBA are considerably different such that they are expected to naturally separate in the environment after a MTBE reformulated gasoline release. (Figures from Fate and Transport of Ethanol in the Environment presented M.C. Kavanaugh and A. Stocking to the USEPA Blue Ribbon Panel, <http://www.epa.gov/air/caaac/mtbe/mtbeethan.pdf>)

Table 5.2: State ratings of SVE and bioremediation used to remediate MTBE contaminated soil (NEIWPCC, 2003)

	Very good	Good	Moderately good	Poor
SVE	12	3	10	-
Biodegradation	-	3	6	12

Remediation activity and natural processes such as volatilization into the atmosphere, can also influence, and significantly change, the mass of contaminants in the unsaturated zone, available to impact groundwater (Eweis *et al.*, 2007). SVE is aimed at “vacuuming” volatile contaminants from the unsaturated zone and has been proven very effective at locally reducing MTBE concentrations in soil. It is the technology most commonly used for treating soil contaminated with MTBE (USEPA, 2004). In fact, in a survey of state experiences with remediation process for MTBE and other oxygenate contamination at LUST sites (NEIWPCC, 2003), soil vapor extraction (SVE)²¹ was the most widely cited technology for treating contaminated soils. Furthermore, in terms of performance, more states rated SVE on the “very good” range of the spectrum, while biodegradation was rated more on the “poor” end of the spectrum (Table 5.2).

As MTBE mass is removed through SVE, less is available to impact groundwater. Conversely, TBA, being much less volatile from water, would likely remain behind, facilitating its migration to the water table (Eweis *et al.*, 2007). This change in contaminant mass (mainly MTBE loss) in the unsaturated zone is expected to be reflected in groundwater, resulting in a rising TBA to MTBE ratio that can mirror what might be expected from biodegradation. Figure 5.4 shows the apparent effects of dual phase extraction (DPE, which is a combination of vapor extraction and groundwater extraction) on MTBE and TBA concentrations in the groundwater monitoring wells.

²¹ Soil vapor extraction (SVE) is a process wherein vapors are pumped from wells screened in the vadose zone above the water table

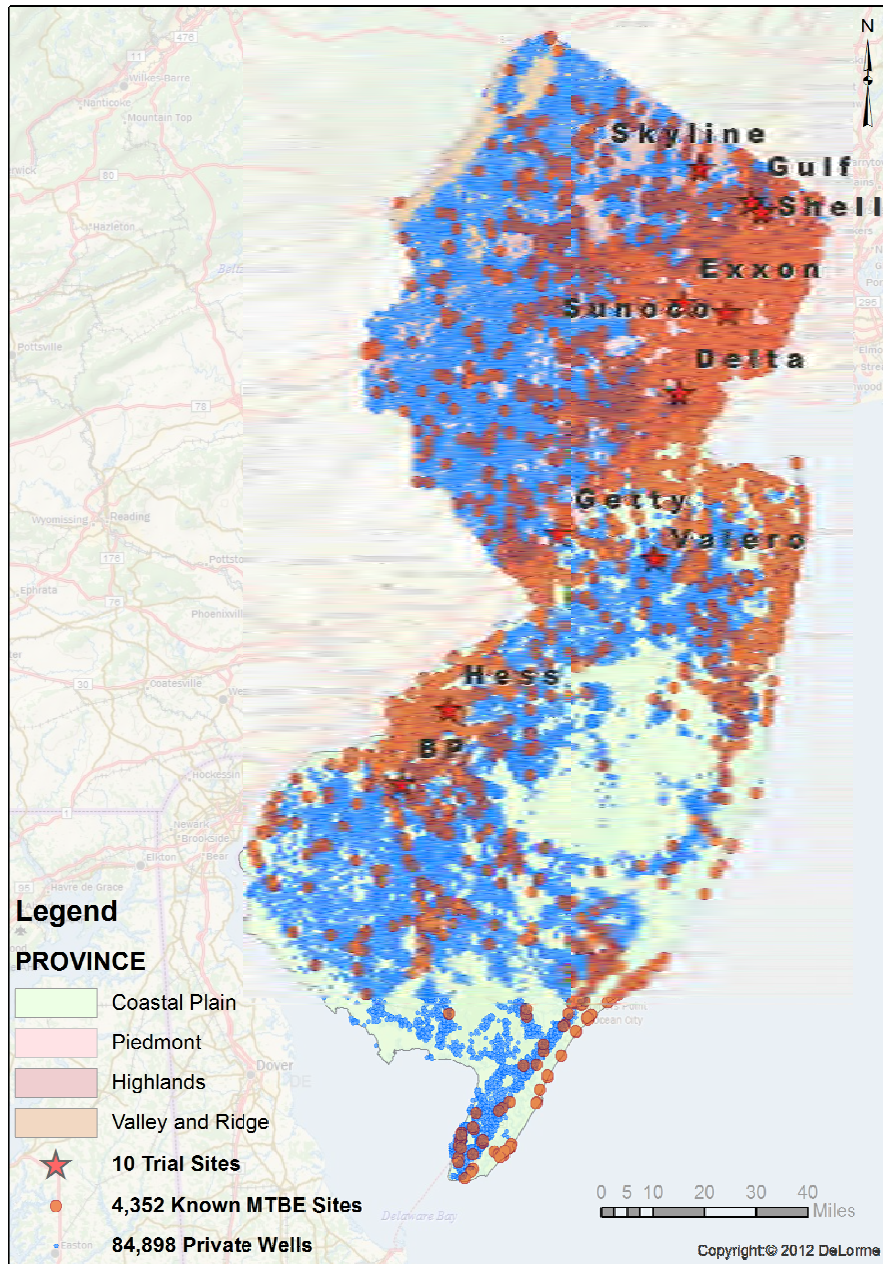


Figure 2.3. Location of the trial sites and other known MTBE contamination sites in the State, in relation to the location of the private wells that have reported groundwater sampling analysis under the Private Well Testing Act (as per the most recent data from the State). Note that the New Jersey has an estimated 400,000 private well, and approximately 20% of those wells are plotted.