Evaluation of Impacts Resulting from Home Heating Oil Tank Discharges

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ABSTRACT

Diesel #2 is used to heat nearly 400,000 dwellings in Virginia. Home heating oil released from leaking underground tanks located adjacent to homes and residing in unsaturated soil adjacent to houses poses a potentially serious health risk. Specifically, the migration of hazardous vapors into buildings, known as vapor intrusion, can negatively impact indoor air quality in homes and public buildings (USEPA 2015). In this look-back study, we assessed the potential for petroleum vapor intrusion by sampling soil vapor at 25 previously remediated spill sites. Residual contaminants, in particular total petroleum hydrocarbons (TPH) and naphthalene, were detected in approximately 1/3 of the samples. Concentration levels were correlated to site variables (building type, time since remediation, physiographic region) including previous abatement measures. Spill category as assigned by the remediation contractor was investigated in conjunction with these three site variables. Remediation time was the most promising predictive site variable, with visible trends downward in DEQ Category 2 sites with increased remediation time. Higher contaminant concentrations were found near basement-style dwellings, which we hypothesize is due to the wall of the basement blocking horizontal migration of contaminants and the flow of oxygen to the release source zone. We found that many sites exceeded the sub-slab risk target threshold in naphthalene concentration, which has negative implications on previous abatement strategy efficacy.

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GENERAL AUDIENCE ABSTRACT

Diesel is used to heat nearly 400,000 residences in Virginia. Diesel released from leaking underground tanks located adjacent to homes and residing in soil adjacent to houses poses a potentially serious health risk. Specifically, the migration of hazardous vapors into buildings can negatively impact indoor air quality in homes and public buildings (USEPA 2015). In this study, we assessed the potential for vapor migration by sampling soil vapor at 25 previously remediated spill sites. Residual contaminants were detected in approximately 1/3 of the samples. Concentration levels were compared to site variables (building type, time since spill, soil type) including previous remediation activity. Spill category as assigned by the remediation contractor was investigated in conjunction with these three site variables. Remediation time was the most promising as a predictive site variable. Higher contaminant concentrations were found near dwellings with basements, which we hypothesize is due to the wall of the basement blocking horizontal migration of vapors. We found that many sites exceeded the target threshold in naphthalene concentration, which has negative implications on previous remediation effectiveness.

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List of Abbreviations

BEN	Benzene, Ethylbenzene, and Naphthalene
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
DEQ	Virginia Department of Environmental Quality
GCMS	Gas Chromatograph and Mass Spectrometer
MCHM	Multi-component Hydrocarbon Mixture
NFA	No Further Action
TD	Thermal Desorption
PAH	Polycyclic Aromatic Hydrocarbons
TPH	Total Petroleum Hydrocarbon
UST	Underground storage tank
VOC	Volatile Organic Carbon

1. Introduction

As of 2011 approximately 400,000 houses in the state of Virginia were using heating oil systems to heat their homes (Virginia DEQ, 2017). Heating oil, known as Diesel No. 2, is a mixture comprised of hundreds or thousands of hydrocarbons with between approximately seven and 20 carbon atoms. It is generally stored in tanks either above or below ground outside the dwelling. These tanks, called "underground storage tanks" (USTs) are usually located within 10 ft of the house and contain upwards of 500 gal of fuel. USTs can develop leaks into the unsaturated zone next to and below the house resulting in the discharge of heating oil into unsaturated soil.

Hazardous vapors are known to enter buildings by migrating through cracks, seams, interstices, and gaps in basement floors, walls, or foundations; through intentional openings (e.g., perforations due to utility conduits, sump pits); and/or within conduits (e.g., drain and sewer lines), resulting in negative impacts to indoor air quality in the homes (EPA 2015). Vapor intrusion is the process by which volatile gaseous compounds can enter homes through imperfections in the foundation (Virginia DEQ, 2017).

The suspected danger of vapor intrusion stems from health effects such as skin, eye, and respiratory irritation and is suspected of causing cancer and genetic defects. Benzene, Toluene, Ethylbenzene, Xylene (BTEX), and naphthalene vapors are noted to be harmful when inhaled, even to the point of mortality (Hess Corporation, 2012). In addition to health effects, vapor intrusion can also increase explosion hazard within the house and increase the degradation of utility lines in the soil (Dhir, 2000).

The Virginia Department of Environmental Quality (DEQ) administers a Home Heating Oil program in response to reports of tank releases. Environmental contractors are contacted to assess spills, remove the tank, and perform other remediation tasks as they deem necessary. In order to contextualize the spills for the contractors' abatement plans, DEQ has developed a category system based upon information at the time the discharge is reported, severity and extent of contamination, and risks from the discharge. There are four DEQ categories: No Further Action (NFA), and Categories 1, 2, and 3. NFA simply means that the concentrations do not pose a threat to the homeowners and the case is closed. Categories 1, 2, and 3 are increasing increments of concern. Generally, Category 1 sites are characterized by low amounts of spilled fuel, and are handled by retiring the tank, cleaning it out, and filling it with inert material.

Category 2 sites are generally characterized by a larger amount of spilled fuel, but no intrusion to the house. These are generally abated by removing the tank as well as excavating the surrounding soil and refilling with clean soil or gravel. Finally, Category 3 sites usually experience some kind of intrusion into the building or very potent olfactory sensation. These sites generally require both indoor and outdoor abatement strategies, and even the temporary relocation of the homeowner for their safety.

DEQ entered into an agreement with the Virginia Tech Department of Civil and Environmental Engineering to perform a look-back study in order to evaluate risk to homeowners. This study investigates the potential for vapor intrusion of below-ground hydrocarbons at the sites of known heating oil spills in the Commonwealth of Virginia. Field samples were collected at sites spanning a range of spill ages, architecture styles, and physiographic regions of Virginia. Headspace vapors were sampled over time to qualitatively assess the expected composition of fresh heating oil soil gas.

The objectives of this study are as follows:

1. measure petroleum vapor concentrations in soil at a range of sites,
2. analyze the correlation of certain site variables to the relative risk of the spills, and
3. determine if certain parameters can serve as predictors for future site abatement projects.

We hypothesized the following with regards to site variables:

1. Basement will have higher concentrations of TPH slab or crawlspace.

This is because we assumed that the presence of the basement wall would restrict lateral movement of the spill, disallowing the natural attenuation due to dispersion and advection.

2. Sites with a larger time since remediation (year of reporting) will have lower concentrations of all compounds.

Natural abatement mechanics will degrade compounds over time, resulting in lower concentrations at sites which have an older report date.

3. Piedmont sites will have higher concentrations than Valley and Ridge sites.

Piedmont soil’s lower porosity and permeability will prevent movement of compounds away from the source zone.

We also hypothesized that overall, Category 3 concentrations would be higher than Categories 2 and 1 concentrations. We hypothesized the variance amongst samples would decrease with remediation time as various remediation mechanics, defined below, decrease concentrations in areas that increase the variance from the background concentration of the site.

2. Literature Review

Upon release into the unsaturated zone, the volatile components of Diesel No. 2 enter the interstitial pore spaces as vapors. Light aromatic compounds, specifically BTEX and Naphthalene, are the focus of this work due to their adverse health effects. Upon entering the unsaturated zone, there are mechanisms by which the compounds can be degraded or removed. However, the mobility of vapor phase benzene, toluene, ethylbenzene, and xylenes (BTEX) and naphthalene in soil poses a threat to human health, as vapor intrusion into structures near the spills is likely given the proximity of the tank. Soil vapor intrusion is a phenomenon often associated with spills of petroleum products, and can have acute and chronic health effects. As the liquid fraction of diesel is often recalcitrant due to its tendency to be held in the interstitial spaces in the soil via capillary forces as a discontinuous phase, exposure can be long-term (Dhir, 2000).

One contaminant of concern is naphthalene, which is a type of polycyclic aromatic hydrocarbon (PAH). The United States Environmental Protection Agency (EPA) characterizes benzene, naphthalene, and ethylbenzene as priority pollutants (EPA 2014) because upon inhalation they can have carcinogenic, teratogeneic, mutagenic, and chronic health effects in humans (Qin et al., 2017, Park et al., 1990). Known short-term potential health effects associated with PAHs include vomiting, diarrhea, eye irritation, nausea, and confusion. Potential long-term health effects associated with the inhalation of naphthalene includes cancers of the skin, gastrointestinal tract, bladder, and lungs, as well as kidney and liver damage, jaundice, and cataracts (Illinois Department of Public Health). PAH inhalation has also been known to adversely affect child mental development (Fluegge 2016). In addition, the presence of hydrocarbon vapors in basements of buildings poses an explosion risk (Dhir 2001), and can have high bioaccumulation potential in soil, which can threaten local ecosystems (Park et al., 1990).

BTEX compounds also pose a serious threat to human health upon inhalation. Benzene is believed to have the most toxic effects on human health, with symptoms of nervous system toxicity, dizziness, narcosis, and cardiac arrhythmias following lethal exposure, behavior disturbances following intermediate exposure, and cytopenia and damage to bone marrow following low, prolonged exposure. Toluene can be readily absorbed from gastrointestinal and respiratory tracts. Exposure can cause neurological impairment, narcosis, structural changes in the brain, tremors, paranoid psychosis, hallucinations, and impaired speech, vision, and hearing.

Ethylbenzene causes similar neurological symptoms upon prolonged inhalation exposure. In addition, exposure to ethylbenzene is hypothesized to cause liver and kidney problems. Finally, xylenes similarly target the central nervous system, causing impairments to short-term memory and equilibrium (U.S.D.H.H.S., 2004).

BTEX, naphthalene, and TPH have different exposure limits, or risk targets, for indoor exposure and sub-slab soil gas. Indoor and sub-slab soil risk target values for BTEX and naphthalene are available in Table 2.1.

Table 2.1: Indoor and sub-slab soil risk target concentrations for vapor phase BTEX, naphthalene, and TPH. Values for BTEX and naphthalene were retrieved from the Vapor Intrusion Screening Level Calculator developed by USEPA (OSRTI, 2014). TPH concentration thresholds were retrieved from Brewer (2013).

Compound Name	**Sub-Slab Risk Target [μg m^{-3}]**
Benzene	12
Ethylbenzene	37
Naphthalene	2.8
TPH	100,000

Aromatic vapors can be mitigated through volatilization, or mineralization and transformation of source zone liquid fraction by biodegradation, as well as chemical and physical processes. These mechanisms are discussed in 2.2.

2.1 MCHM Composition

Diesel fuel is an MCHM comprised primarily of hydrocarbons with 7 to 20 carbon atoms often used in vehicles and sub-slab soil equipment. It is composed of aliphatics, aromatics, resins, and asphaltenes (Chen et al., 2017). Aromatics represent a small fraction of diesel's overall composition; however, this study will focus primarily on the aromatic fraction, as their toxicity and mobility makes them a priority (ATSDR, 1995). Of particular interest to this study are benzene (C_6), ethylbenzene (C_8), and naphthalene (C_{10}) due to their negative impacts on human health upon inhalation, and because we found concentrations of these compounds above sub-slab risk thresholds in our field study. We also consider TPH as a proxy for spill size and severity. This is because TPH is a concentration which represents the abundance of medium-volatility hydrocarbons which comprise the majority of the composition of the diesel.

In a simple physical volatilization system, MCHM composition changes over time with the volatilization of first lower then higher carbon number component compounds. This is reflected in the movement of the unresolved complex mixture “hump” (Figure 2.1) over time from the lower carbon number compounds to the higher carbon number compounds (Jeon et al., 2017). In addition, the signal decreases as the compounds are depleted in the source. In order to demonstrate this, we sampled the headspace of a 2 mL sample of fresh diesel fuel over a time period spanning a week with a flow of air refreshing the headspace at a rate of 5 ccm. Figure 2.1 shows two chromatograms which demonstrate the temporal shift from higher volatility to lower volatility hydrocarbons.

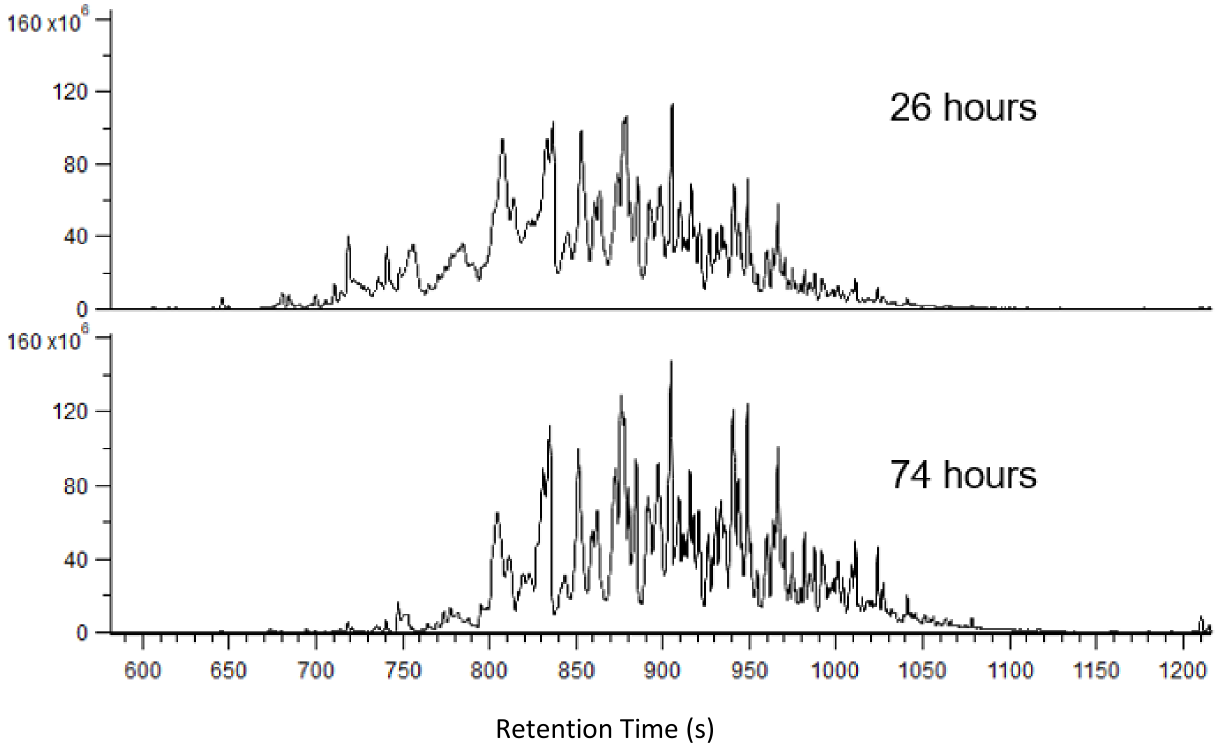


Figure 2.1: Headspace samples were analyzed to demonstrate movement of unresolved hydrocarbon hump from more volatile to less volatile compound composition with time. Between the two chromatograms, 49 hr have passed. Retention time is not corrected to a standard. Y axis units are total ion signal (arbitrary units). The hours indicated in the figure refer time since start.

2.2 Mechanisms of Hydrocarbon Attenuation

A number of mechanisms have been credited with the ability to remove and/or remediate complex multi-component hydrocarbon mixtures (MCHMs) in the unsaturated zone in a process referred to as "abatement," or any process that neutralizes toxicity of a compound or removes it from a system. Mechanisms of note include diffusion, advection, and aerobic biodegradation (Anderson et al., 2016; Choi et al., 2002; Qin et al., 2017). These mechanisms work to attenuate MCHMs by increasing mass transfer out of the source zone or converting the hydrocarbons into either more mobile, less-toxic organic compounds (transformation) or carbon dioxide and water (mineralization) (Madigan, 2015).

2.2.1 Physical Processes

Diffusion is the primary mechanism by which vapors may travel through porous media such as soil. Volatile organic compounds (VOCs) like BTEX and naphthalene are likely to enter soil gas due to of their characteristically high vapor pressures and high air to liquid partitioning coefficients. The diffusion coefficients of the diesel component compounds of interest (benzene, ethylbenzene, and naphthalene) are much higher than those of other hydrocarbons, often resulting in primarily diffusion-driven movement driven by concentration gradients (high source and low background concentrations). The steeper the concentration gradient, the higher resulting diffusion rate (Fick, 1855).

Lower molecular weight (C_6 to C_{12}) compounds have relatively high saturation vapor pressures and high diffusion rates and therefore easily diffuse through the soil into the atmosphere or nearby structures, while heavier compounds may take years to volatilize or diffuse (Sotsky et al., 1994). As evaporation rate of a hydrocarbon is proportional to its vapor pressure, it follows that lower carbon number compounds evaporate at shorter timescales and higher carbon number compounds evaporate at much longer timescales, if at all (de Gouw et al., 2011). Each addition of two carbon numbers decreases vapor pressure drops by approximately an order of magnitude (Pankow et al., 2008), increasing evaporation timescales by an order of magnitude. We divided carbon number into three vaporization classes: The first is carbon number below 8, the second is between 9 and 18, and the third is 19 and above. Table 2.2 below summaries general vaporization times for these classes (de Gouw et al., 2011).

Table 2.2: Hydrocarbon vaporization timescales by number of carbon atoms (de Gouw et al., 2011).

Carbon number class	**Vaporization timescale**
$\leq C_8$	< 1 hour
$C_9 - C_{18}$	1-1000 hours
$C_{19 \leq}$	>1000 hours

Whereas diffusion is the result of random motion of molecules, advection is the result of pressure gradients causing motion of soil gas. It is a mechanism that allows for mass transfer from the MCHM source zone to the pore space in the unsaturated zone. The relative ability of the gas to advect depends almost entirely on the permeability of the soil (Boudouch et al., 2016). Since the unsaturated zone is subject to atmospheric changes in pressure and temperature, pressure gradients form, resulting in gas advection through the soil (Ostendorf et al., 1991). In addition, buildings can create positive pressure on one side of the structure and negative pressure on the other, resulting in a pressure gradient (McHugh et al., 2010).

Density-driven advection causes mass flux of gasses out of the liquid source zone. Soil water content can hinder this process, as it effectively reduces diffusion coefficients of the gaseous MCHM and slows advection (Cotel et al., 2015). In addition, preferential pathways can be created by plant roots, utility lines, and soil macropores, creating points of entry to residences as well as providing direct routes to the atmosphere.

2.2.2 Chemical Processes

Chemical reactions often serve to reduce the size of larger, heavier hydrocarbon molecules which persist in soil, sometimes for decades, due to inherent recalcitrance. For example, branched and cyclic alkanes tend to persist in soil due to their low bioavailability. Contractors can utilize chemical oxidation by injecting a strong oxidant such as ozone into the unsaturated zone. This process increases aromatic compounds’ bioavailability by either directly breaking ring bonds by adding to the double bonds, or indirectly by creating hydroxyl radicals nearby that can react with double bonds within the ring (Chen et al., 2017).

2.2.3 Biotic Processes

Biodegradation occurs in tandem with abiotic processes to decrease concentrations of hydrocarbons near MCHM source zones. Gram-positive bacteria are known to biodegrade hydrocarbons (Hamamura et al., 2006), transforming source hydrocarbons into other (usually lower molecular weight) hydrocarbons, or mineralizing these compounds into inorganic components, chiefly carbon dioxide and water. Volatile compounds enter the vadose zone and undergo biotic aerobic respiration pathways, resulting in a concentration gradient that induces diffusion away from the source zone (Khan et al., 2016, Johnsen et al., 2005). These microorganisms oxidize the hydrocarbons (Qin et al., 2017), then assimilate their carbon. Their respiration processes result in carbon dioxide and water as byproducts (Hamamura et al., 2006). This is due to the presence of reduction-oxidation gradients present in soil (Khan et al., 2016).

The bioavailability of higher molecular weight compounds decreases semi-logarithmically as molecular mass increases (Johnsen et al., 2004). While carbon rings serve as a carbon source for biologic catabolism (Park et al., 1990), high molecular weight hydrocarbons prove difficult for the microorganisms to process, and must be broken down to smaller molecules to become bioavailable (Chen et al., 2017). Each species has a specific series of pathways which allow for the degrading of these molecules. Eventually, the microbes are able to injest the final product of these pathways, catechol, using the enzyme dioxygenase. This enzyme specifically breaks the cyclical bonds in catechol. Chemical reactions in the soil may break apart high molecular weight hydrocarbons, increasing their ability to be utilized in these pathways (Madigan et al., 2015).

Certain suites of bacteria are known to have hydrocarbon degrading capabilities; for example, *Rhodococcus*, *Alcaligenes denitricans*, and *Stenotrophomonas maltophilia* (Qin et al., 2017). *Rhodococcus* in particular is worth noting for its ability to degrade alkanes of various chain lengths and association with crude oil contamination. Most microorganisms can only degrade one class of compounds at a time. Once the compound is depleted, the organism will acclimate to another compound and begin to metabolize it (Dhir 2000). A consortium of microorganisms with different target substrates can degrade a broad range of compounds (Hamamura et al., 2006). Thus, when remediating a MCHM, a robust soil consortium is key in eliminating a wide range of compounds.

When implementing bioremediation systems, soil preparation is especially important in reducing remediation time. When effectively implemented, some bioslurry strategies can reduce concentrations 2- and 3-ring carbon compounds by as high as 80% in a one-year timescale (Loick et al., 2009). However, the logistics of creating a bioslurry from spills that originate from 3-10 ft below ground surface are often prohibitive.

Soil microbiological consortium diversity is important for biodegradation of petroleum vapors. Soils of different localities contain different, characteristic suites of microbes which possess varying hydrocarbon degrading specialties. This variability is because physical and chemical characteristics of soil, such as concentration of hydrocarbon substrate, pH, soil grain composition, and grain rounding, differ geospatially. However, certain species of hydrocarbon degrading microbes such as *Rhodococcus* occur almost ubiquitously, regardless of soil type and chemistry (Hamamura et al., 2006).

Previous studies have determined limiting factors and ideal conditions in soil biological activity. Optimal conditions for microbial growth were found to be at around room temperature, slightly acidic pH, and carbon concentrations around 9 g L^{-1} (Li et al., 2017). In addition, substances like citric acid, ammonium sulfate, and sodium chloride can be added to increase biodegradation efficiency by as much as 50% (Zafar et al., 2010).

Characterization of soil is an important component in determining how biodegradation will affect the contaminant. Biological activity in soil is highly variable with factors like depth, soil moisture, porosity, permeability, and soil grain composition. For example, clayey soil tends to be resistant to most bioremediation techniques (Partovinia et al., 2010), possibly due to lack of connectivity between the pores, preventing petroleum vapors and oxygen from coming into contact with the microbial consortium.

Microbiological metabolic activity changes with time through exposure to the source contaminant material. Diesel’s presence in the soil stimulates soil dehydrogenase, an enzyme often indicative of the presence of hydrocarbon-degrading organisms (Kaczynska et al., 2015). Previously uncontaminated soil often contains relatively small population sizes of hydrocarbon-metabolizing microbes. When contamination occurs, an acclimation period is necessary before the microbes can enter exponential growth phase and begin to metabolize the compounds. Other factors that affect rate of biodegradation include the composition of the microbial community, amount and nature of present hydrocarbons, and environmental conditions (Loick et al., 2009).

Biologic diversity can be lost when a consortium is exposed to high concentrations of hydrocarbon, as competitive microbes with tolerance to stress, hydrocarbon degradation ability, and nitrogen fixation ability often overgrow and dominate the community as the less tolerant species are weakened by the presence of the contaminants (Vazquez et al., 2017).

Diffusive flux out of the source zone is often the driving factor behind abatement. For example, 90% of naphthalene vapors degrade within the first 5-10 centimeters above the water table at a biodegradation rate of 2-26 days^{-1} (Andersen et al., 2006). Rates of degradation increase with increased exposure time. As vapors degrade, the flux out of the source zone can increase 10-300 fold. This information has powerful implications for hydrocarbon vapor remediation: The more hospitable the vadose zone is for naphthalene degrading organisms, the more mass transfer can occur, minimalizing the need for physical remediation measures (Anderson et al., 2016).

Prediction and modelling of diesel component degradation rates is complicated by the bioavailability and physical characteristics of the contaminants. *In situ* microbiological monitoring is a difficult and daunting task associated with many sources of error. In addition, when the MCHM enters the soil, it does not stay as one, cohesive mass; rather, it fills pore spaces and is consequently isolated from the rest of the mass in a discontinuous phase (Dhir, 2001). It is thus crucial to understand the soil and biological parameters of each site to implement remediation protocols.

2.3 Strategies for Abatement

The sites that were visited in this study were generally characterized in a similar manner across all sites in the Commonwealth. A spill was detected, and a contracting company was called in. The contracting company took vapor samples and provided recommendations to DEQ on a course of action for site abatement. DEQ has the responsibility to evaluate these situations and decide if further action or investigation is warranted. DEQ staff determine appropriate actions to protect human health and the environment. At sites where a release of home heating oil is deemed to pose a potential threat and impact, the release or discharge of oil from the tank and piping must be stopped, free product must be removed to the extent practicable (Virginia DEQ Guidance).

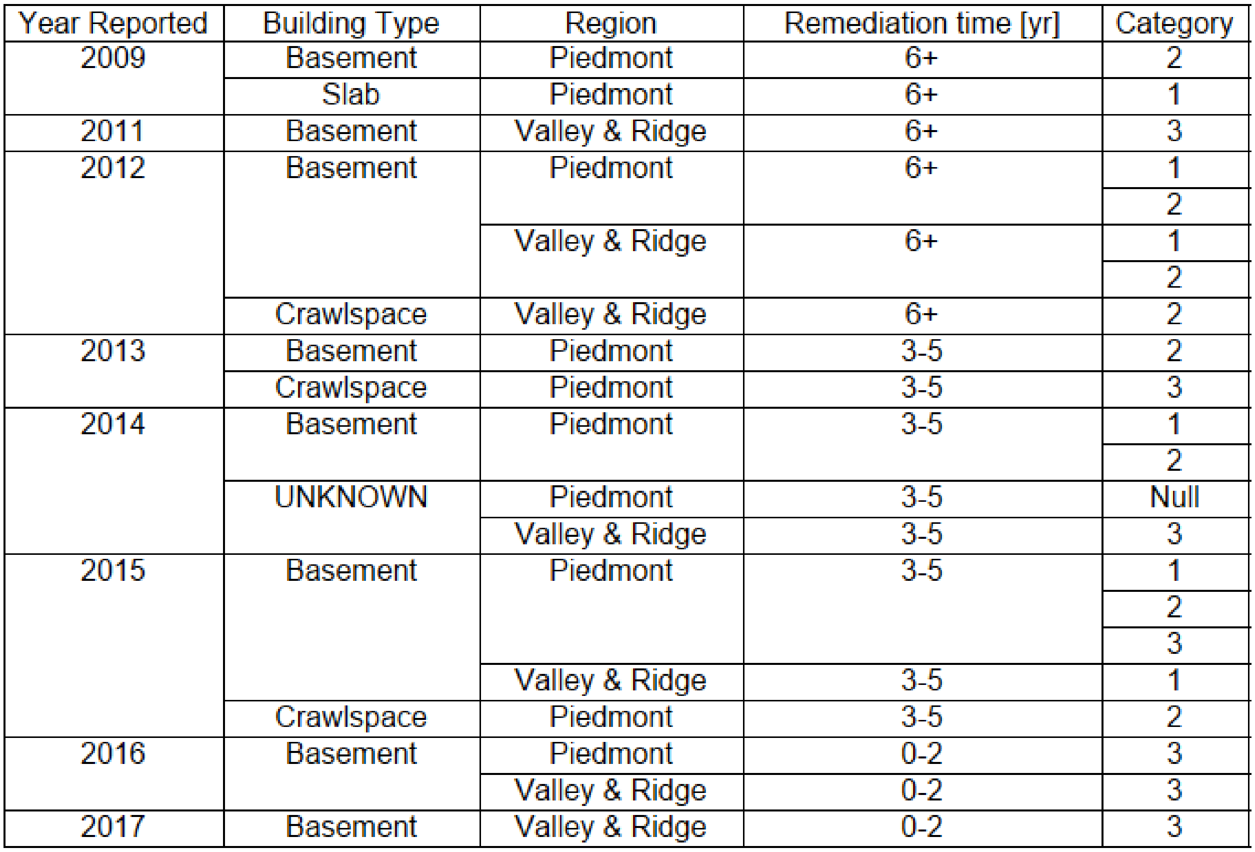
At sites where a confirmed release had occurred, the contractor returned to the site, and the tank was then vacuumed of its contents and cleaned. Depending on the site category, it was either filled with inert material and left in the ground, or it was excavated and removed to the appropriate facility. In the latter case, the soil was removed until no visible trace of the spill was present, then the pit was refilled with clean backfill. In especially dangerous cases, additional steps were taken sub-slab soils, such as the installation of a soil venting system. Steps taken indoors include the physical removal of contaminant, cleaning of surfaces, and extended aeration period for the rooms affected by the spill.

3. Materials and Methods

3.1 Field Site Selection

Soil gas samples were collected at 25 Virginia residences in the Home Heating Oil program. These sites were selected from a database provided by DEQ of known contaminated sites (Smythe, 2017) (Table 3.1). Using a random sample of 400 sites, we assessed the viability of each case for the study, and sent letters to the viable cases. Based on homeowner responses, we chose 35 for the overall study, 25 for the Piedmont and Valley and Ridge sub-section, based on physiographic province, contamination level (category), and accessibility to samples.

Table 3.1: Field site variables including building type, physiographic region, remediation time, and categorization. Individual case numbers have been removed to protect the privacy of homeowners. Year reported was used to calculate remediation time from the year 2017.



Year Reported	Building Type	Region	Remediation time [yr]	Category
2009	Basement	Piedmont	6+	2
	Slab	Piedmont	6+	1
2011	Basement	Valley & Ridge	6+	3
2012	Basement	Piedmont	6+	1
				2
		Valley & Ridge	6+	1
				2
	Crawlspace	Valley & Ridge	6+	2
2013	Basement	Piedmont	3-5	2
	Crawlspace	Piedmont	3-5	3
2014	Basement	Piedmont	3-5	1
				2
	UNKNOWN	Piedmont	3-5	Null
		Valley & Ridge	3-5	3
2015	Basement	Piedmont	3-5	1
				2
				3
		Valley & Ridge	3-5	1
	Crawlspace	Piedmont	3-5	2
2016	Basement	Piedmont	0-2	3
		Valley & Ridge	0-2	3
2017	Basement	Valley & Ridge	0-2	3

Sites were distributed across Virginia, spanning all major physiographical regions as categorized by the DEQ, with the exception of Appalachian Plateau. These regions are known as

Piedmont, Coastal, and Valley and Ridge. The Valley and Ridge and Blue Ridge Mountain regions were grouped together due to the similarity in soil texture and composition.

3.2 Field Sampling Procedure

Details of each release event (e.g. spill) were documented at the time of remediation. The thoroughness and legibility of these reports varied widely. These reports aided in choosing the placement of soil gas probes relative to the spill area. In general, USTs were located within 10 ft of the residence, and samples were collected over the release site and near the house.

Soil gas samples were collected from depths between 4-6 ft below ground surface (bgs) near the release site using soil gas probes. Typically, samples were obtained using an AMS GVP Retract-A-Tip connected to AMS GVP Extensions (5/8-inch x 4-ft stainless steel hollow threaded rods). Teflon tubing (OD: ¼ in.) was connected to the soil probe and was placed through the hollow probe shaft to the land surface for connection to a sampling pump. Bentonite clay was placed around the annulus of the probe shaft at ground level to prevent a preferential pathway from forming to the atmosphere. Soil gas was passed through a stainless steel gas sampling cartridge containing Tenax™ TA adsorbing polymer, which was chosen for its ability to capture a large range of compounds, from C_7 to C_{20}. In some cases, air was also sampled through Carbopack^{TM} adsorbing polymer in order to capture more volatile compounds (e.g. benzene). Flow was sampled for 30 minutes using a handheld sample pump (AirChek XR5000, SKC), with a flow rate maintained at approximately 35 ccm, measured before sampling using a Dwyer Variable Area 65 mm glass flowmeter. This resulted in sample volumes of 1 L. For detailed procedures and figures, see Appendix B.

Variations to sampling technique and sampling depth occasionally occurred where soil was too difficult to drill probes to the full 6 ft depth or when utility line locations prevented installation of a soil probe. Individual probes were placed based on site report diagrams depicting the impacted area and proximity to structure. Background samples were taken from locations at least 15 ft from the residence, typically at a depth of 3-4 ft bgs. Background samples were collected to understand the local concentrations and context at the contaminated sites.

3.3 Data Analysis

3.3.1 Operation of GCMS and TD

Once samples were collected, they were transported on ice and stored in a freezer maintained at approximately -4°C until analysis. Each sample was processed with Agilent Technologies 7820A GC System coupled with a 5977 Mass Spectrometer (GCMS). Samples were thermally desorbed from the Tenax^{TM} and Carbopack^{TM} tubes using a Short Path Thermal Desorption Model TD-4. Helium was used as the carrier gas throughout the TD and GCMS system. During the TD process, the injection inlet was kept at 280°C and 2 psi. Total desorption flow was 130-150 ccm, with 16 ccm captured on a cryotrap (deactivated 0.53 mm ID fused silica, -95°C), and the remainder purged. The ratio of purged to trapped was approximately 8:1 and regularly measured. Before injection, the sample tube is purged for 10 s with the carrier gas. The cryotrap was heated to inject the contaminants to the chromatography column (30m x 0.25 mm x 0.25 um, phase DB-5), which was held at 35°C and during desorption and for 4 subsequent minutes, then heated at a ramp of 15°C min^{-1} to 300°C, then held for 5 min. Compounds are thus separated primarily by their volatility, then analyzed and identified by mass spectrometry.

In some cases, the soil moisture was high enough that liquid water was included in the sample. In these cases, the TD process was slightly altered to prevent the freezing of the cryotrap (and the subsequent loss of the sample). The sample is purged for an additional 5-10 s before the standard procedure to remove some of the excess water.

3.3.2 Integration and calibration of gas chromatograph data

We analyzed BTEX, naphthalene, and TPH; however, this study will focus on benzene, ethylbenzene, naphthalene (BEN), and TPH due to their exceeding the risk target threshold at several sites. It should be noted that our quantification of benzene proved challenging. The cryotrap was unable to quantitatively trap benzene at the temperature used in this work (-95°C), while lower temperatures were subject to freezing due to sampled water vapor. Reported values consequently represent minimum concentrations: Samples below detection could actually have elevated benzene concentrations.

EPA Method TO-17 was used as a guideline for sample processing, conducted by Xin Liu. Compounds of interest were identified by their retention time and unique quantitative ion responses and quantified by integrating GC data peaks using the TERN chromatographic processing package in Wavemetrics Igor Pro 7 (Isaacman et al., 2012). Standards were analyzed at multiple concentrations spanning the range of observed data, and used to calibrate instrument response, from which sampled gas-phase concentrations were calculated.

To quantify TPH, the total ion chromatogram was integrated across the entire range of the chromatogram associated with unresolved complex mixture (Figure 3.1). TPH was calibrated assuming an instrument response identical to the total ion response of tetradecane.

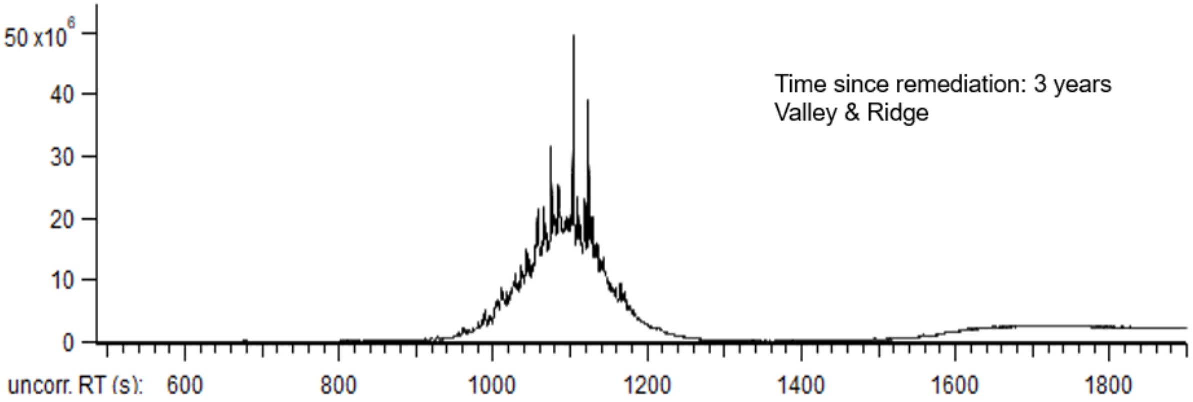


Figure 3.1: Example of the hump in total ion chromatogram data associated with unresolved complex mixtures. Y axis units total ion signal (arbitrary units) and the X axis is retention time in seconds.

Each compound has a risk target concentration determined by EPA for both indoor and sub-slab soil concentrations. These risk targets are recommended as a factor of 33 for residential structures (OSRTI 2004). This is to account for the proportion of gas that does not intrude into the structure. In SVI sites, indoor air concentrations are directly influenced by soil gasses outside the foundation. The risk targets for BEN and TPH are available in Table 2.1.

3.3.2 Statistical Analysis

Sample concentration values were organized in a one to many table in Microsoft Excel, then visualizations were created in Tableau. These were used to contextualize the experimental variables building type, physiographic region, and remediation time with categories and concentration.

Coefficients of variation were calculated for all variables and compounds to characterize variance at individual sites. A Chi-square test was performed to determine the covariance between the two parameters “Building Type” and “Physiographic Region”. The R code used to perform the tests is provided in Appendix D.

4. Results and Discussion

4.1 Data Overview of BEN and TPH Concentrations and Site Variance

On average six samples were collected at each site, including a background sample approximately 5-15 feet away from the spill site. For variability and impact analyses, background sample values were neglected. BEN and TPH were compared across several physical site criteria. Toluene, p-m-xylene, and o-xylene concentrations were not found to be above their respective sub-slab soil exposure limit (OSRTI 2014) and were not evaluated.

As some uncertainty is associated with using the previous contractor reports to locate the areas of the highest concentration, there are some sites where we did not accurately place our probes to find the source zone. In the cases where source zone location was known, one probe would be located in the source zone and one would not, increasing individual site concentration variability. Variability increased at sites with particularly high concentrations in the source zone as well.

4.2 Impact of Site Characteristics on BEN and TPH Concentrations

We hypothesize three variables impact the concentrations found at field sites: building type, remediation time, and physiographic region. First, building type can be divided into three main categories, regarding the interface between the foundation and the soil: basement, slab, and crawlspace. Second, remediation time refers to the amount of time since abatement measures were taken and ranges in value between 0 and 8 years. Finally, the Piedmont and Valley and Ridge physiographic regions were considered.

4.2.1 Building Type

We limited our scope to residential buildings that are part of the DEQ Home Heating Oil Program. At the case investigated, three building foundation styles were noted and thought to impact observed concentrations: basement, concrete slab, and crawlspace. It should be noted that the sample size for basement-style dwellings is much higher than for crawlspace and slab-style dwellings: of the 25 sites investigated in this study, 20 are basement-style, 3 are crawlspace-style, 1 is slab-style, and 1 is unknown (Table 3.1).

To establish if codependence exists between building type and physiographic region, a Chi square test was performed. We were specifically concerned with the relationship between Coastal sites and basement building type. It was found that there is some statistical correlation relationship between the coastal region and building type (Table 4.1), with basements largely absent from the Coastal region. Since building type and the physiographic regions in question (Valley and Ridge and Piedmont) were found independent, controls of region on building type and vice versa were not considered in individual investigations on these variables.

Table 4.1: Results of Chi-square test for dependence between building type and physiographic region.

		Physiographic Region		
		Coastal	***Valley/Ridge***	***Piedmont***
Building Type	***Basement***	1.59E-05	0.170	0.083
	Crawlspace	0.025	0.68	0.327
	Slab	0.003	0.308	0.385

We hypothesized that samples taken near buildings with basements would have higher concentrations than those taken near crawlspace or slab buildings. This is because the adjacent basement wall may disallow the advection of oxygen to the source zone, resulting in anaerobic biodegradation, a much slower process than aerobic biodegradation (Madigan et al., 2015). In addition, the wall may prevent the horizontal movement of the spill via advection or diffusion, causing a hydrocarbon “hotspot” to remain in the same place for a longer period of time. We also hypothesized that DEQ Category 3 sites would have the highest concentrations of each compound and Category 1 sites would have the lowest. Basement sites overrepresented in this analysis. It is worth noting, however, that the basement category has the highest concentrations for all four compounds.

In order to analyze building type and category with regards to all compounds, the maximum concentration values were found for each site and plotted by year of report and foundation style. Many benzene samples were below limits of detection (Figure 4.1), but some values do exceed the sub-slab risk threshold, exclusively in the basement category. The exceedance rate for the basement category was 16%, and the rates for the crawlspace and slab categories were 0%. As noted in methods, these values represent minimum concentrations, and as such provide only a conservative assessment of possible benzene risk.

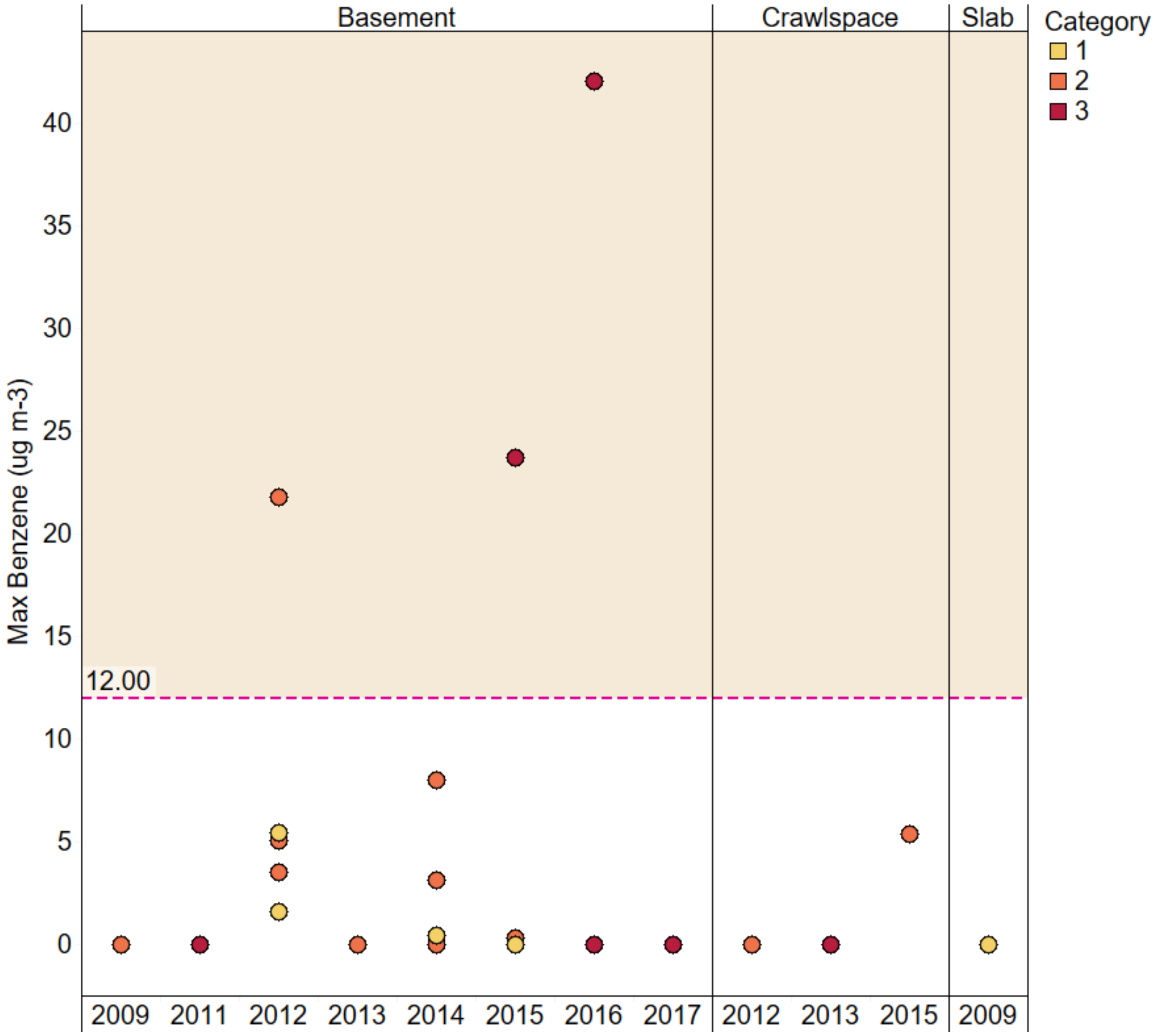


Figure 4.1: Data overview of benzene concentration binned by building type and year reported for ease of viewing. Each point is a maximum concentration value from an individual sampling site. The sub-slab risk threshold of 12 μg m^{-3} is indicated. Most values of benzene are 0 or below the threshold. Those that exceed the threshold are of Categories 2 and 3.

It was expected that Category 1 sites would have the lowest benzene concentrations and that Category 3 sites would have the highest. While benzene was not detected in 5 out of 6 Category 3 sites, the points that do exceed the threshold are of Categories 2 no Category 1 sites exceed the threshold.

Similarly to benzene, ethylbenzene concentrations do not usually exceed the risk target threshold. Categories 1 and 2 behave as expected, with overall higher concentrations in Category 2 than in Category 1 samples (Figure 4.2). Category 3 does not have overall higher concentrations than Category 2 as we had expected. Crawlspace and slab samples have lower average concentrations. Only one site exceeds the treshold, resulting in an exceedence rate of 5% in the basement category and 0% in the slab and crawlspace categories.

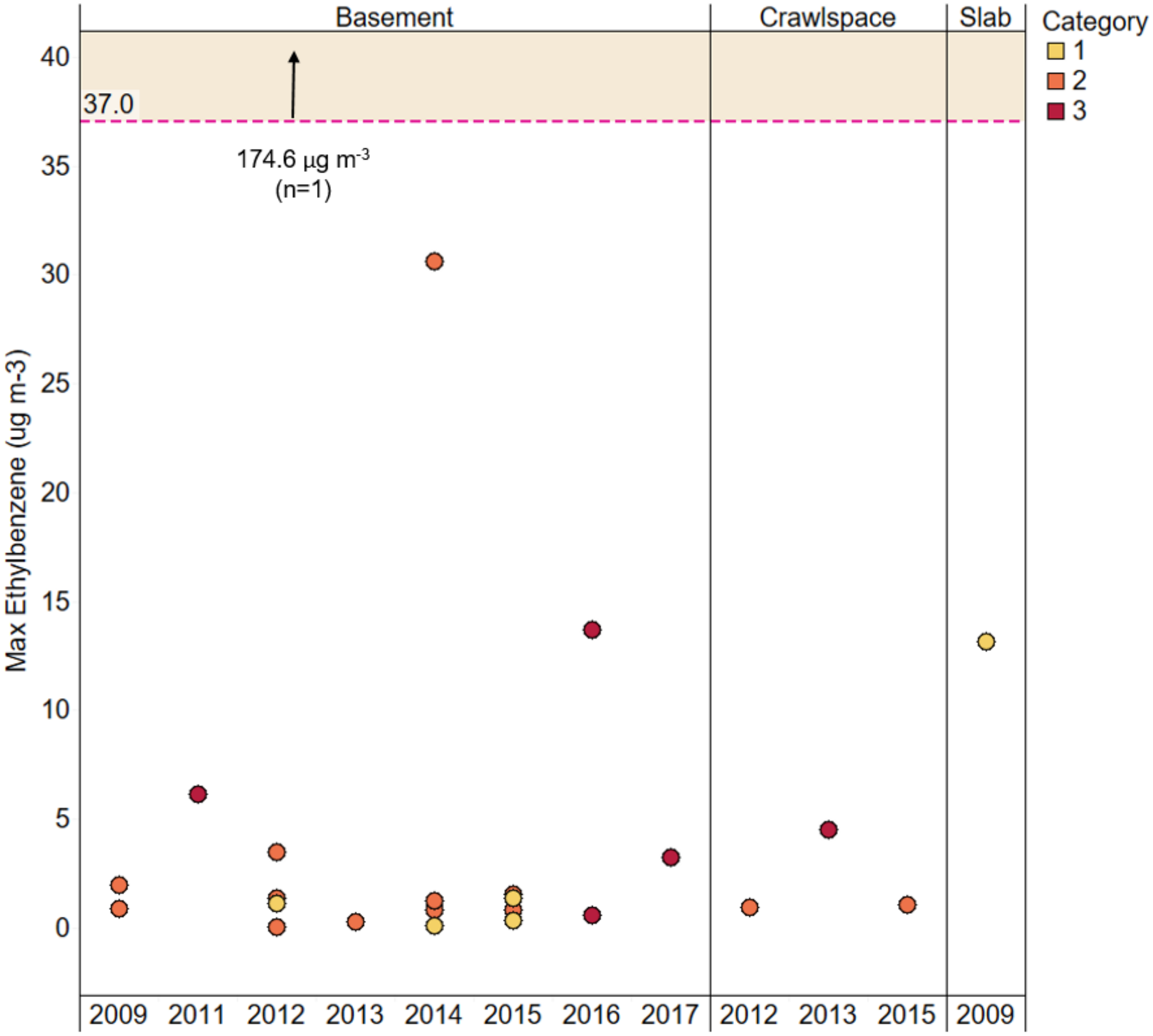


Figure 4.2: Ethylbenzene site maximum concentrations binned by building type and year reported. The sub-slab risk threshold of 37 µg m^{-3} is indicated. One outlier is indicated. Ethylbenzene concentration does not appear to exhibit any notable trends or behaviors regarding to proximity to specific building types or DEQ categorization.

A remarkable number of points exceed the naphthalene risk target threshold. Naphthalene Category 3 sites returned relatively high concentrations. 61% of values in the basement category exceed the naphthalene risk target threshold, and 100% of points exceed the threshold in the crawlspace and slab categories. Category 1 sites tend to have lower concentrations, with only a few points exceeding the threshold (Figure 4.3). However, concentrations reported here have not been corrected for blanks – that is to say, the background contamination found in our equipment have not been subtracted from our values.

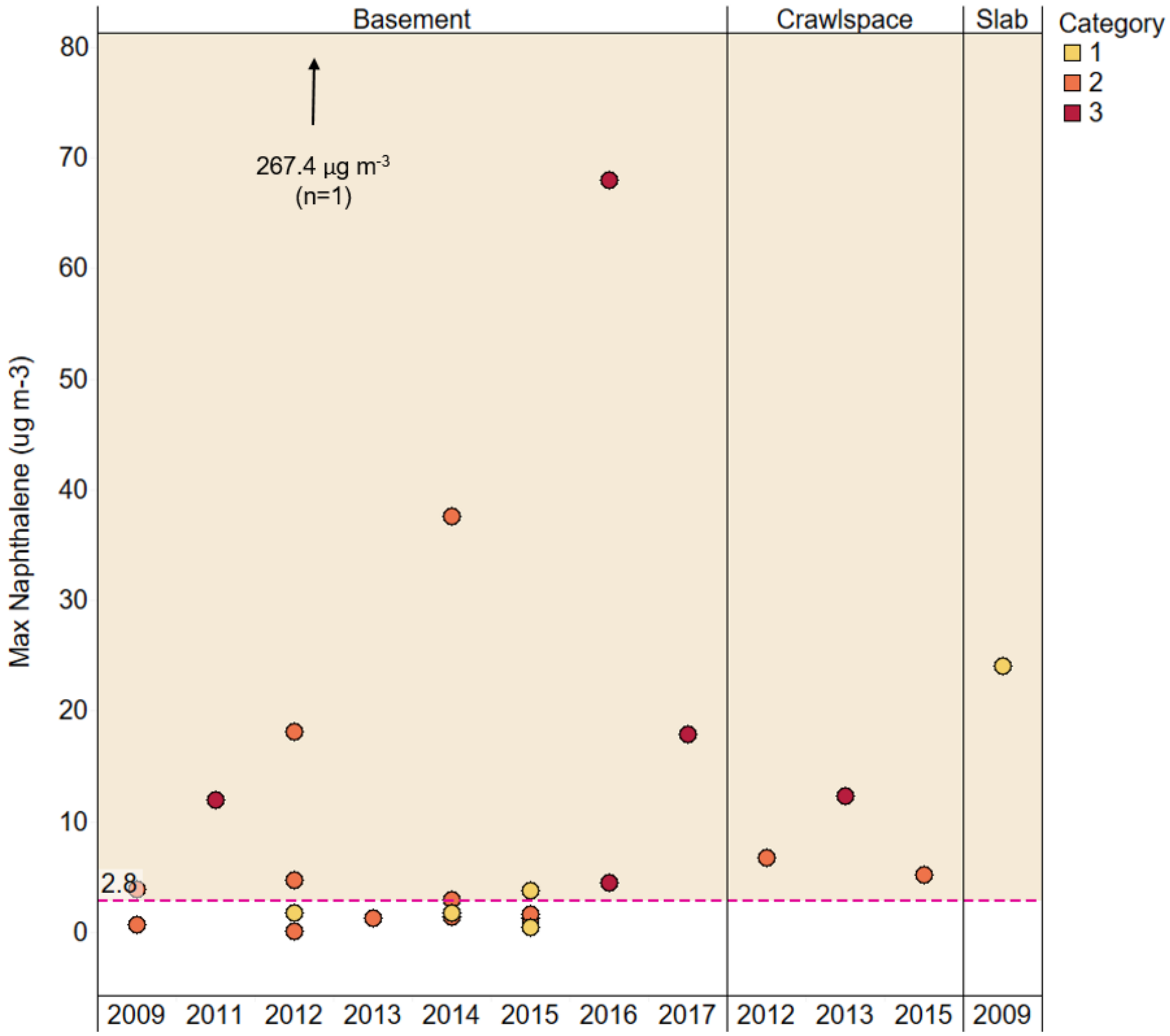


Figure 4.3: Naphthalene site maximum concentrations binned by building type and by year reported. One outlier is indicated. The sub-slab risk threshold of 2.8 µg m^{-3} is indicated. Several Category 3 and Category 2 sites exceed this threshold. Categories behave as expected, with Category 3 having the overall highest concentrations and Category 1 having the lowest concentrations, regardless of building type.

Only 5 TPH values exceed the risk target threshold in the basement category; in fact, no other points exceed the threshold (Figure 4.4). 33% of basement values exceed the sub-slab risk threshold, and 0% of values exceed the threshold in the slab or crawlspace categories. Within these categories, the data did not behave as expected, as Category 1 does not have the lowest overall concentrations, and Category 3 concentrations are not significantly higher than that of Category 2.

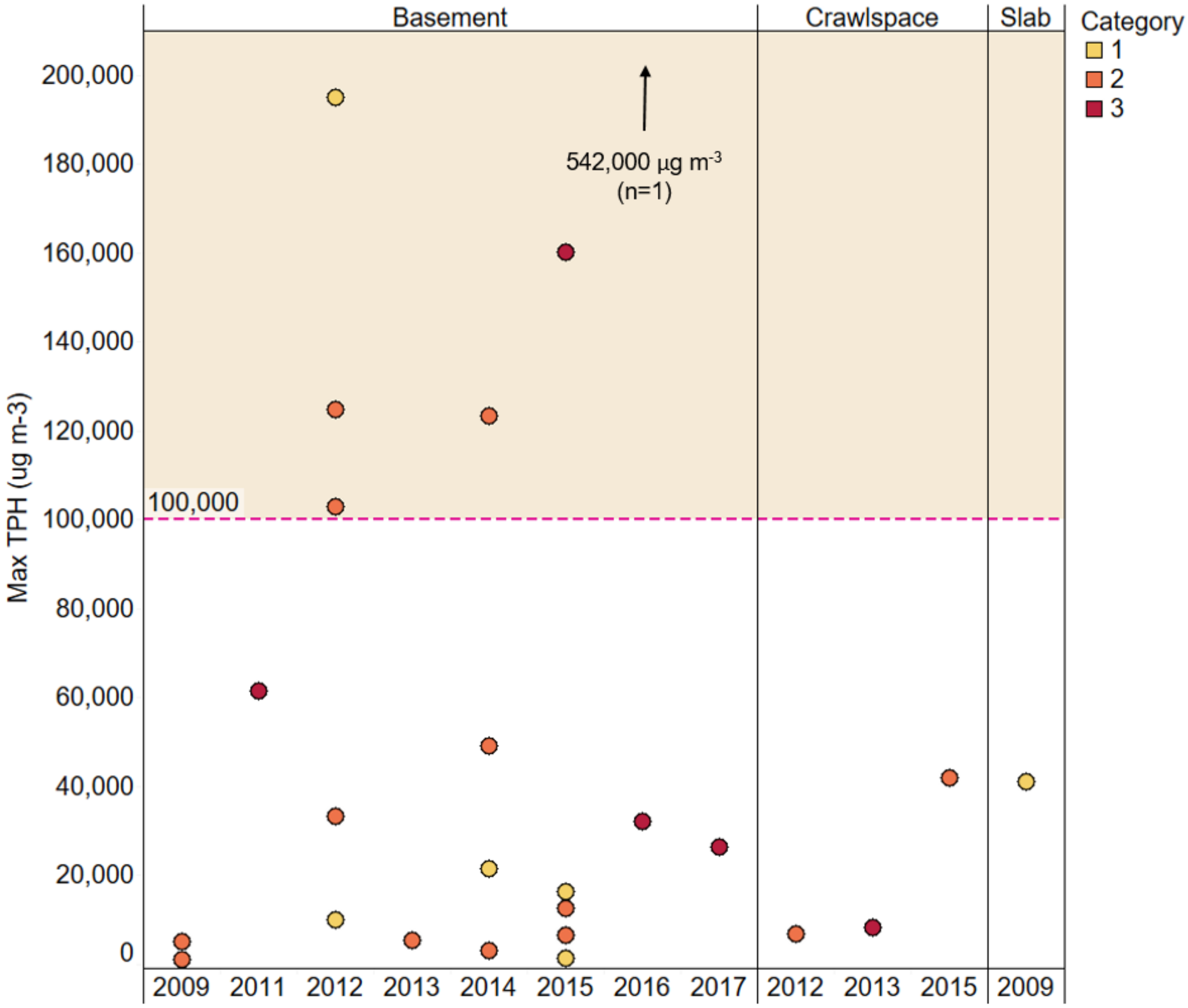


Figure 4.4: TPH site maximum concentration binned by building type and year reported. Few data points exceed the sub-slab risk target threshold of 100,000 μg m^{-3}. One outlier is indicated.

At this time, no conclusions can be drawn regarding slab or crawlspace building types and contaminant concentrations due to lack of data. It is worth noting, however, that basement-style buildings experience higher concentrations of contaminants overall. While building type may have a slight control on the movement and abatement of a tank release, the more obvious control on soil vapor concentrations is remediation time, discussed below.

4.2.2 Time Since Remediation

Our sites range from 0 and 8 years in age, at least with regards to when the spill was reported. The accuracy of the “time since remediation” variable is dependent on how close to the actual spill the site was reported. Generally, no data exists for original spill time, as homeowners may not have been made aware of a spill until they attempted a real estate transaction, smelled contamination, or began to require unusually frequent tank refill service.

Benzene concentration trends over time are difficult to categorize, as most samples were below detection (Figure 4.5). Interestingly, none of the most recent sites demonstrated non-zero benzene concentrations. However, given the small sample size (n=3), no conclusions can be drawn from this lack of data. Overall, category concentration data behaved as expected, as Category 3 had the highest concentrations and Category 1 had the lowest. The threshold exceedance was 0% for Category 1, 8% for Category 2, and 28% for Category 3.).

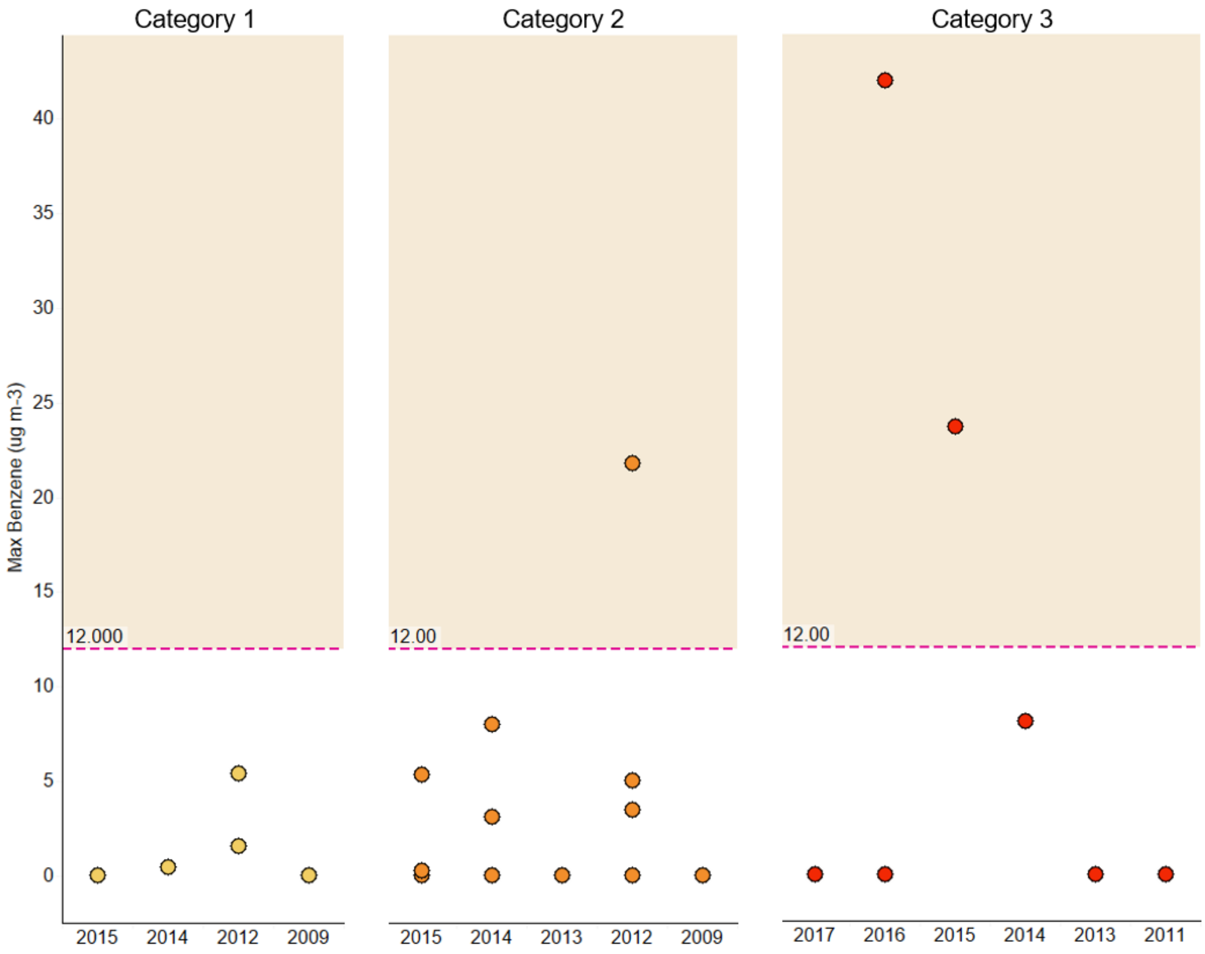


Figure 4.5: Benzene concentrations for each site binned by remediation time and year reported and separated by DEQ category. Note that the years are in reverse chronological order such that time since remediation increases towards the right.

Ethylbenzene behavior is especially interesting when broken down by DEQ category (Figure 4.6). As expected, Category 1 sites exhibit the lowest concentrations of ethylbenzene; however, the highest reported concentration is a Category 1 site. Category 3 would be expected to have the highest concentrations; however, with the median of the 3-5 year bin for Category 3 sites as 0.784 μg m^{-3} and Category 2 as 0.787 μg m^{-3}, it is hard to assert that there is much of a difference in behavior between these two categories.

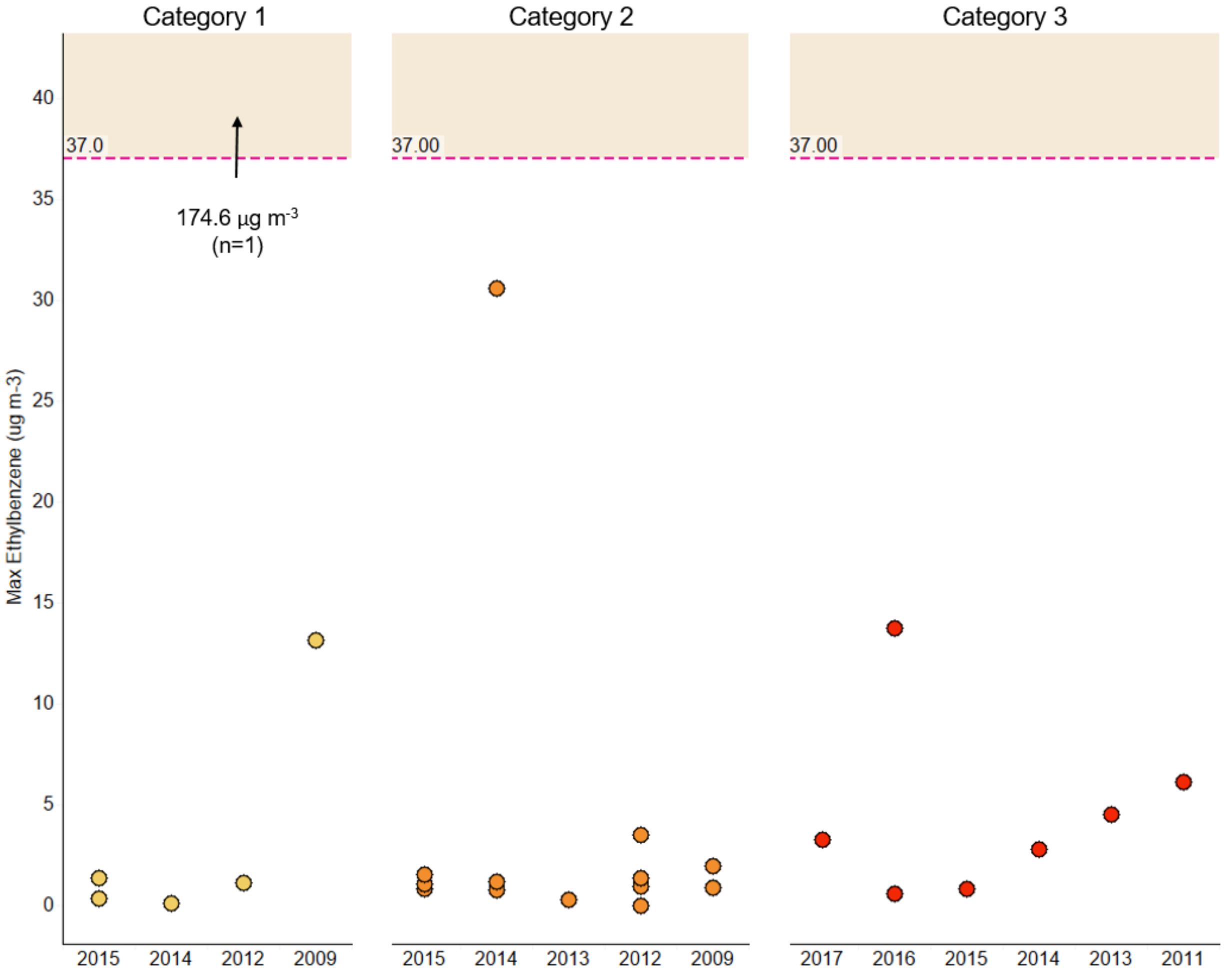


Figure 4.6: Ethylbenzene site maximum concentrations separated by individual categories. Time since remediation increases to the right. Categories 2 and 3 do not show a strong negative trend over time as might be expected.

Naphthalene concentrations over time exhibit a downward trend in Categories 2 and 3. Concentrations for the most part do not exceed the sub-slab risk target threshold for Categories 1 and 2; however, most values exceed it in Category 3, regardless of time since remediation (though the overall downward trend in values does imply that eventually these values would no longer exceed the threshold given more than 8 yrs) (Figure 4.7). The naphthalene sub-slab risk threshold was exceeded by 50% of values in Category 1, 54% in Category 2, and 66% in Category 3.

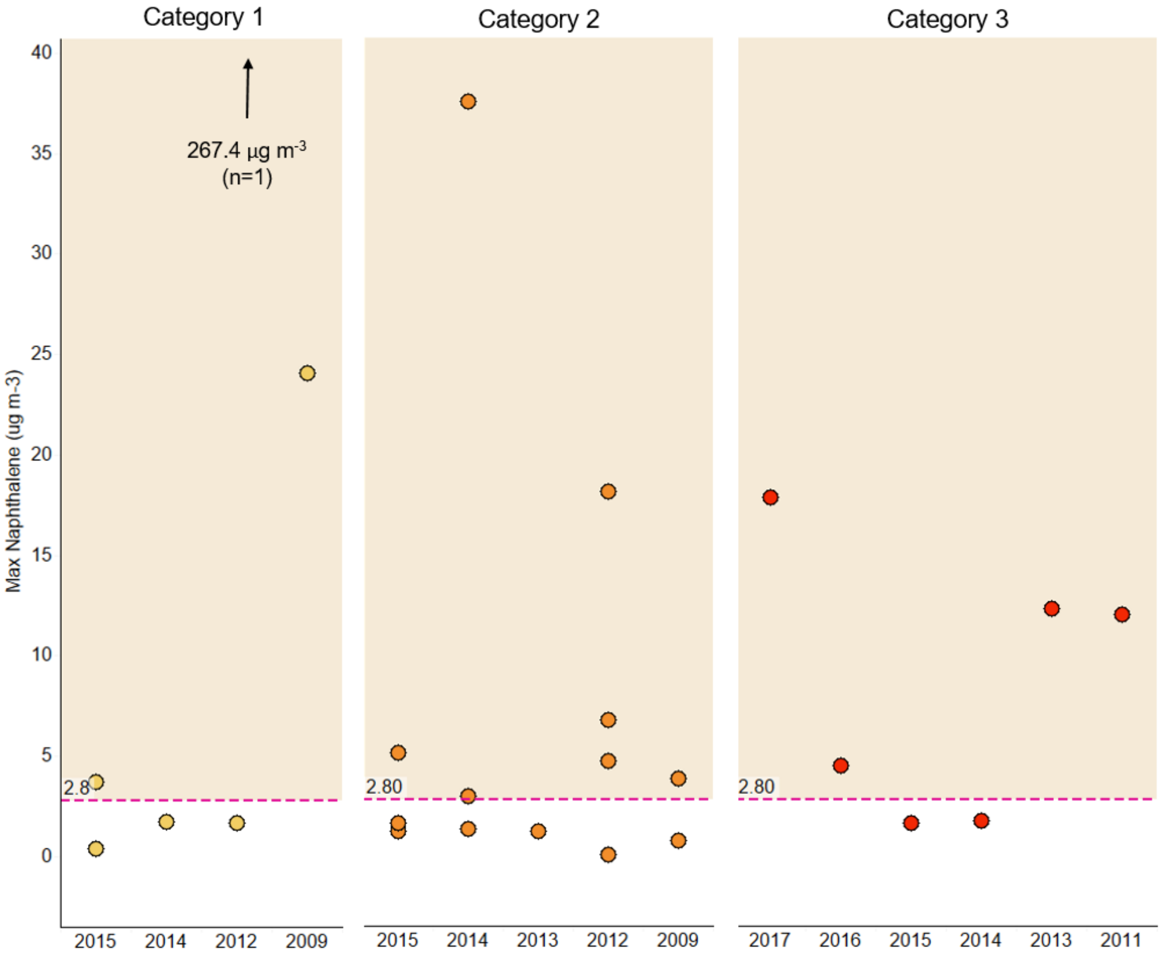


Figure 4.7: Naphthalene site maximum concentrations for each site binned by time of reporting and separated by category. One outlier is indicated. Time since remediation increases to the right.

Some TPH concentration values exceed the sub-slab risk threshold of 100,000 μg m^{-3}, however a large majority of the values do not (Figure 4.8). 17% of values exceed the threshold in Category 1, 21% in Category 2, and 17% in Category 3.

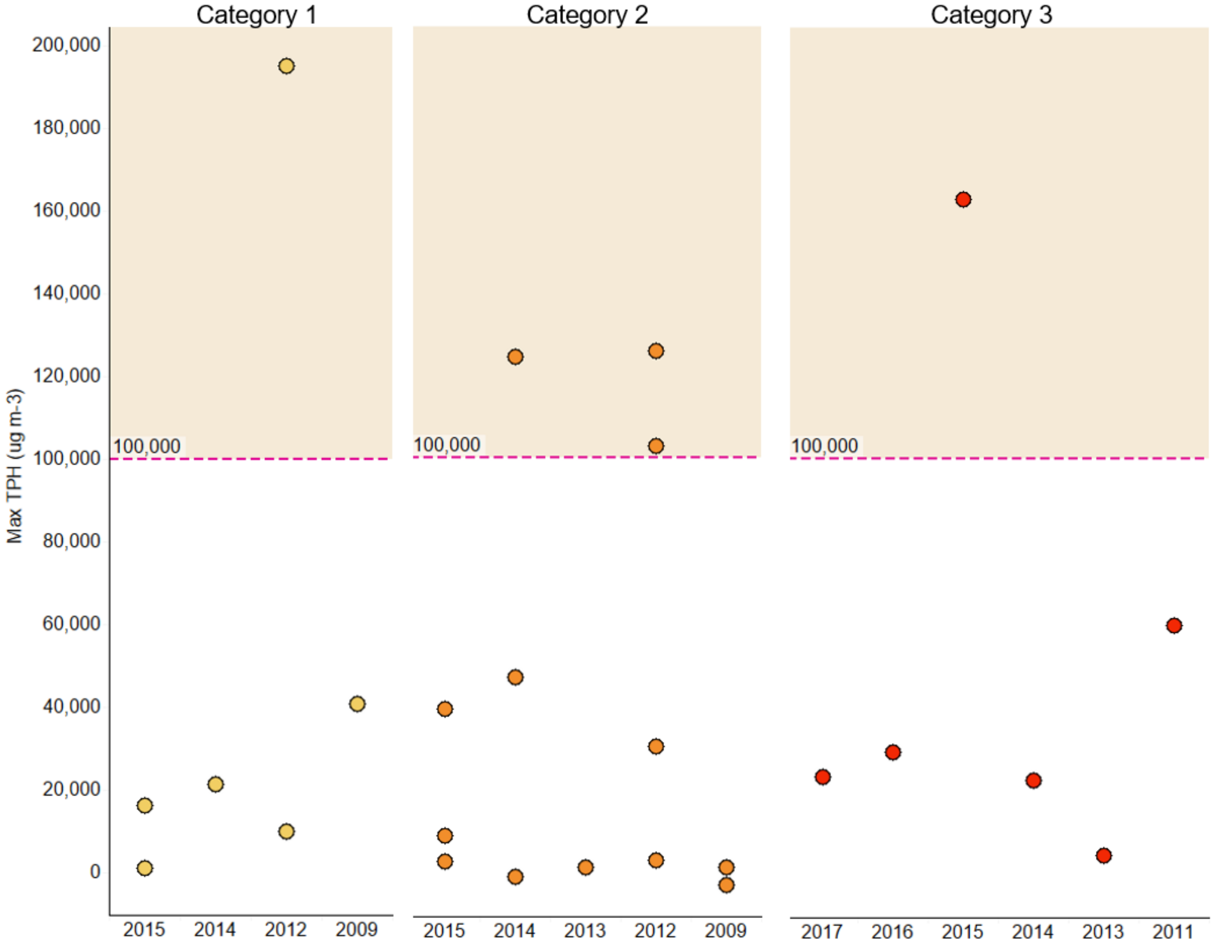


Figure 4.8: Total Petroleum Hydrocarbon site maximum concentrations with increasing remediation time. The sub-slab risk threshold of 100,000 µg m^{-3} is indicated. The median concentration values are very similar across Categories.

We calculated best fit using a linear curve and associated R^2 values for each Category over time (Figure 4.9). We had hypothesized that TPH concentrations would decrease with increased time since remediation; however, we did not observe this phenomenon. It is possible that this behavior would be observable at an individual site. Since each site has a different set of circumstances, no useful predictions can be made based on time since remediation for multiple sites.

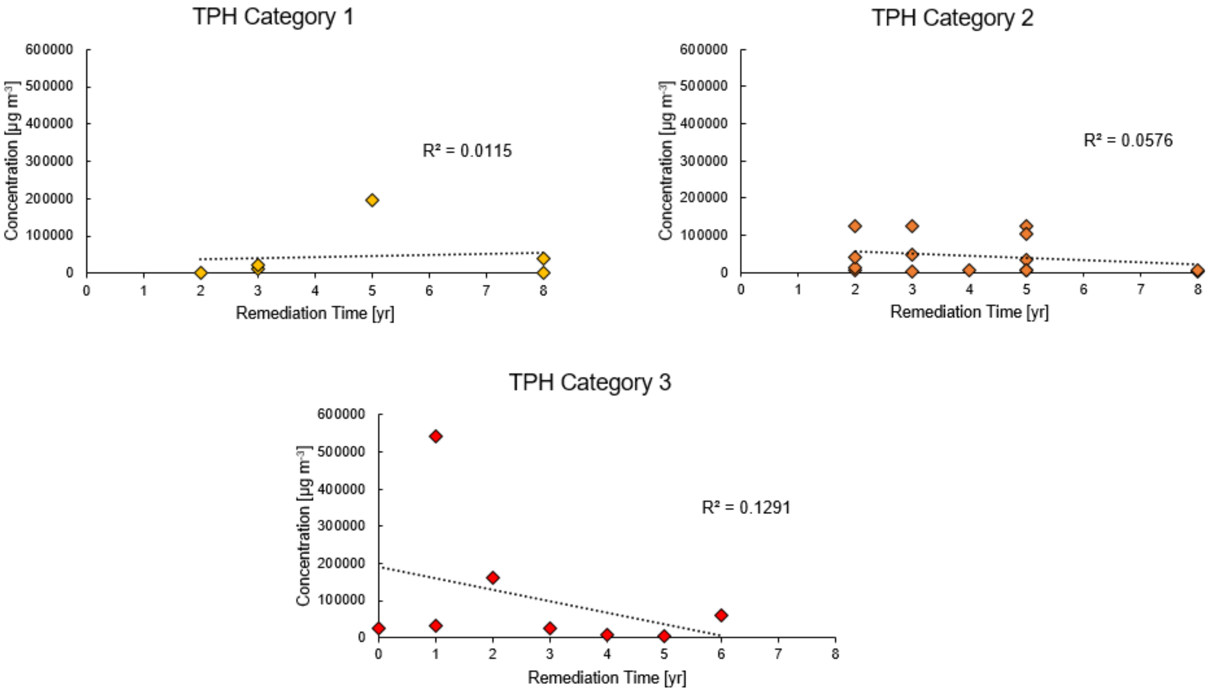


Figure 4.9: Maximum concentrations of TPH plotted against remediation time, years. As expected, DEQ Category 3 shows the relative strongest downward trend in concentration over time. Category 1 has a loose upward trend, which was not expected. Overall, it cannot be said that time since remediation results in a trend in concentration values from different sites.

Coefficients of variance, or relative standard deviations, were calculated for each field site for each compound and plotted on an axis of increasing remediation time. We hypothesized that variability would increase with Category, and decrease over time. Because a large majority of data points for benzene are below detection, most of the coefficients of variation returned are null values. Ethylbenzene variability appears to remain constant over time for all Categories (Figure 4.10). Category 3 does not have the highest overall variability as we had expected. No noteworthy trends over time appear to exist.

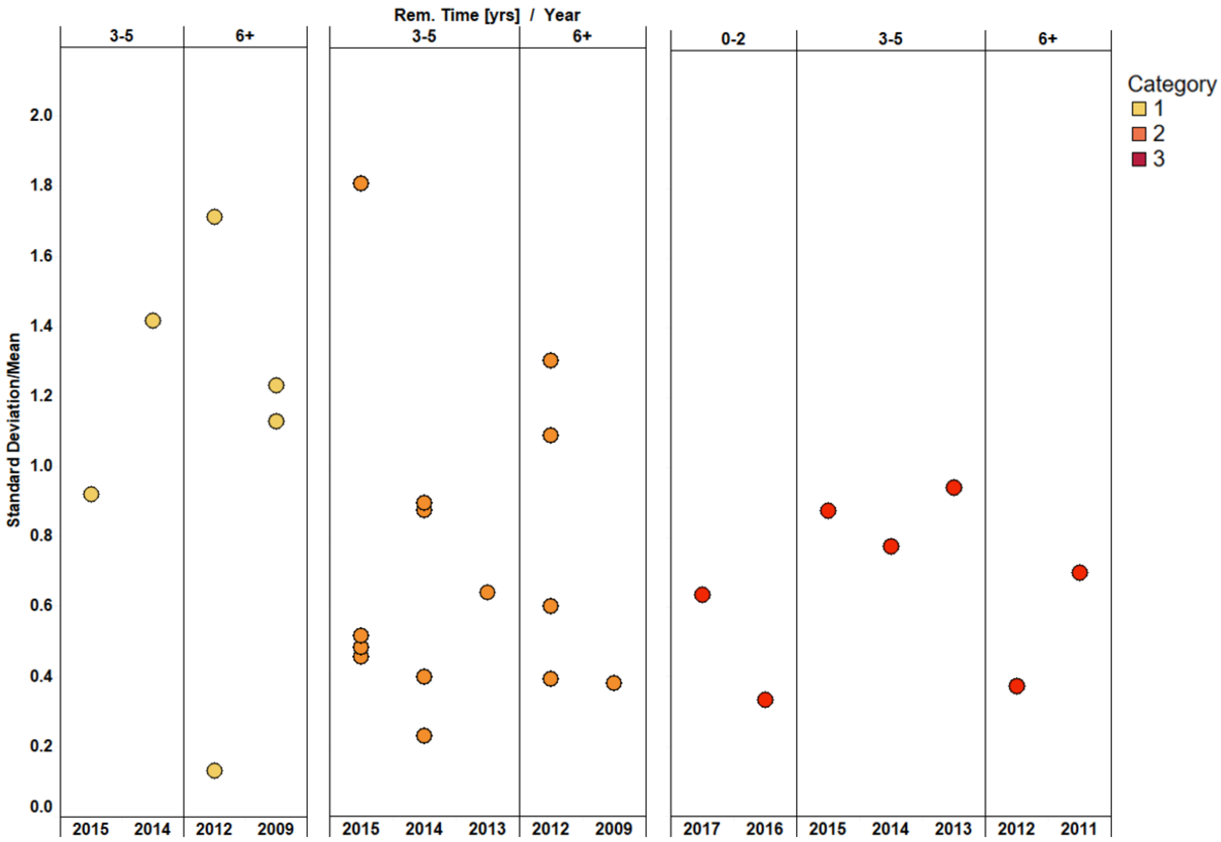


Figure 4.10: Ethylbenzene variance coefficients by increasing remediation time. Unexpectedly, Category 3 sites are not more variable than Categories 1 and 2.

Naphthalene variability stays relatively low for Category 2 sites over time, though it does appear to increase over time. Categories 1 and 3 does not have any discernable trend with time. Naphthalene variability behaves interestingly for Category 2 sites. It was expected that as sites age, bioremediation and volatilization would reduce the concentration of naphthalene, bringing the "hot spot" concentration closer to the background value and thus lowering variability at a given site. However, the results show the opposite: a potential upward trend with remediation time. Naphthalene variability values for Category 3 sites decrease over time with abatement (Figure 4.11). Category 1 variance coefficients do not exhibit a clear trend. We had also expected that Category 3 would have overall higher variability values than Category 2, but this was not observed. Overall, no clear trends occur in variance coefficients; however, future work could potentially result in a different result.

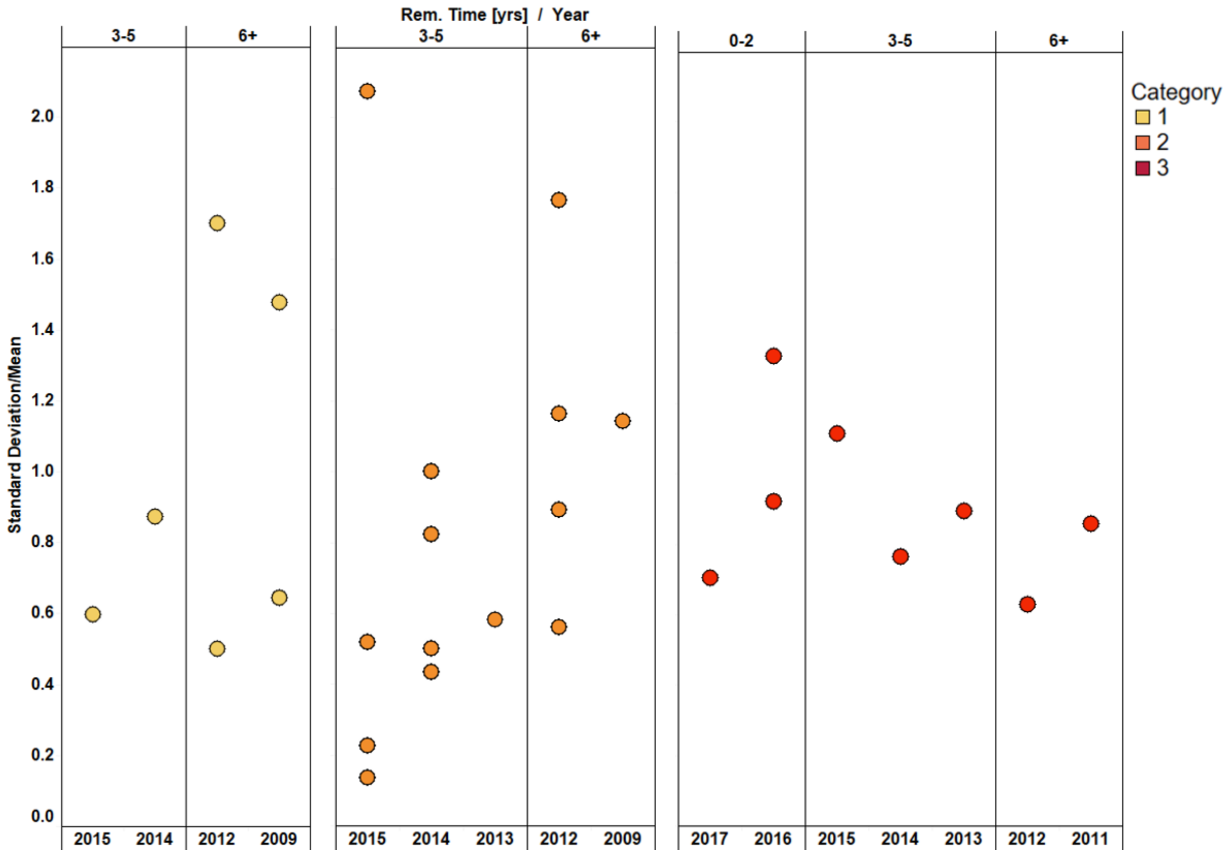


Figure 4.11: Naphthalene variance coefficients separated by category. We expected variability to go up with DEQ Category, but Category 1 showed the highest variability.

Overall, TPH variance coefficients fit expectations for Category and temporal behavior. Category 1 site values returned low variance coefficients, though they did increase over time, which was unexpected. Category 2 sites exhibited the expected downward trend for the 3-5 year remediation time bin, but not for the 6+ year bin. Category 3 sites returned higher variance coefficients overall, with no discernable temporal trend (Figure 4.12).

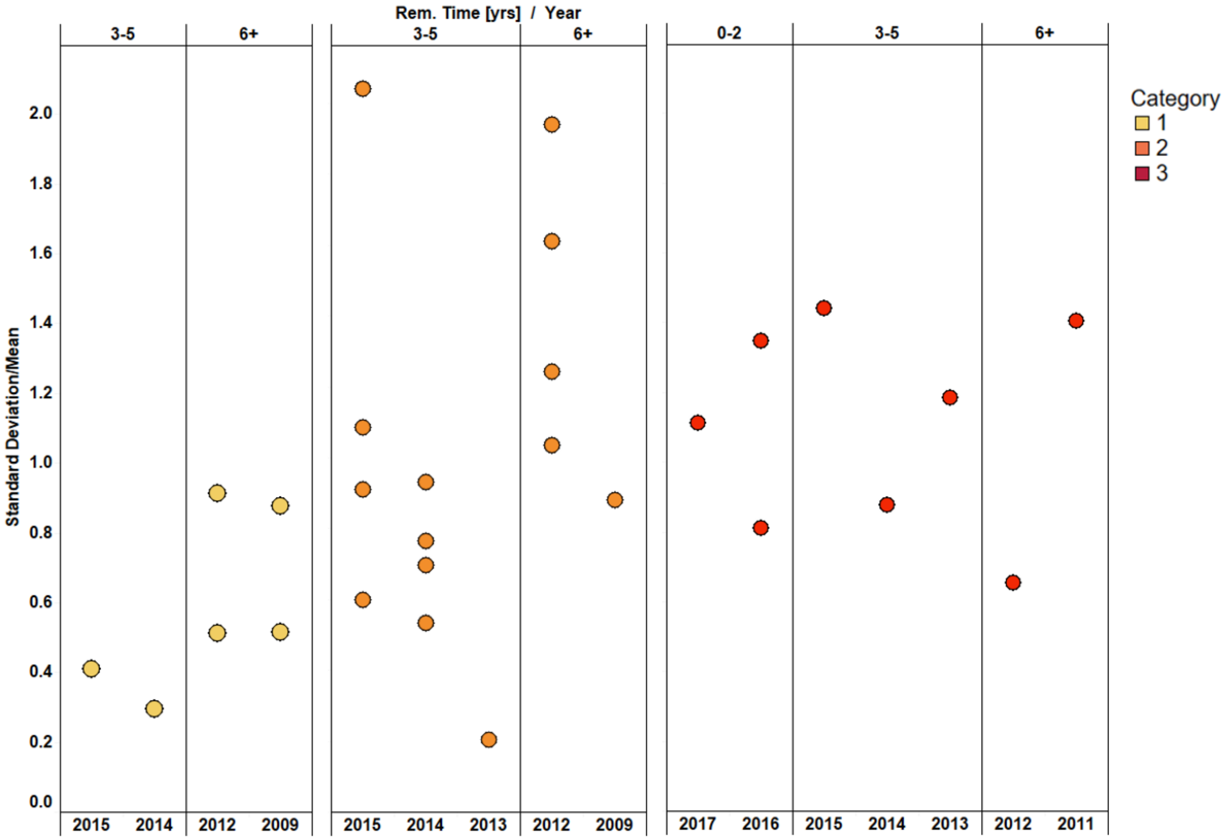


Figure 4.12: Variability coefficients for TPH, binned by remediation time and separated by DEQ category. Overall variance values for each Category behaved as expected, with the lowest values in Category 1 sites and the overall highest values in Category 3 sites. Downward trends in variance were expected over time.

Coefficients of variance seem to indicate mostly upward trends in variance with time, defying our expectations. Category 3 sites do not consistently have higher variability than Category 1 or 2 sites for TPH, again defying expectation. Generally, Category 2 sites range between 0.2-1.8 in variance coefficient with an upward trend.

Remediation time cannot be used as a universal predictor because each site has a different set of variables that affect concentration such as soil texture parameters (porosity, permeability), soil moisture on day of testing, degree of biodegradation, composition of biological consortium, and remediation techniques applied to a given site. Because of these variables' effects on remediation time, remediation time as a variable does not hold much promise as a universal predictor. However, when reviewing the abatement of a single site, it may inform decisions made by a contractor when determining remediation techniques.

4.2.3 Physiographic Region

As discussed above in 4.2.1, we found that the physiographic region often controls for the building type. That is to say, buildings with basements are much less likely to occur in the Coastal region than in the Valley and Ridge region. However, due to the relative lack of Coastal samples (4 out of 28 sites visited in 2017), the scope of this discussion will be limited to Piedmont and Valley & Ridge data (Table 3.1).

Piedmont sites tended to have higher concentrations of ethylbenzene and TPH than Valley and Ridge sites for all categories; yet, physiographic region did not seem to control naphthalene concentration (Figures 4.13, 14, 15). Category 3 sites are more likely to have higher concentrations in all compounds except benzene for both regions. An upward trend in Category 1 TPH concentrations in the Piedmont as remediation time decreases seems to indicate that age plays an important factor in this region.

Benzene does not exhibit any obvious responsive to physiographic region, though this lack of response probably has more to do with lack of data (Figure 4.13). 3 Piedmont region sites exceed the sub-slab risk threshold (21% of sites), and no Valley and Ridge sites exceed the threshold (0%). Those sites that do exceed the threshold are of Categories 2 and 3.

Ethylbenzene values do not exceed the risk target threshold for sub-slab vapors in either region, with one exception in Category 2 Valley and Ridge. Ethylbenzene concentrations for Category 1 were relatively low. Samples for Categories 2 and 3 result in very similar values for ethylbenzene, generally below 5 $\mu g\ m^{-3}$ (Figure 4.13). The highest concentrations are found in Category 3 and the lowest concentrations are found in Category 1. As Valley and Ridge and Piedmont soils are generally very similar in permeability, it was expected that the concentrations would be similar in both regions. With the exception of Category 1 sites, this expectation was fulfilled (Figure 4.14).

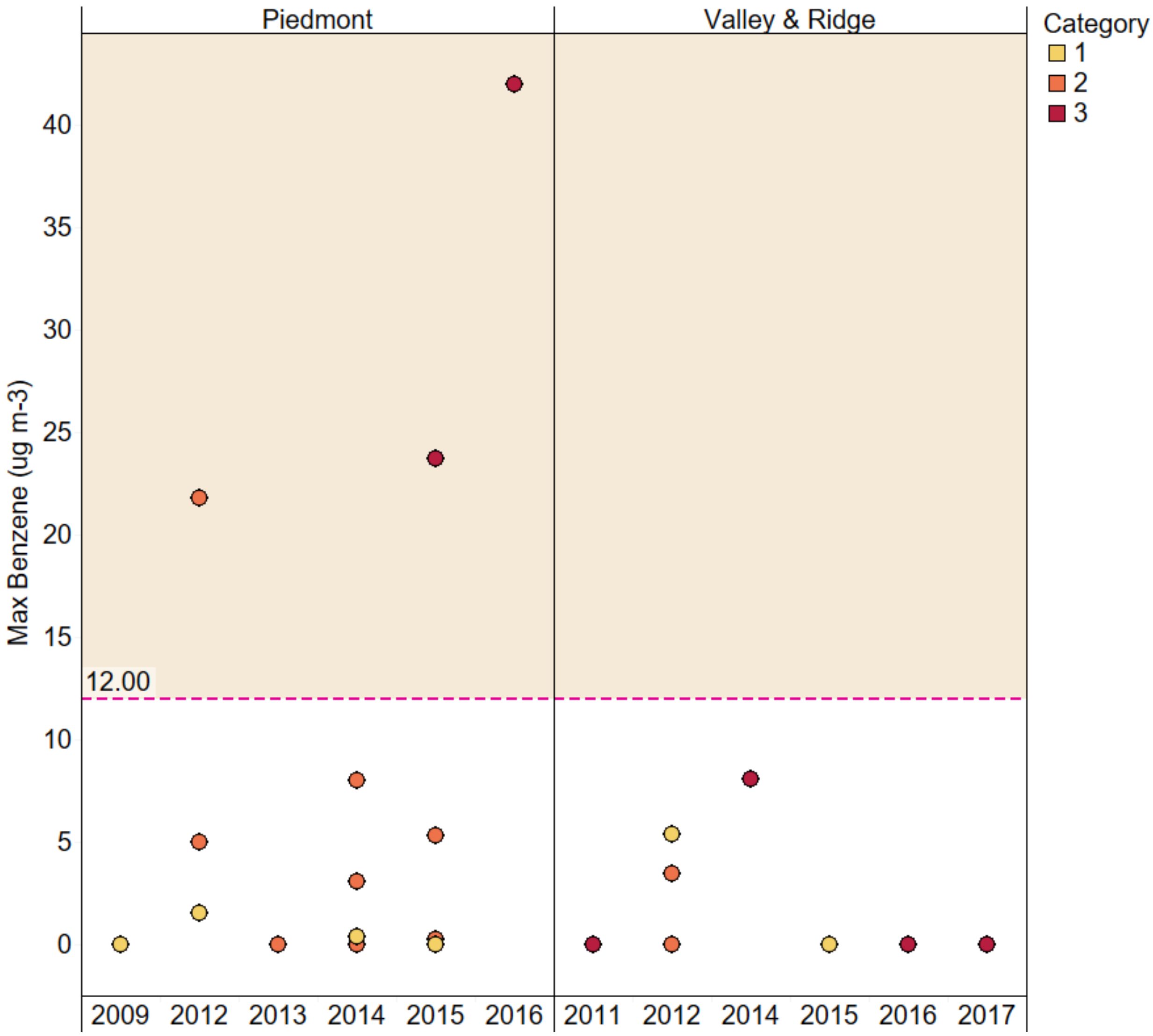


Figure 4.13: Benzene site maximum concentrations, binned by physiographic region and year reported. Category 3 sites have the highest concentrations in benzene in the Piedmont. No Valley and Ridge sites exceed the benzene sub-slab risk threshold of 12 μg m^{-3}.

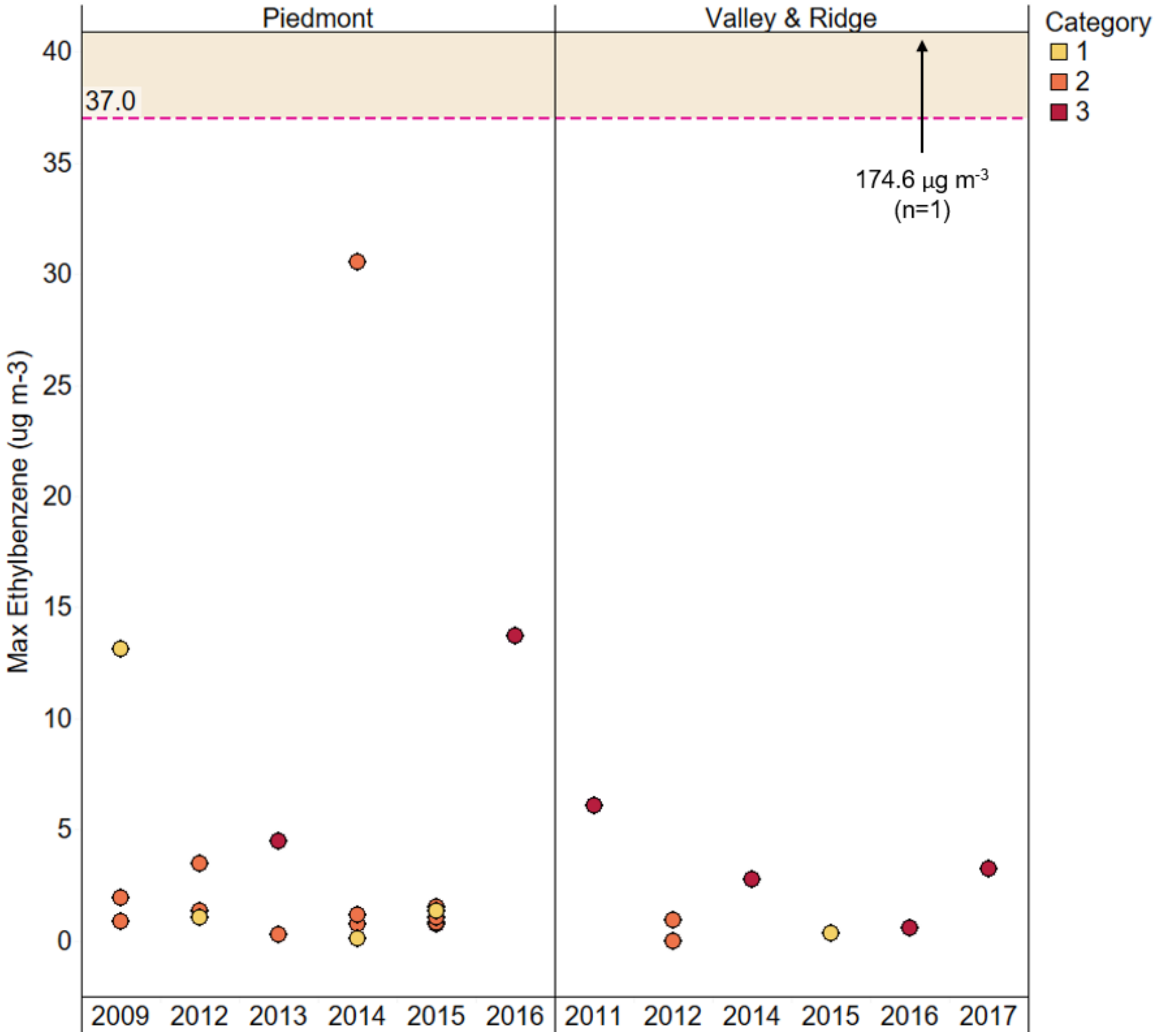


Figure 4.14: Ethylbenzene site maximum concentrations binned by physiographic region and year reported. Category 2 and 3 sites have the highest concentrations in benzene in the Piedmont. No Piedmont sites exceed the ethylbenzene sub-slab risk threshold of 37 µg m^{-3}.

Whereas benzene and ethylbenzene site maximum concentrations tend to be below their respective sub-slab risk thresholds, 58% of Piedmont sites and 63% of Valley and Ridge sites exceed the threshold for naphthalene concentrations (Figure 4.15). Overall, Piedmont region sites have higher maximum concentrations than Valley and Ridge sites.

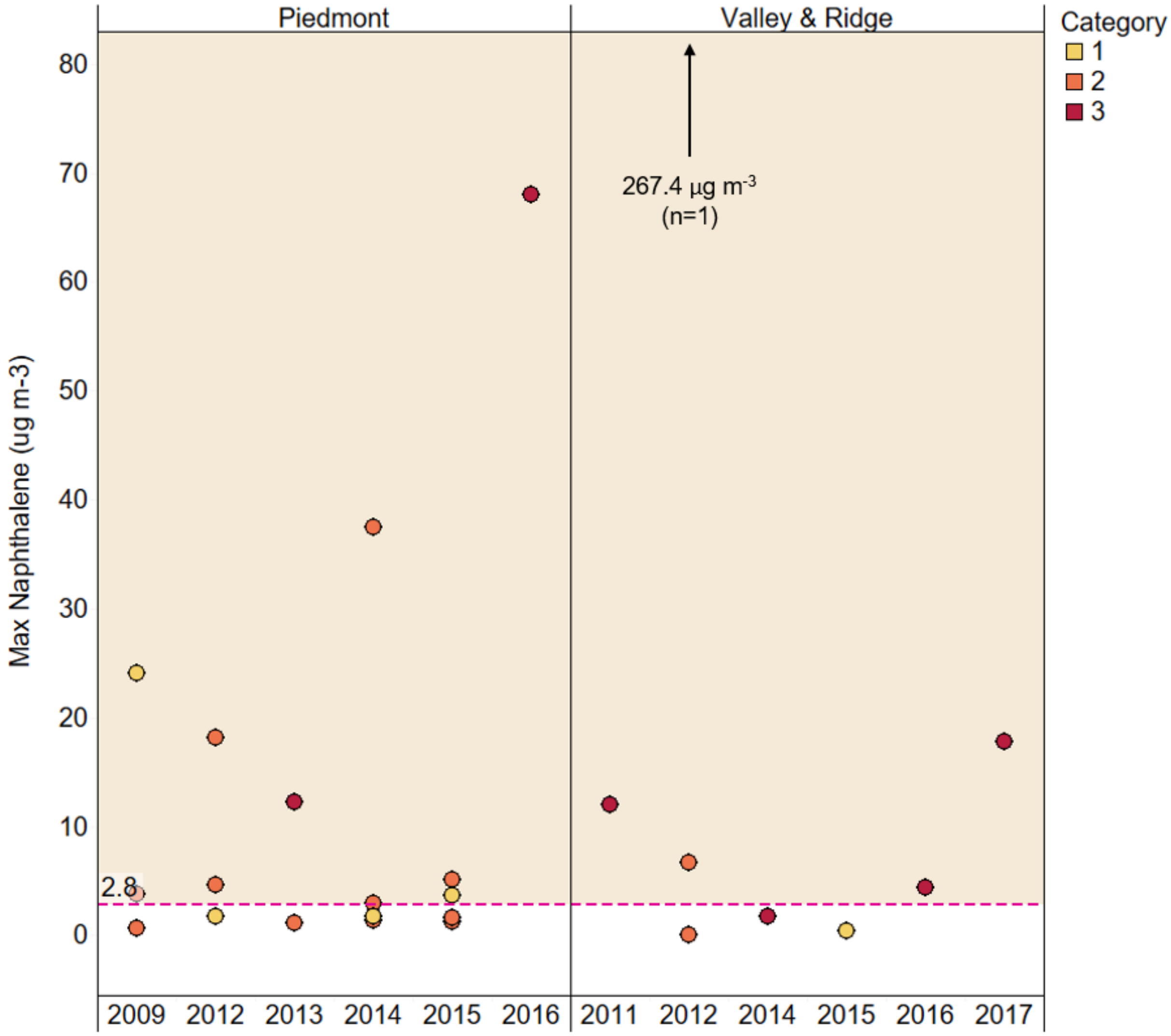


Figure 4.15: Naphthalene concentration binned by physiographic region and year reported. A majority of Category 3 samples exceed the naphthalene sub-slab risk threshold of 2.8 µg m^{-3}.

TPH concentrations broken down by Category returned values which fit our expectations, as each Category results in higher concentrations (Figure 4.16). 28% of Piedmont site maximums exceed the sub-slab risk threshold, while only 13% of Valley and Ridge exceed the threshold. If TPH is to be used as a proxy for heating oil release severity, then it appears that previous abatement efforts were somewhat successful in removing most of the spills at a majority of the sites we visited.

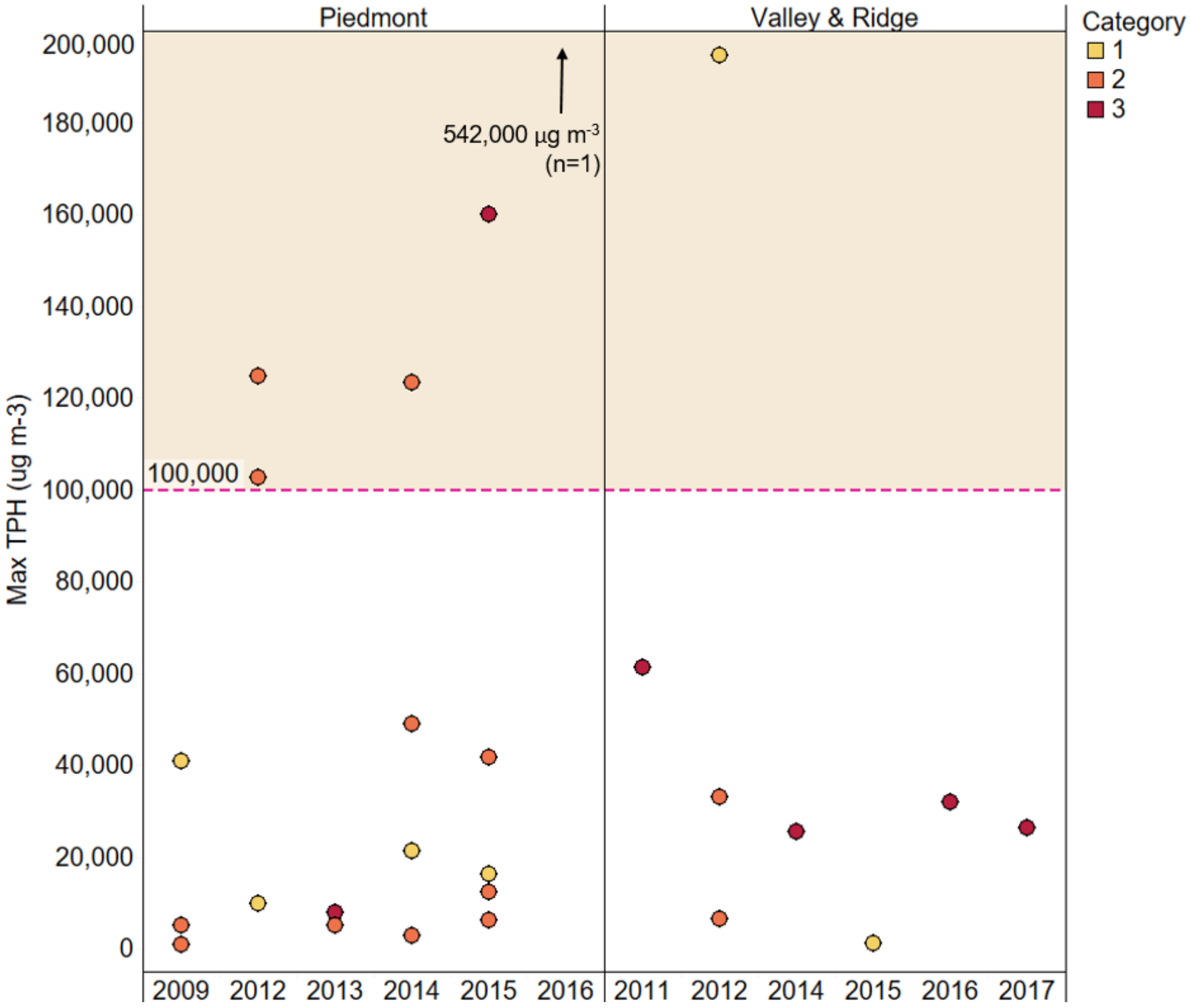


Figure 4.16: TPH site maximum concentrations binned by physiographic region and year reported.

4.3 Site Characteristics as Contamination Predictors

One goal of this study was to determine relationships between Category and contaminant removal (contaminant concentration), building type and/or physiographic region and contaminant concentration, and remediation time and contaminant concentration.

Fitting linear trend lines to the category and concentration data was expected to serve as a tool for predicting concentration based on remediation time. We hypothesized that as time passes, Category 3 sites' TPH concentration will most likely decrease in a predictable manner. We did not observe this behavior (Figure 4.9). Overall, trends were difficult to parse due to small sample size and variability of sites. R^2 values do not exceed 0.2 for any compound of any category, suggesting that contaminants may not exhibit a linear trend between site concentration and residence time during remediation.

Physiographic region, at least with regards to Valley and Ridge and Piedmont, does not exhibit a significant control on contaminant concentration. We hypothesized that Coastal sites would have lower contaminant levels due to high soil permeability and related increased likelihood of aerobic biodegradation due to the increased circulation of oxygen. Due to difficulties in data acquisition, coastal data was not utilized in this study, so no conclusions can be drawn. Because slab-style houses are popular in the coastal region and not as much in the Piedmont and Valley and Ridge regions, no conclusions could be drawn about this style of house.

Building type minimally affects concentrations, if at all. The lack of crawlspace and slab data makes drawing conclusions on the difference between basement, crawlspace, and slab sites impossible. The relationship between region and building type is worth further data collection to develop predictive models.

5. Conclusions

We evaluated the impacts to soil local to residences with previously reported home heating oil spilled from USTs. This study investigates site variables at 25 previously documented UST heating oil release sites in the Commonwealth of Virginia: These variables are building type, remediation time, and physiographic region. They were investigated in order to determine if nearby structures to UST releases, abatement time, and soil type, respectively, serve as predictive tools for contaminant concentrations. In addition, DEQ Category was investigated in conjunction with the three variables.

Building type shows some promise as a predictive variable for site contamination. It is likely that basement-style dwellings impose physical limitations on release abatement, either by preventing horizontal movement of the spill, causing concentrations to remain high for longer periods of time, or disallowing oxygen from entering the source zone, causing the soil microbial consortium to anaerobically biodegrade the compounds instead of aerobically doing so, slowing abatement.

Time since remediation can potentially be used as a predictor once remediation has occurred at an individual site, but it cannot be applied across the Commonwealth as a predictor. It is true that longer a release has been in the unsaturated zone, the more likely it has aerobically biodegraded or volatilized to the atmosphere, depleting overall contaminant concentrations. The relationship between contaminant concentration and remediation time should be empirically modelled in future work.

Physiographic region is potentially a powerful predictive variable, as soil permeability is expected to be a powerful parameter on source zone contaminant depletion. However, a lack of Coastal (sandy soil) sites prevents conclusions from being made.

DEQ Category was investigated in conjunction with the three site variables. Overall, Categories 2 and 3 tended to have higher concentrations, as expected. Category 1 concentrations did not always behave as expected. Site sample variance was difficult to characterize, as “DEQ Category” is a subjective parameter. Sites were expected to have “hot spots” of increased contaminant concentration near the source zone, particularly at Category 3 sites, so it was expected that Category 3 sites would always have higher variability. This was not the case for any of our compounds; generally, Category 2 had the highest variability.

Risk remains for naphthalene, TPH, and possibly benzene exposure. Most samples, regardless of DEQ Category, exceeded the sub-slab risk target threshold for these compounds. This implies that the release source zone was not effectively removed from the soil during excavation.

There is a strong potential for future work for this study. As the category system is subjective, and Category 2 encompasses most sites, future work would require a more thorough sampling of sites aged 0-2 years for Categories 1 and 2. In addition, a more thorough sampling of houses with slab and crawlspace foundations is needed before conclusions can be drawn regarding these styles' potential impact on soil contaminant vapor concentrations. Time since remediation is a variable that should be investigated on an individual site basis over a span of many years in future work.

6. Engineering Implications

Remediation time is the most promising predictive tool for contaminant concentration at a UST release site. Physiographic region could prove as a predictive variable, but more data are needed. It is possible that building type plays a role in how a release is abated, since the highest values were found at sites with basements. In the future, models for these variables could be created to predict whether a site will have concentrations exceeding sub-slab risk target thresholds.

The standard strategy for remediating spilled hydrocarbons does not completely remove risk from naphthalene. Given that naphthalene is extremely detrimental to human health when inhaled, it is concerning that many of the data are above the risk target threshold.

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Appendix A: Data

Table A.1: Calibrated field values in μg m^{-3} for benzene, toluene, ethylbenzene, p-m-Xylene, and o-Xylene. Table does not include background samples.

GCMS File Number	Case Number	Benzene	Toluene	Ethylbenzene	p-m-Xylene	o-Xylene
DEQ_0387	20094134	0.000	5.945	0.552	2.630	0.681
DEQ_0389	20094134	0.000	2.497	13.146	15.939	0.000
DEQ_0424	20094442	0.000	3.956	2.329	3.751	3.069
DEQ_0425	20094442	0.000	0.650	0.766	0.734	0.968
DEQ_0426	20094442	0.000	2.459	0.000	0.000	0.497
DEQ_0427	20094442	0.000	5.164	0.530	1.757	0.033
DEQ_0428	20094442	0.000	0.000	0.369	0.000	0.291
DEQ_0310	20097124	0.000	0.668	0.867	2.194	1.138
DEQ_0312	20097124	0.000	2.368	1.924	4.245	2.625
DEQ_0246	20112079	0.000	1.185	1.648	1.613	1.931
DEQ_0248	20112079	0.000	8.803	6.114	10.179	8.010
DEQ_0250	20112079	0.000	9.475	4.256	6.016	4.123
DEQ_0263	20122193	0.000	0.000	0.949	0.932	1.568
DEQ_0266	20122193	0.000	0.000	0.424	0.000	0.417
DEQ_0224	20122231	0.000	0.000	0.000	0.000	0.118
DEQ_0226	20122231	0.955	0.000	0.000	0.000	0.000
DEQ_0228	20122231	3.484	293.901	0.000	0.000	0.000
DEQ_0216	20122308	1.747	0.000	0.000	0.000	0.000
DEQ_0218	20122308	5.436	0.000	174.601	178.668	415.476
DEQ_0370	20124030	0.000	0.027	1.323	1.093	0.654
DEQ_0372	20124030	0.000	0.000	0.305	0.179	0.312
DEQ_0374	20124030	21.783	0.000	0.000	0.000	0.000
DEQ_0412	20124137	0.152	5.263	1.047	4.467	1.341
DEQ_0414	20124137	1.563	5.534	1.077	8.638	1.878
DEQ_0398	20124212	5.027	11.615	2.217	2.117	1.875
DEQ_0399	20124212	0.000	44.566	3.464	3.942	2.283
DEQ_0401	20124212	3.356	3.414	0.852	0.363	0.559
DEQ_0430	20124298	0.000	5.579	1.119	0.000	1.508
DEQ_0431	20124298	0.000	2.231	0.000	0.000	0.000
DEQ_0433	20124298	0.000	0.000	0.170	0.000	0.100
DEQ_0435	20124298	0.000	0.000	0.533	0.299	0.601
DEQ_0442	20124502	0.000	2.742	2.605	4.556	3.913
DEQ_0443	20124502	0.000	0.341	1.180	1.587	1.733

DEQ_0444	20124502	0.000	0.064	3.912	6.908	5.982
DEQ_0445	20124502	0.000	0.342	3.359	5.258	4.629
DEQ_0446	20124502	0.000	0.031	2.751	3.891	3.473
DEQ_0402	20132080	0.000	0.386	0.282	0.000	0.162
DEQ_0392	20134061	0.000	2.836	4.471	5.598	1.953
DEQ_0393	20134061	0.000	0.000	0.000	0.000	0.000
DEQ_0397	20134061	0.000	2.676	2.714	5.299	2.543
DEQ_0181	20142338	0.000	12.919	2.766	3.771	4.714
DEQ_0182	20142338	0.000	3.182	0.751	0.950	0.730
DEQ_0229	20142338	3.756	35.987	1.917	2.728	3.690
DEQ_0232	20142338	8.097	32.292	0.000	4.404	5.512
DEQ_0301	20142376	3.120	3.344	0.772	1.252	1.001
DEQ_0304	20142376	0.000	0.298	0.660	0.950	0.740
DEQ_0316	20142394	0.000	4.383	1.193	2.542	1.227
DEQ_0319	20142394	8.016	28.810	0.973	1.748	1.255
DEQ_0405	20142475	0.000	6.900	1.404	1.638	1.394
DEQ_0408	20142475	0.000	3.125	1.667	1.882	1.706
DEQ_0410	20142475	0.000	3.206	0.701	2.587	0.744
DEQ_0379	20144415	0.000	0.668	0.098	0.000	0.000
DEQ_0381	20144415	0.434	8.618	0.000	0.000	0.000
DEQ_0342	20146061	0.000	0.684	6.886	9.715	6.196
DEQ_0345	20146061	0.000	2.499	30.566	25.990	27.456
DEQ_0290	20152319	0.285	1.016	1.528	1.972	1.670
DEQ_0292	20152319	0.011	0.393	0.688	1.193	0.816
DEQ_0282	20152345	0.000	0.234	0.787	1.480	1.134
DEQ_0285	20152345	0.000	0.083	0.634	1.143	0.903
DEQ_0307	20152413	0.000	4.660	0.338	0.103	0.280
DEQ_0436	20153154	0.000	3.967	0.842	0.207	1.220
DEQ_0437	20153154	0.000	2.749	1.100	2.180	1.504
DEQ_0438	20153154	2.095	1.122	0.126	0.000	0.000
DEQ_0439	20153154	0.000	5.969	1.644	1.238	0.960
DEQ_0440	20153154	0.000	0.513	20.367	37.196	4.207
DEQ_0350	20156059	23.703	0.716	0.000	0.000	0.000
DEQ_0353	20156059	0.000	2.030	0.784	1.169	0.589
DEQ_0338	20156134	0.000	1.134	1.352	2.406	1.496
DEQ_0339	20156134	0.000	0.380	0.286	0.271	0.335
DEQ_0332	20156135	5.358	17.705	1.068	2.258	1.685
DEQ_0333	20156135	4.467	3.083	0.669	0.956	0.931
DEQ_0254	20162264	0.000	4.501	0.564	0.000	0.452
DEQ_0255	20162264	0.000	0.000	0.349	0.000	0.317
DEQ_0357	20163113	8.895	5.829	13.701	30.299	27.625

DEQ_0359	20163113	42.008	7.457	1.323	1.242	0.950
DEQ_0362	20163113	0.000	0.646	0.840	1.459	3.806
DEQ_0455	20163113	0.000	0.189	0.416	0.000	0.000
DEQ_0456	20163113	0.000	1.383	0.000	0.000	0.000
DEQ_0457	20163113	0.000	3.959	1.363	1.655	1.984
DEQ_0460	20163113	0.000	1.870	0.000	0.000	0.000
DEQ_0461	20163113	0.000	3.637	0.156	0.000	0.000
DEQ_0462	20163113	0.000	5.150	1.513	1.892	2.177
DEQ_0463	20163113	0.000	0.156	0.000	0.000	0.000
DEQ_0464	20163113	0.000	11.407	1.111	0.045	0.000
DEQ_0257	20172038	0.000	0.137	3.230	6.916	5.999
DEQ_0260	20172038	0.000	0.000	2.005	3.910	3.591

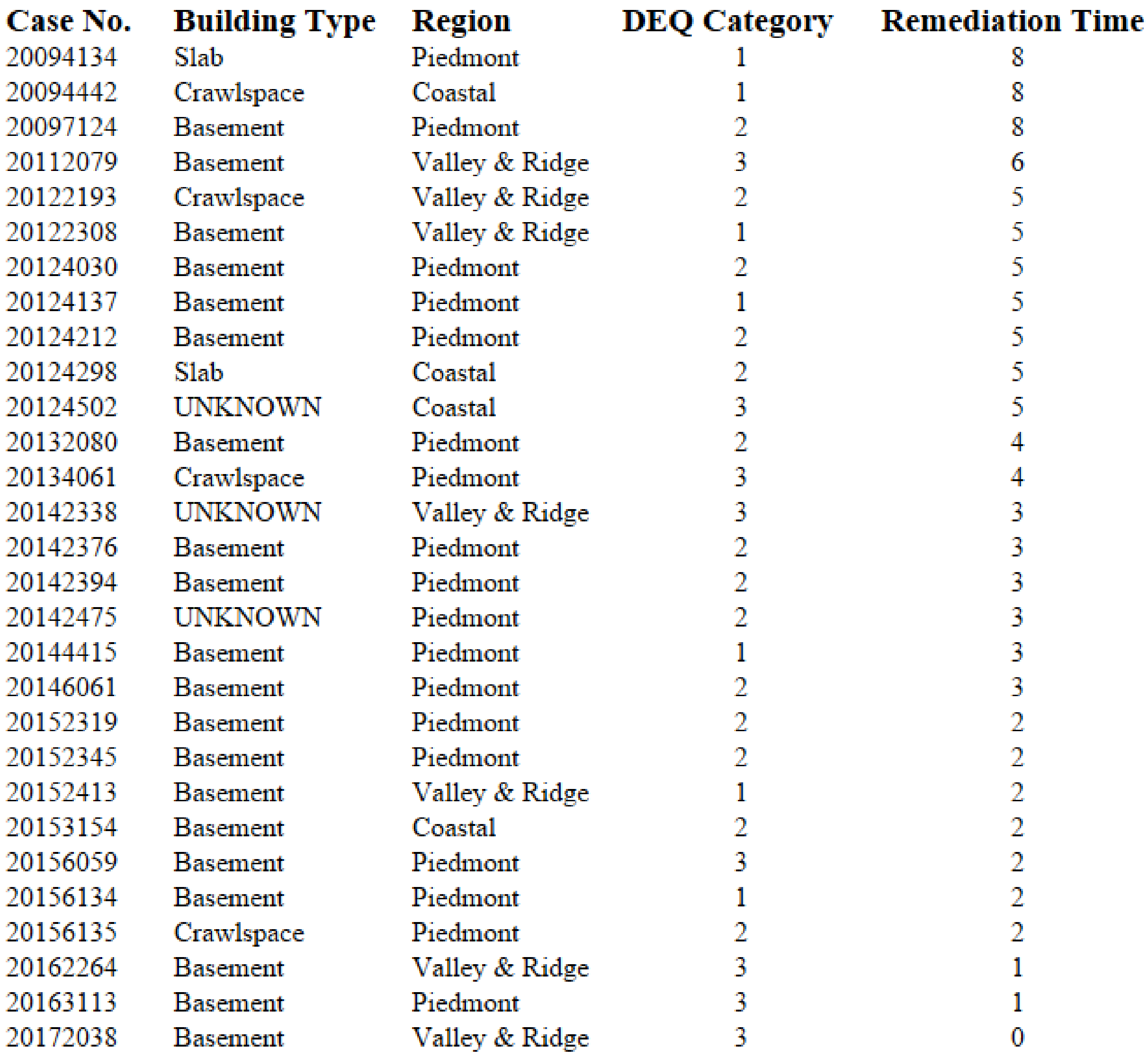
Table A.2: Calibrated field values in µg m-3 for naphthalene and TPH. Table does not include background samples.

GCMS File Number	Case Number	Naphthalene	TPH
DEQ_0387	20094134	0.509	1193
DEQ_0389	20094134	24.056	40761.9
DEQ_0424	20094442	2.574	1256.17
DEQ_0425	20094442	1.520	845.582
DEQ_0426	20094442	1.171	528.654
DEQ_0427	20094442	2.746	1433.11
DEQ_0428	20094442	0.182	369.869
DEQ_0310	20097124	0.706	971.932
DEQ_0312	20097124	3.829	4931.21
DEQ_0246	20112079	0.682	2132.02
DEQ_0248	20112079	11.985	61198.2
DEQ_0250	20112079	7.502	10316.7
DEQ_0263	20122193	6.730	6543.94
DEQ_0266	20122193	0.518	742.36
DEQ_0224	20122231	0.000	4833.08
DEQ_0226	20122231	0.000	33111.6
DEQ_0228	20122231	0.000	2789.79
DEQ_0216	20122308	0.000	194803
DEQ_0218	20122308	267.383	120481
DEQ_0370	20124030	1.198	2173.79
DEQ_0372	20124030	0.311	366.85
DEQ_0374	20124030	18.108	124715
DEQ_0412	20124137	1.430	9708.33
DEQ_0414	20124137	1.686	8575.05
DEQ_0398	20124212	0.928	2302.8
DEQ_0399	20124212	4.682	102747
DEQ_0401	20124212	1.326	2789.95
DEQ_0430	20124298	2.606	5947.71
DEQ_0431	20124298	1.240	3568.74
DEQ_0433	20124298	1.879	614.467
DEQ_0435	20124298	0.545	242.951
DEQ_0442	20124502	6.103	814.798
DEQ_0443	20124502	2.327	363.708
DEQ_0444	20124502	12.027	3108.51
DEQ_0445	20124502	9.542	2040.35
DEQ_0446	20124502	3.081	2043.3

DEQ_0402	20132080	1.185	5087.16
DEQ_0392	20134061	12.245	2382.48
DEQ_0393	20134061	0.000	0
DEQ_0397	20134061	9.164	7932.39
DEQ_0181	20142338	0.000	12596.1
DEQ_0182	20142338	1.706	25541
DEQ_0229	20142338	1.210	4147.61
DEQ_0232	20142338	0.804	6962.57
DEQ_0301	20142376	1.333	2777.64
DEQ_0304	20142376	0.584	680.204
DEQ_0316	20142394	2.948	18946.3
DEQ_0319	20142394	2.212	48947.6
DEQ_0405	20142475	0.358	228.725
DEQ_0408	20142475	0.457	576.856
DEQ_0410	20142475	2.071	787.314
DEQ_0379	20144415	0.408	13836.6
DEQ_0381	20144415	1.727	21169.8
DEQ_0342	20146061	9.907	25353.5
DEQ_0345	20146061	37.527	123279
DEQ_0290	20152319	1.215	1983.82
DEQ_0292	20152319	0.977	6264.54
DEQ_0282	20152345	1.575	3054.58
DEQ_0285	20152345	1.524	12243.7
DEQ_0307	20152413	0.367	1114.51
DEQ_0436	20153154	1.839	2521.91
DEQ_0437	20153154	1.665	1340.99
DEQ_0438	20153154	1.519	4147.13
DEQ_0439	20153154	1.103	1401.38
DEQ_0440	20153154	98.850	124789
DEQ_0350	20156059	0.000	159995
DEQ_0353	20156059	1.584	14771.4
DEQ_0338	20156134	3.683	16268.5
DEQ_0339	20156134	1.500	8944.87
DEQ_0332	20156135	5.120	41699.5
DEQ_0333	20156135	3.304	13270.9
DEQ_0254	20162264	4.450	31999.9
DEQ_0255	20162264	0.129	774.488
DEQ_0357	20163113	28.218	405071
DEQ_0359	20163113	6.727	454396
DEQ_0362	20163113	1.023	15593
DEQ_0455	20163113	30.923	304087

DEQ_0456	20163113	13.120	267428
DEQ_0457	20163113	57.589	12246.5
DEQ_0460	20163113	30.661	318749
DEQ_0461	20163113	20.138	309965
DEQ_0462	20163113	68.002	12149.1
DEQ_0463	20163113	9.959	405740
DEQ_0464	20163113	0.000	542461
DEQ_0257	20172038	17.821	6691.41
DEQ_0260	20172038	13.991	26309.7

Table A.3: Pertinent metadata for each field site, including case number, building type, physiographic region, DEQ Category Number, and remediation time (years).



Case No.	Building Type	Region	DEQ Category	Remediation Time
20094134	Slab	Piedmont	1	8
20094442	Crawlspace	Coastal	1	8
20097124	Basement	Piedmont	2	8
20112079	Basement	Valley & Ridge	3	6
20122193	Crawlspace	Valley & Ridge	2	5
20122308	Basement	Valley & Ridge	1	5
20124030	Basement	Piedmont	2	5
20124137	Basement	Piedmont	1	5
20124212	Basement	Piedmont	2	5
20124298	Slab	Coastal	2	5
20124502	UNKNOWN	Coastal	3	5
20132080	Basement	Piedmont	2	4
20134061	Crawlspace	Piedmont	3	4
20142338	UNKNOWN	Valley & Ridge	3	3
20142376	Basement	Piedmont	2	3
20142394	Basement	Piedmont	2	3
20142475	UNKNOWN	Piedmont	2	3
20144415	Basement	Piedmont	1	3
20146061	Basement	Piedmont	2	3
20152319	Basement	Piedmont	2	2
20152345	Basement	Piedmont	2	2
20152413	Basement	Valley & Ridge	1	2
20153154	Basement	Coastal	2	2
20156059	Basement	Piedmont	3	2
20156134	Basement	Piedmont	1	2
20156135	Crawlspace	Piedmont	2	2
20162264	Basement	Valley & Ridge	3	1
20163113	Basement	Piedmont	3	1
20172038	Basement	Valley & Ridge	3	0

Appendix B: Field Methods (Complete)

B.1 Installation soil vapor sampling probe

- General considerations:
    - Do not use actual sampling probe tip to drill hole – this may result in its loss. Use solid 403 probe segments and simple drilling tip.
    - Be aware of utilities such as water, electric, and cable lines that may run below. Give half a foot grace distance away from marked utility lines. Also be aware of whether the heating oil tank is still in the ground or not.
    - Clay soils will quickly expand into sampling hole, so use time efficiently and consider drilling the hole twice before inserting sampling probe.
    - Do not use duct tape to hold elements together, as the adhesive can outgas and cause problems with your samples.
- Process:
    - Pick site safely away from any utilities, but close enough to either the structure or the hotspot you are sampling.
    - Assemble drilling probe and sampling probe. Be sure Teflon tubing is securely attached to probe tip within the probe shaft, and that at least 1.5 ft of excess tubing is available on the other end to work with the sampling pump.
    - Push drilling probe in as far as you can without a hammer, then install a slide hammer (or use sledge hammer or mallet).
    - Drill probe into ground until hammer piece is about 2 in from the ground surface.
    - If you cannot remove the probe by hand, use a jack to remove the probe.
    - Insert sampling probe to full depth.
        - If you are using a retractable tip, pull up on the probe about 3 in to allow the tip to expand into the soil, then place a vice grip on the probe shaft at ground surface (Figure B-1).

Figure B.1: Vice grip prevents probe from sliding further into ground, which would collapse the probe tip and prevent sample collection.

  - Pack clay around the soil and probe interface.

B.2 Preparing and installing soil vapor sampling equipment

- General considerations:
  - You <u>must</u> test the flow rate for every sorbent tube, as each one has a different head loss.

    - Calibrate your rotameters to an electronic flow meter ahead of time so that the rotameters themselves are not causing head loss that would interfere with later calculations.
    - Rotameter elements tend to “stick” in humid weather – tap it firmly on a hard surface or tap it with the blunt end of a screwdriver to rectify this.
- Split flow sampling:
    - Insert sampling tubes of choice (for our purposes, it was either Tenax™ TA or Carbopack™) into either end of a T fitting, keeping the middle section open. Arrows on the tubes should be pointed away from the fitting.
        - Use the nut that comes with the tube rather than the fitting’s nut.
    - Connect rotameters to open ends of tubes on the “pressure” side of the rotameter (should be the bottom fitting).
    - Hook up pumps to “suction” fittings on the rotameters.
    - Start both pumps at once, adjust flow rate using the pump tube, not the rotameters themselves. Once they both read your target rate, pause both pumps (Figure B-2).

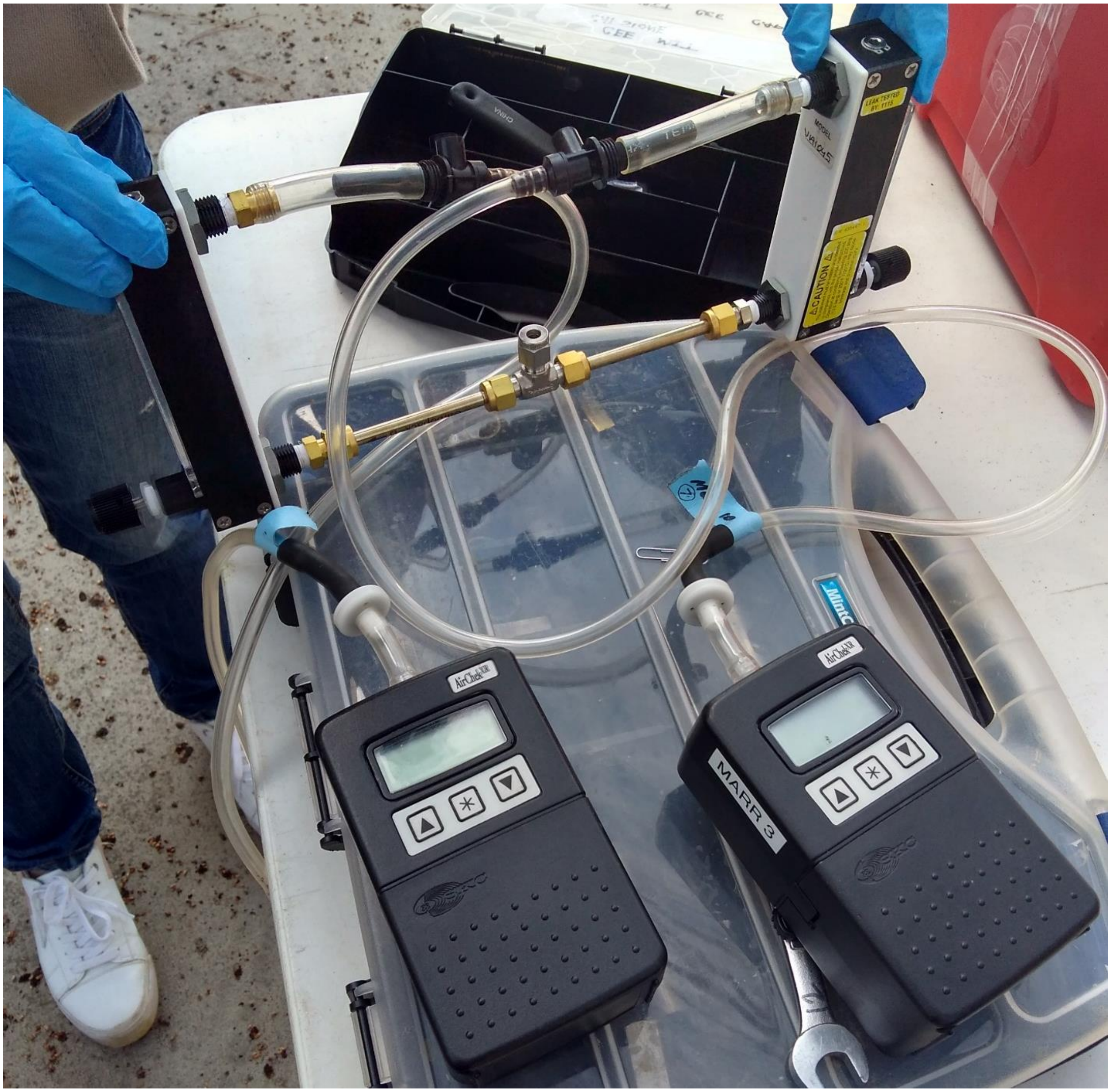


Figure B.2: Flow rate testing setup for split flow sampling. Note the valves for flow rate adjustment and location of pump and sorbent tube connections.

    - Disconnect pump and tubes from rotameter, and attach pumps directly to tubes.
- Single flow sampling:
    - Insert sorbent tube of choice into a union, arrow pointing away from the union.
    - Insert other end into the “pressure” fitting on the rotameter, arrow pointing towards rotameter.
    - Hook pump up to “suction” fitting on the rotameter.
    - Start pump, adjust flow rate using valve on pump tube until your rotameter reads your target flow rate.

- Pause pump, disconnect sorbent tube and pump from rotameter, attach pump directly to sorbent tube (Figure B-3).

Figure B.3: Single flow setup ready to attach to soil probe.

- Connecting to soil probe:
    - Insert Teflon tubing from soil probe into open nut on fitting, secure tightly (tends to slip).
    - Make sure there are no kinks or sharp bends in the tubing.
    - Start pump(s).

B.3 How to operate handheld sampling pumps

The below instructions pertain to the AirChek XR5000, SKC handheld pumps. I am including this because I found the instructions that come with the pumps to be unhelpful.

- Turn on the pump: hold the "star" button until the display says "on".
- Set time: Hit the following, in order: "Star Up Down Star", then hit the star button until you get to the "Run Time" screen. Use the Up and Down arrows to set your time. If you want the pump to start immediately, also navigate to the "Delay Time" screen and bring the number down to 0.
    - To select the time you want, hit "Up" and "Down" simultaneously.
- Clear current timer: Hit "Star Up Down Star". You should see "Clr". Hit Up and Down simultaneously to select "Clr" and your timer will start over.
    - If "Star Up Down Star" isn't bringing up the menu, hit Up and Down simultaneously, then try it again.
- Start the pump/Pause the pump: Hit Up and Down simultaneously.
- Turn off the pump: Hold "Star" until you see "Off 1", then let go.

B.4 Sheets, Scripts, and Checklists

B.4.1 Field Equipment Checklist

Drilling Probe Kit

Drilling probe tip
AMS 403 segments
Probe segment connectors
Slide hammer + connecting piece

Sampling Probe Kit

Sampling probe tip
AMS Hollow 214 segments
Probe segment connectors
Teflon tubing ¼”

Other

Handheld pumps
Pump connecting tubes with valve
Rotameters (2)
Tape measure
Box cutter
Vice grips
First aid kit
Nitrile Gloves
Work Gloves
Teflon tubing cutter (or scissors)
Site Worksheets
Clipboard
Pen/pencil
Foldable table
Utilities map, or call a utility marking company

Pump charger (for overnight trips)
Sorbent Tubes
Screwdriver for pump valve
Duct tape
Wrenches (for sorbent tubes)
Trash bags
Sample baggies (or masking tape and marker)
Clay
Cooler with freeze pack or ice bag
Jack
Site reports with UST location
GPS enabled device
Water, snacks
Insect repellent, sunscreen
Long pants, closed-toed shoes

B.4.2 Site Worksheet

Soil Vapor Site Log

Case #	
Address	
Category	
Date	
Time	
Weather	

Max TPH-DRO	
ID	
Concentration	
Depth	

Sample ID	Tube #	Depth (ft)	Q (ccm)	Start Time	End Time	Pump #	Tube #

Useful information: Stainless steel probe 7’3”. 214 probe + retractable tip is 6’8”.

Notes:

B.4.3 Homeowner Cold Call Script

Good Evening ________,

My name is ______ I am working at Virginia Tech in conjunction with the Virginia Department of Environmental Quality to analyze risks imposed by home heating oil tanks. DEQ has approached us with information regarding home heating oil spills and restoration efforts in your area. We understand that your property has or had a home heating oil tank, and there was restoration efforts in _____ to remove the tank and contaminated soil, or to monitor the contamination levels. DEQ has filed reports for each location, including yours, and categorized the sites based on level of risk (from 1-3).

Our study, with the guidance of DEQ, involves revisiting these restored sites to see if any harmful vapors from the spill still persists. After looking through reports we have determined that your property is of interest for sampling. With your permission we would like to collect soil samples above and near the contamination site on your property.

The sampling is unintrusive and only requires us to work in a small area outside the house. We will be placing 3 small soil probes 3-9 feet in the ground and collecting soil gas samples that will take approximately 60 mins to run. Once the samples have been collected we will leave the site. The three small sampling site holes will be no greater than an inch in diameter. There will be no damage to your yard or home throughout this process. Since we will only be working outside, it is not necessary that someone is at home while we sample.

Your participation would be greatly appreciated as we determine the potential health risks that may linger at these contaminated sites. Would you be willing to participate and allow us to sample at your location?

No: I understand, Thank you for your time.
Yes: Thank you very much, would **date** work for us to come sample? We will leave a message the day/week before to remind you of our visit

Appendix C: Statistical Methods

C.1 Creating Remediation time figures in Tableau

C.2 Chi-Square R code

```
rm(list = ls())

library(readxl)

library(dplyr)     # for data wrangling

library(tidyr)

library(plyr)

x<- read_excel("C:/Users/Ellen/Documents/SVI/research/covariance.xlsx")

View(x)

#Benzene

x1<-filter(x,Region=="Coastal")

x2<-filter(x,Region=="Piedmont")

x3<-filter(x,Region=="Valley & Ridge")

x4<-filter(x,`Building Type`=="Basement")

x5<-filter(x,`Building Type`=="Slab")

x6<-filter(x,`Building Type`=="Crawlspace")


names(x[12])

for(k in 12:18){

print(names(x[k]))

  xtest<-
rbind.fill(as.data.frame(x1[[k]]),as.data.frame(x2[[k]]),as.data.frame(x3[[k]]),as.data.frame(x4[[k]]),as.dat
a.frame(x5[[k]]),as.data.frame(x6[[k]]))

for(i in 1:3){

  for(j in 4:6){

    pv<-wilcox.test(xtest[[i]],xtest[[j]],alternative = "less")

    pv1<-pv$p.value
```

```
    print(pv1)
  }
}
}



thing_to_test_for_1 = "Piedmont"
thing_to_test_for_2 = "Slab"

a = filter(x, Region == thing_to_test_for_1,
           `Building Type` == thing_to_test_for_2)

b = filter(x, Region != thing_to_test_for_1,
         `Building Type` == thing_to_test_for_2)

c = filter(x, Region == thing_to_test_for_1,
         `Building Type` != thing_to_test_for_2)

d = filter(x, Region != thing_to_test_for_1,
         `Building Type` != thing_to_test_for_2)

test_input = data.frame(matrix(c(length(a$X__1),
                        length(b$X__1),
                        length(c$X__1),
                        length(d$X__1)),
                        nrow = 2))

row.names(test_input) = c(thing_to_test_for_1, paste0("Not ", thing_to_test_for_1))
names(test_input) = c(c(thing_to_test_for_2, paste0("Not ", thing_to_test_for_2)))
```

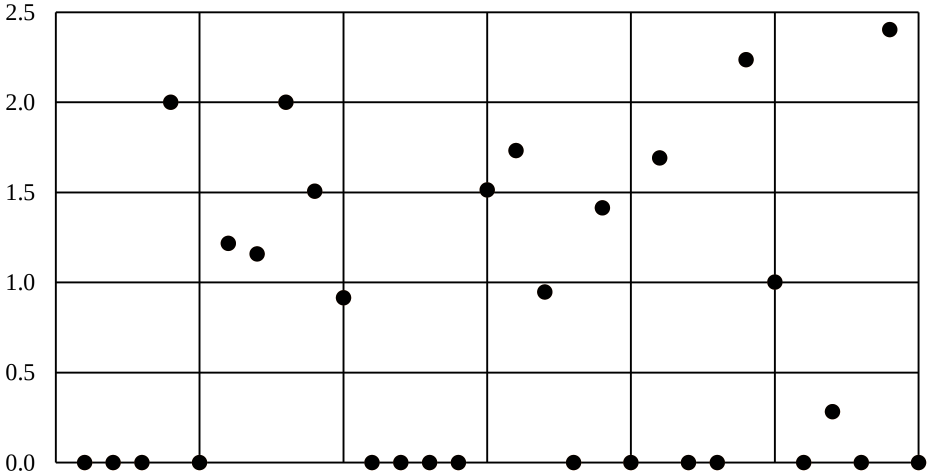
```
test_input

chisq.test(test_input)
```

C.3 Coefficient of Variance Results

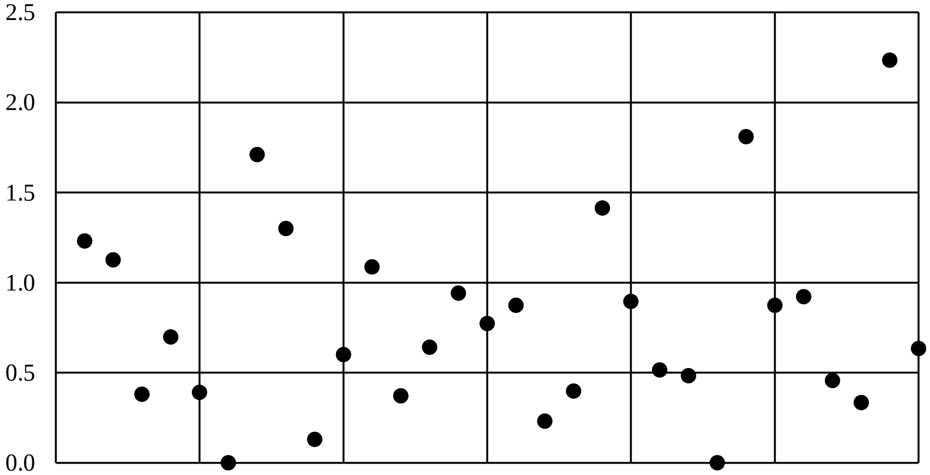
Table C.1: Coefficients of variance for calibrated data as of April 11, 2018.

Case Number	Benzene	Ethylbenzene	Naphthalene	TPH
20094134	0.000	1.231	1.477	0.878
20094442	0.000	1.126	0.644	0.514
20097124	0.000	0.381	1.143	0.879
20112079	2.000	0.699	0.859	1.406
20122193	0.000	0.391	1.165	1.241
20122231	1.217	0.000	0.000	1.248
20122308	1.159	1.711	1.700	0.912
20124030	2.000	1.301	1.767	1.940
20124137	1.508	0.130	0.499	0.513
20124212	0.916	0.600	0.892	1.609
20124298	0.000	1.087	0.562	1.036
20124502	0.000	0.371	0.628	0.653
20132080	0.000	0.640	0.581	0.202
20134061	0.000	0.940	0.893	1.184
20142338	1.515	0.772	0.763	0.877
20142376	1.732	0.874	0.501	0.697
20142394	0.947	0.231	0.433	0.763
20142475	0.000	0.397	1.000	0.531
20144415	1.414	1.414	0.874	0.296
20146061	0.000	0.894	0.823	0.932
20152319	1.692	0.515	0.137	0.911
20152345	0.000	0.483	0.518	1.085
20152413	0.000	0.000	0.000	0.000
20153154	2.236	1.809	2.073	2.040
20156059	1.002	0.874	1.115	1.440
20156134	0.000	0.921	0.596	0.411
20156135	0.284	0.456	0.225	0.597
20162264	0.000	0.334	1.335	1.347
20163113	2.404	2.235	0.920	0.810
20172038	0.000	0.633	0.703	1.112

Benzene Coefficients of Variance



Ethylbenzene Coefficients of Variance



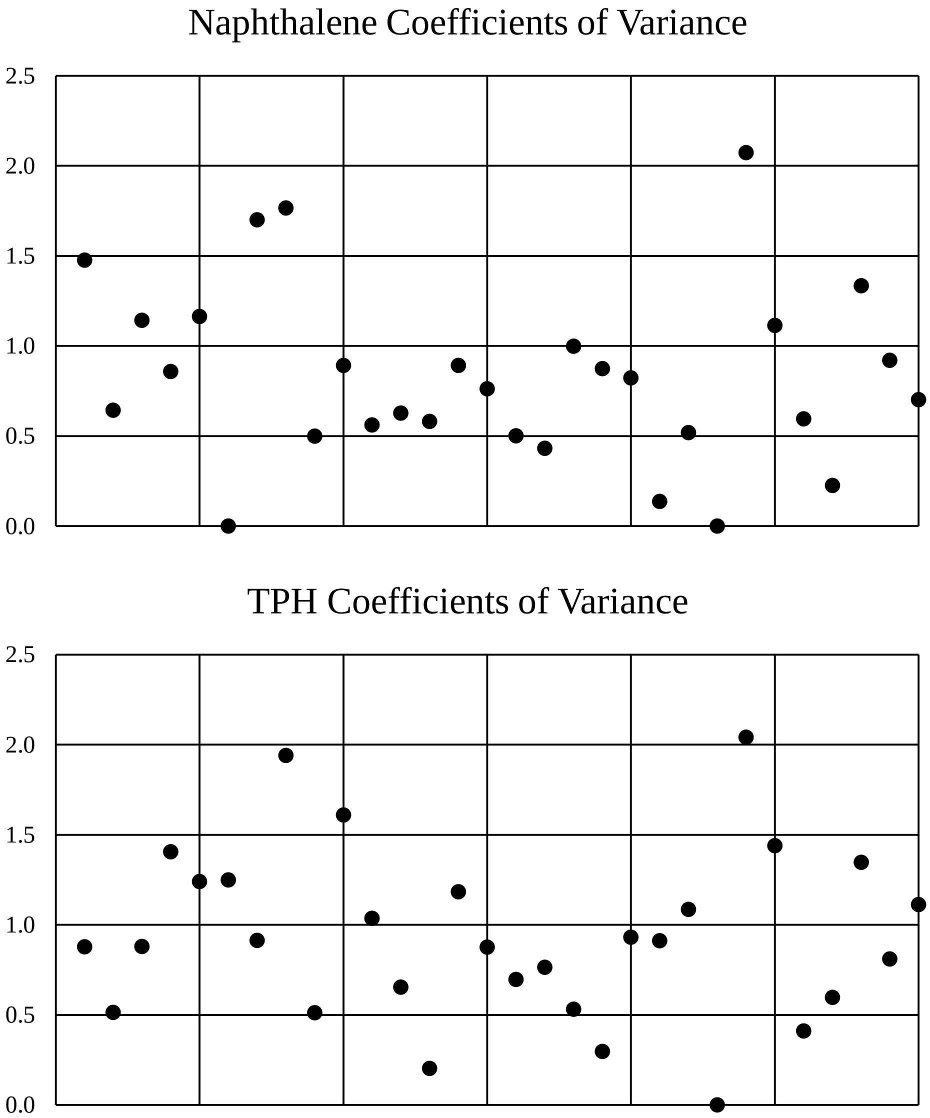


Figure C.1: Variance coefficients for BEN and TPH sorted by case number.