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Characterizing Risks Posed by Petroleum Contaminated Sites:

Implementation of the MADEP VPH/EPH Approach

Policy #WSC-02-411

BACKGROUND/SUPPORT DOCUMENTATION FOR THE DEVELOPMENT OF PUBLICATION GUIDELINES & RULES OF THUMB

October 2002

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Introduction, Background, and Purpose

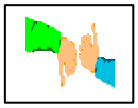
The first draft of the MADEP VPH/EPH Implementation Policy was issued on October 31, 1997. Subsequently, a Final Draft was issued in June 2001, followed by the Final Policy on October 31, 2002.

Although largely unchanged from the 10/31/97 Public Comment Draft, the Final Policy does contain certain revisions, clarifications, and extended subject explanations, based largely on public comments and the agency's experiences in implementing the VPH/EPH approach. This is reflected in the number of pages contained in the various incarnations of this document, as detailed below:

Version	# Pages in Text	# Pages in Appendices
10/31/97 Public Comment Draft	33	5
6/01 Final Draft	43	12
10/31/02 Final Policy	49	14

The origin, reference, and rationale for many of the guidelines and recommendations contained in the Final Policy are detailed directly in that document (e.g., basis of VPH/EPH toxicological approach), and/or otherwise involve subject areas that should be familiar to the intended reader (e.g., principles of gas chromatography). Moreover, recommendations on a number of specific topics and technical items were discussed in detail in the MADEP publication *Issues Paper - Implementation of the EPH/VPH Approach*, May 1996, available at http://www.state.ma.us/dep/bwsc/vph_eph.htm. As such, they will not be addressed here.

Rather, the purpose of this Support Document is to provide insight, reasoning, and justification for heretofore-undocumented decisions and recommendations contained in the Final Policy, including various "Rules of Thumb". Relatively brief discussions on a range of subject areas are summarized within the body of this document, in the order they exist in the Final Policy, followed by a series of Appendices that discuss a specific issue in greater detail. All significant references are noted/footnoted, with complete citations given at the end of the document and each Appendix, including, where available, a web URL citation to obtain the listed source.



Section 3.8: Analytical Screening Recommendations – Table 3-4

Discussions/Rules of Thumb on PID/FID Headspace Development Procedure and Dynamics

☞ Details on PID/FID response and interferences were from *Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure* (Fitzgerald, 1989). The DEP "Jar Headspace Procedure" is from MADEP publication, *Interim Remediation Waste Management Policy for Petroleum Contaminated Soil* (1994).

Statement "For gasoline, excluding clays & organic soils, headspace readings less than 100 ppmv usually means that all VPH fractions are below 100 mg/g."

☞ There are a number of different approaches to relate headspace concentrations of VOCs to soil concentrations, all of which rely basically upon the same concepts and equations. Examples include approaches by (i) Jury et. al. (Lyman et. al., 1982), (ii) Rong, H., California Water Quality Control Board (1996), and (iii) the Fugacity approach by MacKay and

Patterson (Lyman et. al., 1982). An example calculation is provided in Appendix 1 using the Fugacity approach, which demonstrates that a 100 ppmV jar headspace value for benzene (as a reasonable surrogate for gasoline) equates to a level of 1.6 ug/g benzene in soil.

Assumptions on composition of fuel mixtures when interpreting screening data

☞ See Explanation for Section 5.2.2

Section 3.8.2: Recommended VPH/EPH Laboratory Confirmation – Table 3-5

The degree of VPH/EPH data needed to confirm and support assumptions made in analytical screening techniques ranges from 10% to 60%, depending upon the type(s) of petroleum and site conditions.

☞ Analytical screening techniques for individual contaminants (e.g., XRF analysis for lead) can be reasonably correlated with "lab" analytical data (e.g., ICP). However, because petroleum is a complex mixture, and because available VPH/EPH screening techniques cannot provide simultaneous data on the absolute and/or relative concentrations of both aliphatic and aromatic hydrocarbon ranges, sufficient thought and effort must be expended to provide reasonable correlative relationships. This is especially true because of the variation in petroleum chemistry at even a small site, based upon fate and transport processes, and the presence of aerobic/anaerobic micro-environments. This variation is magnified in petroleum products with elevated solubility, mobility, and/or biodegradation potential (e.g., gasoline), necessitating more robust confirmatory efforts, as reflected in these recommendations.

Section 4.2.2: Target Analytes

Basis for Recommended Target Analytes for #2 Fuel/Diesel

☞ 100 ppmV Jar Headspace Criteria to Determine the Need to Test for BTEX: although #2 Fuel/Diesel oil contains BTEX, they are generally present at very low concentrations, usually < 1% total BTEX by weight (Potter and Simmons, 1998). Using the DEP Jar Headspace Procedure, headspace readings of less than 100 ppmV are likely indicative of a total volatile compound concentration in soil of less than 10 ug/g (see Appendix 1). Even if 100% of this 10 ug/g were just Benzene, it would be less than the S-1 cleanup standard. Thus, levels below 100 ppmV can be considered Diminimis, and obviate the need for BTEX analyses.

☞ 500 ug/g TPH Criteria to Determine Need to Test for PAHs: This determination is based upon the concentrations of PAHs in #2 Fuel Oil/Diesel (Potter and Simmons, 1998) and agency experiences at a large residential UST removal project in Natick, MA, that was detailed in MADEP's *Issues Paper - Implementation of the EPH/VPH Approach (1996).* Specifically, it can be seen that the only #2 Fuel Oil/Diesel priority-pollutant PAH compounds that would be expected to exceed a Method 1 Soil Standard are acenaphthene, naphthalene, 2-methylnaphthalene, and phenanthrene, and only above 500 ug/g of total petroluem hydrocarbons (TPH).

☞ Basis for inclusion of MtBE as Target Analyte in GW-1 Areas: The Final Policy document provides multiple notices and notations indicating the gasoline-additive MtBE is not (purposely) added to #2 fuel oil/diesel oil. However, a study conducted by the Connecticut Department of Environmental Protection/University of Connecticut in 2000 found that MtBE was detected in a significant percentage of #2 fuel oil (only) release sites. The results of this study were presented by Robbins et. al. in *Ground Water Monitoring & Remediation (*1999), a peer-reviewed scientific publication of the National Ground Water Association. Key findings contained in this paper are summarized below:

- MtBE was identified at 27 of 37 sites (73%) where releases of fuel oil (exclusively) had contaminated groundwater;
- The concentrations of MtBE in groundwater were found to range from 1 μg/L to 4100 μg/L, with a (geometric) mean value of 42 μg/L;
- In total, 46% of evaluated sites contained levels of MtBE greater than 20 μg/L, which is the lower end of the EPA drinking water advisory range of 20-40 μg/L (which is also the range adopted by MADEP as the secondary drinking water standard for MtBE).

The authors of the Connecticut study hypothesized that the presence of MtBE in the #2 fuel oil was caused by mixing #2 fuel oil with products that contain MtBE during the transportation and/or distribution process. Based upon partitioning calculations, the paper concluded that only 0.8-1.5 cups of residual gasoline in a 5000 gallon tanker truck could contaminate a subsequent shipment of #2 fuel oil with levels of MtBE that, if released to the environment, could pose a groundwater threat (i.e., groundwater concentrations of MtBE in excess of 100 μg/L).

In making the recommendation to list MtBE as a contaminant of concern at #2 fuel oil/diesel oil sites, MADEP assumed that industry practices for the shipment and storage of petroleum products in Massachusetts where similar to industry practices in Connecticut

It should be stressed that the Final Policy identifies MtBE as a contaminant of concern ONLY in groundwater, and ONLY at sites located in sensitive (i.e., GW-1 areas). Since less than 25% of sites regulated by the Massachusetts Contingency Plan are located in GW-1 areas, this will not be an issue or concern at the majority of fuel-oil contaminated sites.

Section 4.2.2.2: Petroleum Product Additives as Target Analytes

The Final Policy recommends a tiered approach to deciding when and how to test for gasoline additives, on the basis of when a spill of leaded gasoline occurred and the sensitivity of soil/groundwater receptors.

☞ LEAD: Beginning in the late 1970s, the USEPA began to enforce regulations to reduce the use of lead in gasoline. The allowable lead content of gasoline began to drop from 1-2.5 grams/gallon (average of all gasoline) to a limit of 0.8 grams/gallon in 1979, followed by a continued reduction through the early 1980s. However, it wasn't until December 31, 1987, that all leaded gasoline for general automotive use was removed from the market (Gibbs, 1990). Accordingly, the Final Policy uses December 31, 1987 as a milestone for when to test media for lead and/or alkyl leads, and EDB.

For releases of leaded gasoline prior to 1998, the policy recommends testing for total lead only in S-1 soils and GW-1 areas. This is based upon the following assumptions:

1. **Alkyl leads are not likely to remain in the environment after more than 15 years**. While little quantitative data are available on the breakdown of alkyl lead in soil and groundwater, it is not considered a persistent compound (USEPA, 1997). Based upon MADEP experiences and inquiries, it is expected that alkyl lead contaminants will be degraded to stable inorganic lead salts within this period of time.

2. **The lead content in gasoline is unlikely to contaminate soils to level significantly higher than the S-1 soil standard of 300 ug/g**. This is based upon agency experiences, and calculations presented in Appendix 2.

3. **Dissolved concentrations of lead in groundwater are unlikely to persist after a 15 year period of time.** This is due to the fact that the more soluble organic leads will have degraded to less soluble salts, in combination with dispersion effects. However, due to the toxicity of lead and environmental sensitivity considerations, confirmation of this assumption is recommended in GW-1 areas.

Conversely, releases of leaded gasoline after 1987 would be exclusively from aviation and specialty (e.g., racing car) fuels that are likely to have relatively high concentrations of alkyl lead (compared to pre-1987 general automotive gasoline). In such cases, concentrations of total and/or organic lead in soil would be of concern due to human exposure <u>and</u> source (leaching) concerns, and concentrations in groundwater would be of concern for human health, ecological exposures, and mobility considerations.

- EDB: The Final Policy recommends testing for EDB in GW-1 areas for pre-1988 releases of leaded gasoline. While EDB levels are likely to be significantly attenuated over this time period, due to this compound's high water solubility, concern still exits because of its extremely low GW-1 standard (0.02 μg/L).

  For post-1988 releases of leaded gasoline, EDB testing is recommended in all soil categories. This is due to the concerns over concentrations of EDB in all soils, with respect to source identification/control (leaching) concerns. It is assumed that leaching concerns of this nature would not be significant for older (pre-1988) release conditions, due to degradation, volatilization, and dispersion processes.

- MtBE: The Final Policy recommends testing for MtBE for all releases of unleaded gasoline after 1979, the year this compound began to be used as an octane enhancing agent; it was later added to gasoline in much higher concentrations as an oxygenate (Gibbs, 1990). An additional recommendation is made to test for MtBE in GW-1 areas where there was a release of #2 fuel oil (post-1979), for the reasons explained in Section 4.2.2: Target Analytes.

Section 4.3.1: Using a Method 2 Approach to Demonstrate "No Impact" to Indoor Air

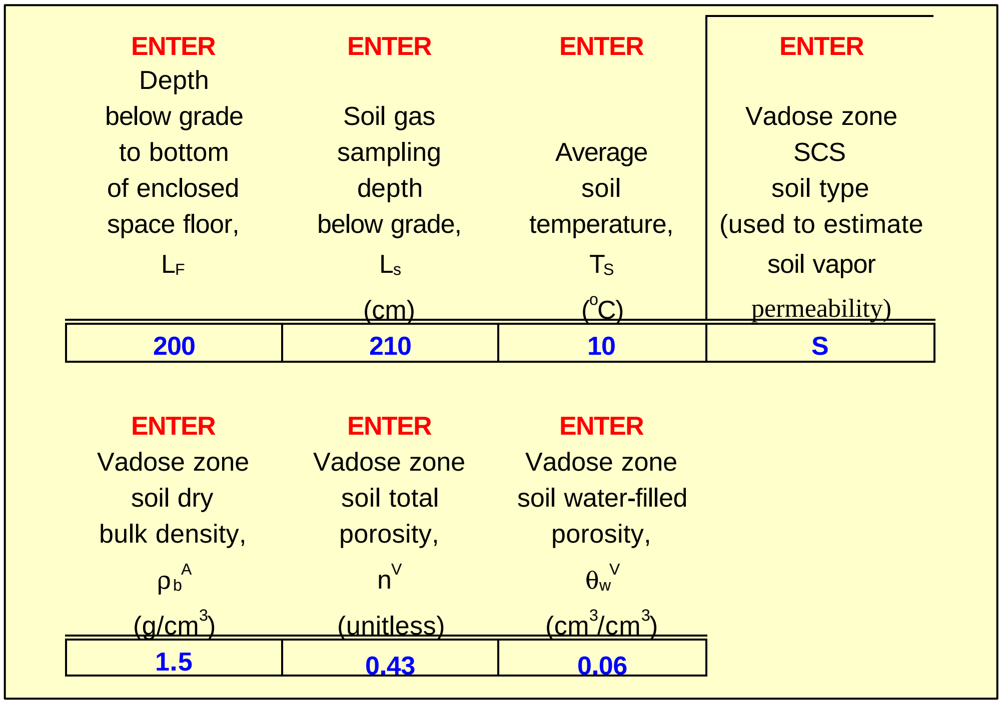
The Final Policy recommends a tiered approach to investigate and assess sites where a subsurface vapor pathway may be measurably impacting the indoor air of a structure. In the Final Policy, a series of criteria are provided for various media using various measurement techniques to characterize the magnitude of this concern, and/or provide the basis to eliminate the pathway from further consideration.

Table 4-9: Soil Gas PID/FID Screening Levels for Evaluating Indoor Air Impacts

☞ DERIVATION OF SOIL GAS CONCENTRATIONS OF CONCERN

<u>Dilution and Attenuation Factors</u>

Toluene, Ethylbenzene, Xylenes: Dilution Factors (i.e., [soil gas]/[indoor air]) for these compounds were calculated based upon use of *SG-Screen*, a spreadsheet adaptation of the Johnson and Ettinger Heuristic model (USEPA, 2000). Key site input factors that were used in this regard are summarized below:



ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Soil gas sampling depth below grade, L_s (cm)	ENTER Average soil temperature, T_S (°C)	ENTER Vadose zone SCS soil type (used to estimate soil vapor permeability)
200	210	10	S

ENTER Vadose zone soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Vadose zone soil total porosity, n^V (unitless)	ENTER Vadose zone soil water-filled porosity, θ_w^V (cm^3/cm^3)
1.5	0.43	0.06

As can be seen above, the scenario used to model this pathway consisted of a structure with a basement floor 200 cm (6.6 feet) below grade, where a soil gas sample is obtained immediately below the floor slab (i.e., 10 cm or 4 inches). The structure is situated on top of a sandy soil with a total porosity of 0.43, and a vadose zone water-filled porosity value of 0.05 cm^3/ cm^3, for a soil saturation level of about 15%. This water-filled porosity value is consistent with the low range of soil moisture data reviewed by MADEP for sub-slab soil samples; this soil saturation level is consistent with the low range of values suggested in a recent publication on this subject (Johnson, P.C., 2002).

Based upon the above user-defined input parameters, in combination with the default parameters incorporated into the SG-Screen model, the following Dilution Factors were obtained:

Compound	Dilution Factor soil gas/indoor air
Ethylbenzene	1300
Toluene	1250
Total Xylenes	1300

A printout of the spreadsheets for each of the above contaminants, which list additional contaminant and site-specific input parameters, is contained in Appendix 3.

Hydrocarbons Ranges: It is not possible to accurately model this pathway for the hydrocarbon fractions, because of the variability in the presence and distribution of the individual hydrocarbon compounds that comprise these ranges, each possessing (slightly) differing properties. Using the average fractional properties recommended in the Final Policy, Dilution Factors range between 1280 and 1350. In consideration of this uncertainty, however, a value of 1300 was used for all hydrocarbon ranges of interest.

Empirical Data: In addition to the estimates provided by the Johnson and Ettinger Model, consideration was also given to site data obtained and reviewed by agency staff (Fitzpatrick and Fitzgerald, 1996). Such data suggest that the Dilution Factor of 2000 used by MADEP to calculate GW-2 standards in 1993 were protective in most, though not every, petroleum contamination situation. This finding further supports use of values in the 1200 – 1300 range, as conservative "screen out" criteria.

These Dilution Factors are deemed appropriate for this generic evaluation of these hydrocarbon compounds and ranges, based upon fate and transport considerations (including biodegradation), and the totality of conservativeness of this generic evaluation. **Note, however, that these values may NOT be used for site-specific evaluations, unless verified as being representative or conservative for the site-specific pathway of interest.**

Acceptable Indoor Air Concentrations

After determining the appropriate Dilution Factor, it is necessary to establish an indoor air concentration as the "ending point" of the vapor intrusion pathway, in order to back-calculate a soil gas level of potential concern.

For the purpose of these guidelines, the indoor air concentration of interest was established as the "background" concentration of each compound and hydrocarbon range. This is consistent with use of these values as conservative "screen out" criterion, and reflective of potential Critical Exposure Pathway (CEP) concerns in residential and school buildings.

Background values for ethylbenzene, toluene, and xylenes were as most recently proposed by MADEP in the development of revised GW-2 standards (MADEP, 2001).

Background concentrations for the hydrocarbon ranges were estimated based upon a limited indoor air sampling effort conducted by MADEP (1997). Full details and all findings and data from this effort are provided in Appendix 4.

A summary of the selected background IAQ concentrations, Dilution Factors, and resultant soil gas action levels is provided below. Concentrations of aliphatic and aromatic fractions are converted from μg/m^3 to ppbV based upon the approach developed by Gustafson et. al. (1997):

Parameter	Dilution Factor	Back IAQ μg/m^3	EC	ECMW (MW)	Soil Gas Action Level		
					μg/m^3	ppbV	ppmV
C5-C8 Aliphatics	1300	85	6.5	93	110,500	29,000	29
C9-C12 Aliphatics	1300	90	10.5	149	117,000	19,200	19
C9-C10 Aromatics	1300	80	9.5	120	104,000	21,200	21
C9-C18 Aliphatics	1300	100	12	170	130,000	18,700	19
Toluene	1250	29	N/A	(92)	36,250	9600	10
Ethylbenzene	1300	10	N/A	(106)	13,000	3000	3
Xylenes	1300	72	N/A	(106)	93,600	21,600	22

Where:

ppbV = [ug/m3][24.45]/MW for individual compounds
ppbV = [ug/m3][24.45]/ECMW for hydrocarbon ranges

EC = Equivalent Carbon number for range (Gustafson et. al., 1997)
ECMW = Molecular Weight for Equivalent Carbon Number (Gustafson et. al., 1997)

PID and FID Instrument Response

Once the soil gas action levels are established, it is necessary to determine how to measure such levels using PID and FID screening instrumentation.

Given that such instrumentation can only provide data for "total organic vapors (TOV)", a conservative assumption is made that 100% of the TOV value is due to the presence of the compound or hydrocarbon range that exceeded a GW-2 standard in the underlying groundwater. Moreover, if more than one compound or hydrocarbon range exceeds GW-2 standards in the underlying groundwater, a conservative assumption is made that 100% of the TOV response could be from any and each compound or hydrocarbon range. In this manner, one would systematically and conservatively isolate each compound or hydrocarbons range of interest, and compare the soil gas TOV reading to a PID or FID action level.

In addition to only providing a totalized reading for organic compounds, the utility of PID and FID instrumentation is further qualified by their degree of response to different types of organic compounds. Thus, additional assumptions need to be made on how a given instrument will quantitate a soil gas vapor sample. For example, if a sample was comprised of 15 ppmV of C5-C8 Aliphatic Hydrocarbons, what ppmV value would be quantitated by a PID or FID instrument? 15 ppmV? More? Less?

To answer this question, the following assumptions were made:

- A properly calibrated and operated FID instrument will respond relatively uniformly to hydrocarbon vapors within the range of concentrations expected in soil gas, although response is somewhat better for aliphatics hydrocarbons than for aromatic hydrocarbons (USEPA, 510-B-97-001, 1997). Thus, 15 ppmV of C5-C8 Aliphatic Hydrocarbons will elicit a response on an FID meter of 15 ppmV;

- A properly calibrated and operated PID instrument will produce a variable response, based upon the intensity of the lamp used in the unit (USEPA, 510-B-97-001, 1997). A PID with a higher energy lamp (e.g., > 11.5 eV) will respond better than a PID unit with a lower energy lamp (e.g., < 10.1 eV). In fact, lower energy PID units will NOT respond at all to certain types of contaminants (e.g., lighter aliphatic hydrocarbons). Thus, 15 ppmV of C5 – C8 Aliphatic Hydrocarbons will produce a negligible response on a PID unit with a 9.7 eV lamp, but will elicit a response approaching 15 ppmV on a PID unit with a 10.6 eV lamp. Moreover, PID units will produce an elevated response to certain classes of compounds, including aromatic hydrocarbons. For example, a soil gas sample containing 15 ppmV of toluene would be expected to elicit a response on a PID unit (10.6 eV lamp) greater than 15 ppmV (unlike the FID unit which responds relatively uniformly to aliphatics and aromatic).

To quantitate the differences in PID response, information on compound-specific ionization energies and detector response were surveyed from available literature. The most complete inventory of such data was found in the technical literature of a manufacturer of field PID units (RAE Systems, 2002). A summary of key data in this regard is provided below, for each of the available PID lamps (9.8, 10.6, and 11.7 eV) used by this manufacturer:

9.8 eV Lamp

	Compound	No. Carbons	Ionization Energy	Calibration Factor[a]	Normalized Response[b]	Average Response[c]
ALIPHATICS	n-pentane	C5	10.35	145	0.013	0.03
	cyclopentane	C5	10.51	N/A		
	n-hexane	C6	10.13	636	0.003	
	cyclohexane	C6	9.86	N/A		
	n-heptane	C7	9.92	85	0.021	
	n-octane	C8	9.82	23	0.077	
	n-nonane	C9	9.72	N/A		0.25
	n-decane	C10	9.65	4	0.250	
	n-undecane	C11	9.56	N/A		
AROMATICS	benzene	C6	9.25	0.55	1.82	
	toluene	C7	8.82	0.54	1.85	
	ethylbenzene	C8	8.77	0.52	1.92	
	avg xylene	C8	8.56	0.54	1.87	
	1,3,5-TMB	C9	8.41	0.65	2.78	2.25
	Cumene	C9	8.73	0.58	1.72	

10.6 eV Lamp

	Compound	No. Carbons	Ionization Energy	Calibration Factor[a]	Normalized Response[b]	Average Response[c]
ALIPHATICS	n-pentane	C5	10.35	8.4	0.119	0.4
	cyclopentane	C5	10.51	N/A		
	n-hexane	C6	10.13	4.3	0.233	
	cyclohexane	C6	9.86	1.4	0.714	
	n-heptane	C7	9.92	2.8	0.357	
	n-octane	C8	9.82	1.8	0.556	
	n-nonane	C9	9.72	1.4	0.714	0.64
	n-decane	C10	9.65	1.4	0.714	
	n-undecane	C11	9.56	2	0.500	
AROMATICS	benzene	C6	9.25	0.53	1.89	
	toluene	C7	8.82	0.5	2.00	
	ethylbenzene	C8	8.77	0.52	1.92	
	avg xylene	C8	8.52	0.49	2.04	
	1,3,5-TMB	C9	8.41	0.35	2.86	2.35
	Cumene	C9	8.73	0.54	1.85	

11.7 eV Lamp

	Compound	No. Carbons	Ionization Energy	Calibration Factor[a]	Normalized Response[b]	Average Response[c]
ALIPHATICS	n-pentane	C5	10.35	0.7	1.429	1.7
	cyclopentane	C5	10.51	0.6	1.667	
	n-hexane	C6	10.13	0.54	1.852	
	cyclohexane	C6	9.86	N/A		
	n-heptane	C7	9.92	0.6	1.667	
	n-octane	C8	9.82	N/A		
	n-nonane	C9	9.72	N/A		2.9
	n-decane	C10	9.65	0.35	2.857	
	n-undecane	C11	9.56	N/A		
AROMATICS	benzene	C6	9.25	0.6	1.67	
	toluene	C7	8.82	0.51	1.96	
	ethylbenzene	C8	8.77	0.51	1.96	
	avg xylene	C8	8.56	0.57	1.75	
	1,3,5-TMB	C9	8.41	0.3	3.33	2.91
	Cumene	C9	8.73	0.4	2.5	

[a] Calibration Factor: PID unit is calibrated with an isobutylene gas standard. Using this calibration procedure, unit reading in (ppmV) x (CF) = compound concentration ppmV. e.g., using a 10.6 eV lamp, a 100 ppmV PID unit reading (based on calibration with isobutylene) would indicate the presence of 53 ppmV of benzene (100 x 0.53).

[b] Normalized Response: normalizes calibration factors to calibration factor for isobutylene, which is the calibration standard specified in the Final Policy when screening soil gas samples.

[c] Average Response: average normalized response of indicated Aliphatic/Aromatic fraction

On the basis of the calibration/response factors detailed above, the established soil gas action levels were adjusted for each compound and hydrocarbon fractions of interest for 3 broad ranges of PID Lamp intensities: < 10.1 eV, 10.1-11.4 eV, and >11.4 eV, as follows:

Normalized Response x Soil Gas Action Level = PID Normalized Value

The PID Normalized Values were further modified to incorporate the effects of elevated humidity (soil moisture) on PID response. This phenomenon is well documented, and appears to be attributable to (a) absorption of ultraviolet radiation by water molecules in the gaseous sample, and/or (b) deactivation of ionized hydrocarbons that collide with water molecules present in the gaseous samples (Barsky, 1985).

Older models of PID units are particularly susceptible to humidity effects, with signal "quenching" up to 40% (Fitzgerald, 1989; and H-nu Systems, undated). In recent years, manufacturers of PID meters have made progress in minimizing impacts of this nature, at least under the range of common atmospheric humidity conditions. However, significant problems remain at very high levels of relative humidity. Literature from at least one major manufacturer continues to identify response quenching of 40% or greater between 90 and 100% Relative Humidity conditions (RAE Systems, 2001). Given that soil gas beneath structures in Massachusetts is likely to be at or near 100% Relative Humidity (Lstiburek, 2002), impacts of this nature must be incorporated into PID action levels. **Accordingly, the normalized PID action levels were reduced by 40%, to account for signal quenching due to high Relative Humidity conditions:**

< 10.1 ev Lamp				
Parameter	Normalized Response (isobutylene)	Soil Gas Action Level (ppmV)	PID Soil Gas Action Level ppmV	
			Normalized Value	- 40% (moisture effects)
C5-C8 Aliphatics	0.03	29	<1	**N/A**
C9-C12 Aliphatics	0.25	19	5	**3**
C9-C10 Aromatics	2.25	21	47	**28**
Toluene	1.9	10	19	**11**
Ethylbenzene	1.9	3	6	**4**
Average Xylene	1.9	22	42	**25**
10.1-11.4 eV Lamp				
C5-C8 Aliphatics	0.4	29	12	**7**
C9-C12 Aliphatics	0.64	19	12	**7**
C9-C10 Aromatics	2.35	21	49	**29**
Toluene	2.0	10	20	**12**
Ethylbenzene	1.9	3	6	**4**
Average Xylene	2.0	22	44	**26**
> 11.4 eV Lamp				
C5-C8 Aliphatics	1.7	29	49	**29**
C9-C12 Aliphatics	2.9	19	55	**33**
C9-C10 Aromatics	2.9	21	61	**37**
Toluene	2.0	10	20	**12**
Ethylbenzene	2.0	3	6	**4**
Average Xylene	1.8	22	40	**24**

The values presented above were used as the basis of the guidelines provided in Table 4-9 of the Final Policy. As can be seen from this table, action levels provided for C9-C12 Aliphatic Hydrocarbons were also used for the C9-C18 Aliphatic range, given that it is unlikely that there will be significant gaseous-phase concentrations of >C12 hydrocarbons that would migrate through soil gas and impact an overlying structure. It can also be seen that no value has been provided for C5-C8 Aliphatic Hydrocarbons when using a PID with a lamp energy less than 10.1 eV, as this range of hydrocarbons cannot be reliably detected or quantitated with such instrumentation:

Table 4-9: Soil Gas PID/FID Screening Levels for Evaluation Indoor Air Impacts

Hydrocarbon Fraction(s) and Target Analytes which exceed applicable Method 1 GW-2 Standards and/or are present in proximate soils	**Indoor air impacts unlikely if below listed value for each hydrocarbon fraction & Target Analyte of Interest**			
	PID ppmV (Isobutylene response)			**FID ppmV (as methane)**
	< 10.1 eV	**10.1 – 11.4 eV**	**≥11.5 eV**	
C5-C8 Aliphatic Hydrocarbons	N/A	7	29	29
C9-C12 Aliphatic Hydrocarbons	3	7	33	19
C9-C10 Aromatic Hydrocarbons	28	29	37	21
C9-C18 Aliphatic Hydrocarbons	3	7	33	19
Toluene	11	12	12	10
Ethylbenzene	4	4	4	3
Total Xylenes	25	26	24	22

Example

In order to clarify this approach, and illustrate use of the recommended action levels, consider the following example:

- Groundwater beneath a structure contains levels of C5-C8 Aliphatic Hydrocarbon and toluene greater than the GW-2 standards. It may also contain other contaminants below the applicable GW-2 standards.

- A soil gas sample obtained immediately below the structure indicates 15 ppmV TOV using an FID meter. Two "worst case" scenarios are possible:

  1. the 15 ppmV TOV value is 100% attributable to C5-C8 Aliphatic Hydrocarbon vapors (i.e., the concentration of C5 – C8 Aliphatic Hydrocarbons was 15,000 ppbV, using the "Equivalent Carbon Number" method to convert $\mu g/m^3$ to ppbV); or

  2. the 15 ppmV TOV value was 100% attributable to toluene vapors (i.e., the concentration of toluene in the soil gas sample was 15,000 ppbV).

- Both worst-case scenarios are systematically isolated and evaluated.

  - Assuming the soil gas TOV is 100% C5-C8 Aliphatic Hydrocarbons, the 15 ppmV FID value is compared to the soil gas action level of 25 ppmV in Table 4-9 of the Final Policy. Since it is below the action level, it is unlikely that 15 ppmV of C5-C8 Aliphatic Hydrocarbon vapors would infiltrate and contaminate the indoor air of the overlying structure at a concentration that would be discernable (i.e., greater than) an expected background condition (i.e., 85 $\mu g/m^3$). Thus, it is possible to conclude that this pathway in unlikely to be of concern for this particular contaminant.

  - The next parameter is then evaluated, and an assumption is made that 100% of the 15 ppmV FID value is now attributable to the presence of toluene in the soil vapor sample. The 15 ppmV value is compared to the 10 ppmV action level provided in Table 4-9 for toluene, and indicates that if this assumption is true, one CANNOT rule out this pathway of concern. Specifically, based upon a reasonably conservative modeling exercise, there is some possibility that soil gas concentrations of toluene greater than 10 ppmV could infiltrate into the overlying building, contaminating indoor air with concentrations of toluene greater than an expected background condition (i.e., >7.5 ppbV or 29 $\mu g/m^3$)

- Based upon the above, it would NOT be possible to "screen out" this pathway using this level of assessment. This does NOT mean that an indoor air impact is or is even "likely" occurring. Rather, given that the worst-case assumptions used are an impossibility (i.e., all of the TOV value CANNOT be simultaneously due to the presence of C5-C8 Aliphatic Hydrocarbons AND toluene), the appropriate conclusion from this exercise is simply that additional evaluation is needed to better define the actual chemistry of the soil gas sample, for comparison with action levels provided for individual compounds and hydrocarbon ranges (i.e., in Table 4-10 of the Final Policy).

Table 4-10: Soil Gas GC Screening Levels for Evaluating Indoor Air Impacts

The screening levels provided are expected indoor air background concentrations of each compound/range multiplied by the expected indoor air/soil gas dilution factor, as discussed and documented previously.

Parameter	Dilution Factor	Back IAQ ($\mu g/m^3$)	EC	ECMW (MW)	Soil Gas GC Screening ($\mu g/m^3$)
C5-C8 Aliphatics	1300	85	6.5	93	110,500
C9-C12 Aliphatics	1300	90	10.5	149	117,000
C9-C10 Aromatics	1300	80	9.5	120	104,000
C9-C18 Aliphatics	1300	100	12	170	130,000
Toluene	1250	29	N/A	(92)	36,250
Ethylbenzene	1300	10	N/A	(106)	13,000
Xylenes	1300	72	N/A	(106)	93,600

Where: ppbV = [ug/m3][24.45]/MW for individual compounds
ppbV = [ug/m3][24.45]/ECMW for hydrocarbon ranges
EC = Equivalent Carbon number for range (Gustafson et. al., 1997)
ECMW = Molecular Weight for Equivalent Carbon Number (Gustafson et. al., 1997)

Table 4-11: Estimated Background Indoor Air Concentrations

As previously discussed, background concentrations for the hydrocarbon ranges were estimated based upon a limited indoor air sampling effort conducted by MADEP (1997). Full details, findings, and all data of this effort are provided in Appendix 4.

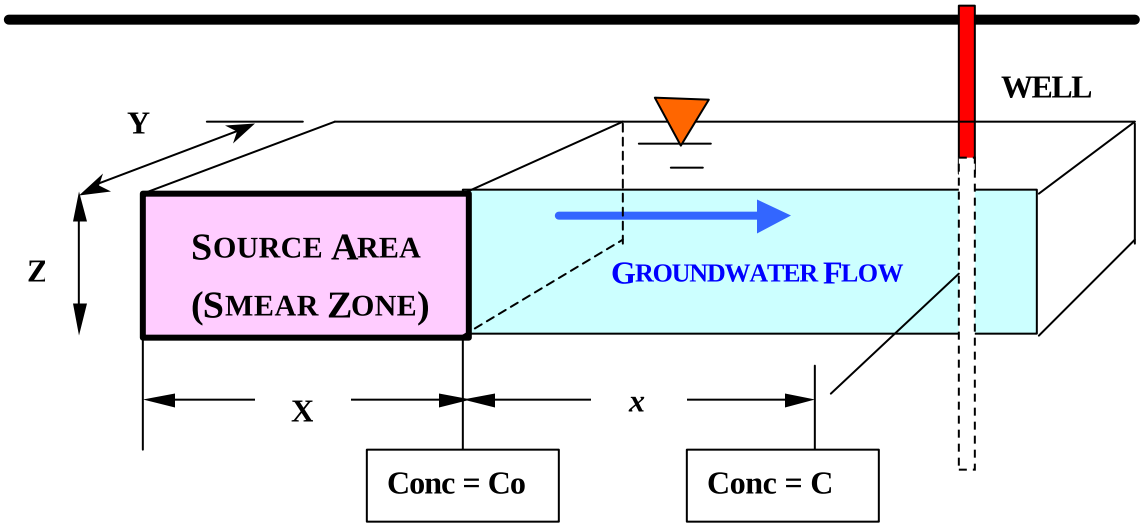
Background concentrations for benzene, toluene, ethylbenzene, xylenes, and naphthalene were those most recently proposed by MADEP in the development of revised GW-2 standards (MADEP, 2002).

Because no literature citations could be found identifying indoor air background concentrations of MtBE, data for ambient air concentrations were used (Zogorski, J.S., et. al., 1996). This is not viewed as overly limiting, since MtBE is not otherwise present in building materials or consumer products, and would likely be present in homes due solely to its presence in the ambient air, unless there is a source of gasoline located within the structure (e.g., a 5 gallon can of gasoline in a resident's basement).

Figure 4-4: Groundwater Dilution Factors for Dissolved Hydrocarbons

The dilution factors and plots detailed in Figure 4-4 were developed using the Domenico and Robbins analytical transport model (Domenico, P.A., and Robbins, G.A., 1985). To be conservative, this evaluation was premised upon an infinite source assumption, and considered ONLY solute attenuation that results from hydrodynamic dispersion processes (i.e., additional attenuation from sorption, biodegradation, volatilization, etc., was NOT considered). In this manner, a number of site-specific factors (e.g., soil type) are not relevant, and the only factor that affects dilution is the configuration of the source area (i.e., contaminated soil).

The scenario that was modeled is graphically illustrated below:



The objective of this effort was to determine the concentration of a dissolved contaminant at the water table at distance x from the source area, as a function of the concentration of that contaminant at the source area (i.e., C_o/C). To simulate a site where an underground storage tank had impacted soil and groundwater, the thickness of the source area (dimension **Z**) was assumed to be 6 feet, consistent with a typical NAPL "smear zone". In assuming an infinite source condition, the dimension of the source area parallel to groundwater flow (dimension **X**) is not relevant.

Thus, the only remaining variable is the width of the source area perpendicular to the groundwater flow direction (dimension **Y**). In this regard, three scenarios were assumed:

Y = 10 feet, to simulate a small residential fuel oil UST site
Y = 30 feet, to simulate a mid-sized commercial UST site; and
Y = 60 feet, to simulate a larger multi-tank UST site.

The results and complete details on this modeling effort are provided in Appendix 5. Two details are worth noting:

- The dilution graphs included in Figure 4-4 of the Final Policy contain not only the **Y** dimension, but also the **X** dimension, assuming a square source area (e.g., 10 foot by 10 foot). Even though the **X** dimension is irrelevant because of the assumption of an infinite source, use of an area term was chosen to minimize confusion.

- MADEP has chosen to prohibit use of these graphs for an evaluation of subsurface saturated zone transport over a distance (x) of less than 100 feet, in recognition of the modeling assumption of a homogeneous and isotropic aquifer. Specifically, the existence of preferred flow paths and/or small-scale heterogeneities could lead to situations where application of these graphs over such a short distance could result in a non-conservative conclusion.

Table 4-13: Recommended VPH/EPH Toxicological & Risk Assessment Parameters

Recommended values were those most recently proposed by MADEP in the development of revised MCP Method 1 standards (MADEP, 2001).

Table 4-14: Recommended VPH/EPH Fractional Properties for Modeling Purposes

The recommended values were calculated using the equations and compound-specific properties published by the TPH Criteria Working Group (Gustafson, J.B., et. al., 1997).

Section 5.2.2: Converting TPH Data into EPH Fractional Ranges

The assumptions on the percentages of aliphatic and aromatic hydrocarbons in common products contained in Table 5-1 of the Final Policy are based upon the information and data published by the TPH Criteria Working Group for "fresh" petroleum Potter and Simmons, 1998). Professional judgement was then used to provide a conservative estimate of "weathering" impacts, where the aliphatic fraction degrades prior to the aromatic fraction (i.e., the weathered materials become more "enriched" in their aromatic content).

Assumptions on the composition of “fresh” Mineral Oil Dielectric Fluids was taken from a publication of the Electric Power Research Institute (EPRI, 1996).

Section 5.4.1: Numerical Ranking System (NRS)

The criteria and scores for the Hydrocarbon Ranges in Table 5-2 of the Final Policy were developed using the method specified in 40.1514(4) of the MCP, using fate and transport properties developed per the procedures and criteria recommended by the TPH Criteria Working Group (Gustafson, J.B., et. al., 1997).

Section 5.4.3: Characterization of Remedial Air Emissions

MADEP has previously published guidance on how to evaluate point-source remedial air emissions (MADEP, May, 1994). In this policy, a series of emission-distance graphs have been provided to evaluate groups of common contaminants. In total, 4 contaminant-specific groupings were established, based upon the commonality of contaminant properties (Casey and Fitzgerald, 1992). Each emission-distance graph was designed to ensure that no group contaminant is likely to be present in the ambient air at a given distance in excess of (a) threshold health effects levels, (b) non-threshold health effects levels, or (c) odor thresholds (i.e., whatever is lower). As this policy pre-dated the VPH/EPH approach, there are no recommendations provided for hydrocarbon ranges.

At present, MADEP does not consider any of the hydrocarbon ranges to pose non-threshold (i.e., carcinogenic) health effects. While it is not possible to establish an “odor threshold” for an aliphatic or aromatic hydrocarbon range, it is possible to associate each fraction with one of the existing groupings based upon its Reference Concentration (an inhalation threshold effects level).

Below is the basis of the contaminant groupings in the 1994 policy:

Category of Air Contaminant	Emission Graph protective of contaminants with Ambient Air Action Level of
Group 1	< 13 μg/m3
Group 2	13 μg/ m3 - 32 μg/m3
Group 3	33 μg/m3 - 118 μg/m3
Group 4	> 118 μg/m3

Below are the recommended inhalation toxicity values (Reference Dose or RfD) for the fractions of interest:

Hydrocarbon Range	RfD (μg/m3)
C5-C8 Aliphatic Hydrocarbons	200
C9-C12 Aliphatic Hydrocarbons	2000
C9-C18 Aliphatic Hydrocarbons	2000
C9-C10 Aromatic Hydrocarbons	60

Based upon the above tabulations, it can be seen that C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C18 Aliphatic Hydrocarbons possess toxicity values within the range of “Group 4” contaminants, and C9-C10 Aromatic Hydrocarbons posses a toxicity value within the range of “Group 3” contaminants. Note that the C19-C36 Aliphatic Hydrocarbons and C11-C22 Aromatic Hydrocarbons were not evaluated, since they are not likely to be volatile enough to be present in remedial air emissions.

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Appendix 1 –Soil Headspace Partitioning

OBJECTIVE: Using the Fugacity Approach developed by Mackay and Patterson (1981), determine the concentration of benzene in soil for a sample yielding 100 pmmV headspace vapors via the MADEP Jar Headspace procedure

Assumptions

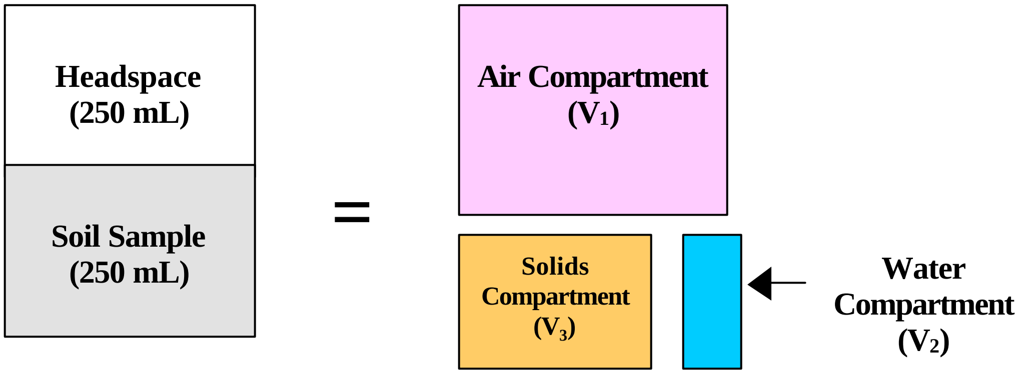
SOIL

- soil particle density =2.65 g/cm3
- soil porosity = 0.3 cm3/cm3
- volumetric soil moisture content = 10%
- soil organic carbon content (oc) = 0.005

HEADSPACE/PID UNIT

- Headspace Development Temperature = 20°C
- assume 50% of equilibrium headspace conditions were achieved during the jar headspace development period (Fitzgerald, 1989)
- assume the jar headspace reading by the FID/PID unit represents 50% of the true jar headspace reading of benzene (Fitzgerald, 1989)
- assume soil is filled exactly half way in a 500 mL (approx 16 oz) sampling jar

STEP 1 - Determine Volumes of 3 Compartments of Interest:



(A) Volume of Solids Compartment (f_3)

250 mL x 0.3 = 75 mL = volume of void spaces in soil sample

250 mL - 75 mL = 175 mL = 175 cm3 = volume of soil solids

175 cm3 x $\frac{1\text{ m3}}{10^{6}\text{ cm3}}$ = 1.75 x 10-4 m3 = volume of soil solids compartment = V_3

(B) Volume of Water Compartment (f_2)

250 mL x 0.1 = 25 mL = 25 cm3 = volume of water in soil sample

25 cm3 x $\frac{1 \text{ m3}}{10^{6} \text{ cm3}}$ = 2.5 x 10-5 m3 = volume of soil water compartment = V_2

(C) Volume of Air Compartment (f_1)

volume of void spaces in soil sample = (250)(0.3) = 75 mL
volume of water in soil sample = (250)(0.1) = 25 mL
Thus, volume of air-filled pore spaces = 75mL - 25 mL = 50 mL

250 mL (headspace volume) + 50 mL (pore air volume) = 300 mL = 300 cm 3 = total volume of air

300 cm3 x $\frac{1 \text{ m3}}{10^{6} \text{ cm3}}$ = 3.0 x 10-4 m3 = volume of air compartment = V_1

Step 2 - Determine Fugacity Capacity of Compartments

Z_1 = 1/RT = 1/(8.21 x 10-5)(293) = 41.5 mol/atm-m3

Z_2 = 1/H = 1/5.6 x 10-3 = 179 mol/atm=m3

Z_3 = (ρ Kd)/H

Kd = (Koc)(oc) = (83)(0.005) = 0.415 mL/g

Z_3 = (1.58)(0.415)/5.6 x 10-3 = 117 mol/atm-m3

Σ(ViZi) = V_1Z_1 + V_2Z_2 + V_3Z_3

= (3 x 10-4)(41.5) + (2.5 x 10-5)(179) + 1.75 x 10-4)(117)

= 3.74 x 10-2 atm/mol

Step 3 - Determine Mole Fraction Distribution Among Compartments

M_1/M = Soil Air Fraction = V_1Z_1/Σ(ViZi) = (3 x 10-4)(41.5)/3.74 x 10-2 = 0.33 = 33% in air compartment
M_2/M = Soil Water Fraction = V_2Z_2/Σ(ViZi) = (2.5 x 10-5)(179)/3.74 x 10-2 = 0.12 = 12% in soil water compartment
M_3/M = Soil Solids Fraction = V_3Z_3/Σ(ViZi) = (1.75 x 10-4)(117)/3.74 x 10-2 = 0.55 = 55% in soil solids compartment

Step 4 - Determine Concentration Distributions Among Compartments

100 ppmv headspace = 100,000 ppbv headspace

ug/m3 = (ppbv)(MW)/24.45 = (100,000)(78)/24.45 = 319,000 = headspace conc = conc in air compartment

(319,000)(3 x 10-4) = 96 ug = total mass of benzene in air compartment

96 ug x 1 mg/1000 ug x 1 g/1000 mg = 9.6 x 10-5 g = total mass of benzene in air compartment

9.6 x 10-5 g x $\frac{1 \text{ mole benzene}}{78 \text{ g benzene}}$ = 1.2 x 10-6 moles benzene in air compartment moles benzene in soil solids = (1.2 x 10-6) x $\frac{55\%}{33\%}$ = 2.0 x 10-6

moles benzene in soil water = (1.2 x 10-6) x $\frac{12\%}{33\%}$ = 4.4 x 10-7

grams benzene in soil solids = 2.0 x 10-6 mol x $\frac{\text{78 g benzene}}{\text{1 mol benzene}}$ = 1.6 x 10-4 g

1.6 x 10-4 g x $\frac{\text{1000 mg}}{\text{1 g}}$ x $\frac{\text{1000 ug}}{\text{1 mg}}$ = 160 ug benzene is soil solids

grams benzene in soil water = 4.4 x 10-7 mol x $\frac{\text{78 g benzene}}{\text{1 mol benzene}}$ = 3.4 x 10-5 g

3.4 x 10-5 g x $\frac{\text{1000 mg}}{\text{1 g}}$ x $\frac{\text{1000 ug}}{\text{1 mg}}$ = 30 ug benzene is soil solids

TOTAL MASS BENZENE IN SOIL SAMPLE = mass in solid compartment + mass in soil water compartment

= 160 + 30 = 190 ug

CONCENTRATION IN SOIL SAMPLE = mass benzene in soil sample/mass soil sample

mass soil sample = (2.65 g/cm3)(175 cm3) = 464 grams

concentration = 190 ug/464 g = 0.41 ug/g

- ASSUMING HEADSPACE READING = 50% EQUILBRIUM CONDITIONS

Soil Concentration = (0.04)(2) = 0.82 ug/g

- ASSUMING JAR HEADSPACE PROCEDURE YIELDS 50% OF TRUE HEADSPACE CONCENTRATION

Soil Concentration = (0.82)(2) = 1.64 ug/g

Thus, 100 ppmV jar headspace benzene equates to an approximately 2 ug/g bulk soil benzene concentration, indicating a 1-2 order of magnitude partitioning relationship between gasoline in soil and gasoline in a jar headspace

Appendix 2 –Maximum Concentrations of Lead in Soils from Releases of Leaded Gasoline

Assumptions:

SOIL

- soil particle density =2.65 g/cm3
- soil porosity = 0.3 cm3/cm3
- volumetric soil moisture content = 0% (i.e., all pore spaces filled with gasoline)

GASOLINE

- lead conc. in gasoline product = 4.3 grams/gallon (peak allowable level; 1959, per Gibbs, 1990)
- density of gasoline = 6.5 pounds/gallon (API, 1993)

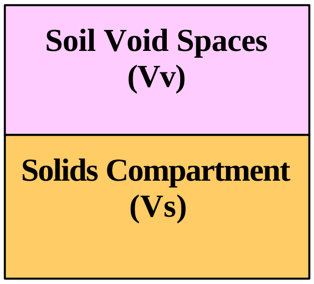
PARTITIONING

- Assume 100% of lead from NAPL sorbs onto soil solids

CALCULATIONS

6.5 pounds/gal gasoline X 454 grams/pound = 2951 grams gasoline/gallon

4.3 grams lead/2951 grams gasoline = 0.0015 (0.15%) = level of lead in gasoline



Assume 1 cm^3 soil block

@ 0.3 porosity, Vv = 0.3 cm3 and Vs = 0.7 cm^3

mass of soil solids = [Vs] [2.65 g/ cm^3] = 1.86 g = 0.00186 kg

0.3 cm^3 X 6.5 lb/gal X 1 gal/3785 cm^3 X 454 g/lb = 0.23 g = mass of gasoline in pore space (assuming worst case condition of 0% moisture)

0.23 g X 0.0015 = 0.00035g X 1000 mg/g = 0.35 mg = mass of lead in gasoline in pore space

[0.35 mg lead] / [0.00186 kg soil] = 188 mg/kg lead concentration in soil

Thus, up to 200 ug/g lead possible in soil in contact with leaded gasoline NAPL. Continued releases of new NAPL over a number of years could “enrich” soil with additional lead, approaching and/or exceeding the MCP Method 1 S-1 Cleanup standard of 300 ug/g.

Appendix 3 - Johnson and Ettinger SG-Screen Model, Version 1.0 (USEPA, 2000)
Contaminant: Ethylbenzene (at presumed soil gas level of 10 ppmV)

Source-building separation, L_T (cm)	Vadose zone soil air-filled porosity, θ_a^V (cm^3/cm^3)	Vadose zone effective total fluid saturation, S_{te} (cm^3/cm^3)	Vadose zone soil intrinsic permeability, k_i (cm^2)	Vadose zone soil relative air permeability, k_{rg} (cm^2)	Vadose zone soil effective vapor permeability, k_v (cm^2)	Floor-wall seam perimeter, X_{crack} (cm)	Soil gas conc. ($\mu g/m^3$)	Bldg. ventilation rate, $Q_{building}$ (cm^3/s)
10	0.370	0.019	9.92E-08	0.987	9.79E-08	3,844	4.57E+04	5.63E+04

Area of enclosed space below grade, A_B (cm^2)	Crack-to-total area ratio, η (unitless)	Crack depth below grade, Z_{crack} (cm)	Enthalpy of vaporization at ave. soil temperature, $\Delta H_{v,TS}$ (cal/mol)	Henry's law constant at ave. soil temperature, H_{TS} ($atm\text{-}m^3/mol$)	Henry's law constant at ave. soil temperature, H'_{TS} (unitless)	Vapor viscosity at ave. soil temperature, μ_{TS} (g/cm-s)	Vadose zone effective diffusion coefficient, D^{eff}_V (cm^2/s)	Diffusion path length, L_d (cm)
1.69E+06	2.27E-04	200	10,155	3.18E-03	1.37E-01	1.75E-04	1.48E-02	10

Convection path length, L_p (cm)	Source vapor conc., C_{source} ($\mu g/m^3$)	Crack radius, r_{crack} (cm)	Average vapor flow rate into bldg., Q_{soil} (cm^3/s)	Crack effective diffusion coefficient, D^{crack} (cm^2/s)	Area of crack, A_{crack} (cm^2)	Exponent of equivalent foundation Peclet number, $\exp(Pe^f)$ (unitless)	Infinite source indoor attenuation coefficient, α (unitless)	Infinite source bldg. conc., $C_{building}$ ($\mu g/m^3$)
200	4.57E+04	0.10	6.50E+01	1.48E-02	3.84E+02	3.35E+74	1.12E-03	5.14E+01

Appendix 3 - Johnson and Ettinger SG-Screen Model, Version 1.0 (USEPA, 2000)
Contaminant: Toluene (at presumed soil gas level of 10 ppmV)

Source-building separation, L_T (cm)	Vadose zone soil air-filled porosity, θ_a^V (cm^3/cm^3)	Vadose zone effective total fluid saturation, S_{te} (cm^3/cm^3)	Vadose zone soil intrinsic permeability, k_i (cm^2)	Vadose zone soil relative air permeability, k_{rg} (cm^2)	Vadose zone soil effective vapor permeability, k_v (cm^2)	Floor-wall seam perimeter, X_{crack} (cm)	Soil gas conc. (µg/m^3)	Bldg. ventilation rate, $Q_{building}$ (cm^3/s)
10	0.370	0.019	9.92E-08	0.987	9.79E-08	3,844	3.97E+04	5.63E+04

Area of enclosed space below grade, A_B (cm^2)	Crack-to-total area ratio, η (unitless)	Crack depth below grade, Z_{crack} (cm)	Enthalpy of vaporization at ave. soil temperature, $\Delta H_{v,TS}$ (cal/mol)	Henry's law constant at ave. soil temperature, H_{TS} (atm-m^3/mol)	Henry's law constant at ave. soil temperature, H'_{TS} (unitless)	Vapor viscosity at ave. soil temperature, μ_{TS} (g/cm-s)	Vadose zone effective diffusion coefficient, D^{eff}_V (cm^2/s)	Diffusion path length, L_d (cm)
1.69E+06	2.27E-04	200	9,154	2.92E-03	1.26E-01	1.75E-04	1.72E-02	10

Convection path length, L_p (cm)	Source vapor conc., C_{source} (µg/m^3)	Crack radius, r_{crack} (cm)	Average vapor flow rate into bldg., Q_{soil} (cm^3/s)	Crack effective diffusion coefficient, D^{crack} (cm^2/s)	Area of crack, A_{crack} (cm^2)	Exponent of equivalent foundation Peclet number, $\exp(Pe^f)$ (unitless)	Infinite source indoor attenuation coefficient, α (unitless)	Infinite source bldg. conc., $C_{building}$ (µg/m^3)
200	3.97E+04	0.10	6.50E+01	1.72E-02	3.84E+02	1.76E+64	1.13E-03	4.48E+01

Appendix 3 - Johnson and Ettinger SG-Screen Model, Version 1.0 (USEPA, 2000)
Contaminant: Total Xylenes (at presumed soil gas level of 10 ppmV)

Source-building separation, L_T (cm)	Vadose zone soil air-filled porosity, θ_a^V (cm^3/cm^3)	Vadose zone effective total fluid saturation, S_{te} (cm^3/cm^3)	Vadose zone soil intrinsic permeability, k_i (cm^2)	Vadose zone soil relative air permeability, k_{rg} (cm^2)	Vadose zone soil effective vapor permeability, k_v (cm^2)	Floor-wall seam perimeter, X_{crack} (cm)	Soil gas conc. ($\mu g/m^3$)	Bldg. ventilation rate, $Q_{building}$ (cm^3/s)
10	0.370	0.019	9.92E-08	0.987	9.79E-08	3,844	1.68E+05	5.63E+04

Area of enclosed space below grade, A_B (cm^2)	Crack-to-total area ratio, η (unitless)	Crack depth below grade, Z_{crack} (cm)	Enthalpy of vaporization at ave. soil temperature, $\Delta H_{v,TS}$ (cal/mol)	Henry's law constant at ave. soil temperature, H_{TS} ($atm\text{-}m^3/mol$)	Henry's law constant at ave. soil temperature, H'_{TS} (unitless)	Vapor viscosity at ave. soil temperature, μ_{TS} (g/cm-s)	Vadose zone effective diffusion coefficient, D^{eff}_V (cm^2/s)	Diffusion path length, L_d (cm)
1.69E+06	2.27E-04	200	22,944	1.22E-06	5.26E-05	1.75E-04	2.64E-03	10

Convection path length, L_p (cm)	Source vapor conc., C_{source} ($\mu g/m^3$)	Crack radius, r_{crack} (cm)	Average vapor flow rate into bldg., Q_{soil} (cm^3/s)	Crack effective diffusion coefficient, D^{crack} (cm^2/s)	Area of crack, A_{crack} (cm^2)	Exponent of equivalent foundation Peclet number, $\exp(Pe^f)$ (unitless)	Infinite source indoor attenuation coefficient, α (unitless)	Infinite source bldg. conc., $C_{building}$ ($\mu g/m^3$)
200	1.68E+05	0.10	6.50E+01	2.64E-03	3.84E+02	#NUM!	1.01E-03	1.69E+02

Appendix 4

Estimating Background Concentrations of Hydrocarbons in the Indoor Air of Homes with Oil Heat

February 1997

A limited investigation was undertaken by the Massachusetts Department of Environmental Protection (MADEP) to gain insight into background concentrations of hydrocarbons present in the basement of residential homes containing a free-standing fuel oil tank and oil combustion furnace. Conservative assumptions were used to differentiate aliphatic from aromatic hydrocarbons, and derive upper-limit background concentrations for the hydrocarbon ranges detected using the MADEP VPH/EPH approach.

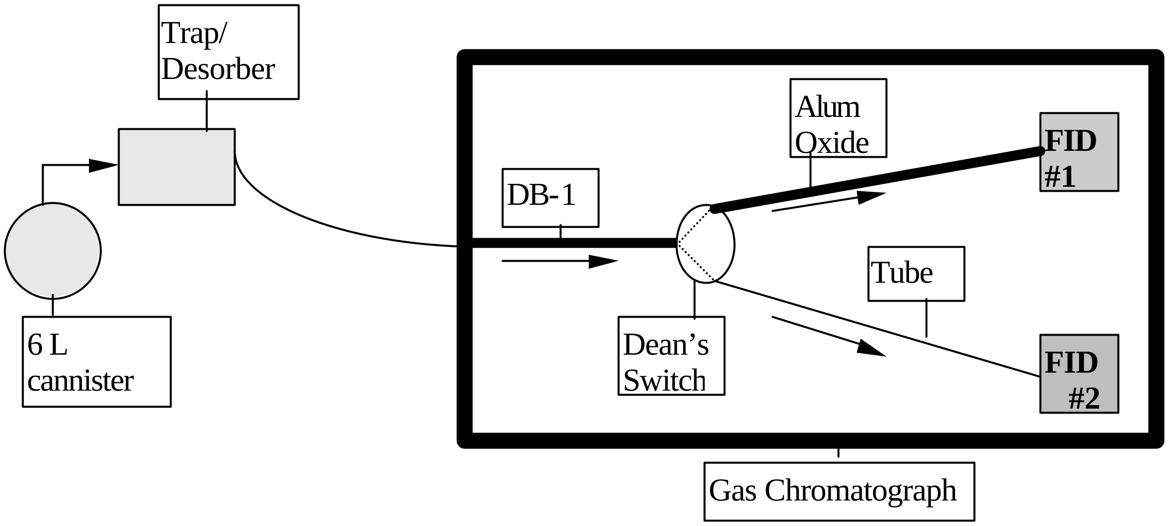
Sample Collection

In February 1997, indoor air samples were obtained from the basements of 5 DEP employees. A 275 gallon free-standing oil tank was present in each (open and unfinished) basement. Time-weighted air samples were obtained in 6-liter evacuated stainless-steel canisters with mechanical regulators, per EPA Method TO-14. Air samples were obtained within the breathing zone, at least 10 feet from the oil tank and/or furnace. Small quantities of paint, stain, gasoline, and other typical household chemical/cleaning products were present to some degree in all basements sampled.

Sample Analyses

Samples were analyzed at the DEP Wall Experiment Station using a dual-column GC/FID procedure employing a "Deans Switch" technique, as detailed in Figure 1.

Figure 1: Instrument Setup



In this procedure, a 6 Liter canister is overpressurized with an inert gas, and a 600 mL sample is metered onto a trap. Subsequently, the trap is rapidly heated to desorb the sample and direct it into a gas chromatograph, where it travels through a (DB-1) non-polar chromatographic column, through a (Dean's) switch, onto a second aluminum oxide chromatographic column, and finally into FID #1. After about 12 minutes, the switch is automatically activated, and the flow out of the DB-1 column is re-directed to an uncoated column (hollow tube), and into FID #2.

In this manner, light hydrocarbons (<C6) elute from the DB-1 column quickly, and then travel more slowly through the aluminum oxide column, allowing for greater chromatographic separation of these analytes on FID #1. After activation of the switch, flow from the DB-1 column is routed directly to FID #2, and additional flow to the aluminum oxide column is terminated (although compounds through C5 continue to elute from this column into FID #1 for some time). The run is terminated after about 48 minutes, eluting through C11 hydrocarbons.

Estimating Aliphatic/Aromatic Split

All of the compounds detected by FID #1 will be <C6, and, since the smallest aromatic compound has 6 carbons (benzene), all of these compounds are aliphatic. Compounds eluting on FID #2 will be a mixture of aliphatic/aromatic hydrocarbons in the C6-C11+ range. A 56-component standard mixture is used to calibrate the GC, comprised of both aliphatic and aromatic analytes, including BTEX. Since the BTEX peaks are individually identified and quantitated, all unknown compounds less than C8 are assumed to be aliphatics. Between C8 and C11, individual component standard peaks are identified and quantitated as either aliphatic or aromatic, and the rest of the peaks are then assumed to be 50% aromatic and 50% aliphatic.

Quantitation/Reporting of Range Concentrations

Reported results are in ppb-carbon (ppbc), a technique used in air analyses to normalize FID response to allow comparison over a broad range of hydrocarbons. Specifically, while an FID will respond relatively uniformly to all hydrocarbons on a molar basis, it is necessary to provide a common quantitation benchmark when analyzing a range of compounds, since one mole of a C3 hydrocarbon will weigh considerably less than 1 mole of a C10 hydrocarbon (that is, for the same mass of analytes, the FID response will be much greater for the lighter hydrocarbons, since it will have more atoms).

The conversion is:

$$\text{ppbc} = (\text{ppbv})(\#\ \text{carbons})$$

Thus, 100 ppbc of propane will result in the same chromatographic response (peak area) as 100 ppbc of nonane, even though the ppbv (and ug/m3) concentration for nonane will be less than the ppbv (and ug/m3) concentration of propane.

Results

The results are presented in Table 1.

Table 1 - Reported Concentrations of Hydrocarbons in Sampled Homes

Location	TNMHC* (ppbc)	Estimated total Aliphatic (ppbc)	Estimated total Aromatics (ppbc)	Notes
Methuen #1	358	219	139	
Methuen #2	410	248	162	Duplicate
Saugus	1094	353	234	Natural gas likely present
Reading	1213	781	432	Gasoline likely present
North Reading	160	96	63	
West Newbury	208	103	106	

* TNMHC = Total non-methane hydrocarbons

To further refine the data, and convert it into ranges more consistent with the VPH/EPH approach, individual chromatograms and data report sheets were examined. Hydrocarbons lighter than C5 were eliminated, and hydrocarbons greater than C5 were apportioned into aliphatic and aromatic fraction, as presented in Table 2.

Discussion

Key assumptions/limitations

The following assumptions and limitation are integral to this study/analysis:

- The chromatographic runs were terminated at 48 minutes, although peaks were only integrated to about 45 minutes; a point approximately mid-way between n-C11 and n-C12. It is noted that small peaks were still eluting after C12. It is assumed that naphthalene (C11) elutes near n-C12, and thus the aromatics eluting during these runs were all C9-C10.

- Although it was not possible to differentiate all aliphatics from aromatic hydrocarbons, it was possible to definitively establish C5-C8 Aliphatics (since all compounds not BTEX would be aliphatics). In the C9-C11(+) range, the concentration of aliphatic and aromatic “Target Compounds” (i.e., those compounds contained in the calibration standard, and therefore identified and quantitated by the GC/FID) were collectively summed, and the remaining unknown hydrocarbons were assumed to be 50% aliphatic and 50% aromatic. This is believed to be a suitably conservative, though not “worst case” assumption.

Data Analysis and Interpretation

The following observations and conclusions are noted:

- A can of gasoline was being stored in the basement of the Reading home, and there is evidence of significant concentrations of gasoline vapors in the air sample. Specifically, the BTEX compounds were higher than in any other home, and on the high side of typical “background” ranges. Moreover,

Table 2 - Actual and Estimated Breakdown of Indoor Air Data

	Methuen #1	Methuen #2[b]	Saugus	Reading	North Reading	West Newbury
Dilution Factor[a]	2.0	2.2	2.5	2.25	1.5	2.15
C5-C6 Aliphatics (ppbc)	36	35	44	127	13	9
C6-C8 Aliphatics (ppbc)	58	61	96	202	18	19
C5-C8 Aliphatics (ppbc)	94	96	140	330	31	28
C9-C11+ Total Hydrocarbons (ppbc)	145	196	282	486	48	102
C9-C11 Target Aliphatics (ppbc)	27	30	71	118	7	12
C9-C11 Target Aromatics (ppbc)	47	50	63	136	17	35
Remaining C9-C11+ Hydrocarbons (ppbc)	71	115	147	232	25	55
% of unknown C9-C11+ Hydrocarbons	49%	59%	52%	48%	52%	54%
Estimated C9-C11+ Aliphatics[c] (ppbc)	63	88	145	234	19	39
Estimated C9-C10+ Aromatics[c] (ppbc)	83	108	137	253	29	63
n-C9 (ppbc)	5.2	5.7	16.5	43.4	0.8	4.5
n-C10 (ppbc)	11.2	9.2	25.3	43.7	2.0	4.5
n-C11 (ppbc)	11.0	15.6	29.5	30.4	3.9	2.6
C9+C10+C11	27.4	30.5	71.3	117.5	6.7	11.6
C9+C10+C11 C9-C11+ Hydrocarbons	18.9%	15.6%	25.3%	24.1%	14%	11.3%
benzene (ppbc)	5.12	4.84	5.85	17.9	2.88	2.97
toluene (ppbc)	23.5	21.9	56.5	67.4	22.1	21.6
ethylbenzene (ppbc)	3.90	3.81	4.43	9.79	1.25	2.15
xylenes (ppbc)	21.2	21.1	26.2	71.3	6.62	12.9
n-octane (ppbc)	2.70	2.73	4.28	6.23	0.75	1.27
n-nonane (ppbc)	5.20	5.74	16.4	43.5	0.81	4.49
1,3,5-TMB (ppbc)	4.58	3.94	7.52	17.0	0.90	2.19
n-decane (ppbc)	11.1	9.17	25.3	43.7	1.95	4.62
1,4-diethylbenzene (ppbc)	4.16	5.96	3.45	7.90	1.50	3.55

Notes:

(a) Dilution Factor = Pressure of canister after pressurization/initial pressure of canister (absolute pressures)

(b) Methuen #1 and #2 are sample duplicates

(c) Remaining hydrocarbons assumed to be 50% aliphatic and 50% aromatic there were elevated concentrations of light (<C6) hydrocarbons in this sample range, in numerous peaks consistent with a gasoline mixture

- All chromatograms have the signature chromatographic “grass” in the C9-C11 range, indicating the presence of numerous compounds typically associated with a complex mixture like petroleum (as opposed to large, well-defined peaks of individual compounds). Given the predominance of normal alkanes in fresh #2 fuel oil, one would expect to see significant and well-defined peaks for n-C9, n-C10, and n-C11, if a significant portion of background was being contributed by this source. The Saugus home appeared to have the most pronounced presence of #2 fuel oil, as indicated by the relatively high percentage of n-nonane (C9), n-decane (C10), and n-undecane (C11), relative to the total concentration of all C9-C11+ hydrocarbons. Although the Reading home had a similar high percentage, it is noted that the high concentration of n-C9 (relative to n-C10 and n-C11) may be indicative of the presence of gasoline vapors mixed in with the #2 fuel oil “background”.

- At lower “background” concentrations, the influence of #2 fuel oil seems to diminish somewhat, as evidenced by the lower relative percentages of n-C9, n-C10, and n-C11 compounds in the North Reading and West Newbury homes. At these lower levels, gasoline, paints, paint thinners, and other household products may comprise a higher percentage of background hydrocarbon concentrations

Representativeness of Sampled Homes/Study

Given the limited nature of this study, and the variations that may be expected in “background” concentrations of indoor air contaminants, the results of this study cannot be considered conclusive. However, some insight into the representativeness of study data can perhaps be discerned by comparing the concentrations of well-studied “benchmark” compounds with values and ranges reported in national databases.

Based upon data available from the National Ambient Volatile Organics (VOCs) Database[1], a comparison of key aliphatic and aromatic compounds throughout the ranges of interest is presented in Table 3.

Table 3 - Comparison of Study Data to National VOC Database

Compound	National VOC Database for Indoor Air			Range in Study (ppbc)	Range in Study (ug/m3)*	Range in Study excluding Reading data (ug/m3)
	# data points in database	Median conc (ug/m3)	75% conc (ug/m3)			
benzene	2128	10.03	21.06	2.9-18	1.5-9.6	1.5-3.1
ethylbenzene	2278	4.8	9.63	1.3-10	0.7-5.5	2.1-2.5
total xylenes	2216	4.8	9.3	6.6-71	3.6-39	3.6-14
octane	605	2.4	4.3	0.8-6	0.5-3.5	0.5-2.4
1,3,5-TMB	178	1.43	5.41	0.9-17	0.5-9.3	0.5-4.1
Nonane	134	3.67	6.29	0.8-44	0.5-26	0.5-9.8
1,4-diethylbenzene	2305	17.07	31.61	1.5-8	0.8-4.4	0.8-3.3
decane	710	1.63	4.07	2-44	1.2-26	1.2-15

Note: ug/m3 = [(ppbc/#carbons)(MW)]/24.45

Except for the Reading home, all sample data appear consistent with the national database. Since the Reading home appears to have been contaminated with significant concentration of gasoline vapors, it is not believed to be representative of a typical background condition. Excluding the Reading data, only xylenes, nonane, and decane concentrations are above the 75% percentile concentration in the next highest home (Saugus), and of these three compounds, only decane is significantly above the listed value. It is possible that homes with oil heat are not sufficiently represented in the national database, which may explain the relatively high concentrations of decane observed in this study.

Given these data, except for the Reading home, the concentration of well-studied hydrocarbons within the homes sampled are within expected ranges. Such a finding suggests that the concentrations and collective concentrations of less-studied hydrocarbons reported in this study are also likely to be within typical background ranges.

Heavier Hydrocarbons

Because this effort was limited to the quantitation of hydrocarbons in indoor air less than C12, an issue arises over the possible presence of heavier hydrocarbons in "background" indoor air, including PAH/aromatic compounds in the C11-C22 range.

Given that vapor pressures decrease with increasing molecular weight, the concentrations of heavier hydrocarbons compounds would also be expected to decrease with increasing molecular weight. However, at increasing molecular weights, hydrocarbons may be present and measured in both the vapor and/or particulate phases.

Limited information is available on background indoor-air concentrations of these heavier hydrocarbons. Available studies include the following:

- In a 1992 report prepared by the California Air Resource Board (CARB)[2], PAH concentrations were measured within the indoor air of 125 residential dwellings in Riverside, California. Based upon this study, the 90th percentile (combined) vapor and particulate phase concentrations of the 17 Hazardous Substance List (HSL) PAH compounds were well below 1 ug/m3. However, it is reasonable to speculate that most homes in this study did not have oil storage or furnace systems, and it is noted that no detectable concentrations of naphthalene or 2-methylnaphthalene were reported.

- In a 1991 study conducted by the US EPA[3], indoor air concentrations of PAHs were measured in 33 homes in Azuza, California and Columbus, Ohio. Once again, the combined concentrations of all 17 HSL PAH compounds were well below 1 ug/m3, even for homes with smokers, gas heat, and gas stoves.

- In a 1995 study funded by MADEP[4], indoor air concentrations of PAHs and other Tentatively Identified Compounds (TICs) were determined for 3 homes in Braintree, Massachusetts. All homes had oil tanks and furnaces in the basement. Although this study was undertaken to determine if waste oil contamination beneath the homes was adversely impacting indoor air quality, the data obtained suggested that all detected compounds were unrelated to environmental (site) contaminants. The results of this effort documented levels of naphthalene in basement air up to 19 ug/m3 (above the 5 ug/m3 typically cited as background by MADEP), and combined levels of all remaining HSL PAHs once again well below 1 ug/m3. TIC data reported on 7 compounds heavier than C11 that were found in the basements or first floors of the 3 sampled homes, at collective concentrations of N.D. to 80 ug/m3. These TIC compounds included various isomers of Trimethyl Decane, Dodecane, and various unknown C12 hydrocarbons.

- The National VOC Database provides information on two compounds in this range: Dodecane (n-C12), with a 75 percentile concentration of 2.30 ug/m3, and Hexadecane (n-C16), with a 75 percentile concentration of 5.55 ug/m3.

Based upon these findings, other than naphthalene, significant concentrations of HSL PAHs are likely not present in most homes. Nevertheless, significant concentrations of other heavier (>C11) hydrocarbons may be present within the indoor air as a "background" condition. The concentrations of these hydrocarbons, however, and whether they are present in the vapor or particulate phase, is difficult to discern.

Uncertainty

Beyond the uncertainty inherent in a small data set, additional uncertainty is introduced when making assumptions on the proportions of aliphatic and aromatic hydrocarbons in the >C9 ranges.

As presented in Table 2, approximately 50% of hydrocarbons in the C9-C11+ range were not identified as aliphatic or aromatic (target) compounds, and were therefore assumed to be half aliphatic and half aromatic. Under a worst-case scenario, where all of the remaining compounds were 100% aliphatic or 100% aromatic, the estimated range concentrations of C9-C12 aromatics and C9-C10 aromatics could be higher or lower by a factor of 33%. Given all of the other uncertainties in estimating "typical" background indoor air concentrations, and limitations and uncertainties in analytical precision and accuracy, such a deviation is not considered to be excessive. Moreover, it would appear highly unlikely that such extremes would in fact exist in the homes evaluated.

Conclusions and Recommendations

Based upon this limited effort, it is concluded that, except for the Reading home, hydrocarbons detected within the sampled homes appear to be representative of "background" conditions. It is recommended that the data from the Saugus home be considered a suitable "upper limit" on indoor air background in homes with oil heat. (Note that although light hydrocarbons were present in this home at high concentrations, apparently due to the use of natural gas in a basement dryer, it did not affect the concentration of hydrocarbons >C5).

In order to provide a conservative accounting of hydrocarbons eluting after the termination of the analytical runs, and up to C12, it is recommended that the values estimated for >C9 hydrocarbon ranges be increased by 10%. This is based upon an evalution of the chromatograms. (Note that even though integration of peaks was terminated between C11 and C12, peak elutions are still recorded on the chromatogram to just beyond C12).

To estimate heavier hydrocarbon concentrations beyond C12, it is recommended that the C9-C12 value be increased by 10 ug/m3, based upon the data from the National VOC database, and limited data from the Braintree homes.

These recommended values and calculations are tabulated in Table 4.

Table 4 - Recommended Conservative Upper Limit Background Concentrations

Range	Saugus house (ppbc)	upper limit background (ppbc)	EC	EC MW	upper limit background concentration (ppbv)	upper limit background concentration (ug/m3)
C5-C8 Aliphatics	140	140	6.5	93	22	85
C9-C12 Aliphatics	145	160	10.5	149	15	90
C9-C10 Aromatics	137	150	9.5	120	16	80
C9-C18 Aliphatics	N/A					100

Note:

EC = Equivalent Carbon number (average carbon number for range)[5]
EC MW = Molecular Weight for Equivalent Carbon Number

ug/m3 = [(ppbc/EC)(MW)]/24.45

Based upon these values, a recommended conservative upper limit "TPH" value would be 200 ug/m3.

REFERENCES FOR APPENDIX 4

[1] USEPA, *National Ambient Volatile Organic Compound (VOCs) Database Update*, EPA/600/3-88/010(a), 1988

[2] Air Resources Board, California Environmental Protection Agency Air Resources Board Research Division,. *PTEAM: Monitoring of Phthalates and PAHs in Indoor and Outdoor Air Samples in Riverside, CA*. Final Report (1992)

[3] United States Environmental Protection Agency Research and Development, *Radon Reduction Methods*, OPA-86-005 (1991).

[4] Environmental Health and Engineering, Inc., *Indoor/Outdoor Ambient Air Testing for Polynuclear Aromatic Hydrocarbons at the Braintree Pearl Street Site*, DEP Site No. 3-0261 (1995)

[5] Total Petroleum Hydrocarbon Criteria Working Group, Volume 3, *Selection of Representative TPH Fractions Based on Fate and Transport Considerations*, (1997)

Appendix 5

BASIS FOR DERIVATION OF THE METHOD-2 GW-3 DILUTION FACTORS FIGURE 4-4 VPH/EPH IMPLEMENTATION GUIDANCE DOCUMENT.

NIHAR MOHANTY, MADEP

SUMMARY

In this paper, generalized groundwater transport Dilution Factors are developed for typical site conditions in Massachusetts using a conservative scenario. The Domenico & Robbins simplified 3-dimensional analytical groundwater transport model is used to derive a family of curves for three different source configurations under steady-state conditions. The use of these curves is illustrated by an example. Site conditions where the derived Dilution Curves may not be applicable are also identified.

BACKGROUND AND OBJECTIVE

The MCP Method 1 GW-3 groundwater standards were derived by assuming that a disposal site is located upgradient from a surface water body and that groundwater from the disposal site will eventually reach and discharge into the surface water body. A Dilution and Attenuation Factor (DAF) was then designated for each Method 1 standard, as a conservative estimate of contaminant attenuation via (1) subsurface transport to, and (2) dilution in, the surface water body. For most contaminants, a 10-fold dilution condition is assumed (DAF = 10). The Method 1 GW-3 standards were then simply calculated as the Dilution Factor multiplied by the acceptable ambient water concentration of the contaminants of concern.

Using a Method 2 Risk Characterization process, a Method 1 GW-3 standard can be modified by justifying a different site-specific Dilution and Attenuation Factor. The objective of this evaluation is to develop a means for parties to quickly and easily justify a conservative groundwater transport Dilution Factor for a disposal site, based upon the size and configuration of the contaminated soil “source area”, and distance to the nearest downgradient surface water body, using the Domenico and Robbins transport model, and a series of conservative assumptions on site hydrogeological conditions. This effort is limited to dilution that occurs via groundwater transport only, and does NOT consider additional dilution effects that may be present at a site due to the flowrate and/or volume of the receiving surface water body.

THE DOMENICO & ROBBINS MODEL

The mass balance equation (commonly called the dispersion-convection equation) governing the transport of an ideal non-reactive conservative solute by a homogeneous fluid flow through saturated porous medium is given by:

$$\frac{\partial C}{\partial t} + \mathrm{v}\frac{\partial C}{\partial \mathrm{x}} - \mathrm{D}_{\mathrm{x}}\frac{\partial^2 C}{\partial \mathrm{x}^2} - \mathrm{D}_{\mathrm{y}}\frac{\partial^2 C}{\partial \mathrm{y}^2} - \mathrm{D}_{\mathrm{z}}\frac{\partial^2 C}{\partial \mathrm{z}^2} = 0 \qquad (1)$$

where:

C = the solute concentration,
v = seepage velocity
D_X, D_Y and D_Z = the principal values of the dispersion tensor, and
t = time.

Domenico and Robbins (1985(b)) used an extended pulse approximation to the continuous finite source problem. The source has constant dimensions in a transverse and a vertical direction with respect to the groundwater flow direction, and has infinite dimension in the groundwater flow direction. It describes a semi-infinite contaminated area that moves with a one-dimensional velocity in the positive x direction under uniform flow conditions. Contaminant concentrations at distances x, y, z from a source at time t may be estimated from equation 2 given below. The equation accounts for advection and dispersion only and does not account for biodegradation.

$$C(x, y, z, t) = \left(\frac{C_0}{8}\right) erfc\left[\frac{(x - vt)}{2\sqrt{a_x vt}}\right] \left\{ erf\left[\frac{y + \frac{Y}{2}}{2\sqrt{a_y x}}\right] - erf\left[\frac{y - \frac{Y}{2}}{2\sqrt{a_y x}}\right]\right\} * \left\{ erf\left[\frac{z + \frac{Z}{2}}{2\sqrt{a_z x}}\right] - erf\left[\frac{z - \frac{Z}{2}}{2\sqrt{a_z x}}\right]\right\} \qquad (2)$$

where:

x = distance of the point of compliance from the source in the direction of groundwater flow
y = distance transverse to the groundwater flow
z = distance vertical (in the direction of gravity) to the groundwater flow
v = groundwater velocity
Y = width of the source in a direction transverse to the groundwater flow
Z = Thickness of the source in a direction vertical to the groundwater flow
a_x = longitudinal dispersivity in the direction of flow
a_y = transverse dispersivity in the direction transverse to the flow
a_z = vertical dispersivity in the vertical direction to the flow
erf = error function
erfc = complementary error function

Equation (2) may be simplified for estimating contaminant concentrations along the plume center line (y =0) in the direction of groundwater flow (x) at the water table (z= 0). For a source at the water table, Z/2 is replaced by Z (Domenico and Robbins (1985(b)) in equation 2. Under steady-state conditions i.e., at receptor distances x << vt, the *erfc* term (second term) of equation 2 approaches 2. The simplified equation is given below:

$$C = C_0 \left\{ \mathrm{erf}\left(\frac{Y}{4\sqrt{a_y x}}\right)\right\} * \left\{ \mathrm{erf}\left(\frac{Z}{2\sqrt{a_z x}}\right)\right\} \qquad (3)$$

Under a steady-state condition, as seen from equation 3, contaminant concentrations at distances x from a source is solely a function of source geometry (width and thickness) and dispersivity (transverse and vertical). Note that to estimate contaminant concentrations using equation 3, the longitudinal dispersivity coefficient is not a variable and is not required directly. However, transverse dispersivity and vertical dispersivity are directly related to longitudinal dispersivity, and are usually expressed as a fraction of the longitudinal dispersivity value. Using equation 3, aquifer properties (e.g. organic carbon content of aquifer material, porosity, hydraulic conductivity, hydraulic gradient) and the partitioning coefficient of a contaminant do not affect predicted contaminant concentrations.

MODELING SCENARIO AND INPUT ASSUMPTIONS

A. Scenario and source

Common scenarios were evaluated for leaking underground storage tank (LUST) sites. At such sites, petroleum products leak from an underground storage tank and contaminate surrounding soils. It is not uncommon for non-aqueous phase liquids (NAPL) to exist at the water table interface, creating a “smear zone” as the groundwater elevation rises and falls. Contamination within this smear zone then acts as a continuing source of contamination of the groundwater.

A reasonably conservative “smear zone” for Massachusetts was assumed to be 6 feet, which was used as “source thickness” term (Z) for all modeling scenarios. Three scenarios were then evaluated with different combinations of length and width, as indicated below

10ft. (length) x 10ft.(width) x 6ft. (thick)	Residential USTs
30ft. x 30ft. x 6ft.	Commercial USTs at gas stations
60ft. x 60ft. x 6ft	Larger Commercial USTs

B. Dispersivity coefficients:

Once the source configuration parameters were established, it was necessary to designate dispersivity coefficients, which are the key input variables in equation 3, and controlling element in all models which seek to characterize contaminant transport solely on the basis of dispersion.

Dispersivity coefficients may be estimated by two approaches: theoretical derivation and empirical observation. Ideally, values derived by both means should be roughly comparable.

<u>Theoretical Derivation</u>

Dispersion in groundwater occurs as a consequence of two different processes: mechanical dispersion and molecular diffusion, as shown in equation 4. (Pickens and Grisak, 1981):

$$D_x = a_x v + D^* \qquad (4)$$

Where:

D_X = coefficient of hydrodynamic dispersion,
a_x = longitudinal dispersivity in the x-direction; and
D^* = coefficient of molecular diffusion.

Mechanical dispersion is caused by local variations in velocity, which in turn is caused by the non-idealities or heterogeneity of a medium. Some of the geological features contributing to heterogeneity of a medium are pore size distribution, non-uniform stratification, directional and non-uniform permeability, etc. Hydraulic conductivity is the most important variable contributing to the heterogeneity of a medium.

In a recent geo-statistical approach, longitudinal macro-dispersion, A^*_L is given by (Domenico, Swartz, 1998) as follows:

$$A^*_L = A_L + \alpha_L + \frac{D^*_d}{v} \qquad (5)$$

where

α_L = local scale (Sudicky, 1986), pore scale (Domenico and Schwartz, 1998), microscopic and column scale dispersion (Smith and Schwartz,1980). [Local scale dispersion is generally assumed to be insignificant (Gelhar and Axness, 1983).]

D_d^* = diffusion coefficient; is generally assumed to be negligible (Domenico and Schwartz, 1998), (Pickens and Grisak, 1981).

A_L = asymptotic longitudinal dispersivity (Gelhar and Axness, 1983) given by:

$$A_L = \frac{\sigma_Y^2 \lambda}{\gamma^2} \qquad (6)$$

where:

γ =1 (Dagan, 1982)

σ_Y^2 = variance of the log-transformed hydraulic conductivity ($Y = \ln K$)

λ = correlation length in the mean direction of flow.

In the same manner, A^*_T, transverse macro-dispersivity, is given by:

$$A^*_T = \alpha_T + \frac{D^*_d}{v} \qquad (7)$$

A similar derivation does not currently exist for vertical dispersivity.

From equation 6, the asymptotic longitudinal dispersivity, A_L is affected by the heterogeneity or variability of a medium. Spatial mean and variance of hydraulic conductivity and correlation lengths have been used to describe the heterogeneity of a medium. The correlation length is a measure of spatial persistence of zones of similar properties.

Empirical Observations and Scale Effects

Empirical data are available from laboratory experiments and a limited number of (well characterized) sites. A review of this data indicates that dispersion varies with distance. Specifically, the greater the distance over which dispersivity is measured, the greater the observed value, which is called the *scale effect* (Anderson, 1979).

In laboratory column experiments, dispersion is reported to be controlled by fluid flow velocity and grain size distribution. Local scale dispersion is in the centimeter range and is generally two or more orders of magnitude smaller than dispersivity at a macro scale (Smith and Schwartz, 1980). For example, longitudinal dispersivities for a *medium sand* were measured using an in-situ single-well injection-withdrawl tracer test and a laboratory column test (Pickens and Grisak, 1981). Longitudinal dispersivities were found to be an order of magnitude higher when measured in-situ (0.7 cm) than the column scale study (0.035 cm). Based on the scale of measurements reported by researchers, there is evidence that dispersivity coefficients are scale dependent (Pickens and Grisak, 1981, Gelhar et.al. 1985).

Theoretically, from equation 6, longitudinal dispersivity initially increases linearly with distance and gradually approaches a constant asymptotic value (Gelhar and Axness, 1983, Dagan, 1986, 1988). Therefore, groundwater must move a substantial distance before it is able to fully interact with the heterogeneity to the extent necessary to produce a macro-scale mixing. That would explain the increase in dispersivity away from a source before approaching an asympotic (or fixed) value. For example, the asymptotic value had not been reached even after 90m (300ft) of contaminant travel at the Borden site (Freyberg, 1986).

Gelhar et al (1992) reviewed 106 field observations of dispersivities from 59 sites and classified the data points into three groups of varying reliability levels: high, intermediate, and low. They concluded that, in general, field scale dispersion appears to be scale-dependent although the relation may not be linear.

Xu and Eckstein (1995) have proposed a weighted least-squares data fitting method using the data reviewed by Gelhar to provide an improved statistical model of the relationship between field scale and dispersivity given as equation 8. Their equation incorporates the general asymptotic nature of dispersion; their analysis indicates when the flow distance exceeds 1,000 meters (300 feet), the increase in longitudinal dispersivity is practically negligible.

$$\alpha_x = 3.28 * 0.83\left[\log_{10}\left(\frac{L_p}{3.28}\right)\right]^{2.414} \qquad (8)$$

where:

L_P = Scale of study, feet; and

α_x = Longitudinal dispersion coefficient, feet.

Field-measured variance of hydraulic conductivity, correlation lengths, and longitudinal dispersivities of four well-characterized sites are shown in Table 1:

Table 1
Field measured variance of hydraulic conductivity, correlation lengths and longitudinal dispersivities

Site Location	Variance of conductivity	Horizontal correlation scale,m	L,T,V[a] Dispersivity, m	Reference
Cape Cod, MA	0.24	2.6	0.96, 0.018, 0.0015	Garabedian et.al., 1991
Borden, Canada	0.29	2.8	0.43,0.039	Freyberg et.al., 1986
Borden, Canada	0.29	2.8	0.5, 0.05, 0.0022	Gelhar et.al. 1991
Columbus, MI	4.5	12.8	7.5	Gelhar et.al., 1992
Denmark	0.37	1.5	0.45, 0.001,0.0005	Jensen et.al., 1993

[a] Independently measured longitudinal, transverse, and vertical dispersivity, where reported.

As discussed earlier (also equation 6), longitudinal dispersivity is proportional to heterogeneity, which is indicated by variance of conductivity. Based on the estimated variances of hydraulic conductivity measurements of the four sites presented in Table 1, the Columbus site is the most heterogeneous (highest value of variance) with a field-measured longitudinal dispersivity (7.5m) an order of magnitude higher than the rest of the sites. In a reliable study conducted at a sand and gravel aquifer in Cape Cod, at a scale of 250m (820 feet), the longitudinal, transverse, and vertical dispersivities were measured to be 0.96m, 0.018m, and 0.0015m, respectively. For the Cape Cod site, using equation 6, the estimated longitudinal dispersivity value is 0.63m, which is close to the measured value of 0.96m.

For groundwater modeling of contaminant migration in the subsurface, it is a common practice to select constant values for the ratio of longitudinal-to-transverse dispersivities. Gelhar et. al., (1992) in a review of all available field-scale studies noted that transverse dispersivities are at least an order of magnitude smaller than the longitudinal dispersivity values. From field data considered to be highly reliable, the ratio of horizontal to transverse dispersivity was observed to be approximately 10.

From results of available field studies, vertical dispersivity was noted to be 1-2 orders of magnitude smaller than the transverse dispersivity. In media with pronounced horizontal stratification, values of vertical dispersivity may be similar to diffusion (Sudicky, 1986). To date, only 9 field-scale vertical dispersivity data points have been reported in the literature. Of the 9 points, only 2 data points were classified as highly reliable: the Borden (Freygerg, 1986) and the Cape Cod (Garabedian, 1991) sites. All of the vertical dispersivities reported in the literature are less than 1 meter and the two highly reliable values (according to Gelhar et. al.) are only a few millimeters, which is the same order of magnitude as the local transverse dispersivity for sandy materials.

Selected Dispersivity Coefficients

The Dispersivity coefficients selected for this modeling effort are indicated in Table 2.

TABLE 2
Dispersivity Assumptions

Dispersivity	Value
Longitudinal	Based on Xu & Eckstein's equation
Transverse	0.1* longitudinal dispersivity (Field scale data, Gelhar et. al. 1992)
Vertical	0.025 * longitudinal dispersivity (EPA, 1986)

Note that a slightly higher value of vertical dispersivity (0.025 * long. Disp. instead of 0.002 * long. Disp. measured at the Cape Cod site) is assumed for the following reasons:

- The Domenico model does not account for vertical mixing of contaminants in a plume due to infiltration and vertical velocity gradients found at sites. Such plumes are sometimes described as "diving plumes". Such vertical mixing in plumes would result in additional dilution (than predicted by dispersion) of contaminant concentrations at a site.

- The direction of groundwater flow is not constant and there are reports of temporal variations in the flow direction in field conditions (Garabedian, 1991). This change in flow direction would further dilute contaminant concentrations at a site.

- As discussed earlier, longitudinal dispersivity is a function of heterogeneity. Since most sites in Massachusetts are not as homogeneous as the Cape Cod site, dispersivity values measured at Cape Cod can, at best, be assumed to be a conservative estimate for most sites in the state.

- Currently, well screens in monitoring wells are typically of 10ft lengths and are seldom less than 5ft. When groundwater samples are collected from a monitoring well with a 10ft screen length placed below the water table, the measured contaminant concentration is expected to be lower due to dilution over a 10-foot stratum. The degree of dilution however, is dependent on the vertical distribution of a contaminant.

C. Other Assumptions and Discussion:

In addition to the source configuration and dispersivity values discussed above, additional key assumptions used during this effort and incorporated into the Dilution curves are identified below:

- ✓ The aquifer is assumed to be homogeneous and isotropic and the groundwater flow direction does not vary.

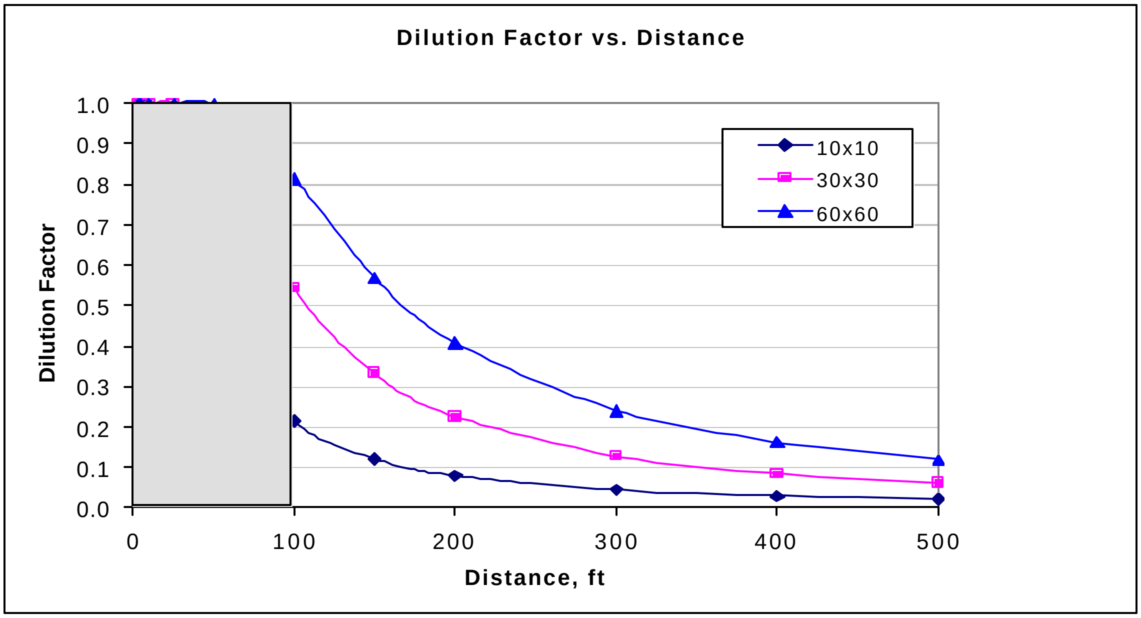
- ✓ Although it is known that VPH and EPH compounds biodegrade in the environment, as a conservative measure, it was assumed that biodegradation of the VPH/EPH fractions does not occur.

- ✓ The point of compliance is assumed to be located at the center of the plume at the water table.

MODELING RESULTS

Contaminant concentrations were estimated at the plume centerline at distances ranging from 3.3 ft. to 500 ft. from the edge of a source using equation 3 and Microsoft Excel. The graphs of three source widths (10 feet, 30 feet, and 60 feet) are shown in Figure 1. In the context of these graphs, the Dilution Factor is the [concentration of a solute at some distance]/[concentration at the source area.], which is C/Co in equation 3. Note that use of this generic Dilution Factor approach is not recommended for distances less than 100 feet, and is therefore not shown in the figure. At distances less than 100 feet from a source, it is usually possible (and preferable) to monitor site conditions directly.

Figure 1
Dilution Curves for 3 Different Source Configurations



Regression equations were fit to the three Dilution Factor curves for distances greater than 100 feet based on the sample coefficient of determination, R^2. The equation, R^2, and the type of equation are shown in Table 2.

Table 2
Regression Equations for Dilution Factor Curves

Source Width, ft.	Equation	R^2	Type Equation	Comments
10	DF=177.2 Distance$^{(-1.4555)}$	0.9999	Power	For Distance >=100ft
30	DF=303.33 Distance$^{(-1.3654)}$	0.999	Power	For Distance >=100ft
60	DF=236.99 Distance$^{(-1.2137)}$	0.9936	Power	For Distance >=100ft

EXAMPLE

Groundwater at a site is contaminated with benzene at 15 mg/l. The source/site is 25 ft. wide in the direction transverse to the groundwater flow direction. The expected concentration of benzene based on the Dilution curve at a distance of 160 ft. from the edge of the source/site may be estimated as shown below:

From Table 3, for a source width of 30ft,

$$DF = 303.33 * Distance^{(-1.3654)} = 303.33 * 160^{(-1.3654)} = 0.3 = C/Co$$

Therefore, the concentration at 160ft = 0.3 * Co = 15 mg/l * 0.3 = 4.5 mg/l

SENSITIVITY ANALYSIS

Under a steady-state assumption, the DFs are sensitive to the source geometry and the dispersivity coefficients, particularly the transverse and vertical dispersivity coefficients

A. Effect of dispersivity coefficients on DFs

Different agencies and researchers have recommended and used different ratios of transverse to longitudinal (T:L) and vertical to longitudinal (V:L) dispersivity values. For example, T:L values of 0.33 (ASTM, 1995 and EPA, 1986), 0.12(EPACMTP, 1996), 0.1(BIOSCREEN, 1996, Gelhar, 1992) have been recommended for use. V:L ratios of 0.1 (Pickens and Grisack, 1981), 0.025 - 0.1(EPA, 1986), 0.05 (ASTM, 1995), 0.006 (EPACMTP, 1996) and 0.002 (measured at the Cape Cod site) have been recommended.

Figures 2 and 3 show the variation of DF with variation of the ratios of T:L and V:L.

Figure 2

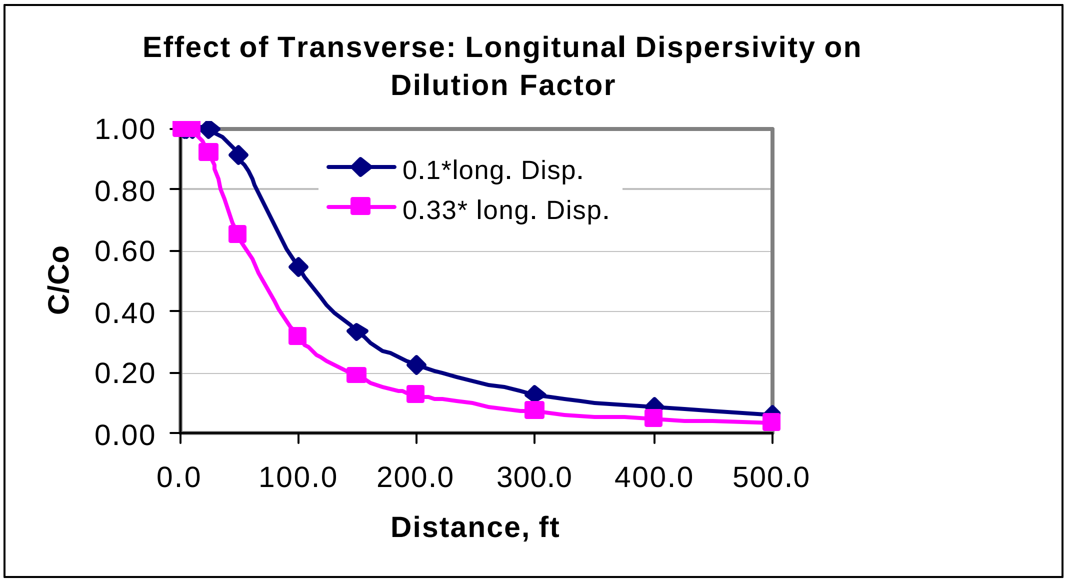
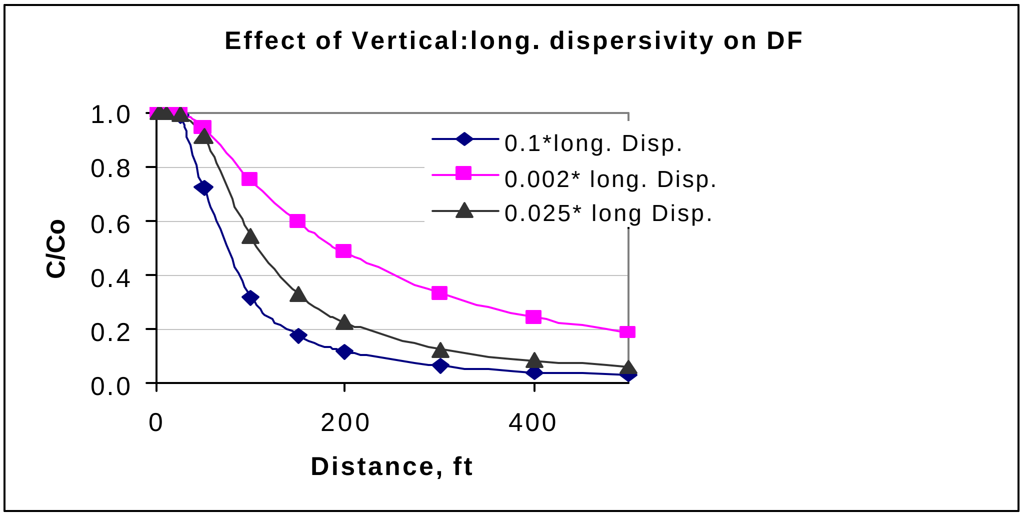


Figure 3

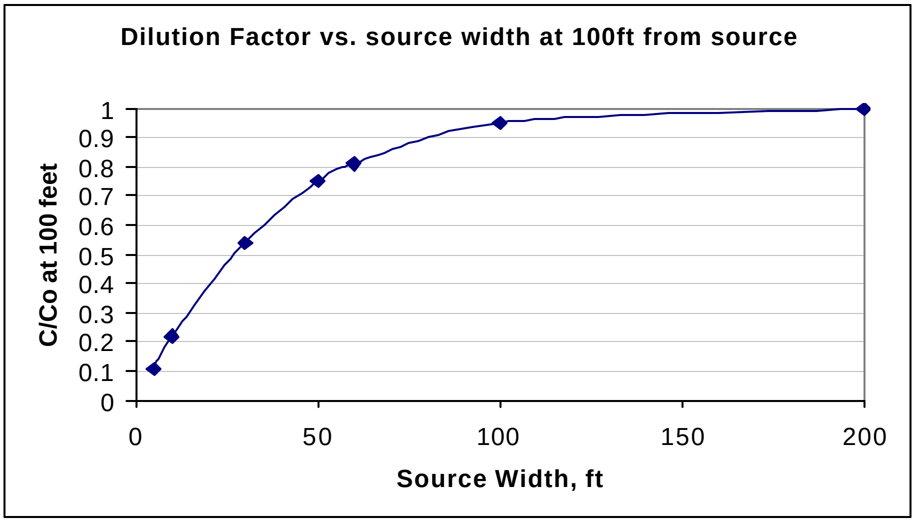


Using equation 3, unit changes in either transverse or vertical dispersivity results in similar values of predicted the DF. The ratios used for the sensitivity analysis (in Figures 2 and 3) have been selected from the sources mentioned above. In general, the effect of vertical dispersivity on the DF is more pronounced compared to the effect of transverse dispersivity. This may be explained by the variation of the input range reported in the literature. For example, T:L ratios generally range between 0.1 and 0.33 (a smaller range) whereas the V:L ratios range between 0.002 and 0.1 (2 orders of magnitude). DFs are most affected between distances of 50 feet and 200 feet; at distances greater than 200 feet, the effect appears to be less significant.

B. Effect of source width and thickness on DF:

Figure 4 shows the variation of DF with source width at a distance of 100 ft. from a source edge. From Figure 4, generally, the DF decreases with source width, however, at distances greater than 75 ft. from the source, there is no significant increase in DF.

Figure 4



Figures 5a and 5b show the variation of DF with source thickness. Figure 5b shows the variation of DF at a distance of 100 feet from the source edge. From Figure 5b, it can be seen that the DF does not increase significantly at thickness greater than 6 feet.

Figure 5a

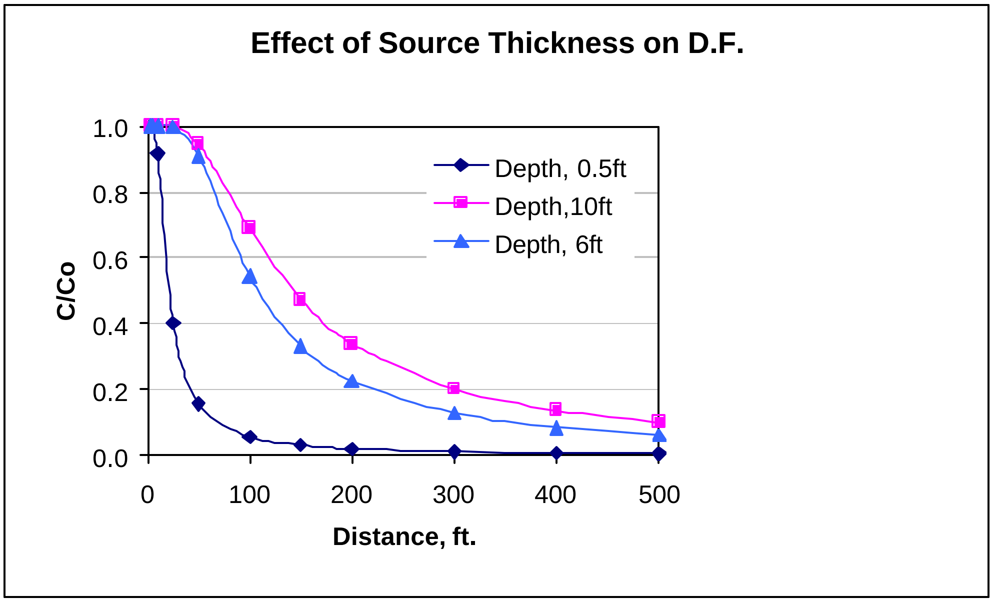


Figure 5b

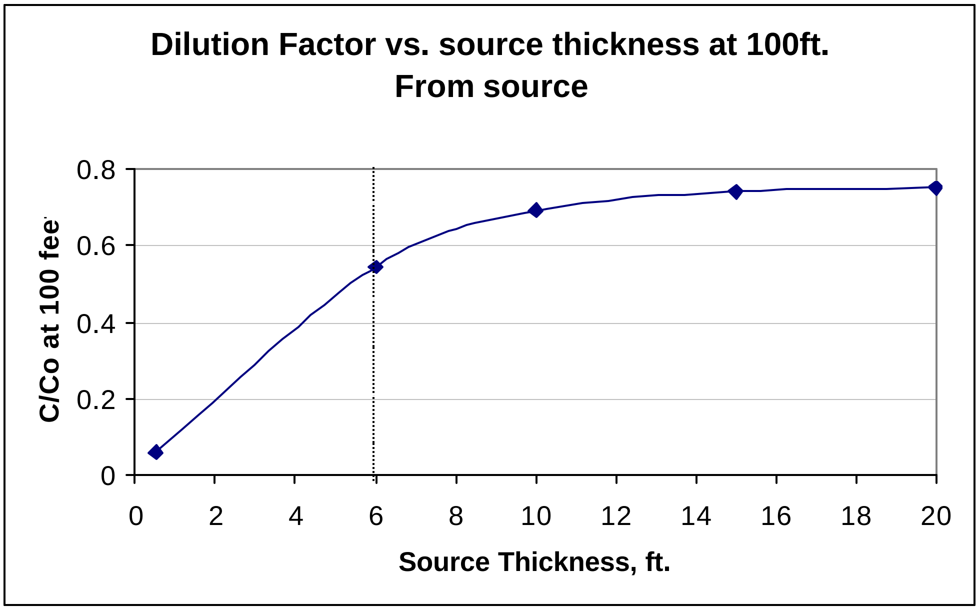


Figure 5b shows the variation of DF at a distance of 100 feet from the source edge. From Figure 5b, it can be seen that the DF does not change significantly at a thickness greater than 6 feet.

CONDITIONS WHERE DFs MAY NOT BE CONSERVATIVE

Based upon the preceding analysis, the use of the Dilution Factor/Curves may not be conservative under the following site conditions:

- The width of the contaminated zone is greater than 60ft;
- Contaminant transport is occurring in bedrock;
- Contaminant transport is occurring along preferred flow paths; or
- The site otherwise has complex groundwater flow conditions.

CONCLUSIONS

The three source widths of 10ft, 30ft and 60ft should be appropriate for most UST sites in Massachusetts. For sites that have unique conditions, for example, contaminant transport in bedrock, the Dilution Factor/Curves may not be conservative and site-specific modeling/evaluation is recommended to establish site-specific dilution factors. On the other hand, at sites where flow is occurring in relatively homogeneous and isotropic formations, it should be possible to derive a site-specific dilution factor that is less conservative than the recommended values estimated using the Domenico's equation and yet be protective.

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