5.0 FATE AND TRANSPORT OF CHEMICAL CONSTITUENTS

5.1 Introduction

This section presents a description of the physical, chemical and biological processes that affect the fate and transport of chemical constituents within and adjacent to the Sag Harbor former MGP site. Integrating these processes along with information regarding the distribution of the chemical constituents detected in environmental media (e.g., soil and groundwater), as described in **Section 4.0**, provides insight into the fate and transport mechanisms at work in the environment. The basic factors affecting the fate and transport of chemicals in the environment include:

- Physical properties of the chemicals, including state (e.g., solid, liquid, gas), density/specific gravity, solubility in water, propensity for volatilization and adsorption to soil.
- The environmental media in which the chemicals are present (e.g., soil, water) and the spatial and temporal changes in media as the chemical moves through the environment.
- The physical, chemical and biological processes that degrade or limit the mobility of the chemicals.

Based on the results of the investigation presented in **Section 4.0**, along with current site conditions, the primary affected environmental media include subsurface soil and groundwater. Off-site, the primary affected media is groundwater and, to a lesser degree, subsurface soil. The primary chemical constituents affecting on-site and off-site environmental media are BTEX and PAH compounds. While metals and cyanide were detected in on-site subsurface soil and groundwater, concentrations were generally low with metals being generally within typical background concentrations. Therefore, this discussion focuses on the behavior of BTEX and PAH compounds within the environment, including surface soil, subsurface soil, soil vapor and groundwater.

The basic processes and chemical properties affecting the fate and transport of BTEX and PAH compounds within the environment are described below. **Table 5-1** summarizes the relative degree to which each process affects BTEX compounds, low molecular weight PAHs, mid or transitional weight PAHs and high molecular weight PAHs.

- *Sorption* - Sorption is the process by which chemicals in one phase (i.e., liquid or gas) become associated with a solid phase. The organic carbon partition coefficient (K_{oc}) reflects the propensity of an organic compound to sorb to the organic matter found in soil and, therefore, governs the degree of dissolution and mobility of the compound. Chemicals that sorb onto organic materials in soil or sediment have reduced mobility in groundwater and surface water. Therefore, the greater the K_{oc}, the greater degree of reduction in the mobility of a compound within these media. In general, BTEX and low molecular weight PAH compounds have relatively low to moderate K_{oc} values indicating that these compounds have reduced mobility to some degree. The high molecular weight PAH compounds generally exhibit a significant reduction in their mobility. Therefore, high molecular weight PAHs would not be expected to migrate to any significant degree within most soil regimes. An exception to this general rule is if the PAH compounds are a component of a NAPL, such as tar and oil, which may migrate through the soil media if a sufficient quantity is released to the subsurface environment.

- *Aqueous Solubility* - Aqueous solubility is a measurement of the degree to which a compound will dissolve in water. Solubility controls the amount of a given chemical that can "partition" into the aqueous environment and, therefore, the degree to which it can be transported in groundwater or surface water. The degree of solubility will also have an influence on the ability of a compound to be degraded within an aqueous environment. Compounds having low solubilities generally have low degradation rates due to limited mass being available to chemical or biological processes. In general terms, BTEX compounds have relatively high rates of solubility, low molecular weight PAH compounds such as naphthalene, acenaphthylene, acenaphthene and methylnaphthalene have moderate rates of solubility and higher molecular weight PAH compounds, such as fluoranthene, pyrene and chrysene, have low to very low rates of solubility.

- *Volatilization* - Volatilization is the process of a compound partitioning into a gaseous phase from a liquid or solid phase. The rate of volatilization can be estimated through the use of the vapor pressure of the compound. BTEX compounds have high vapor pressures. As a result, BTEX compounds will readily vaporize into the atmosphere when present in shallow soil and surface water. Additionally, BTEX dissolved in groundwater will have a propensity to vaporize and migrate through unsaturated soil eventually releasing to the atmosphere. Low molecular weight PAHs tend to have low vapor pressures, therefore, while volatilization of these compounds does occur, their rates are negligible when compared to BTEX. High molecular weight PAHs have very low vapor pressures indicating virtually no volatilization under most conditions.

TABLE 5-1
SAG HARBOR FORMER MGP SITE REMEDIAL INVESTIGATION

RELATIVE INFLUENCE OF CHEMICAL PROPERTIES AND PROCESSES RELATED TO THE FATE AND TRANSPORT OF BTEX AND PAH COMPOUNDS

COMPOUND GROUP/SPECIES	MOLECULAR WEIGHT (g/mol)[1]	SORPTION	Log K_{oc}[1][2]	SOLUBILITY	SOLUBILITY IN WATER (mg/L)[1]	VOLATILIZATION	BIOLOGICAL DEGRADATION	NET EFFECT
BTEX								
Benzene	78.11	**Low**	1.89	**High**	1,780	**High**	**High**	Mobile within most environments. Degrades quickly under favorable conditions.
Toluene	92.14		2.12		515			
Ethylbenzene	106.17		2.2		152			
Xylenes	106.17		2.54		174.3[3]			
LOW MOLECULAR WEIGHT PAHs								
Naphthalene	128.18	**Moderate**	3.14	**Moderate**	30	**Low**	**Moderate**	Moderate mobility within most environments. Degrades at moderate rates under favorable conditions.
Acenaphthylene	152.2		3.68		3.93			
Acenaphthene	154.21		1.25		3.47			
2-Methylnaphthalene	142.2		3.4		24.6			
MID OR TRANSITIONAL MOLECULAR WEIGHT PAHs								
Phenanthrene	178.24	**High**	4.22	**Low**	1.6	**Very Low**	**Low**	Immobile within most enviroments. Recalcitrant to biodegradation.
Dibenzofuran	168.2		3.91 - 4.10		10			
Fluorene	166.22		3.7		1.69			
Anthracene	178.24		4.3		0.075			
HIGH MOLECULAR WEIGHT PAHs								
Fluoranthene	202.26	**High to Very High**	4.62	**Low to Very Low**	0.265	**Very Low**	**Very Low**	Immobile within most enviroments. Recalcitrant to biodegradation.
Pyrene	202.26		4.84		0.16			
Chrysene	228.3		5.39		0.0015			
Benzo (b) fluoranthene	252.32		5.74		0.0012			
Benzo (k) fluoranthene	252.32		6.64		0.00055			
Benzo (a) anthracene	228.3		6.14		0.014			
Indeno (1,2,3-cd) pyrene	276.34		7.49		0.062			
Dibenzo (a,h) anthracene	278.36		6.22		0.0005			
Benzo (g,h,i) perylene	276.34		6.89		0.00026			
Benzo(a)pyrene	252.32		5.60 - 6.29		0.0038			

Notes

(1) From: Montgomery, John H., and Linda M. Welkom.*Groundwater Chemicals Desk Reference* (Chelsea, MI: Lewis Publishers, Inc., 1990), 640 p.

(2) Sorption Coefficient - The ratio of adsorbed chemical per unit weight of organic carbon to the aqueous solute concentration.

(3) Taken from average solubility of all three xylenes at or around 20° C.

- *Biodegradation* - Biodegradation is a process that has been well documented in reducing concentrations of a wide range of organic compounds within soil, groundwater and surface water. Biological processes which take place in the natural environment can modify and destroy organic compounds at the point of introduction or during their transport within soil, groundwater or surface water. The available body of information suggests that the major agents causing the biological transformations in soil, sediment, surface water, and groundwater are the indigenous microorganisms that inhabit these environments (S.S. Suthersan, 1997). While rates of degradation are highly variable and are directly influenced by the conditions of the environmental media, BTEX compounds are readily degraded under aerobic (oxygen-rich) conditions within groundwater and surface water. However, benzene and ethylbenzene appear to be relatively resistant to degradation under anaerobic (oxygen deprived) conditions (R.C. Bordern, et al., 1995). Low molecular weight PAHs have been shown to naturally degrade at moderate rates under aerobic conditions. However, naphthalene was found to be recalcitrant to degradation under anaerobic conditions (J.E. Landmeyer, et al., 1997). High molecular weight PAHs are generally found to be highly recalcitrant to degradation under most natural aerobic and anaerobic conditions (S.S. Suthersan, 1997).

Based on the processes and properties of the chemicals of interest described above, along with the current understanding of the on-site and off-site hydrogeologic conditions, the following sections describe conceptual fate and transport models and transport mechanisms applicable to the site.

5.2 On-site Source Areas

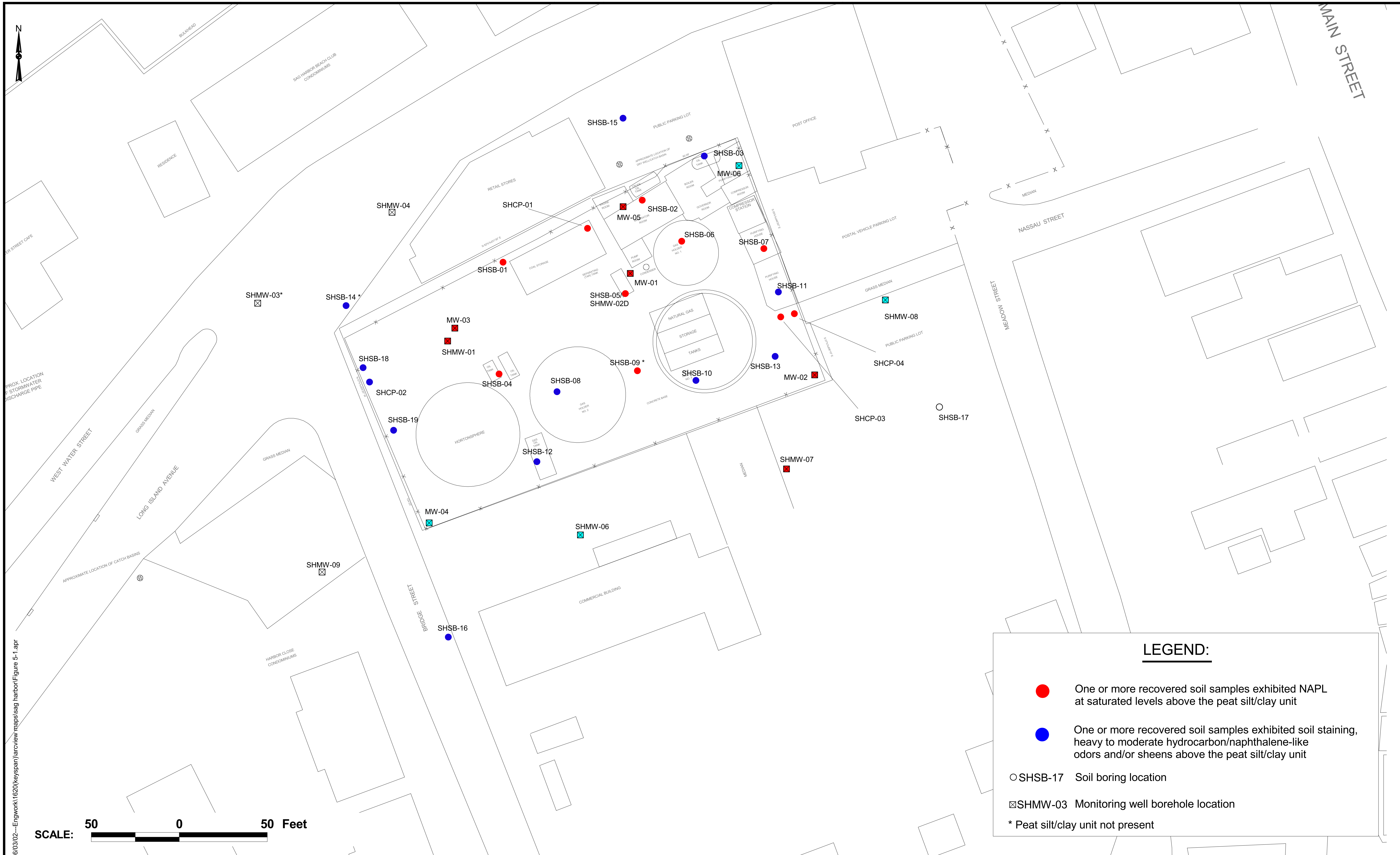
5.2.1 Transport and Fate of NAPL

Low viscosity tar and oil that may have been discharged to the site would have behaved as NAPLs migrating vertically through the soil column under the force of gravity until contacting the water table which is less than 2 feet below grade across the majority of the site. If denser than water, the NAPL would likely continue to migrate below the water table and through the fill material reaching the peat/silt/clay unit where vertical migration would likely be impeded. The NAPL would likely become trapped in the pore spaces of the peat/silt/clay unit as well as the fill material. However, due to the relatively shallow nature of the peat/silt/clay unit, the accumulation of NAPL within and above this stratum may promote lateral movement of the NAPL away from source areas. In areas where the peat/silt/clay unit is absent or relatively thin, the dense NAPL (or DNAPL) may continue to migrate vertically through the confining unit and into the underlying shallow sand unit. As discussed in **Section 3.2**, the shallow sand unit contains discontinuous fine-sand/silt lenses which may act as “traps” for DNAPLs that penetrate the peat/silt/clay unit. If the DNAPL is not trapped, vertical migration may continue until the volume required to sustain gravity-driven migration becomes inadequate either due to solubilization or the loss of mass as the result of the DNAPL being immobilized in pore spaces.

NAPL which is less dense than water (LNAPL) that reaches the groundwater water table tends to spread laterally on the surface of the water table. The LNAPL would become further immobilized in soil pores as the water table naturally fluctuated in the vertical direction in response to changes in rates of groundwater recharge as well as tidal influences. This would create a vertical zone of residual LNAPL, typically referred to as a “smear zone.”

Upon release, NAPLs typically distribute quickly within the subsurface (P.V. Noort, et al., 1994). Therefore, given that gas production operations ceased at least 70 years ago, it can be concluded that virtually all the NAPL present in the subsurface is likely to be at residual saturation levels within subsurface soil, and therefore, relatively immobile.

Figure 5-1 identifies boring and probe locations where NAPL or indirect evidence of NAPL (i.e., staining, strong to moderate odors, etc.) was observed in one or more subsurface soil samples recovered above the peat/silt/clay unit. As indicated by this figure, the majority of on-site locations included at least one sample collected above the peat/silt/clay unit which exhibited some evidence of NAPL. However, the strongest evidence of NAPL was observed within the eastern portion of the site centered around the former Tar Separating Tank, Gas Holder No. 3 and Generator Room/Crude Oil Tank area. Soil recovered from off-site probe SHSB-15 suggests that lateral migration of NAPL to the north of these former MGP structures has occurred above the peat/silt/clay unit. Additionally, soil recovered from off-site wells SHMW-06, SHMW-07 and, to a lesser degree, off-site probe SHSB-16 suggests that lateral migration of NAPL may have occurred to the south as well. While isolated zones of NAPL saturated soil were encountered above the peat/silt/clay unit throughout much of the site, shallow on-site monitoring wells exhibited little evidence of any measurable separate-phase NAPL. The only exception to this



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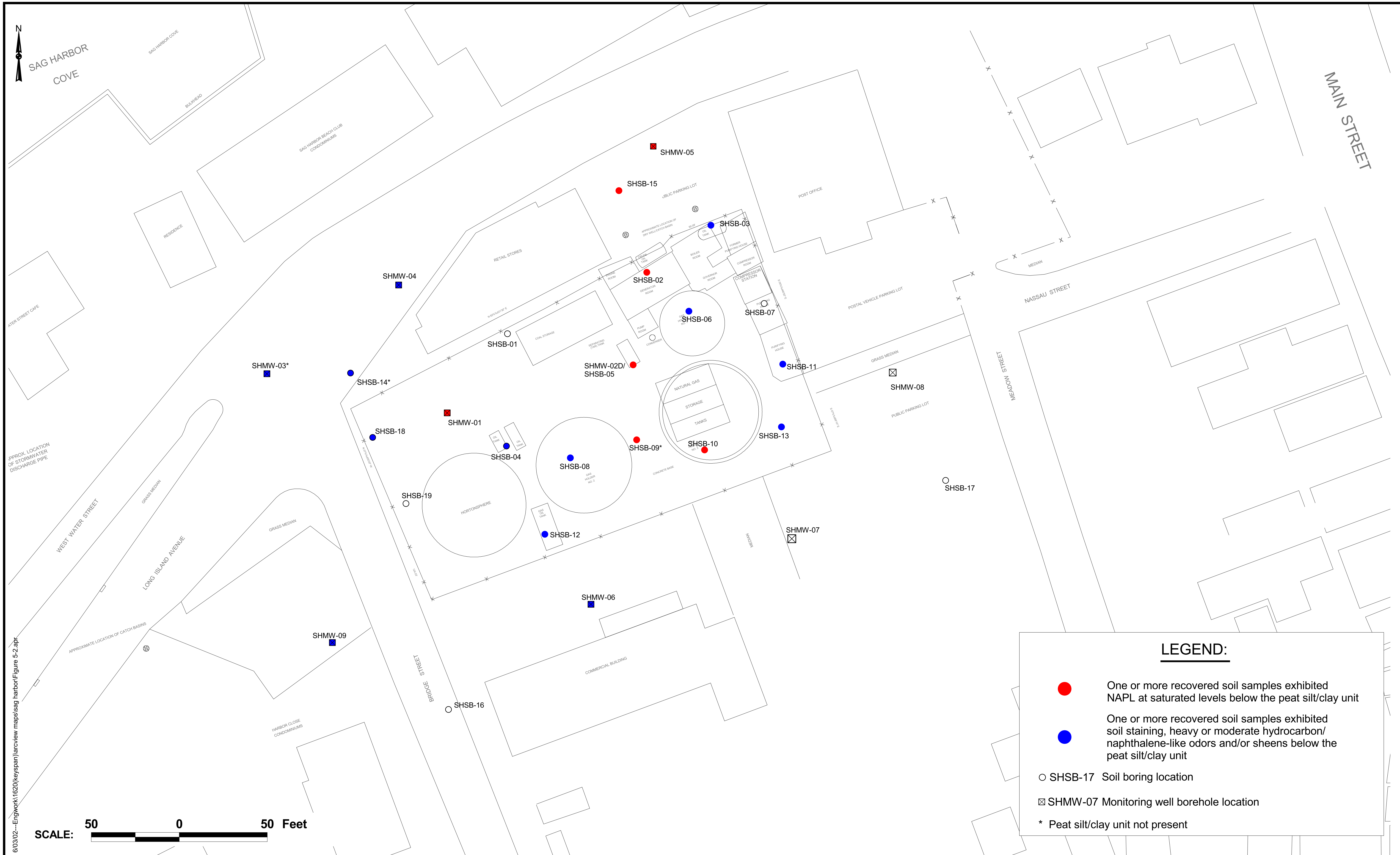
LOCATIONS WHERE EVIDENCE OF NAPL AND SOIL STAINING WAS OBSERVED ABOVE THE PEAT SILT/CLAY UNIT

FIGURE 5-1

was observed during the December 18, 2000 round of water level measurements where less than 0.1-foot of LNAPL was measured at existing well MW-5. This indicates that while NAPL is present above the peat/silt/clay unit, it appears to be currently in an immobile residual saturation state trapped within subsurface soil. Therefore, continued off-site migration of NAPL is unlikely beyond its current extent.

Figure 5-2 identifies locations where direct or indirect evidence of NAPL was observed in soil samples recovered below the peat/silt/clay unit. A comparison of **Figure 5-1** with **Figure 5-2** indicates considerably fewer locations where NAPL was observed below the peat/silt/clay unit. This suggests that the stratum likely behaves as a partial confining unit limiting or retarding the vertical migration of NAPL. The majority of borings exhibiting NAPL below the peat/silt/clay unit are located in the eastern portion of the site where this unit is relatively thin or possibly absent. The only off-site boring exhibiting any evidence of NAPL below the peat/silt/clay unit was SHSB-15, located directly north of the eastern portion of the site, again in an area where this stratum is relatively thin. These field observations suggest that vertical migration of NAPL may continue in areas where the peat/silt/clay is thin or absent. However, no intermediate or deep monitoring wells set below the peat/silt/clay unit exhibited measurable separate-phase NAPL, indicating that while NAPL has been observed below this stratum in subsurface soil, it appears to be currently in a relatively immobile residual saturation state.

As discussed in **Section 4.2.2**, while a number of probes/borings within the eastern portion of the site exhibited evidence of NAPL below the peat/silt/clay unit, it did not extend below a depth of 32 feet with the exception of the boring completed for SHMW-02D. During the installation of SHMW-02D, evidence of NAPL, including tar blebs, staining and sheens were noted to a depth of 90 feet bgs. A review of the boring log for SHMW-02D also indicates the presence of NAPL-saturated soil immediately above and within a fine-sand/silt lens encountered at approximately 50 feet bgs. This suggests that the fine-sand silt lenses present in the shallow sand unit may act as NAPL "traps" in locations where NAPL penetrates the peat/silt/clay unit.



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LOCATIONS WHERE EVIDENCE OF NAPL AND SOIL STAINING WAS OBSERVED BELOW THE PEAT SILT/CLAY UNIT

FIGURE 5-2

5.2.2 Transport of Chemical Constituents from Source Areas to the Atmosphere

While BTEX, and to a lesser degree, low molecular weight PAH compounds, may volatilize from residual NAPL and associated subsurface soil containing these compounds in a sorbed phase, the majority of the BTEX/PAH source is several feet below grade, as well as being below the water table. As a result, BTEX and PAHs present in source areas are not directly exposed to the atmosphere. Therefore, while some volatile emissions may intermittently discharge to the atmosphere within the site, it does not appear to be a major migration pathway. This is supported by the fact that on-site ambient air results did not identify elevated levels of BTEX or naphthalene.

5.2.3 Transport of Chemical Constituents from Source Areas to Groundwater

While the loss of BTEX and PAH compounds from on-site source areas through volatilization may occur, the primary transport mechanism or migration pathway for these compounds is dissolution through direct infiltration of precipitation, as well as groundwater flow through the soil containing the residual NAPL and sorbed BTEX and PAH compounds. Soil within the BTEX/PAH source areas which include organic-rich peat deposits and fill material with relatively high levels of total organic carbon (TOC) will have a relatively high capacity to adsorb and retain much of the BTEX/PAHs, limiting their off-site migration in groundwater. Due to these conditions, the relatively soluble compounds such as BTEX and low molecular weight PAHs which become dissolved in groundwater will have a much greater propensity to stay in solution and migrate via the natural flow of groundwater. In contrast, the high molecular weight PAHs with lower rates of solubility and a higher potential for sorption would have a tendency to remain within the immobile NAPL present in the soil matrix or only migrate a limited distance from this source and become sorbed onto organic material present in the soil. This is supported by the groundwater data which indicates on-site and near-site groundwater collected from areas which contain evidence of NAPL exhibit elevated levels of BTEX and low molecular weight PAHs in addition to relatively high concentrations of high molecular PAHs. In contrast, off-site groundwater data collected at least 50 feet from the site indicates the majority of groundwater exhibiting BTEX and PAHs primarily contain low molecular weight PAHs such as naphthalene, 2-methylnaphthalene and acenaphthylene.

5.2.4 Weathering of Source Areas

As discussed above, dissolution of BTEX and PAHs from the on-site source areas into groundwater is the major transport mechanism for these compounds. This process has been ongoing since the compounds had entered the subsurface environment at least 70 years ago. Therefore, it can be concluded that dissolution along with volatilization and biodegradation processes, (collectively referred to as "weathering") have been continuously reducing the overall concentration of these compounds within on-site source areas. As discussed in **Section 4.2.3**, historical on-site groundwater data, while limited, does suggests that BTEX and PAH concentrations within the site have decreased in on-site groundwater over the 5-year period for which data is available.

In summary, the NAPL present in subsurface soil beneath the site represents a highly weathered source of BTEX and PAHs compounds. The overall result of the weathering process is a general decrease in the contribution of BTEX and PAH compounds from on-site source areas to groundwater.

5.3 Off-site Transport Mechanisms

5.3.1 Transport of Chemical Constituents Present in Surface Soil

As discussed in **Section 4.2.1**, PAH compounds were detected in on-site surface soil samples up to a maximum concentration of 950.79 mg/kg total PAHs. However, the site is covered by 6 to 8 inches of crushed stone, effectively eliminating the transport of soil particulates containing sorbed PAH compounds via wind erosion. Due to the periodic flooding of the southwestern portion of the site, there is a potential for off-site migration of site constituents via overland flow of storm water during periods of heavy precipitation and/or coastal flooding.

However, due to the relatively high organic carbon partition coefficient (k_{oc}) of most PAHs and their low aqueous solubility, this does not appear to be a major transport mechanism.

5.3.2 Transport of Chemical Constituents in Groundwater

On-site groundwater containing BTEX and PAHs will migrate off-site in the direction of groundwater flow. As discussed in **Section 3.3**, both the shallow groundwater (i.e., above the peat/silt/clay unit) and intermediate groundwater zones (i.e., below the peat/silt/clay unit) flow in multiple directions from the site, with the predominant flow being to the north and northwest and minor flow components to the west and south. An easterly component of flow within the intermediate groundwater zone was also noted in the extreme eastern portion of the site. As a result, off-site migration of groundwater is primarily occurring to the north, northwest, south and west, with an easterly component within the intermediate groundwater zone as well. The majority of off-site migration of BTEX and PAHs appears to be occurring in the shallow groundwater zone. This is likely due to the semi-confining nature of the peat/silt/clay unit as well as due to the upward or groundwater discharging conditions observed in the intermediate and deep groundwater zones. Based on these conditions, flow of groundwater from on-site source areas to off-site locations is considered an important migration pathway of BTEX and PAH compounds.

The migration of BTEX and PAHs in groundwater will continue in the direction of groundwater flow away from the site until the compounds are attenuated by natural processes occurring in groundwater or until the groundwater discharges to a surface water body. Hydrocarbons, such as BTEX and PAHs, have been shown to degrade in groundwater as the result of biological and geochemical processes which naturally occur in aquifer systems. Research concerning the evolution of hydrocarbon plumes in groundwater indicate:

- Plumes tend to reach a stable shape and size even when a source is present;
- Plumes "shrink" or narrow (frequently longitudinally) when a source is reduced or removed; and

- Studies have shown that natural biodegradation process occurring within aquifers can be responsible for the reduction of 80 to 100 percent of the hydrocarbon mass of a plume within 1 to 1.5 years after source removal. Volatilization and advective dispersion each could account for only 3 to 5 percent of the BTEX losses in the plume studies (P.M. McAllister, C.Y. Chang, 1994; J.P. Salanitro, 1993; Rifai, et al., 1988).

BTEX and PAHs present in groundwater that may discharge to surface water will be rapidly attenuated as the result of the following fate and transport factors:

- Groundwater containing BTEX and PAHs which discharges to surface water will be diluted as the result of mixing with the surface water and other discharging water sources.
- BTEX and PAHs dissolved in surface water will have the propensity to volatilize from the water and undergo biological decay. Studies have shown that BTEX compounds such as benzene readily degrade through natural processes within surface water (L.Y. Wick, et al., 2000).

5.3.3 Transport of Chemical Constituents from Groundwater to Soil Vapor

While volatilization of BTEX and low molecular weight PAH compounds are likely occurring to some degree within off-site areas, the maximum total BTEX concentration in soil vapor of 154.7 ppbv was detected immediately adjacent to the site. Furthermore, soil vapor samples collected at least 50 feet from the site were found to have total BTEX concentrations below 17 ppbv and naphthalene was nondetectable. Therefore, the volatilization of BTEX and naphthalene from groundwater to soil vapor does not appear to be a major transport mechanism.