MASSACHUSETTS DEPARTMENT OF
ENVIRONMENTAL PROTECTION

Evaluation of MassDEP Volatile Petroleum Hydrocarbon (VPH) Methods

VPH by GC/PID/FID

VPH by GC/MS

June 2016

Executive Summary

In January 1998, the Massachusetts Department of Environmental Protection (MassDEP) issued a *Volatile Petroleum Hydrocarbon* (VPH) analytical testing method for water and soil samples, which involved the use of a gas chromatograph and in-series PID and FID detectors (GC/PID/FID). In February 2012, MassDEP released a draft of a new VPH test method that utilizes a mass spectrometer (MS) in lieu of the PID/FID. Both methods were designed to provide moderately conservative/health-protective data to support risk characterization efforts conducted under the Massachusetts Contingency Plan.

A “single blind” Round Robin study was conducted in June 2012 to evaluate the performance of both methods, focusing on the draft GC/MS procedure. A total of 5 commercial laboratories in the New England area were voluntary participants in this study.

On the basis of this effort, the following observations and conclusions are offered:

- A majority of the participating laboratories had difficulties properly running the MS method and processing raw data. While increased emphasis of key and novel procedures in the MS method may help mitigate this problem, increased diligence by and training of analysts appears to be strongly warranted.

- When properly run, both the GC/PID/FID and GC/MS VPH methods appear capable of providing reasonably similar, accurate and health-protective data for gasoline contaminated samples.

- The MS method appears to have a moderate positive bias in quantifying C_9-C_{12} Aliphatic Hydrocarbons (at least in soil samples), while the GC/PID/FID method has a moderate positive bias in quantifying C_9-C_{10} Aromatic Hydrocarbons. Both methods appear to provide similar results for C_5-C_8 Aliphatic Hydrocarbons and the Target Analytes (e.g., BTEX).

- The positive bias in the MS method for C_9-C_{12} Aliphatic Hydrocarbons appears to be attributable to an increased total ion response for aromatic hydrocarbons that elute in the C_9 to C_{12} hydrocarbon range, compared to the total ion response of aliphatic hydrocarbons. It is not clear if this bias will exist for all mass spectrometers in all states of tune. However, this is unlikely to be an issue at most sites, given that C_9-C_{12} Aliphatic Hydrocarbons are not expected to be a risk or cleanup driver.

- The positive bias in the PID/FID method for C_9-C_{10} Aromatic Hydrocarbons is attributable to minor though collectively significant PID response to aliphatic hydrocarbons that elute within this range. Due to the low solubility of aliphatics, this is unlikely to be a significant issue in water samples, though it may be more of a concern in soil samples classified as “S-1” under the MCP.

- Some minor adjustments can and should be made to the GC/MS method to optimize performance and reduce biases.

Abbreviations and Acronyms	
AMU	Atomic Mass Unit
BFB	4-Bromofluorobenzene
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
EI	Electron Impact
eV	Electron volt
FID	Flame Ionization Detector
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
m/z	Mass to charge (also notated as m/e)
MassDEP	Massachusetts Department of Environmental Protection
MCP	Massachusetts Contingency Plan
MS	Mass Spectrometer
N.D.	Not Detected
NA	Not Analyzed
NIST	National Institute of Standards and Technology
PID	Photoionization Detector
RL	Reporting Limit
RPM	Revolutions per Minute
RRF	Relative Response Factor
RSD	Relative Standard Deviation
TIC	Total Ion Chromatogram
uV	Ultra violet
VOA	Volatile Organic Analysis
VPH	Volatile Petroleum Hydrocarbons

MassDEP Volatile Petroleum Hydrocarbons by GC/MS	
C_5 – C_8 Aliphatic Hydrocarbons	All aliphatic petroleum hydrocarbon compounds that elute from n-pentane to just before n-nonane (C_9). C_5 through C_8 aliphatic hydrocarbons are determined using the total ion chromatogram.
C_9 – C_{12} Aliphatic Hydrocarbons	All aliphatic petroleum hydrocarbon compounds that elute from just before n-nonane to just before naphthalene. C_9 through C_{12} aliphatic hydrocarbons are determined using the total ion chromatogram.
C_9 – C_{10} Aromatic Hydrocarbons	All aromatic petroleum hydrocarbon compounds that elute from just after o-xylene to just before naphthalene. Although naphthalene is an aromatic compound with 10 carbon atoms, it is excluded from this range because it is evaluated as a separate target analyte. C_9 through C_{10} aromatic hydrocarbons are determined using the extracted ions 120 and 134.

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OVERVIEW

Background

In January 1998, the Massachusetts Department of Environmental Protection (MassDEP) issued a *Volatile Petroleum Hydrocarbon* (VPH) analytical testing method for water and soil samples. This procedure enabled the quantification of not only the "Target Analyte" components of fuels, such as Benzene and Toluene, but also the collective ranges of aliphatic and aromatic hydrocarbon compounds, for comparison to heath-based cleanup standards. Updated by the agency in 2004, this gas chromatography (GC) method employs in-series Photoionization and Flame Ionization Detectors (PID/FID), using the universal response characteristics of the FID to quantify collective concentrations of C_5 – C_8 and C_9 – C_{12} aliphatic hydrocarbons, and the selectivity of the PID to quantify the collective concentration of C_9 – C_{10} aromatic hydrocarbons.

In February 2012, MassDEP released a draft of a new VPH test method that utilizes a mass spectrometer (MS) in lieu of a PID/FID. Under this approach, the collective ranges of aliphatic hydrocarbons are quantified using total ion area counts, and the collective range of C_9 – C_{10} aromatic hydrocarbons is quantified using extracted ions (m/z) 120 and 134.

Round Robin Program Summary

In June 2012, a "single blind" Round Robin testing program was undertaken to evaluate performance of the draft GC/MS VPH method, and compare results to the GC/PID/FID VPH method. Five commercial laboratories in the New England area volunteered to participate in this study.

Each laboratory was provided with:

- Triplicate 40-mL VOA vials containing an acidified water sample; and
- Duplicate 40-mL VOA vials containing a 15 gram soil sample in 15 mL of Methanol.

The water sample was obtained from a groundwater monitoring well at a gasoline-contaminated site in Wilmington, MA. A small volume of neat gasoline (2 µL in a 1 Liter sample) was added to this groundwater sample, to increase the aliphatic hydrocarbon content. This solution was mixed with a magnetic stirrer at 700 RPMs for 30 minutes, and then passed through a 0.45 micron filter, to help ensure that any un-dissolved gasoline globules were removed from the final stock solution.

The soil sample was prepared by spiking sand in a VOA vial with a gasoline/methanol solution. The gasoline was obtained from a commercial dispensing station in Wilmington, MA (Regular Unleaded grade). Each soil sample contained approximately 3000 µg/g of gasoline.

See Appendix B for additional details on sample preparation.

Results

Each laboratory that participated in the Round Robin program was requested to analyze the provided samples for VPH using both the GC/PID/FID and draft GC/MS procedures.

Initial data reports from all participants, identified as Laboratories 1 through 5, were received by MassDEP in early August, 2012. These data are summarized in Tables 1 through 4, along with revisions made after reviewing each data package in detail. Note that Laboratory #1 did not provide GC/PID/FID data.

Table 1 – Water Data by GC/MS (µg/L) – Initial Data Submission/Revised Values

	Unadjusted Range Data			Target Analytes							Adjusted Range Data		Total[a]
Lab#	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	Naphthalene	C5-C8 Aliphatics	C9-C12 Aliphatics	
1	120/124	180/345	<100	39	5	8	44	57	34	<5	<100	<100/160	450 +/-
2	51/59	199/198	55/51	32.6	3.56	6.49	36.4	44.7	27.5	3.3	<50	<50	256 +/-
3	156	203/141	<100	39.9	5.92	6.11	32.1	22	16.7	6.37	104	114/<100	333 +/-
4	992/192	1870/340	24/<100	38.6	4.09	8.24	47.6	61.4	38.1	3.54	941/141	1700/168	561 +/-
5[d]	67/<100	450/484	240/<100	42	5.2	8	40	52	31	4.1	<50/<100	86/296[b]	578 +/-

Table 2 – Water Data by GC/PID/FID (µg/L) – Data Submission

	Unadjusted Range Data			Target Analytes							Adjusted Range Data		Total[a]
Lab#	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	Naphthalene	C5-C8 Aliphatics	C9-C12 Aliphatics	
2	119	188	58	35.9	6	7.7	36.4	41.9	25.6	4	69.8	<50	310 +/-
3	135	467	107	36.1	5.82	8.21	43.3	57.1	33.8	4.62	84.6	226	607
4	195	109	73.9	33.8	5.5	7.6	39.5	51.3	31.7	4.4	26.1	34.8	309
5	110	280	<100	32	4.6	7	35	47	29	<5	<100	170	427 +/-

Table 3 – Soil Data by GC/MS (µg/g) – Initial Data Submission/Revised Values

	Unadjusted Range Data			Target Analytes							Adjusted Range Data		Total[a]
Lab#	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	Naphthalene	C5-C8 Aliphatics	C9-C12 Aliphatics	
1	2700/2795	590/1000	280/250	20	<5.7	235	48	175	63	12	2400/2540	<280/464	3810
2	2130/2478	844/864	305/272	22.2	<0.05	298	53.9	193	69.7	5.84	1990/2160	222/275	3350
3	3458/3462	1145	275	23.7	<2.5	268	51	185	70.3	6.65	3171[c]	564[c]	4616
4	19200/2710	6750/1029	<509/116	21.4	<5.1	248	51.1	185	66	7.5	18800/2440	6250/610	3748
5[d]	1600/2048	1900/1545	<1000/264	24	<1	250	53	202	66	5.6	1400/1775[b]	<1000/959[b]	3599

Table 4 – Soil Data by GC/PID/FID (µg/g) – Data Submission

	Unadjusted Range Data			Target Analytes							Adjusted Range Data		Total[a]
Lab#	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	Naphthalene	C5-C8 Aliphatics	C9-C12 Aliphatics	
2	1760	646	241	19.7	< 0.05	202	47.1	144	55.4	4.97	1540	158	2412
3	1940	717	263	21.8	<1.07	222	40.5	153	55.2	<4.27	1690	202	2652
4	3280	650	420	40.7	<1	324	65.9	242	90.4	12.4	2520	230	3945
5	2700	590	280	27	<0.05	250	50	180	71	4.5	2400	17	3280

[a] Total = summation of revised “Adjusted Range Data” plus Target Analytes; approx only (+/-) for summations containing N.D. data points (assumes N.D. = ½ of Reporting Limit)

[b] may be biased high due to subtraction of extracted ion area counts for internal standards and surrogates instead of total ion area counts

[c] may be biased high due to incorrect GC/MS AMU scanning range [d] Lab 5 used an unapproved column; Aliphatic Range data cannot be used.

GC/MS DATA

While the Round Robin program included the production and evaluation of data from the “conventional” GC/PID/FID method, its primary focus was on the performance of the draft GC/MS procedure. As such, the GC/MS submittals were closely examined, while the PID/FID data were assumed to be accurate.

As can be seen in Tables 1 through 4, some of the data initially provided for the draft GC/MS procedure appeared to be anomalous, particularly from Laboratory #4 and Laboratory #5. In order to further explore the reasons for these anomalies, and otherwise ensure that all data and calculations were generated in conformance with method requirements, a follow-up request was made to all laboratories for additional information and “raw” data on operational systems, parameters, procedures, calculations, and results.

After a number of months and review iterations, significant issues were in fact identified with the GC/MS data packages from 4 of the 5 participating laboratories, which resulted in minor to major changes in the quantification of hydrocarbon range and Target Analyte concentrations. All of these problems were the result of not following the draft GC/MS method, as written.

The most anomalous data package – from Laboratory #4 – was in large part due to the use of extracted (quantitation) ion areas to calculate hydrocarbon range response factors, as opposed to the use of total ion areas specified by the method. This explained the very high positive bias in the initial sample results. Other problems noted for this and other laboratories included: improper hydrocarbon range integration, incorrect calculations of response and linear regression factors, mistakes in hydrocarbon range adjustment procedures, and mistakes in (soil) dry-weight calculations.

GC/MS Operating Systems and Parameters

Details on GC/MS and Purge-and-Trap parameters for the 5 participating laboratories are summarized in Tables 5 and 6, respectively.

Of note in Table 5 was the use of a non-specified capillary column, an Agilent DB-624, by Laboratory #5, a high scanning mass limit (550 atomic mass units [AMUs]) for Laboratory #3, and low injection port temperature for Laboratory #5. Of note in Table 6 is the low trap desorption temperature of 180ºC for Laboratory #2.

Each of these deviations can, and, it appears, did result in biases and inaccuracies in the reported GC/MS data:

Chromatographic Column

The draft GC/MS method specifies use of either an RTX-502.2 or VOCOL capillary column. Previous Round Robin efforts had indicated that the chromatographic column had a significant impact on whether certain C_7 to C_{10} aliphatic hydrocarbons eluted in the C_5-C_8 or C_9-C_{12} Aliphatic Hydrocarbon Range. As such, the use of other columns is permissible only if a demonstration is made proving equivalent chromatography and apportionment of aliphatic hydrocarbons.

The GC/MS data from Laboratory #5 – which used a non-specified DB-624 column – is indicative of this concern. While the total concentration of aliphatic hydrocarbons is consistent with the other laboratories (who used an RTX-502.2), the allocation between the C_5-C_8 and C_9-C_{12} aliphatic hydrocarbon ranges is significantly different, with Laboratory #5 reporting substantially lower concentrations of C_5-C_8 Aliphatic Hydrocarbons, and substantially higher concentrations of C_9-C_{12} Aliphatic Hydrocarbons. For this reason, *the aliphatic range data from this laboratory were not used in the assessment of method performance*.

Table 5: Summary of GC/MS Parameters[1]

	Lab #1	Lab #2	Lab #3	Lab #4	Lab #5
Oven Temperature Program	35°C/4 min 15°C/min to 220°C for 2 min	35°C/5 min 9°C/min to 160°C 20°C/min to 250°C for 2 min	45°C/3 min 20°C/min to 130°C 35°C/min to 250°C for 5 min	35°C/4 min 15°C/min to 220°C for 0.17 min	45°C/5 min 15°C/min to 210°C for 0.3 min
Run time	21.5 min	25.39 min	15.679 min	16.5 min	14.30 min
Column	Restek RTX 502.2 30 m x 0.25 mm x 1.4 um	Restek RTX 502.2 30 m x 0.25 mm x 1.4 um	Restek RTX 502.2 40 m x 0.18 mm x 1 um	Restek RTX 502.2 30 m x 0.25mm x 1.4 um	Agilent DB-624 20 m x 0.18 mm x 1.0 um
Injection port temperature	180°C	240°C	240°C	175°C	100°C
Split ratio	45/1	20/1	50/1	80/1	50/1
Column flow	1 mL/min, constant	0.9 mL/min, constant	1 mL/min	NP	1 mL/min, constant
Split flow	NP	18 mL/min	50 mL/min	38.2 mL/min	50.5 mL/min
Solvent Delay	NP	3.0 min	3.0 min	NP	0.9 min
Low Mass	NP	35 amu	35 amu	NP	35 amu
High Mass	NP	330 amu	550 amu	NP	260 amu
Threshold	NP	600	150	NP	150
MS Source Temp	NP	230°C	230°C	NP	230°C
MS Quad Temp	NP	150°C	150°C	NP	150°C

[1] NP = Not provided

Table 6: Summary of Purge & Trap Parameters for GC/MS Method[1]

	Lab #1	Lab #2	Lab #3	Lab #4	Lab #5
	VOCARB 3000 (Carbopack B, 1000, 1001)	#9: Tenax/silica gel/charcoal	NP	Tekmar Stratum #9 U-shaped	NP
Purge flow	40 mL/min	40 mL/min	NP	40 mL/min	40 mL/min
Purge time	11 min	11 min	11 min	11 min	11 min
Purge temp	NP	NP	NP	20°C	35°C
Dry purge time	2 min	1 min	1 min	2 min	1 min
Desorb time	0.5 min	1 min	1 min	4 min	NP
Desorb temp	260°C	180°C	250°C	250°C	260°C
Bake time	8 min	8 min	8 min	8 min	8 min
Bake temp	265°C	200°C	260°C	280°C	230°C
Transfer line temp	NP	NP	150°C	140°C	130°C
Valve oven temp	NP	NP	150°C	140°C	130°C

[1] NP = Not provided

Scanning Masses

The draft VPH by GC/MS method specifies the use of a 70 eV Electron Impact mass spectrometer that is "capable of scanning from 35 to 250 amu every three seconds or less". In theory, extending the scanning range to 550 amu, as was done by Laboratory #3, could result in a high bias, by quantifying masses greater than 250 amus. In this regard, it is noted that the soil hydrocarbon range concentrations reported by Laboratory #3 were in fact significantly higher than other laboratories, though primarily in the C_5-C_8 range. While it is not completely clear that the high scanning mass was the reason for this bias – as even 250 AMUs is presumably beyond the molecular weight of even the heaviest gasoline components – it is possible that such a high scanning range could pick up natural organic materials in samples and/or system contaminants, creating a high bias.

Trap Desorption Temperature

The draft VPH by GC/MS method specifies a trap desorption temperature of 260ºC – which was used (or approached) by all laboratories except Laboratory #2, which used a temperature of only 180ºC. A low temperature would be expected to produce a low bias for heavier hydrocarbons, i.e., the C_9-C_{12} Aliphatic Hydrocarbons. This is indeed the case for the soil data submitted by this laboratory.

EVALUATION AND COMPARISON OF GC/MS and GC/PID/FID DATA

Revised GC/MS data values were evaluated and compared to the GC/PID/FID results.

Key data are graphically presented in Figures 1 and 2. In Figure 3, total ion chromatograms are presented for the groundwater and soil samples from one of the data packages. In Table 7, mean and Percent Relative Standard Deviation (%RSD) values are summarized for each analyte in each sample.

Review of Total Ion Chromatograms (TICs)

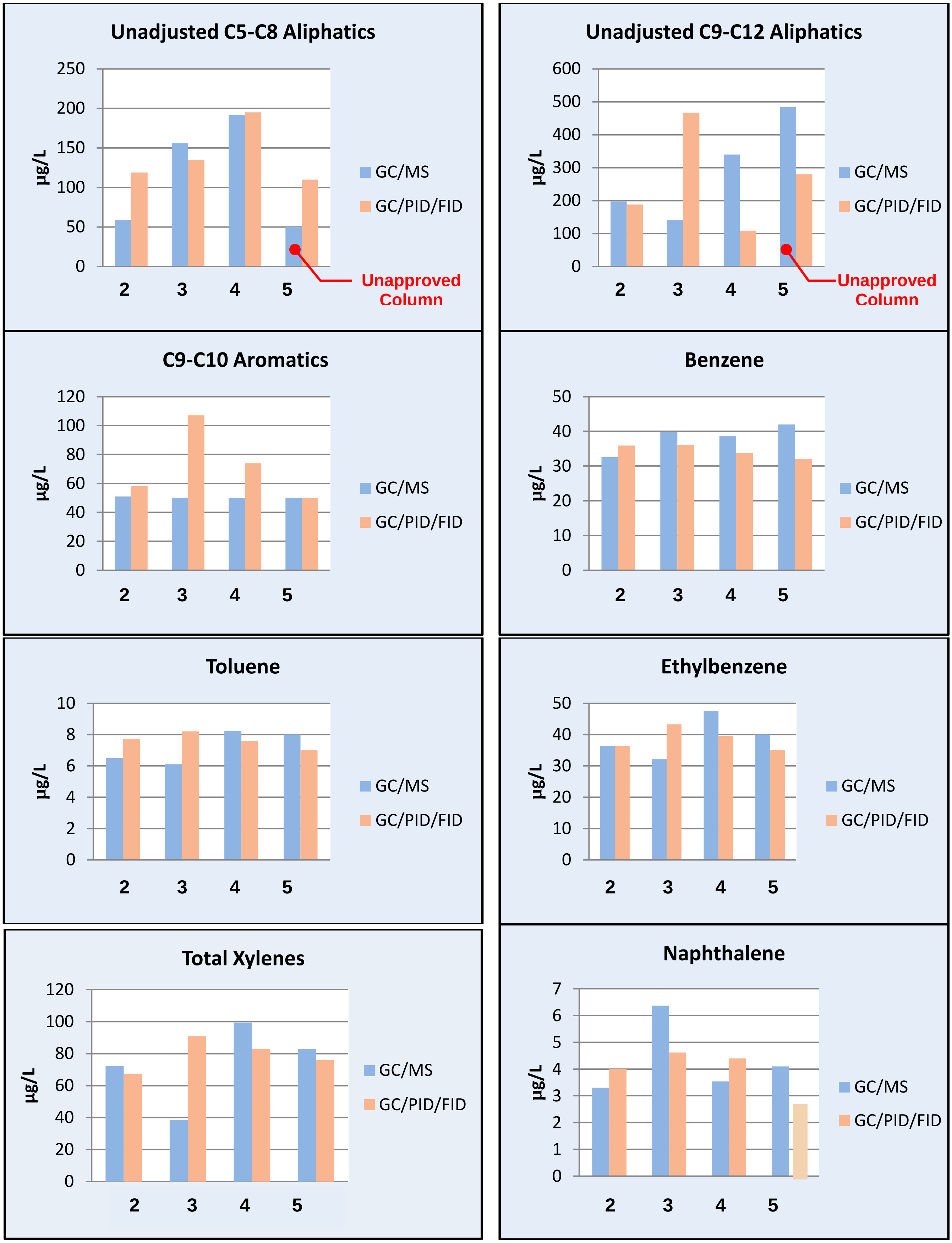
A review of the Total Ion Chromatograms from the GC/MS VPH method submitted by four of the five participating laboratories showed good qualitative agreement in the water and soil samples (Laboratory #5 did not submit total ion chromatograms.) As expected, the water sample chromatograms were dominated by the water soluble fraction (i.e., BTEX), while the soil sample chromatograms had many more hydrocarbon peaks (see Figure 3).

One issue was noted in the chromatograms for Laboratories #1 and #4 – the existence of an additional peak near the first internal standard (see Figure 3), which the method specifies as being either Fluorobenzene or 1,4-Difluorobenzene. Subsequent inquires confirmed that both laboratories had procured internal standard mixtures that contained both of these compounds (though only one was used as an Internal Standard). Other than this finding, all laboratories otherwise used the recommended internal standards and surrogate standard, though there were differences in the length of runs, from a low of 15 minutes for Laboratory #3, to a high of 25 minutes for Laboratory # 2.

Total Hydrocarbons

A VPH Total Hydrocarbon concentration for the groundwater and soil samples can be determined by summing the (adjusted) aliphatic hydrocarbon ranges, the aromatic hydrocarbon range, and Target Analyte concentrations, (see Tables 1-4). In some cases, this value is only an estimate (+/-) because "N.D." results for hydrocarbon range and/or Target Analyte data were assigned an estimated concentration of ½ of the Reporting Limit (RL). Although the total concentration of hydrocarbons in the "real world" groundwater sample is unknown, the soil sample was spiked with 3050 µg/g of gasoline, which can be compared to the estimated VPH soil hydrocarbon value (Table 8).

Figure 1: Water Data (µg/L) for Laboratories #2 through #5



Unadjusted C5-C8 Aliphatics

Unadjusted C9-C12 Aliphatics

C9-C10 Aromatics

Benzene

Toluene

Ethylbenzene

Total Xylenes

Naphthalene

Figure 2: Soil Data (µg/g) for Laboratories #2 through #5 (Dry Weight Basis)

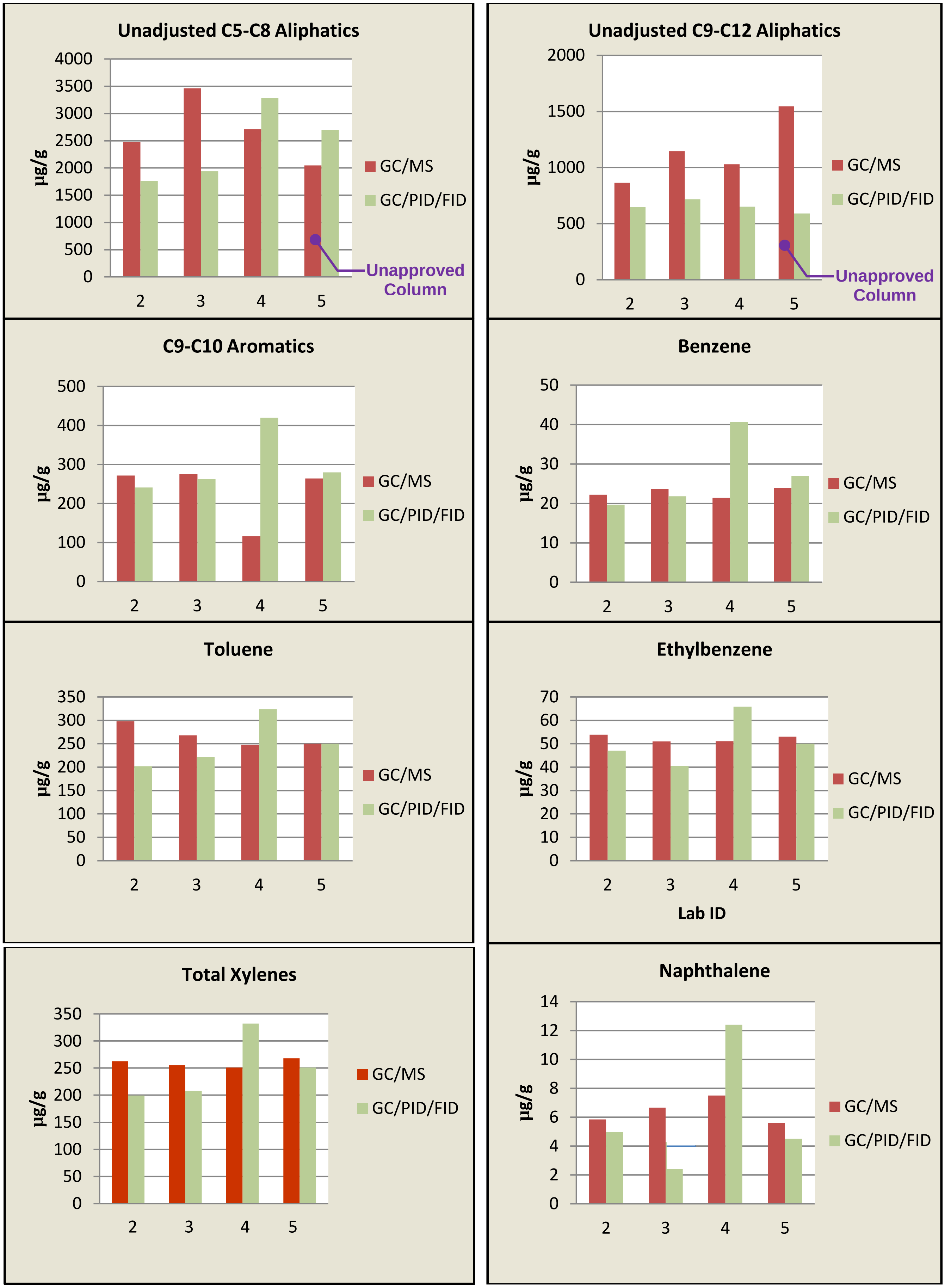


Figure 3: Total Ion Chromatograms for Water and Soil Samples (Laboratory #1)

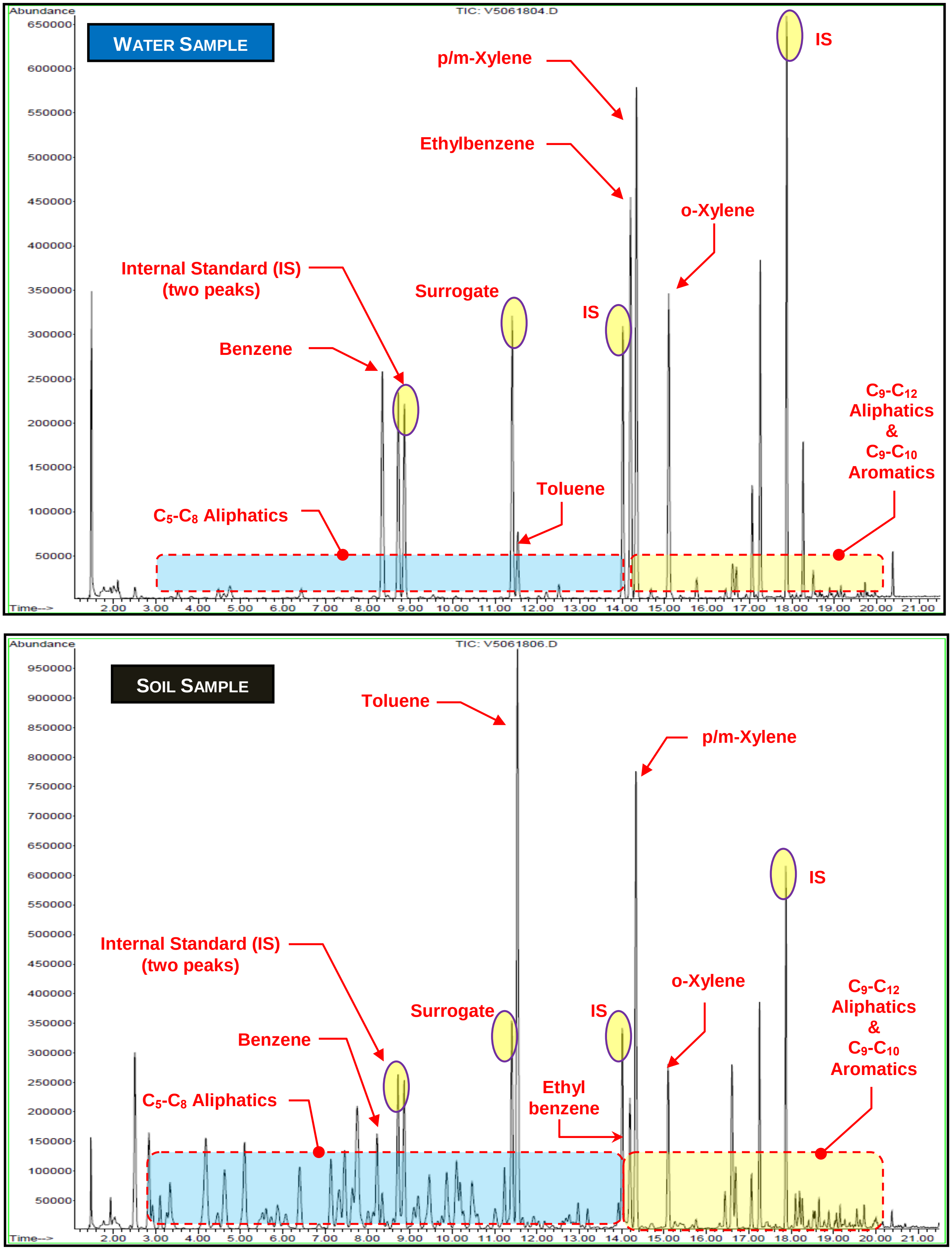


Table 7 – Data Statistics[a]

Water by GC/MS (µg/L)

	Unadjusted Aliphat		Adjusted Aliphat		C_9-C_{10} Aromatics	Target Analytes[c]					
Lab#	C_5-C_8	C_9-C_{12}	C_5-C_8	C_9-C_{12}		Ben	MtBE	Tol	EB	XYL	Naph
1	124	345	(50)	160	(50)	39	5	8	44	91	(2.5)
2	59	198	(25)	(25)	51	33	4	6	36	72	3.3
3	156	141	104	(50)	(50)	40	6	6	32	39	6.37
4	192	340	141	168	(50)	39	4	8	48	100	3.54
5[b]	NA	NA	NA	NA	(50)	42	5.2	8	40	83	4.1
Mean	133	256	80	100	50	38	5	7	40	77	4
S Dev	56	103	52	74	0	4	1	1	6	24	1
%RSD	43	40	65	74	1	9	20	13	15	31	28

Water by GC/PID/FID (µg/L)

	Unadjusted Aliphat		Adjusted Aliphat		C_9-C_{10} Aromatics	Target Analytes[c]					
Lab#	C_5-C_8	C_9-C_{12}	C_5-C_8	C_9-C_{12}		Ben	MtBE	Tol	EB	XYL	Naph
2	119	188	70	(25)	58	35.9	6	7.7	36.4	68	4
3	135	467	85	226	107	36.1	5.82	8.21	43.3	91	4.62
4	195	109	26	35	73.9	33.8	5.5	7.6	39.5	83	4.4
5	110	280	(50)	170	(50)	32	4.6	7	35	76	(2.5)
Mean	140	261	58	114	72	34	5	8	39	83	4
S Dev	38	154	25	100	25	2	1	0	4	10	0
%RSD	27	59	44	88	35	6	11	7	10	12	7

Soil by GC/MS (µg/g)

	Unadjusted Aliphat		Adjusted Aliphat		C_9-C_{10} Aromatics	Target Analytes[c]					
Lab#	C_5-C_8	C_9-C_{12}	C_5-C_8	C_9-C_{12}		Ben	MtBE	Tol	EB	XYL	Naph
1	2795	1000	2540	464	250	20	(d)	235	48	238	12
2	2478	864	2160	275	272	22.2	(d)	298	53.9	263	5.8
3	3462	1145	3171	564	275	23.7	(d)	268	51	255	6.7
4	2710	1029	2440	610	116	21.4	(d)	248	51.1	251	7.5
5[b]	NA	NA	NA	NA	264	24	(d)	250	53	268	5.6
Mean	2861	1010	2577	479	235	22.3	-	260	51	255	7.5
S Dev	422	115	427	149	67	2	-	24	2	12	3
%RSD	15	11	17	31	29	7	-	9	4	5	35

Soil by GC/PID/FID (µg/g)

	Unadjusted Aliphat		Adjusted Aliphat		C_9-C_{10} Aromatics	Target Analytes[c]					
Lab#	C_5-C_8	C_9-C_{12}	C_5-C_8	C_9-C_{12}		Ben	MtBE	Tol	EB	XYL	Naph
2	1760	646	1540	158	241	19.7	(d)	202	47.1	199	4.97
3	1940	717	1690	202	263	21.8	(d)	222	40.5	208	(2.1)
4	3280	650	2520	230	420	40.7	(d)	324	65.9	332	12.4
5	2700	590	2400	17	280	27	(d)	250	50	251	4.5
Mean	2420	651	2038	152	301	27	(d)	250	51	248	6
S Dev	703	52	494	95	81	9	-	53	11	61	5
%RSD	29	8	24	62	27	35	-	21	21	25	74

(a) Values in parentheses are ½ the Reporting Limit

(b) GC/MS data from unapproved column; Aliphatic data not applicable

(c) XYL is Total Xylenes, i.e., summation of m/p and o-Xylene

(d) MtBE was not detected and assumed to be zero

Mean hydrocarbon range and Target Analyte data and Total Hydrocarbon estimates for the water and soil samples are provided in Table 8, which summarizes values for the 4 laboratories providing GC/PID/FID data, and 5 laboratories providing GC/MS data. Similar data from a 1997 Round Robin effort (for the original GC/PID/FID method) are also provided for comparative purposes.

Table 8 – Mean Values for Water (μg/L) and Soil (μg/g) in Round Robin Studies

	Data package (Ranges/Analytes)	Adjusted		C_9-C_{10} Aro	Target Analytes						Total +/-	% Recovery
		C_5-C_8 Ali	C_9-C_{12} Ali		Ben	MtBE	Tol	EB	XYL	Nap		
2012	GC/MS water (4/5)	80	100	50	38	5	7	40	77	5	402	NA
	PID/FID water (4)	58	114	72	34	5	8	39	83	4	417	NA
	GC/MS soil (4/5)	2577	479	235	22	ND	260	51	255	8	3887	127
	PID/FID soil (4)	2038	152	301	27	ND	250	51	248	6	3073	101
1997	PID/FID water (23)	936	1700	560	102	232	606	179	921	95	5331	NA
	PID/FID soil (23)	1327	926	265	99	226	318	131	362	11	3665	120

Note that in Table 8, the number of participating laboratories is indicated in parentheses in the first column (the 4/5 notation indicates that the Aliphatic Hydrocarbon data were not used from Laboratory #5, though all other results are included). A *"% Recovery*" value is also provided in both tables for the soil data, which is equal to [the estimated Total Hydrocarbon concentration] divided by [the gravimetric concentration of total gasoline spiked into the soil sample] multiplied by 100.

As can be seen, the GC/MS water sample had a mean total hydrocarbon concentration of about 402 μg/L, which is similar to the GC/PID/FID value of about 417 ug/L. While encouraging, this degree of agreement is tempered by a significant number of "Non Detect" values for the C_9-C_{10} Aromatic hydrocarbon range, necessitating the use of estimated values in the calculation of total hydrocarbon concentrations.

Soil data are deemed to be more insightful, given not only the higher spiking concentrations, but also the fact that actual (true) total hydrocarbon concentrations were known. As detailed in Table 8, there was good agreement between the methods and with the actual spiking concentration. For the soil samples, the mean GC/MS total hydrocarbon concentration of about 3887 mg/kg was 26% higher than the GC/PID/FID value of 3073 mg/kg. The percent recovery values for the soil sample for both methods were good: 127% for the GC/MS procedure, and 101% for the GC/PID/FID procedure. These values were comparable to the 120% recovery documented in the 1997 Round Robin study, which involved a much larger universe of participants (i.e., 23 laboratory packages).

In theory, the summation of the (adjusted) hydrocarbon ranges and Target Analytes should be less than the total amount of spiked gasoline, given the existence of non-hydrocarbon components, as well as hydrocarbon compounds that elute before C_5 and after C_{12}. This is especially true for the 2012 gasoline soil sample, which was spiked with a product that presumably contained 10% ethanol, which would be difficult to purge from the sample.

These percent recovery values provide some confidence that the overall reported data are consistent with expected concentrations, with a moderate conservative bias, as is the goal.

Hydrocarbon Ranges

As indicated in Table 8, there was relatively good agreement between the GC/MS and GC/PID/FID hydrocarbon range data for the water sample, though the summary statistics suggest the possibility of a slight positive bias for the C_9-C_{10} Aromatic Hydrocarbon concentration for the PID/FID method. However, the low hydrocarbon levels in the water samples (near or below hydrocarbon range Reporting Limits) prevent definitive conclusions in this regard.

The higher hydrocarbon concentrations in the soil samples allow for a more meaningful comparison of potential methodological differences and biases. As can be seen in Table 8, there was relatively good agreement (< 30% difference) between the hydrocarbon range data using both methods, except for C_9-C_{12} Aliphatic Hydrocarbons, where the GC/MS results were significantly higher than the GC/PID/FID results.

Target Analytes

As presented in Table 8, and graphically illustrated in Figures 1 and 2, there was very good correlation for Target Analyte values between both procedures. This would be expected for the water data, in which the water soluble-fraction of gasoline is dominated by the Target Analyte compounds, but is noteworthy for the soil sample, where co-eluting hydrocarbons could inflate PID response and potentially produce a positive bias.

Precision

Statistics on reproducibility (% Relative Standard Deviation) are provided in Table 9, and graphically illustrated for the hydrocarbon ranges in Figure 4.

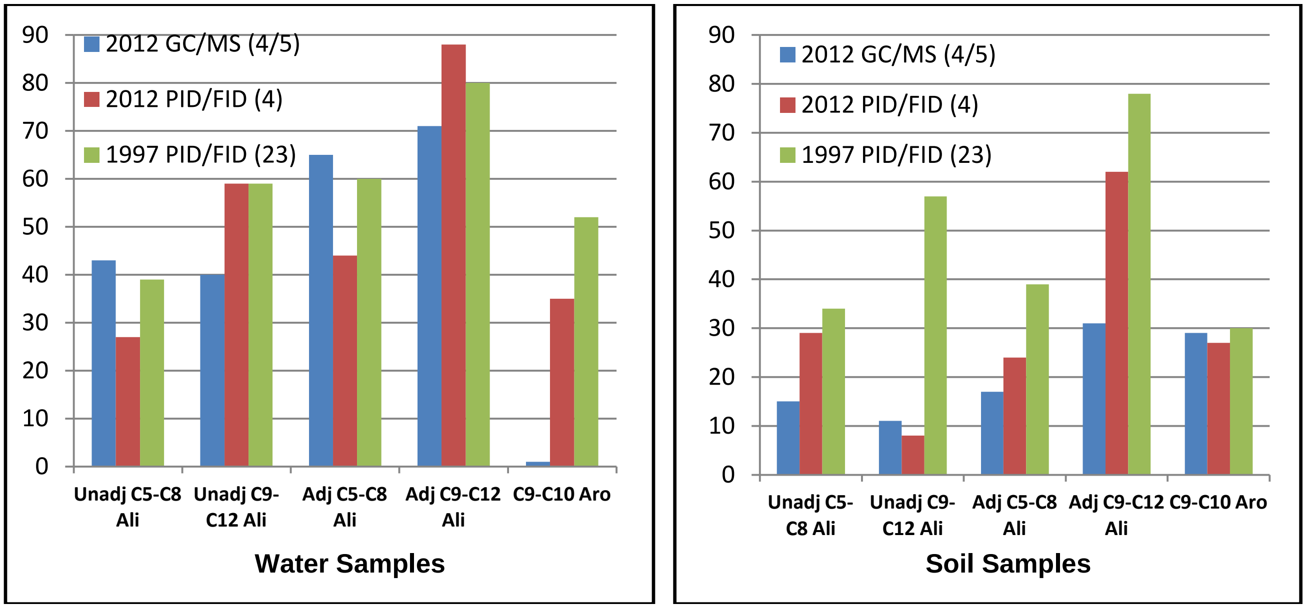
Table 9 – %RSD Values for 2012 and 1997 VPH Round Robin Studies

	Data package (number of labs)	Unadjusted		Adjusted			Target Analytes						
		C_5-C_8 Ali	C_9-C_{12} Ali	C_5-C_8 Ali	C_9-C_{12} Ali	C_9-C_{10} Aro	Benzene	MtBE	Toluene	EB	pm-XYL	o-XYL	Naph
2012	GC/MS water (4/5)	43	40	65	74	1	9	20	13	15	33	28	28
	PID/FID water (4)	27	59	44	88	35	6	11	7	10	13	12	7
	GC/MS soil (4/5)	15	11	17	31	29	7	NA	9	4	5	5	35
	PID/FID soil (4)	29	8	24	62	27	35	NA	21	21	25	25	74
1997	PID/FID water (23)	39	59	60	80	52	14	16	14	10	13	19	19
	PID/FID soil (23)	34	57	39	78	30	-	40	17	18	15	15	45

As can be seen, the overall trends for the 2012 and 1997 hydrocarbon range data are similar: greater variability in the water data, compared to the soil data, with the most variability for the adjusted C_9-C_{12} Aliphatic Hydrocarbon ranges (in both media). The reproducibility of the 2012 "Adjusted" hydrocarbon range data – which are compared to cleanup standards – are reasonably good for the soil sample, at 30% or less, except for C_9-C_{12} Aliphatic Hydrocarbons. The 2012 water data are more variable, with %RSD values up to 88% for the C_9-C_{12} Aliphatic Hydrocarbons. Notably, the %RSD values for C_9-C_{10} Aromatics in the 2012 soil samples were less than 30% by both procedures.

While there was more variability in the water samples, the low levels of hydrocarbons present in the water sample (and resulting non-detect data points) limit the relevance of this calculation.

Figure 4: %RSD for Hydrocarbon Range Values from 2012 & 1997 Round Robin Studies



EVALUATION AND COMPARISON OF GC/MS and GC/PID/FID METHODS

The VPH by GC/PID/FID and draft VPH by GC/MS methods are based upon EPA SW-846 8000 series environmental testing protocols, and employ conventional detection and calibration techniques to identify and quantify individual "Target" analytes, such as Benzene and Toluene. However, both methods also use simple, innovative approaches to identify and quantify collective ranges of aliphatic and aromatic hydrocarbon compounds. While the simplicity of these approaches allows for the cost-effective and health-protective assessment of petroleum contaminated sites, it also provides the potential for analytical biases in the reporting of data, depending on the specific hydrocarbon chemistry of individual samples, such that reported hydrocarbon range concentrations may be higher or lower than the true concentration. This "systemic bias" is in addition to the precision and accuracy limitations and variability that exist when reporting the concentration of individual analytes using conventional methods.

Procedural elements in both VPH methods have been formulated to address these systemic biases, and, ideally, allow for the reasonably conservative quantification of hydrocarbon ranges, such that both methods are more likely to over-report than under-report contaminant levels, for most samples from most sites. While the universe of usable data packages for the VPH GC/MS method and Round Robin program is small (i.e., 5 submittals each for soil and water), some preliminary conclusions are possible, when integrating these empirical data with theoretical expectations

FID vs PID vs MS Response

The FID provides almost uniform response (by mass) to most of the petroleum hydrocarbons present in fuels; a C_6 alkane (e.g., Hexane) will produce a response almost identical to a C_6 aromatic (e.g., Benzene). This has led to the long-standing use of an FID to provide accurate and consistent quantification of hydrocarbon mixtures, including in the VPH by GC/PID/FID procedure.

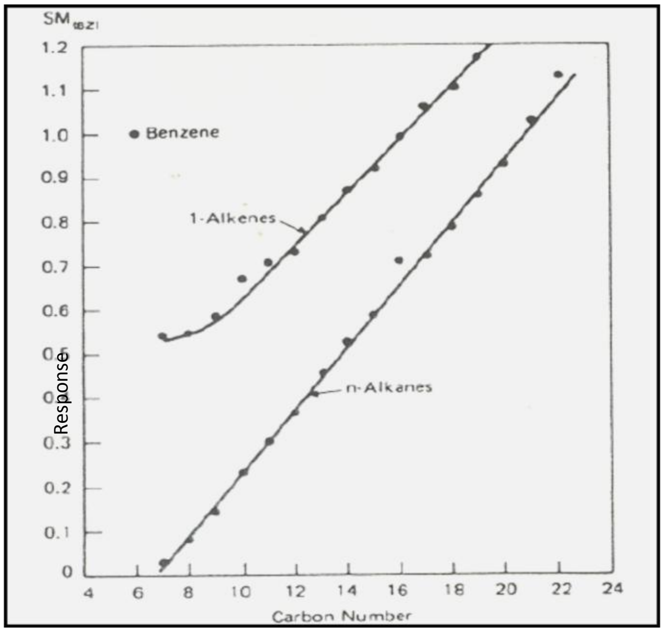
The PID is more selective, with response a function of molecular weight and structure, the presence of functional groups, and the type of chemical bonds (e.g., single vs double), as illustrated in Figure 5.

Most GC/PID techniques, including the VPH by GC/PID/FID method, use a PID lamp with an ionization energy of 10+/- eV, to provide optimum discrimination between C_5 – C_{12} aliphatic and aromatic hydrocarbon compounds. In such systems, PID response is:

- greater for aromatics than for aliphatics;
- greater for alkenes than for alkanes;
- greater for cyclic alkanes than for normal alkanes; and
- greater for branched (iso) alkanes than for normal alkanes

This leads to a significant disparity in PID response between aliphatic and aromatic hydrocarbons, with the BTEX compounds and other alkylated benzenes possessing response factors 5 to 15 times higher than the lighter C_5 and C_6 alkanes (e.g., n-Pentane and n-Hexane), and 2 to 4 times higher than the heavier (>C_9) alkanes.

Figure 5: PID Sensitivity (Molar Basis)
(Langhorst, Journal. of Chromatography, 1981)



Like PIDs and FIDs, an MS detector works by ionizing compounds, then quantifying the number of ions formed. However, an MS adds an additional and complex intermediary step: separating the generated ions by their mass/charge (m/z) ratio, before they are quantified.

Historically, MS detectors have been coupled with gas chromatographs to provide positive identification and quantification of *individual* organic compounds. While this functionality is employed in the VPH by GC/MS method (for Target Analytes), the MS is also used to quantify *collective ranges* of hydrocarbon compounds, by quantifying total and extracted ions.

When quantifying total ion response, ideally, an MS detector would respond in a consistent, near-universal manner to most aliphatic and aromatic hydrocarbons, similar to an FID. While this is not the case, the degree and significance of variations in MS detector response are not at this time completely clear.

Mass Spectrometer (MS) Total Ion Response

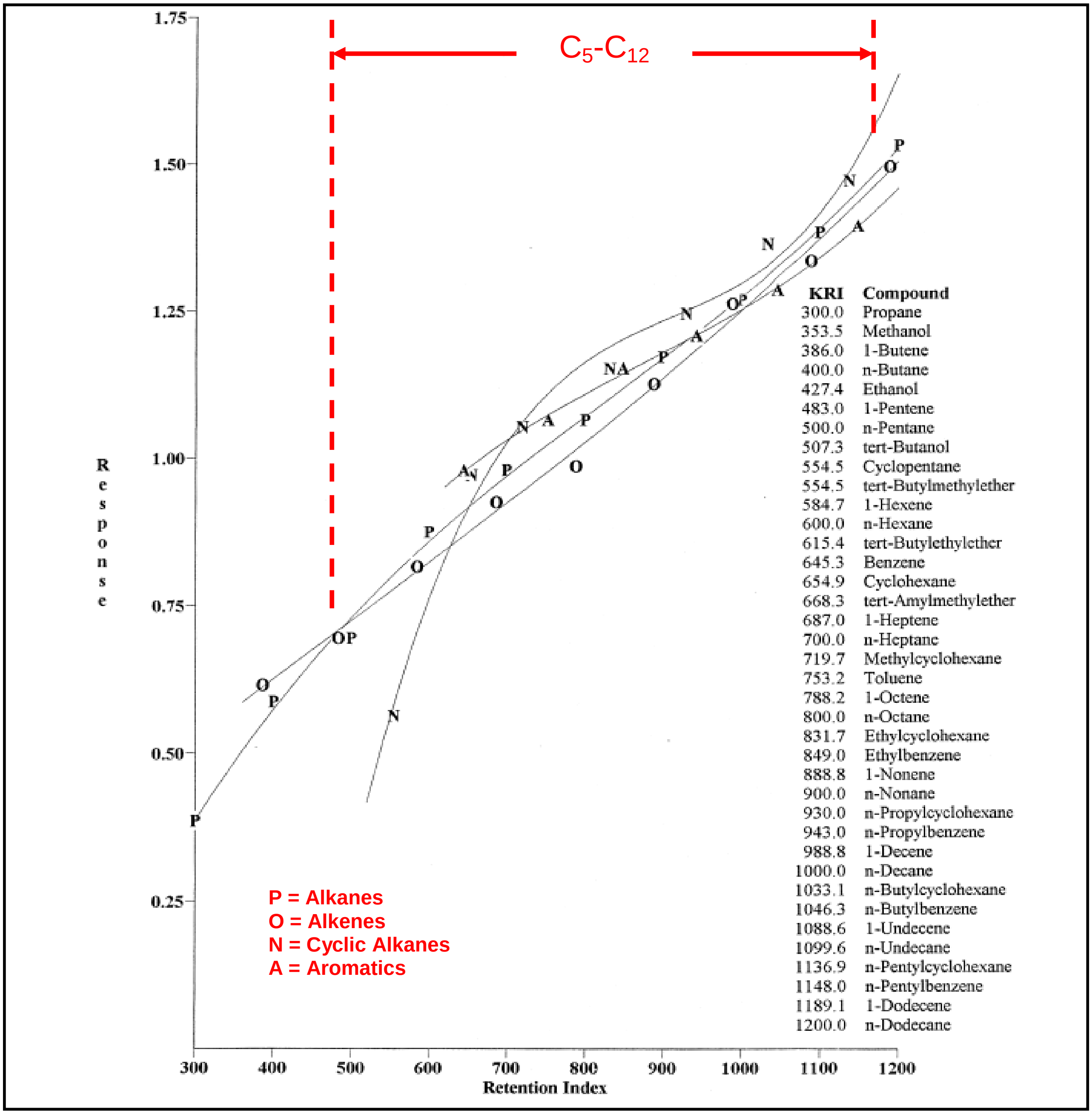
An MS unit can employ a variety of approaches to produce and separate ions. The draft VPH by GC/MS method, like EPA Method 8260, specifies use of a 70 eV *Electron Impact* (EI) ionization technique, a “hard” process that tends to split organic compounds into a number of smaller ionic fragments. While the production (and separation) of many smaller fragments aids in the qualitative identification of individual organic compounds, it can lead to differences in how various instruments quantify the total amount of all fragments produced in a given sample or in a given hydrocarbon range, which is a key element in the VPH methods.

In theory, in a 70 eV EI mass spectrometer, certain hydrocarbon structures would be expected to fragment to a higher degree than others, though the amount of ions that will be produced, transported through the mass analyzer, and ultimately contribute to a total ion current appears to be significantly influenced by MS operational and tuning parameters.

Empirically, the nature and uniformity of MS total ion response in 70 eV EI environmental applications are not something that appears to have been well studied by others. In one of the few peer-reviewed articles indentified, researchers reported a more than 3 fold difference in response factors for various classes of petroleum hydrocarbons in the C_5 to C_{12} hydrocarbon range, with response (total ion area counts) increasing with molecular weight. (*P. J. Schoenmakers et al*., *J. Chromat, A* 892 [2000] 29–46).

A plot of retention index (retention time/molecular weight) vs MS response presented in the Schoenmakers paper for gasoline-range hydrocarbons is reproduced in Figure 6.

Figure 6: MS Response to Gasoline Range Hydrocarbons
(Schoenmakers et. al., Journal. of Chromatography, 2000)

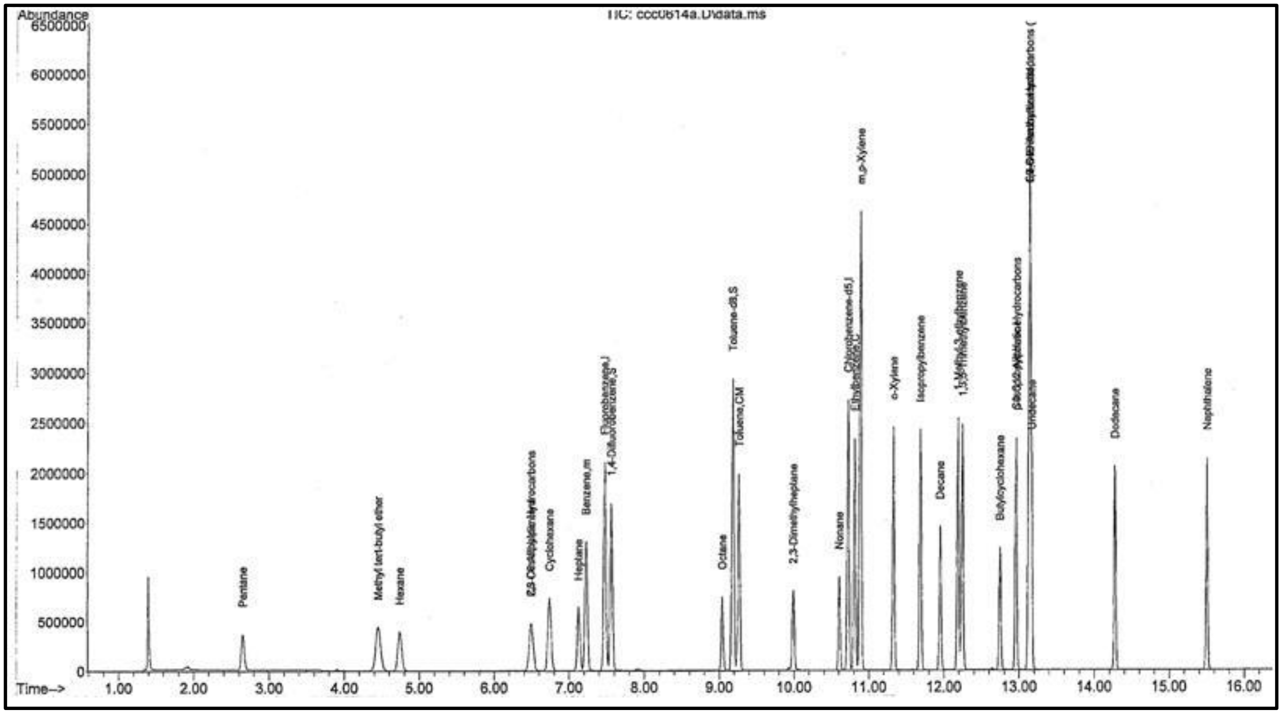


KRI	Compound
300.0	Propane
353.5	Methanol
386.0	1-Butene
400.0	n-Butane
427.4	Ethanol
483.0	1-Pentene
500.0	n-Pentane
507.3	tert-Butanol
554.5	Cyclopentane
554.5	tert-Butylmethylether
584.7	1-Hexene
600.0	n-Hexane
615.4	tert-Butylethylether
645.3	Benzene
654.9	Cyclohexane
668.3	tert-Amylmethylether
687.0	1-Heptene
700.0	n-Heptane
719.7	Methylcyclohexane
753.2	Toluene
788.2	1-Octene
800.0	n-Octane
831.7	Ethylcyclohexane
849.0	Ethylbenzene
888.8	1-Nonene
900.0	n-Nonane
930.0	n-Propylcyclohexane
943.0	n-Propylbenzene
988.8	1-Decene
1000.0	n-Decane
1033.1	n-Butylcyclohexane
1046.3	n-Butylbenzene
1088.6	1-Undecene
1099.6	n-Undecane
1136.9	n-Pentylcyclohexane
1148.0	n-Pentylbenzene
1189.1	1-Dodecene
1200.0	n-Dodecane

This finding would suggest that MS response increases with increasing molecular weight, which is consistent with an assumption that bigger molecules produce more fragments. As presented in Figure 6, this increase is about a factor of 2 to 3 over the VPH range of interest (i.e., C_5 through C_{12}). Less clear is the response characteristics based upon structure; most notably aliphatic vs aromatic. While some differences are noted in that regard in this publication, they do not appear to be significant. However, no information was provided on MS operational parameters or tuning, which is likely of relevance in this calculus.

To further explore this issue, the chromatograms and area counts provided by Round Robin participants for the VPH calibration standards were evaluated. This standard contains a mixture of 25 aliphatic and aromatic compounds throughout the C_5-C_{12} hydrocarbon range. A total ion chromatogram from Laboratory #4 is provided in Figure 7.

Figure 7: Total Ion Chromatogram for VPH Calibration Standards (Laboratory #4)

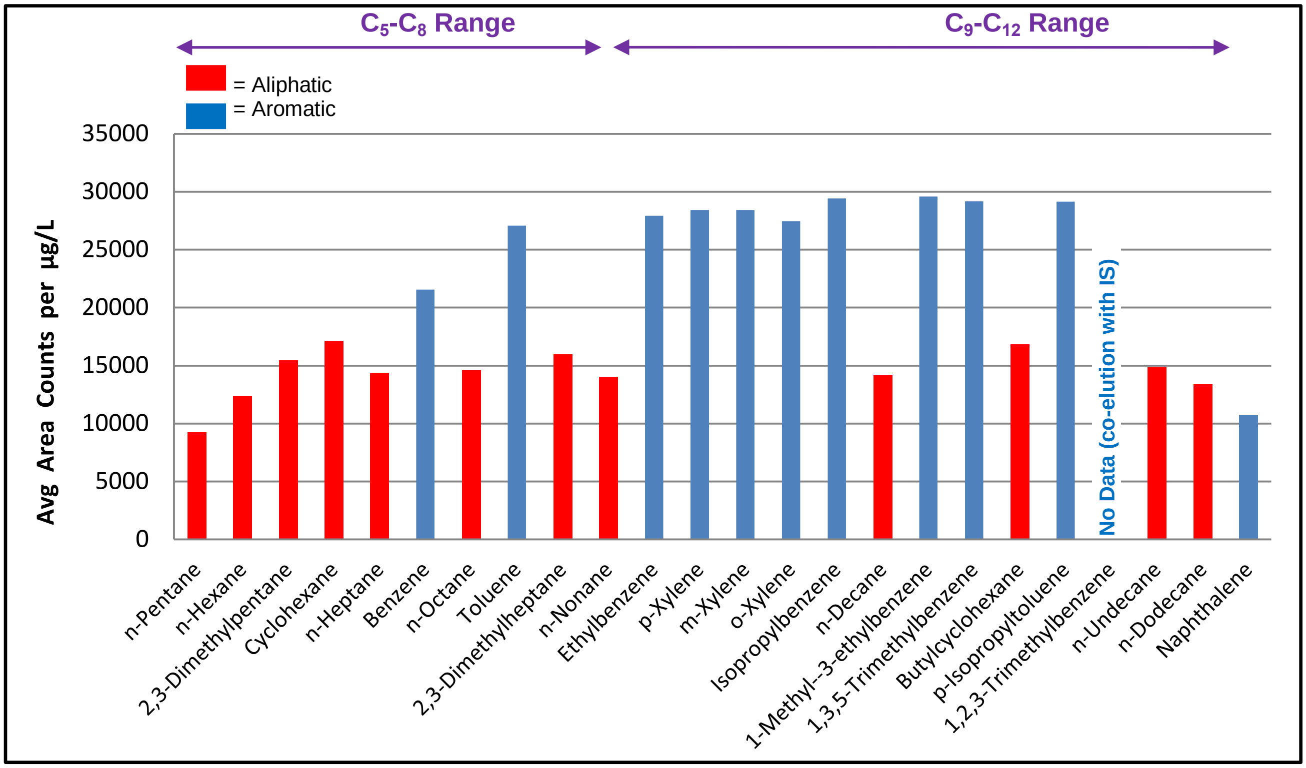


This chromatogram – in which each compound is present at the same concentration - provides visual confirmation of the Schoenmakers finding on increasing MS response with increasing molecular weight.

A more quantitative evaluation can be made by plotting total ion area counts for the VPH calibration standards. Unfortunately, only two laboratories provided reliable data in this regard: Laboratory #1 and Laboratory #4. Nonetheless, the results from both submittals were very similar, and somewhat consistent with the Schoenmakers finding that, overall, MS response increases with increasing molecular weight (though not uniformly). What is different, however, is the significantly increased response for aromatic compounds, particularly in the C_9-C_{12} hydrocarbon range. This is illustrated in Figure 8 for Laboratory #1, which is a plot of the average total ion area per µg/L of each standard over the 5 specified calibration levels.

The reasons for the positive bias for the aromatic compounds is unclear, but it likely due to MS design and operational parameters, and, perhaps most importantly, tuning characteristics. A key finding in the Schoenmakers study was that MS response changed "dramatically" every time the unit was tuned.

Figure 8: Average Total Ion Response for VPH Calibration Standards
(Laboratory #1)



Mass Spectrometer Tuning

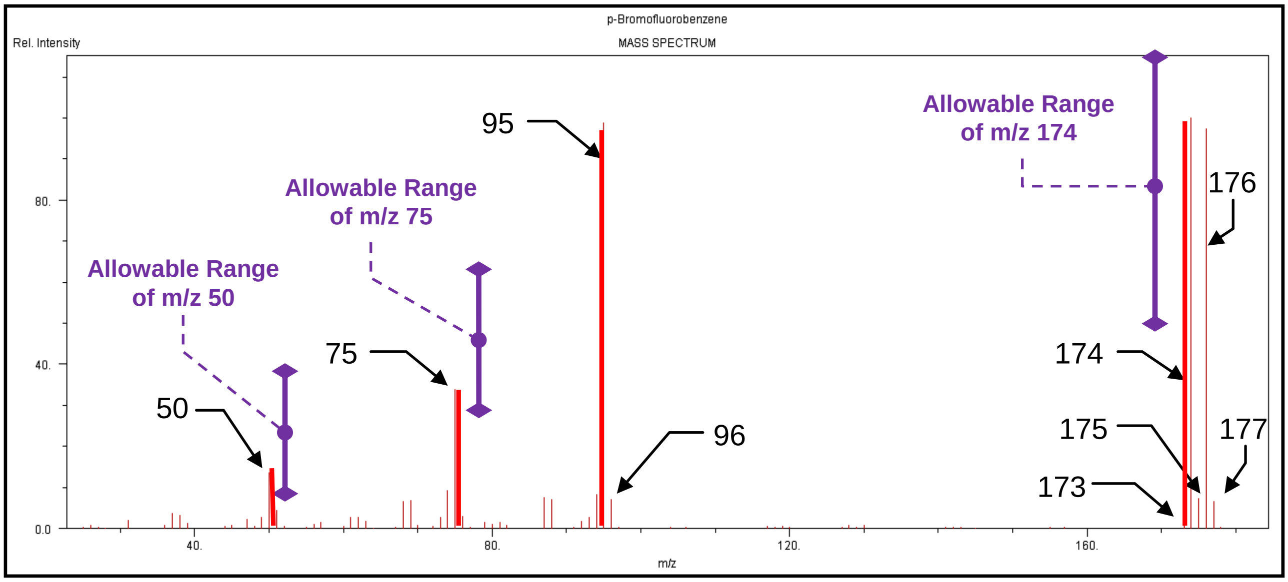
In the Round Robin evaluation, all 5 participating laboratories used Agilent mass spectrometers, either series 5973 or 5975, which incorporate a quadrupole mass analyzer and High Energy Dynode for signal processing. “Tuning” of the MS is accomplished by adjusting a number of instrument parameters and settings involving voltages, currents, and flows. A key element is the balancing of DC and RF voltages in the quadrupole to ensure proper resolution of extracted ions. This involves a trade-off between selectivity and sensitivity.

It is neither possible nor practicable to produce and maintain all system components at optimum settings. Rather, ranges of acceptability are defined and demonstrated via the twice-daily analysis of a tuning standard. In the draft VPH by GC/MS method, the tuning standard is 4-Bromofluorobenzene (BFB). Proper operation of the MS unit is confirmed based upon the relative abundances (ratio) of 9 specific ions, as depicted in Table 10, and illustrated in Figure 9.

Table 10 – VPH by GC/MS BFB Tuning Criteria

Mass	Ion Abundance Criteria	Mass	Ion Abundance Criteria
50	8.0 to 40.0 percent of m/z 95	173	Less than 2.0 percent of m/z 174
75	30.0 to 66.0 percent of m/z 95	174	50.0 to 120.0 percent of m/z 95
95	Base peak, 100% relative abundance	175	4.0 to 9.0 percent of m/z 174
96	5.0 to 9.0 percent of m/z 95	176	93.0 to 101.0 percent of m/z 174
		177	5.0 to 9.0 percent of m/z 176

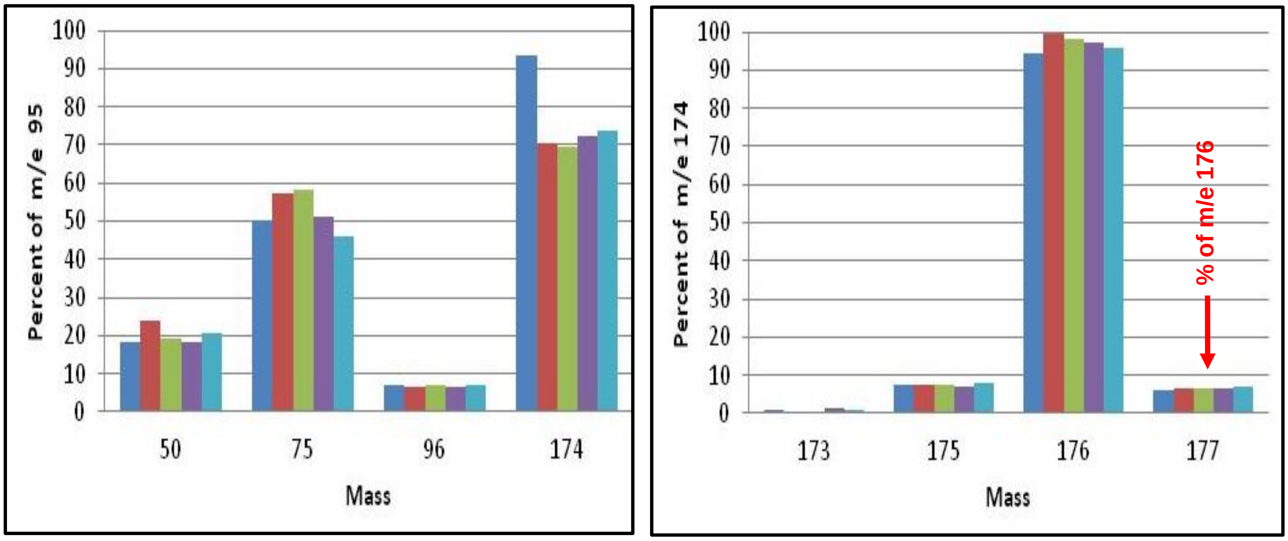
Figure 9: Mass Spectrum for 4-Bromofluorobenzene (BFB) and Allowable Tune Range



While these ranges have proven to be a satisfactory metric for “conventional” GC/MS procedures (e.g., EPA 8260) that focus on the identification and quantification on a limited number of target analytes, it is not clear what effect variations in ion ratios will have on total ion response for a large number of compounds.

To obtain some insight in this regard, the BFB tuning data were obtained from participating laboratories for the VPH sample analyses. These data are displayed in Figure 10.

Figure 10: Tuning Data for the 5 Round Robin Laboratories



As can be seen, all BFB mass ratios for all laboratories were within method specifications. Moreover, the state of tune was similar for all laboratories; perhaps a reflection of the use of the same or simillar MS model (i.e., Agilent series 5973 or 5975). The only notable difference was the higher value for Laboratory #1 (blue column) for m/z 174, with respect to m/z 95. However, it is not clear what effect this had on total ion area, or whether the use of different types of mass spectrometers would lead to different tuning conditions and significantly different MS responses.

Extracted Ions

In the VPH by GC/MS method, two ions (m/z 120 and m/z 134) are extracted from the total ion chromatogram (TIC) over a specified interval, from just after the elution of o-Xylene to just before the elution of Naphthalene. These specific ions were chosen because they are indicative of C_9 (m/z 120) and C_{10} (m/z 134) aromatic structures. Peaks of these ions in an extracted ion chromatogram are qualitative evidence of the presence of C_9-C_{10} Aromatic Hydrocarbons in a sample. The method then attempts to quantify the concentration of such hydrocarbons by integrating the areas of these extracted ion peaks, and comparing these areas to a pre-established area-count/concentration relationship for these extracted ions from a calibration standard that contains 5 aromatic compounds – *compounds that may or may not be present in the sample being analyzed.*

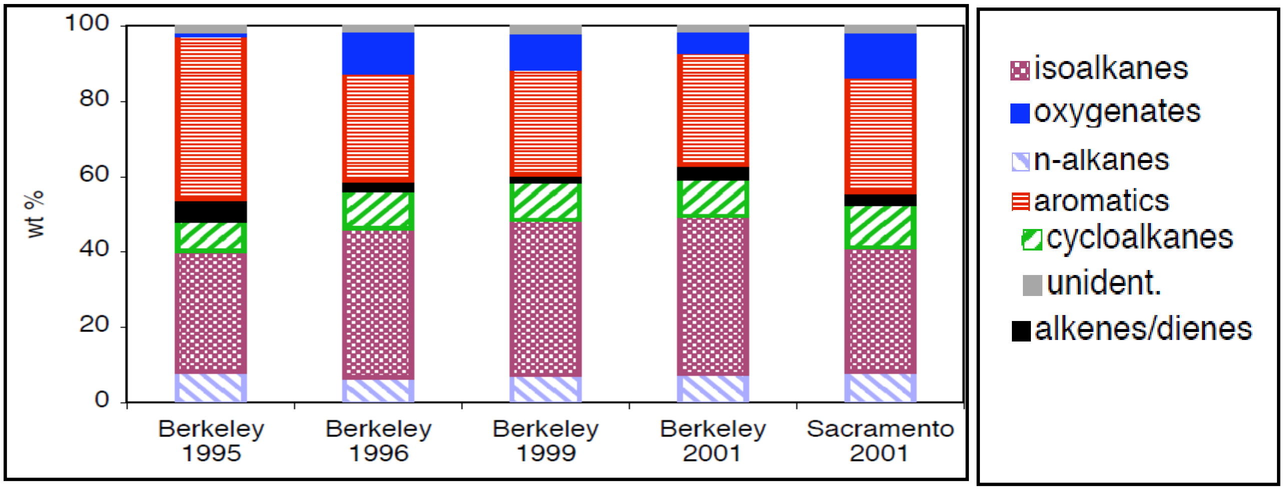
Thus, with respect to the quantification of C_9-C_{10} Aromatic Hydrocarbons using extracted ions, variability and bias may be present due not only to MS operational and tuning conditions, but also due to the specific chemistry of any given sample, with respect to the representativeness of the m/z 120 and m/z 134 area/concentration calibration relationship for the range and ratios of aromatic hydrocarbon compounds that can be expected in “real world” samples. Of interest are the nature and significance of these potential biases, and whether they would on balance result in conservative/ health-protective data.

METHODOLOGICAL BIASES

Although one of the benefits of the VPH hydrocarbon range approach is its applicability to any sample, even if the type/weathered state of the fuel release is unknown, a consideration of gasoline chemistry can provide insight into the biases and protectiveness of the VPH procedures, given that gasoline is the most widely spilled and most toxic light hydrocarbon mixture.

While the composition of gasoline varies over time and between refineries, it is composed primarily of branched (iso) alkanes, aromatics, cyclic (cyclo) alkanes, normal alkanes, and oxygenates, as presented in Figure 11, which provides composition data from gasoline samples obtained in Berkeley and Sacramento California between 1995 and 2001. (http://www.arb.ca.gov/airways/ccos/docs/ii5_0014_aug04_fr.pdf). A listing of specific gasoline constituents presented in this publication is provided in Appendix A.

Figure 11: Composition of Gasoline, California Air Research Board, 2004



As can be seen, gasoline is dominated by isoalkanes and aromatic hydrocarbons, though the aromatic content has decreased over time as the percentage of oxygenates (e.g., Ethanol) has increased. Alkenes may also be present in small to moderate percent levels, depending upon refinery operations (e.g., catalytic cracking of high molecular weight aliphatic hydrocarbons).

Once released into the environment, the chemistry of the gasoline and impacted media will be affected by various and variable physical, chemical, and biological processes. In soil samples, lower-molecular weight alkanes (C_5-C_8) will volatilize and biodegrade, with the normal alkanes most degradable, followed by branched and then cyclic alkanes, resulting in weathered samples dominated by aromatic and heavier-molecular-weight branched and cyclic alkanes. Conversely, groundwater samples will be dominated by the soluble mono aromatic (BTEX) hydrocarbons.

Expected Systemic Bias

Systemic bias can result from two factors:

- Detector response and selectivity, which can influence the quantification of Target Analytes and hydrocarbon ranges; and
- The data manipulation steps in each method, which requires the subtraction of Target Analytes from both Aliphatic Hydrocarbon ranges, and subtraction of C_9-C_{10} Aromatic Hydrocarbons from the C_9-C_{12} Aliphatic Hydrocarbon range.

GC/PID/FID Procedure

Detector Response and Selectivity

Since identification is via a PID, the quantification of Target Analytes (BTEX, MtBE, and Naphthalene) may be biased high, given the possibility of co-eluting aliphatic hydrocarbons. This concern is relatively minimal in water samples, in which the water-soluble fraction is dominated by the BTEX Target Analytes. Soil samples can contain many more components and chromatographic peaks, leading to a higher likelihood that non-aromatic hydrocarbons could co-elute with a Target Analyte. Interference and over-quantification in this manner is however likely to be modest, at best, given the selectivity of the PID, and likelihood that co-eluting compounds will be poorly-responding alkanes. An exception could occur in soil samples impacted by gasoline blends that contained appreciable quantities of alkenes, which will respond well on the PID. Notwithstanding that possibility, it is noteworthy that PID Target Analyte over-quantification was not shown to be a significant problem in the 1997 and 2012 Round Robin testing programs.

With respect to hydrocarbon range data, the FID quantification of C_5-C_8 and C_9-C_{12} Aliphatic Hydrocarbons is expected to be reasonably accurate, regardless of the matrix or degree of weathering, given the response characteristics of the FID to the alkanes and aromatics that will dominate this hydrocarbon range.

Conversely, the PID will likely over-quantify the concentrations of aromatics in the C_9-C_{10} hydrocarbon range, especially in soil samples, given the presence of aliphatic compounds. While PID response to such compounds is relatively low on a 10 +/- eV uV lamp, compared to the response to aromatic hydrocarbons (see Table 11), the *collective* ion signal can become significant if many aliphatics are present – as can be the case in fresh and moderately weathered gasoline-contaminated soil samples. The presence of better-responding alkenes will also add to this positive bias, though this is appropriate, given that the toxicity of alkenes is closer to aromatics than to aliphatic hydrocarbons.

Data Manipulations

Because the (likely over-quantified) C_9-C_{10} Aromatic Hydrocarbon concentrations are subtracted from the unadjusted C_9-C_{12} Aliphatic Hydrocarbon levels, the final (adjusted) C_9-C_{12} Aliphatic Hydrocarbon range is likely to be biased low, particularly in soil samples.

Similarly, over-quantification of the Target Analytes by the PID could lead to a slight negative bias in the calculation of C_5-C_8 and C_9-C_{12} (adjusted) Aliphatic Hydrocarbon values, as the concentration of (PID determined) Target Analytes are subtracted from the collective unadjusted hydrocarbon range concentrations.

GC/MS Procedure

Detector Response and Selectivity

Given the use of a mass spectrometer, Target Analytes should be accurately detected, without any significant positive bias attributable to co-eluting compounds. MS hydrocarbon range quantification data are however subject to more variability and bias, based upon operational and tuning parameters, as previously discussed.

Of particular note is the potential for a positive bias in the quantification of C_9-C_{12} Aliphatic Hydrocarbons, if indeed total ion area response to aromatic compounds in this hydrocarbon range is significantly greater than the aliphatic response. In such a case, the Response Factor developed for the C_9-C_{12} Aliphatic Hydrocarbons range, which is based on the total ion area/mass response of 6 alkanes, will translate the elevated peak area counts of the aromatics as higher-than-actual concentrations of hydrocarbons. This bias will likely be highest in water samples, where most of the water soluble fraction in this hydrocarbon range is aromatic compounds.

Contrary to the above, the use of extracted ions 120 (m/z) and 134 (m/z) to quantify C_9-C_{10} Aromatic Hydrocarbons should minimize the potential for systemic bias (high or low), assuming that the tuning state of the MS does not significantly impact the detection and quantification of these ions. Of greater concern in this regard is the representativeness of the C_9-C_{10} Aromatic Hydrocarbon calibration standard to "real world" sample chemistries. This is especially true given that the 120 (m/z) and 134 (m/z) ions are not generally among the most abundant fragmentation ions in C_9-C_{10} Aromatic Hydrocarbon compounds. Once again, an understanding of the likely chemistry of real-world samples can provide perspective in this matter.

As presented in Figure 11, aromatic hydrocarbons comprise between 25% and 35% of a fresh gasoline. As detailed in Appendix A, this aromatic fraction is dominated by the BTEX compounds, which comprise about 15 to 20% of gasoline, by weight, or 45 to 60% of the aromatic fraction, as presented in Figure 12. Beyond the BTEX components, about 70 additional aromatic compounds are likely to be found in a fresh gasoline product. However, this remaining fraction is in turn dominated by 10 specific compounds, which collectively comprise about 6% of gasoline by weight, or about 30% of the aromatic content (Figure 12). The concentrations of these ten aromatic gasoline constituents are presented in Figure 13.

Figure 12: Aromatic Content of Gasoline

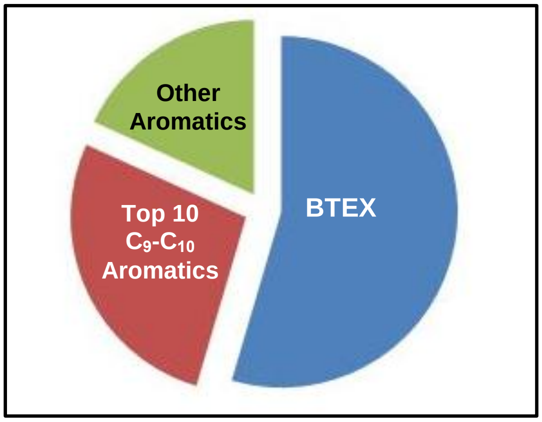
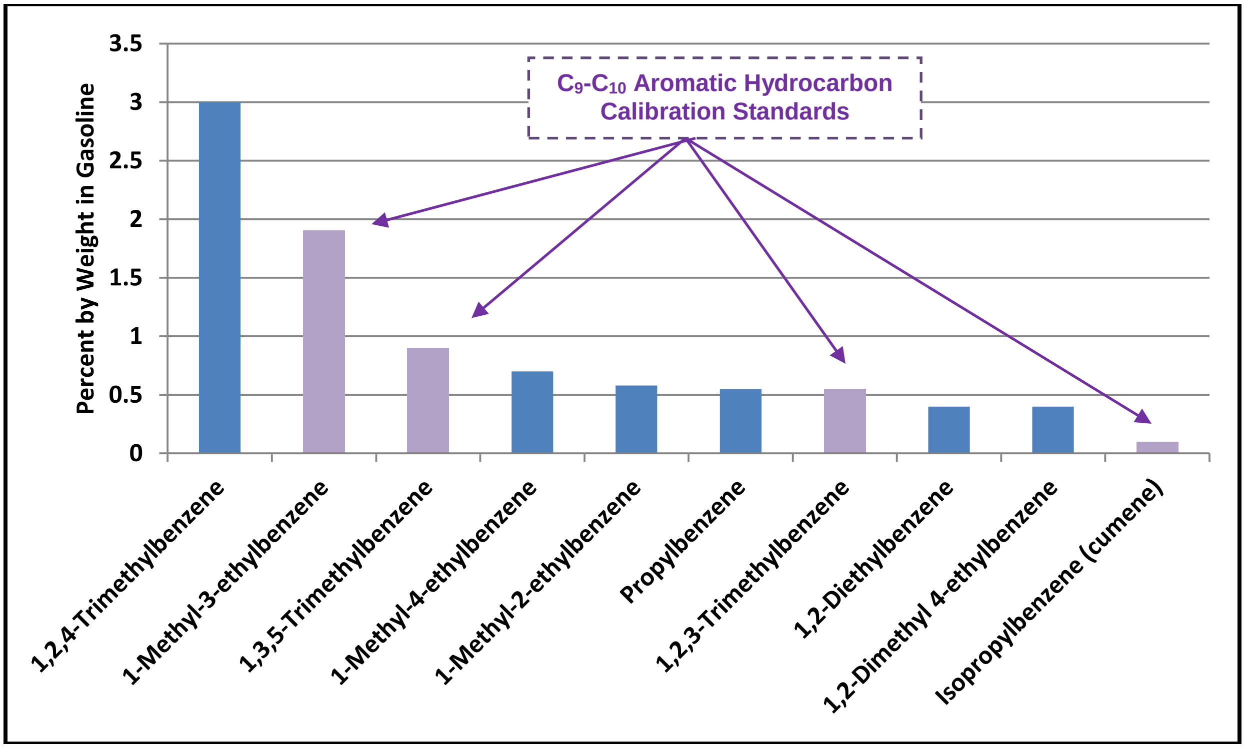


Figure 13: Top Ten C_9-C_{10} Aromatic Hydrocarbon Compounds in Gasoline (CARB, 2004)



Further information on these 10 aromatic compounds is provided in Table 11, including the abundance (percent) of ions m/z 120 and m/z 134 among all ionization fragments produced by a 70 ev EI mass spectrometer, excluding ions less than m/z 35, which are not detected in the VPH by GC/MS method. These data, obtained from the NIST Chemistry Web Book (http://webbook.nist.gov/chemistry/), are graphically displayed in Figure 14.

Figure 14: Ionization of Top Ten C_9-C_{10} Aromatic Hydrocarbon Compounds in Gasoline

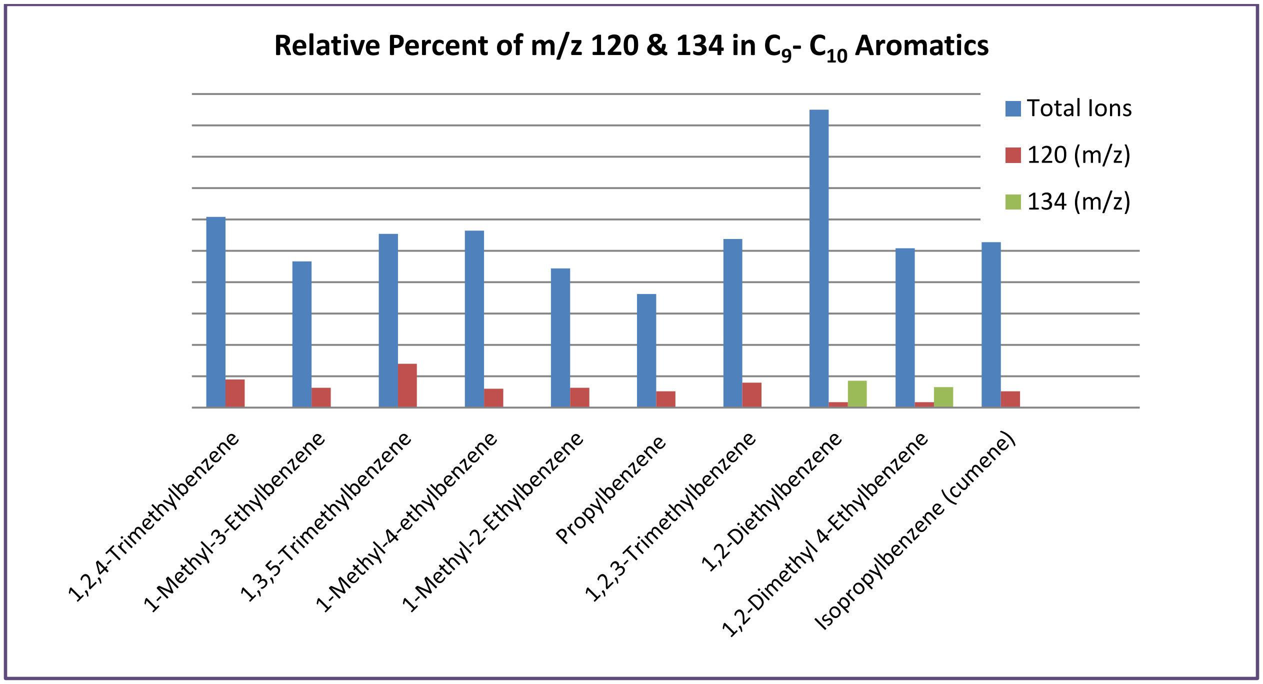


Table 11: Aromatic Hydrocarbon Compounds in Gasoline

Compound			#C	CAS #	Wt % in Gasoline	% m/z[1]		Response	
						120	134	MS TIC[2]	PID RF[3]
BTEX		Benzene	C6	71-43-2	0.5	-	-	-	-
		Toluene	C7	108-88-3	6 - 9	-	-	-	-
		Ethylbenzene	C8	100-41-4	1.5 - 2	-	-	-	-
		p/m Xylenes	C8	-	5 - 7	-	-	-	-
		o-Xylene	C8	95-47-6	2 - 3	-	-	-	-
$C_9 - C_{10}$ Aromatics	Top Ten C_9-C_{10} Aromatics	1,2,4-Trimethylbenzene	C9[a]	95-63-6	2.4 - 3.5	15	0	+/- 25%	4.0
		1-Methyl-3-Ethylbenzene	C9[b]	620-14-4	1.5 - 2.3	14	0	+/- 25%	NA
		1,3,5-Trimethylbenzene	C9[b]	108-67-8	0.8 - 1.2	25	0	+/- 25%	4.0
		1-Methyl-4-Ethylbenzene	C9	622-96-8	0.6 - 0.9	11	0	+/- 25%	NA
		1-Methyl-2-Ethylbenzene	C9	611-14-3	0.4 - 0.8	14	0	-	NA
		Propylbenzene	C9	103-65-1	0.4 - 0.7	14	0	-	2.7
		1,2,3-Trimethylbenzene	C9[b]	526-73-8	0.4 - 0.7	15	0	+/- 25%	NA
		1,2-Diethylbenzene	C10	135-01-3	0.3 - 0.6	2	9	-	NA
		1,2-Dimethyl 4-Ethylbenzene	C10	934-80-5	0.2 - 0.5	4	13	-	NA
		Isopropylbenzene (Cumene)	C9 [b]	98-82-8	0.09 - 0.1	10	0	+/- 25%	NA
	p-Isopropyltoluene		C10 [b]	99-87-6	0.01 - 0.03	4	10	+/- 25%	NA

[1] indicates the % abundance of 120 and 134 extracted ions > 35 AMUs among all fragments for compound (NIST)
[2] expected consistency of Total Ion response for range components, within the range of interest, based on Figure 8
[3] response factor on PID normalized to n-Nonane, from RAE Systems, 10.6 eV PID lamp (NA = Not Available)
[a] calibration standard in GC/PID/FID VPH method for C_9-C_{10} Aromatic Hydrocarbons
[b] calibration standard in GC/MS VPH method for C_9-C_{10} Aromatic Hydrocarbons

In the VPH by GC/MS procedure, the C_9-C_{10} Aromatic Hydrocarbon standard consists of four C_3-alkybenzenes (i.e., C_9 aromatics) and one C_4 alkylbenzene (i.e., C_{10} aromatic), as indicated by purple shading in Table 11. This table also lists MS and PID response characteristics for these components, along with the other aromatic compounds that are most abundant in gasoline (see Appendix A).

As can be seen in Table 11, 4 of the 5 calibration standards are among the most abundant C_9 aromatic compounds in gasoline, with the 5th standard, p-Isopropyltoluene, a less abundant C_{10} aromatic compound. Notably, the most abundant C_9 aromatic, 1,2,4-Trimethylbenzene, is not part of the calibration mixture.

Of interest in the C_9-C_{10} Aromatic hydrocarbon fraction is the representativeness of the ion fragments from the 5 calibration standards. In this regard, the *% m/z* column in Table 11 indicates the prevalence of ions m/z 120 and m/z 134 among all compound fragments greater than m/z 35, the lower limit of scanning in the VPH by GC/MS method. For example, ion m/z 120 represent 14% of the ion fragments for 1-Methyl-3-Ethylbenzene (that are more than m/z 35 in size).

For most of the listed C_9-C_{10} Aromatic Hydrocarbons, the m/z 120 and/or m/z 134 ions represent about 15% of all fragmentation ions. A notable exception is 1,3,5-Trimethylbenzene, for which the ion m/z 120 represents 25% of all fragmentation ions greater than m/z 35. This elevated abundance of m/z 120 in 1,3,5-Trimethylbenzene leads to an increase in the area count of the m/z 120 ion for this compound, which somewhat increases the hydrocarbon Range Response Factor, and therefore may potentially *decrease* the range concentration value – a negative (non-conservative) bias, if most aromatic hydrocarbon compounds in gasoline produce the m/z 120 ion at a lower percentage of total fragments. However, this negative bias is not likely to be substantial, given the relatively high concentrations of 1,3,5-Trimethylbenzene in gasoline, and because this compound is only one of 5 calibration standards. Consideration should nonetheless be given to eliminating this compound from the calibration standard.

Conversely, as indicated in Table 11, only one of the C_9-C_{10} Aromatic Hydrocarbon calibration standards – p-isopropyltoluene – produces a significant number of ion m/z 134 (i.e., m/z 134 comprises 10% of the > m/z 35 fragmentation ions of p-isopropyltoluene). However, 3 of the most abundant aromatic compounds in gasoline (1,2-Diethylbenzene, 1,2-Dimethyl 4-Ethylbenzene, and 1-Methyl 3-Propylbenzene) generate somewhat higher levels of this ionic fragment (about 15%). This leads to a somewhat low RRF value, which in turns leads to a positive bias in quantification of aromatic hydrocarbons in real-world samples. While it appears that the low RRF for m/z 134 may lead to a significant over-reporting of some aromatic compounds in real world samples (mostly C_{10} compounds), the overall effect appears to be moderate, given the predominance of the C_9 aromatics in this hydrocarbon range.

Based upon the totality of the above considerations, notwithstanding any affects of MS operational and tuning issues, it is likely that the VPH by GC/MS method will produce C_9-C_{10} Aromatic Hydrocarbon data that are reasonably accurate to moderately conservative (and thus health protective) for most “real world” samples.

Data Manipulations

Significant bias is not expected in the quantification of Target Analytes, and thus in the adjustment of the aliphatic hydrocarbon ranges by subtraction of the Target Analytes. Furthermore, a significant bias is not expected in the adjustment of the C_9-C_{12} Aliphatic Hydrocarbon range, based upon subtraction of the of the C_9-C_{10} Aromatic Hydrocarbon range (though, as previously noted, there may be a high bias in the calculation of C_9-C_{12} Aliphatic Hydrocarbons, if MS response is as depicted in Figure 8).

Observed Data Biases

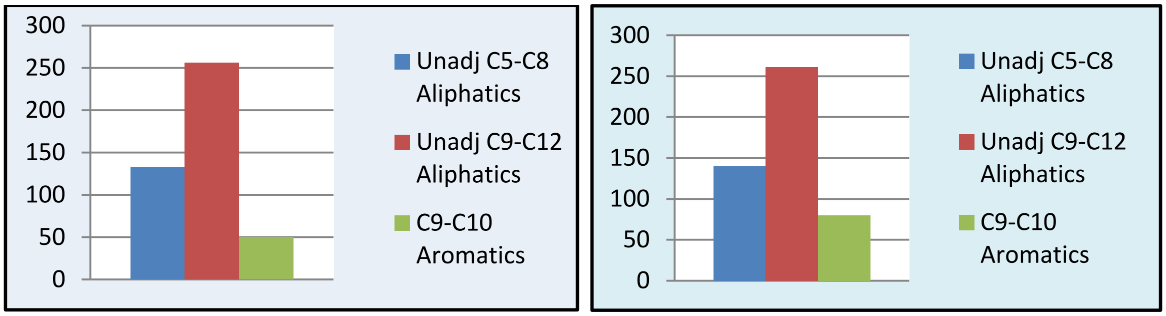
An examination of the Round Robin study data provides additional insight into potential biases, at least for gasoline contaminated media.

Hydrocarbon range data from the GC/MS and GC/PID/FID procedures are displayed in Figures 15 through 17. The unadjusted hydrocarbon range data best represents “raw” detector responses, while the adjusted data best illustrates the effects of hydrocarbon range data manipulation steps as well as the “bottom line” concentration values that are compared to cleanup standards. Note that GC/MS data from Laboratory #5 was not used for the Aliphatic Hydrocarbon ranges, given the use of an inappropriate chromatographic column, and that Laboratory #1 did not provide data for the GC/PID/FID method.

Of interest is how data from the draft GC/MS method compare to the existing GC/PID/FID procedure.

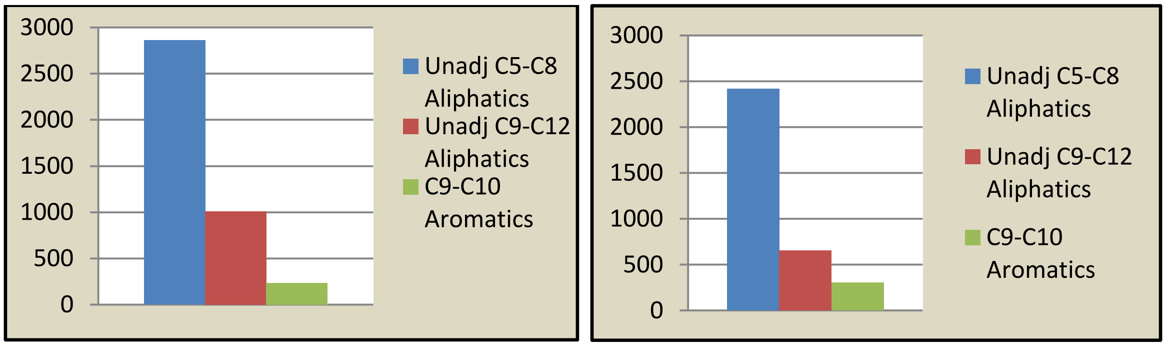
In order to graphically display positive and negative differences, percent difference values were calculated comparing the draft GC/MS method to the existing GC/PID/FID method. These data are graphically presented in Figure 18, using the following equation:

Figure 15: Mean Concentration Data for Unadjusted Hydrocarbon Ranges



Water Samples by GC/MS, µg/L (4 Labs)

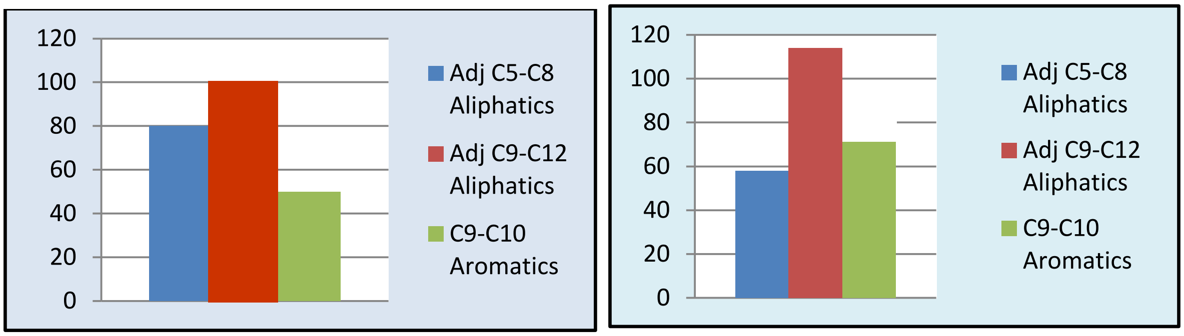
Water Samples by GC/PID/FID, µg/L (4 Labs)



Soil Samples by GC/MS, mg/kg (4 Labs)

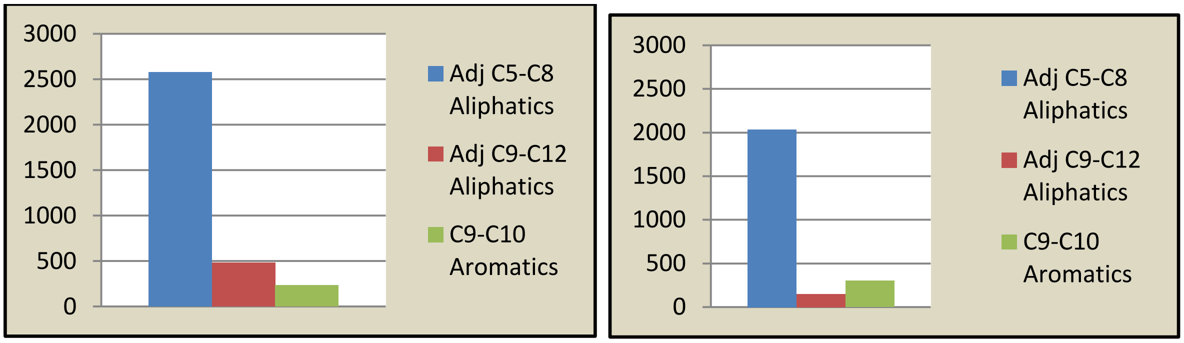
Soil Samples by GC/PID/FID, mg/kg (4 Labs)

Figure 16: Mean Concentration Data for Adjusted Hydrocarbon Ranges



Water Samples by GC/MS, µg/L (4 Labs)

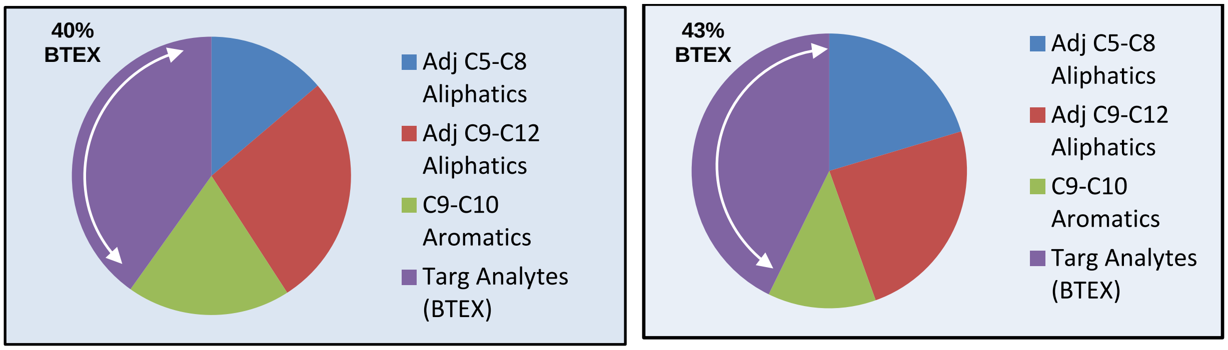
Water Samples by GC/PID/FID, µg/L (4 Labs)



Soil Samples by GC/MS, mg/kg (4 Labs)

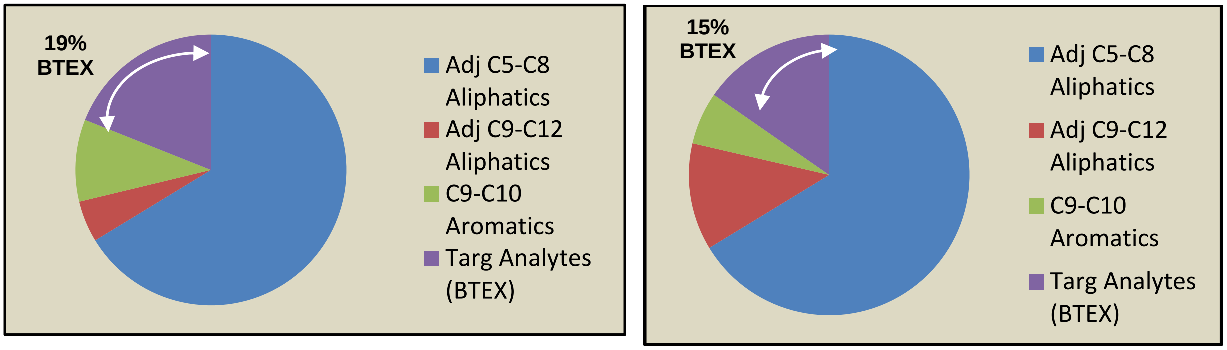
Soil Samples by GC/PID/FID, mg/kg (4 Labs)

Figure 17: Relative Percentages of Hydrocarbon Ranges and Target Analytes



GC/PID/FID Water Data

GC/MS Water Data



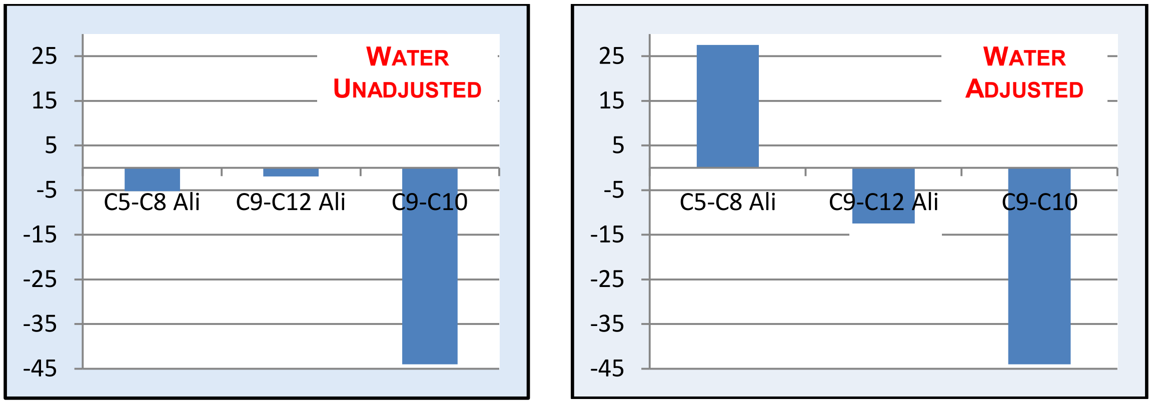
GC/PID/FID Soil Data

GC/MS Soil Data

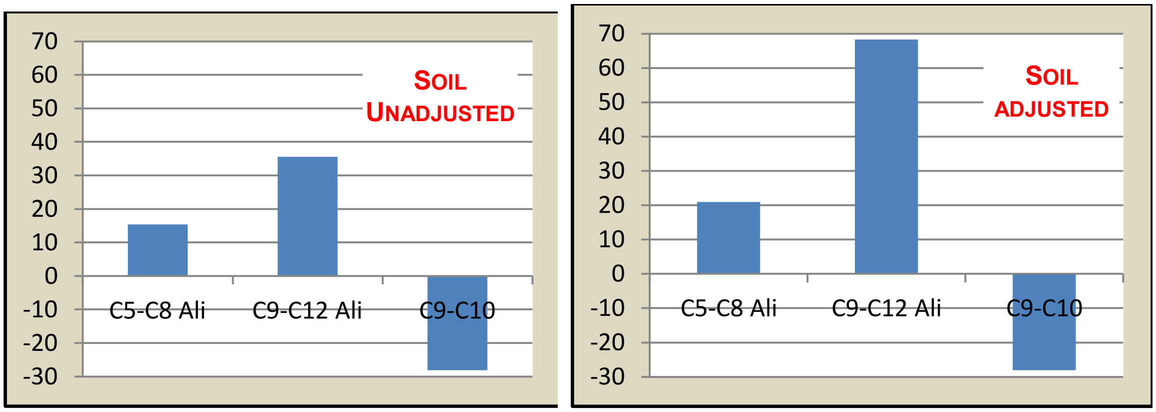
Figure 18: Percent Difference: GC/MS vs. GC/PID/FID Method

(Positive Value Means GC/MS is More Conservative)

Water Samples



Soil Samples



$$\%D \;=\; \frac{[\text{GC/MS Conc}] - [\text{GC/PID/FID Conc}]}{\text{GC/MS Conc}} \quad \text{X } 100$$

The data presentations in Figures 14 through 17 provide the basis for certain broad conclusions:

- Both methods provide similar results for C_5-C_8 Aliphatics, with respect to relative and absolute concentration values;
- As predicted, the PID/FID method provides a consistently more conservative quantification of C_9-C_{10} Aromatics; and
- As predicted, the MS method provides more conservative values for C_9-C_{12} Aliphatics in soil, especially for the "Adjusted" concentration value. The results from the water samples are not deemed to be instructive, given the low/non-detect levels of hydrocarbons present.

It is not surprising that PID/FID results for C_9-C_{10} Aromatics are consistently higher (more conservative) than the MS method results. It has always been known that the presence of non-aromatics in this carbon range will inflate the PID value for this hydrocarbon range; these data suggest this bias is in the order of 30 to 40%, assuming the extracted-ion MS method produces a more accurate quantification of these analytes.

Since the "Adjusted" C_9-C_{12} Aliphatic concentration involves the subtraction of the C_9-C_{10} Aromatics concentration, it was expected that the Adjusted C_9-C_{12} Aliphatics MS method value may be higher than the PID/FID value. Moreover, as predicted, the data from this Round Robin study also indicate a high bias in the MS response to the "Unadjusted" C_9-C_{12} Aliphatics for soil (compared to the FID response in the PID/FID method), due to the significantly higher MS response to aromatic compounds than to aliphatic compounds in this hydrocarbon range (the water data is inconclusive due to low concentrations and data values below Reporting Limits). This synergistic combination of independent factors creates a significant difference in the reported concentrations of C_9-C_{12} Aliphatic Hydrocarbons between the GC/PID/FID and GC/MS methods.

Significance of Bias

The VPH method is designed to support risk assessment and cleanup decisions in the Massachusetts Contingency Plan. The significance of the absolute and relative biases in the PID/FID and MS procedures can be best evaluated by an examination of the VPH standards in the key groundwater and soil cleanup categories provided in Table 12.

Table 12: VPH Cleanup Standards for Key Groundwater/Soil Categories

MCP Groundwater Cleanup Standards (µg/L)

	Adjusted Aliphatics		C_9-C_{10} Aromatics	Target Analytes				
	C_5-C_8	C_9-C_{12}		Ben	Tol	EB	XYL	Naph
GW-1	300	700	200	5	1000	700	10,000	140
GW-2	3000	5000	4000	1000	50,000	20,000	3000	700
GW-3	50,000	50,000	50,000	10,000	40,000	5000	5000	20,000

MCP Soil Cleanup Standards (µg/g)

	Adjusted Aliphatics		C_9-C_{10} Aromatics	Target Analytes				
	C_5-C_8	C_9-C_{12}		Ben	Tol	EB	XYL	Naph
S-1/GW-1	100	1000	100	2	30	40	400	4
S-1/GW-2	100	1000	100	40	500	500	100	20
S-2/GW-2	500	3000	500	200	1000	1000	100	20

Groundwater Samples

For groundwater, MCP category GW-1 refers to drinking water resource areas, which applies to perhaps 10% to 20% of gasoline contaminated sites in Massachusetts. GW-2 refers to areas near buildings, which applies to more than half of all sites.

As indicated in Figure 17, BTEX components and C_9-C_{10} Aromatics comprise the bulk of the water-soluble fraction of gasoline. As such, in GW-1 areas, it appears that the risk/cleanup drivers are Benzene, followed by C_9-C_{10} Aromatic Hydrocarbons. In very “fresh” spills, C_5-C_8 Aliphatic Hydrocarbons may also be a driver. In the more prevalent GW-2 areas, the most likely drivers are Benzene and C_9-C_{10} Aromatics, given that the solubility limit of the C_5-C_8 and C_9-C_{12} Aliphatics are likely less than the 3000 and 5000 µg/L standards, respectively. Even the 4000 µg/L standard for C_9-C_{10} Aromatics is pushing the theoretical solubility limits of these compounds. Finally, in GW-3 areas (all sites), the only possible driver would appear to be Ethylbenzene, though once again the 5000 µg/L standard is pushing the boundaries of its solubility (even though its single-component solubility is higher, its dissolution in groundwater from gasoline is controlled by its mole fraction in gasoline as characterized in Raoult’s law).

C_9-C_{12} Aliphatic Hydrocarbons are unlikely to be a risk or cleanup driver in groundwater.

Soil Samples

There are 9 categories of soil standards in the MCP, comprised of a matrix of 3 soil categories (S-1, S-2, and S-3) overlying the 3 groundwater categories (GW-1, GW-2, and GW-3). The most stringent category is generally S-1/GW-1, which applies to “residential” areas situated over a drinking water resource area. The more common “residential” category is S-1/GW-2. The most common overall category is probably S-2/GW-2.

As indicated in Figure 17, “fresh” gasoline spills in soil are dominated by C_5-C_8 aliphatics, with BTEX comprising about 15% of the mixture. However, as the contaminated soil weathers, the lighter aliphatics volatilize and biodegrade, increasing the relative percentages of the C_9-C_{12} Aliphatics and C_9-C_{10} Aromatics.

In the most stringent cleanup areas (S-1/GW-1), it is likely that the BTEX/naphthalene components would be the risk and cleanup drivers, followed by C_5-C_8 Aliphatic Hydrocarbons for fresh spills, transitioning to C_9-C_{10} Aromatic Hydrocarbons as weathering occurs. In the S-1/GW-2 and S-2/GW-2 areas, it appears the C_5-C_8 Aliphatic Hydrocarbons will be the initial driver, transitioning to C_9-C_{10} Aromatics over time.

C_9-C_{12} Aliphatics are unlikely to be a risk or cleanup driver in soil.

In light of the above, while the GC/MS method appears to have a moderate overall positive bias, compared to the PID/FID method, it responds similarly to the C_5-C_8 Aliphatic Hydrocarbons, and is less conservative (and more accurate) for C_9-C_{10} Aromatics – the two hydrocarbon ranges that are likely to drive risk and cleanup decisions. The other drivers – the BTEX components – were very closely correlated for both procedures in this study, though, in theory, the PID/FID method could over-quantify these analytes for samples where non-aromatics are co-eluting with the BTEX compounds.

CONCLUSIONS AND RECOMMENDATIONS

On the basis of the information and data presented and discussed in this report, the following conclusions are offered:

- A majority of the participating laboratories had difficulties properly running the MS method and processing raw data. While increased emphasis of key issues in the MS method may help mitigate this problem, increased diligence by and training of analysts appears to be strongly warranted.

- When properly run, both the GC/PID/FID and GC/MS VPH methods appear capable of providing reasonably similar, accurate and health-protective data for gasoline contaminated samples.

- Both methods produced similar results for C_5-C_8 Aliphatics and the BTEX/Naphthalene Target Analytes.

- As always known, the PID/FID method tends to over-quantify C_9-C_{10} Aromatic Hydrocarbons, at concentrations that are perhaps 30% higher than the MS method. The positive bias in the PID/FID method for C_9-C_{10} Aromatic Hydrocarbons is attributable to minor though collectively significant PID response to aliphatic hydrocarbons that elute within this range. Due to the low solubility of aliphatics, this is unlikely to be a significant issue in water samples, though it may be more of a concern in soil samples classified as "S-1" under the MCP.

- The MS method appears to over-quantify C_9-C_{12} Aliphatic Hydrocarbons, due to the increased MS total ion area counts for aromatic compounds in this hydrocarbon range. It is not clear if this bias will exist for all mass spectrometers in all states of permissible tuning. However, in any event, this is unlikely to be an issue at most sites, given that C_9-C_{12} Aliphatic Hydrocarbons are not expected to be a risk or cleanup driver.

- Additional efforts are needed to evaluate variability and biases that may be present in the GC/MS procedure based upon operational and tuning considerations.

- Consideration should be given to changing the C_9-C_{10} Aromatic Hydrocarbon calibration standard mixture for the VPH by GC/MS method, substituting 1,2,4-Trimethylbenzene for 1,3,5-Trimethylbenzene:

  - ☞ 1,2,4-Trimethylbenzene is significantly more abundant in gasoline than 1,2,3-Trimethylbenzene.

  - ☞ The fragmentation of 1,3,5-Trimethylbenzene (with respect to the abundance of extracted ion m/z 120) can lead to a somewhat non-conservative hydrocarbon Range Response Factor, which is not the case with 1,2,4-Trimethylbenzene.

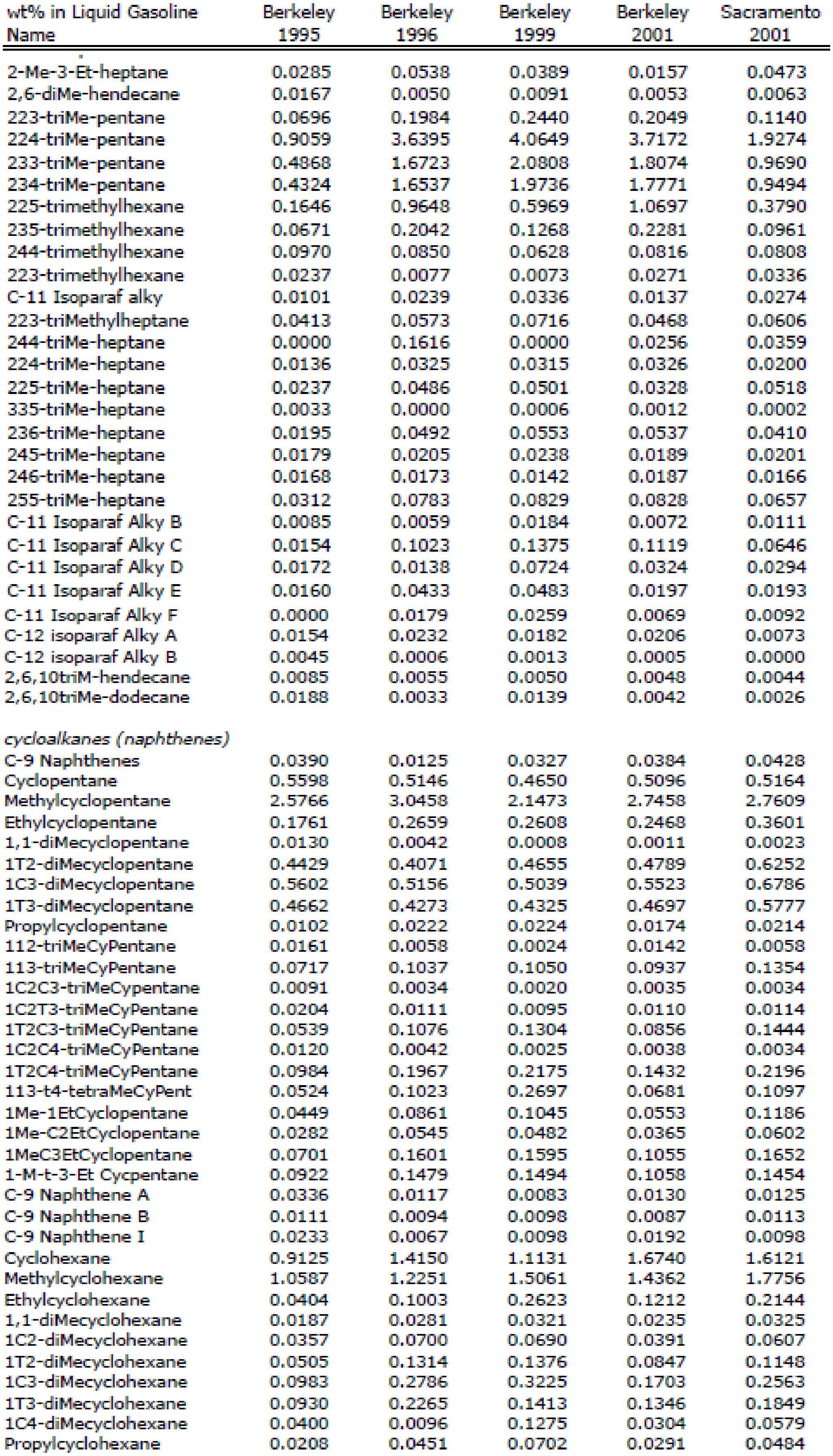
  - ☞ As noted by Laboratory #1, 1,3,5-Trimethylbenzene can co-elute with the recommended Internal Standard 1,4-dichlorobenzene-D4.

  - ☞ As noted by Laboratory #1, 1,2,4-Trimethylbenzene is a Target Analyte in EPA Method 8260, and use in the VPH method will facilitate "cross-over" methodologies.

Appendix A – Composition of Gasoline (California Air Research Board, 2004)

wt% in Liquid Gasoline Name	Berkeley 1995	Berkeley 1996	Berkeley 1999	Berkeley 2001	Sacramento 2001
n-alkanes					
Propane	0.0283	0.0076	0.0126	0.0103	0.0183
Butane	1.0099	0.6300	0.9723	0.7871	0.8893
Pentane	3.1572	2.4246	2.3479	2.8888	2.8296
Hexane	1.9974	1.5031	1.3979	1.7116	1.9026
Heptane	1.3789	1.2453	1.4922	1.4562	1.6101
Octane	0.4683	0.5173	0.6515	0.4724	0.6452
Nonane	0.1570	0.2007	0.3296	0.1859	0.2801
Decane	0.0551	0.0399	0.0776	0.0766	0.1191
Hendecane	0.0448	0.0307	0.0627	0.0473	0.0541
Dodecane	0.0213	0.0097	0.0119	0.0116	0.0179
Tridecane	0.0088	0.0044	0.0044	0.0000	0.0000
Tetradecane	0.0029	0.0000	0.0011	0.0000	0.0000
Pentadecane	0.0061	0.0027	0.0052	0.0000	0.0000
isoalkanes					
2-methylpropane	0.2382	0.0935	0.0886	0.0660	0.1737
2-methylbutane	9.4849	8.8111	8.9207	9.3192	7.5069
2,2-dimethylpropane	0.0109	0.0137	0.0186	0.0054	0.0078
2-methylpentane	4.4643	4.2655	4.0664	4.5749	3.5513
3-methylpentane	2.8354	2.6060	2.4876	2.7622	2.1913
2,2-dimethylbutane	0.9596	0.8159	1.2452	1.3265	0.9615
2,3-dimethylbutane	1.0921	1.3624	1.5084	1.6169	1.1369
2-methylhexane	1.8286	1.5372	1.3902	1.5340	1.4939
3-methylhexane	2.0119	1.8010	1.7750	1.9432	1.8991
3-ethylpentane	0.1714	0.1058	0.0802	0.0748	0.1326
2,2-dimethylpentane	0.1512	0.0938	0.1003	0.1141	0.1147
2,3-dimethylpentane	0.9950	1.4178	1.6668	2.0713	1.7083
2,4-dimethylpentane	0.5121	0.7625	0.8777	0.9339	0.7323
33-Dimethylpentane	0.1462	0.1135	0.0000	0.1123	0.1132
223-Trimethylbutane	0.0000	0.0418	0.0000	0.0463	0.0362
2-Methylheptane	0.6309	0.7821	0.8162	0.7197	0.8474
3-methylheptane	0.7882	0.8442	0.8276	0.7614	0.8389
4-Methylheptane	0.3221	0.3853	0.3806	0.3463	0.3798
2,2-dimethylhexane	0.0643	0.0465	0.0493	0.0493	0.0481
2,4-dimethylhexane	0.3332	0.5962	0.6593	0.5834	0.4218
2,5-dimethylhexane	0.2767	0.5786	0.6862	0.5719	0.3805
3,3-dimethylhexane	0.0654	0.0509	0.0508	0.0535	0.0554
2-Me-3-Et-pentane	0.3160	0.5834	0.6658	0.6099	0.4214
2,4-dimethylheptane	0.0813	0.2388	0.0917	0.0728	0.0568
2,6-dimethylheptane	0.0734	0.1778	0.2117	0.1351	0.2164
2,5-dimethylheptane	0.0089	0.0099	0.0061	0.0128	0.0044
3,5-dimethylheptane	0.2148	0.3556	0.3461	0.2747	0.3080
2,3-dimethylheptane	0.0668	0.1161	0.1126	0.1086	0.1022
3,4-dimethylheptane	0.0350	0.0726	0.0695	0.0594	0.0662
3,3-dimethylheptane	0.0266	0.0420	0.0479	0.0241	0.0381
4,4-dimethylheptane	0.0031	0.0339	0.0285	0.0173	0.0248
2-methyloctane	0.1955	0.2788	0.2784	0.2271	0.2767
3-methyloctane	0.2217	0.3214	0.3443	0.2976	0.3480
4-methyloctane	0.1647	0.2304	0.2337	0.1882	0.2333
3-ethylheptane	0.0592	0.0901	0.0984	0.0644	0.0919
4-ethylheptane	0.0393	0.0459	0.0433	0.0387	0.0467
2,2-dimethylheptane	0.0197	0.0151	0.0159	0.0165	0.0181
3-Me-4-Et-hexane	0.0181	0.0086	0.0137	0.0135	0.0070
2-methylnonane	0.0760	0.0851	0.1196	0.0876	0.1153
3-methylnonane	0.0756	0.0749	0.1134	0.0833	0.1096
4-methylnonane	0.0992	0.2251	0.2963	0.2612	0.2310
3-ethyloctane	0.0000	0.0000	0.0076	0.0000	0.0000
4-ethyloctane	0.0318	0.0453	0.0648	0.0356	0.0461
2,2-dimethyloctane	0.0301	0.0489	0.0179	0.0241	0.0454
2,3-dimethyloctane	0.0220	0.0233	0.0443	0.0243	0.0370
2,6-dimethyloctane	0.0000	0.0207	0.0336	0.0012	0.0210
4,4-dimethyloctane	0.0150	0.0199	0.0269	0.0147	0.0219
2-methyldecane	0.0098	0.0659	0.0764	0.0760	0.0200
3-methyldecane	0.0339	0.0182	0.0368	0.0277	0.0315
2,6-dimethylnonane	0.0166	0.0118	0.0495	0.0185	0.0336
C-11 Isoparaffins	0.0087	0.0095	0.0073	0.0120	0.0119
C-10 Isoparaffin O	0.0025	0.0201	0.0282	0.0181	0.0189

Appendix A – Composition of Gasoline (California Air Research Board, 2004)

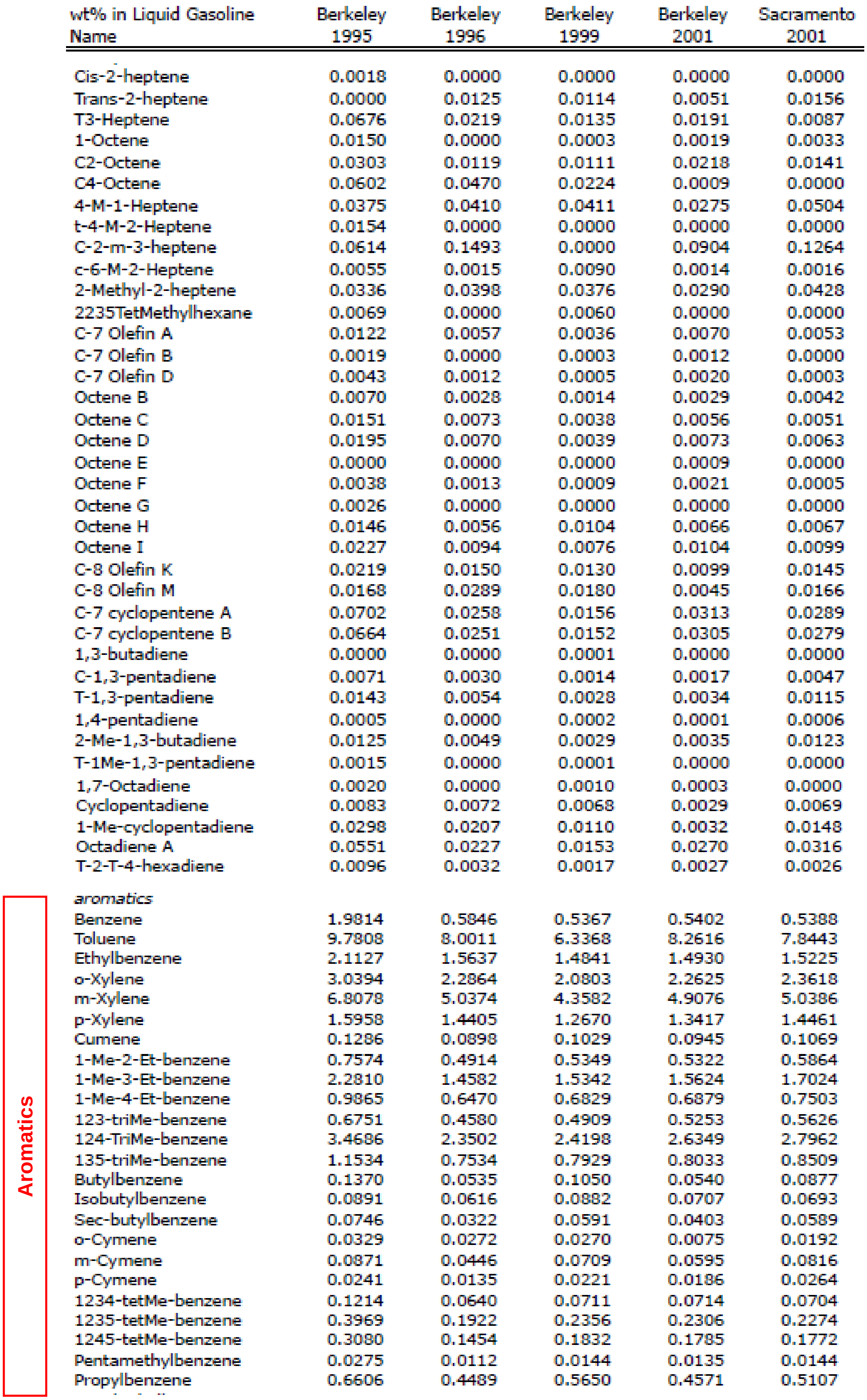


wt% in Liquid Gasoline Name	Berkeley 1995	Berkeley 1996	Berkeley 1999	Berkeley 2001	Sacramento 2001
2-Me-3-Et-heptane	0.0285	0.0538	0.0389	0.0157	0.0473
2,6-diMe-hendecane	0.0167	0.0050	0.0091	0.0053	0.0063
223-triMe-pentane	0.0696	0.1984	0.2440	0.2049	0.1140
224-triMe-pentane	0.9059	3.6395	4.0649	3.7172	1.9274
233-triMe-pentane	0.4868	1.6723	2.0808	1.8074	0.9690
234-triMe-pentane	0.4324	1.6537	1.9736	1.7771	0.9494
225-trimethylhexane	0.1646	0.9648	0.5969	1.0697	0.3790
235-trimethylhexane	0.0671	0.2042	0.1268	0.2281	0.0961
244-trimethylhexane	0.0970	0.0850	0.0628	0.0816	0.0808
223-trimethylhexane	0.0237	0.0077	0.0073	0.0271	0.0336
C-11 Isoparaf alky	0.0101	0.0239	0.0336	0.0137	0.0274
223-triMethylheptane	0.0413	0.0573	0.0716	0.0468	0.0606
244-triMe-heptane	0.0000	0.1616	0.0000	0.0256	0.0359
224-triMe-heptane	0.0136	0.0325	0.0315	0.0326	0.0200
225-triMe-heptane	0.0237	0.0486	0.0501	0.0328	0.0518
335-triMe-heptane	0.0033	0.0000	0.0006	0.0012	0.0002
236-triMe-heptane	0.0195	0.0492	0.0553	0.0537	0.0410
245-triMe-heptane	0.0179	0.0205	0.0238	0.0189	0.0201
246-triMe-heptane	0.0168	0.0173	0.0142	0.0187	0.0166
255-triMe-heptane	0.0312	0.0783	0.0829	0.0828	0.0657
C-11 Isoparaf Alky B	0.0085	0.0059	0.0184	0.0072	0.0111
C-11 Isoparaf Alky C	0.0154	0.1023	0.1375	0.1119	0.0646
C-11 Isoparaf Alky D	0.0172	0.0138	0.0724	0.0324	0.0294
C-11 Isoparaf Alky E	0.0160	0.0433	0.0483	0.0197	0.0193
C-11 Isoparaf Alky F	0.0000	0.0179	0.0259	0.0069	0.0092
C-12 isoparaf Alky A	0.0154	0.0232	0.0182	0.0206	0.0073
C-12 isoparaf Alky B	0.0045	0.0006	0.0013	0.0005	0.0000
2,6,10triM-hendecane	0.0085	0.0055	0.0050	0.0048	0.0044
2,6,10triMe-dodecane	0.0188	0.0033	0.0139	0.0042	0.0026
cycloalkanes (naphthenes)					
C-9 Naphthenes	0.0390	0.0125	0.0327	0.0384	0.0428
Cyclopentane	0.5598	0.5146	0.4650	0.5096	0.5164
Methylcyclopentane	2.5766	3.0458	2.1473	2.7458	2.7609
Ethylcyclopentane	0.1761	0.2659	0.2608	0.2468	0.3601
1,1-diMecyclopentane	0.0130	0.0042	0.0008	0.0011	0.0023
1T2-diMecyclopentane	0.4429	0.4071	0.4655	0.4789	0.6252
1C3-diMecyclopentane	0.5602	0.5156	0.5039	0.5523	0.6786
1T3-diMecyclopentane	0.4662	0.4273	0.4325	0.4697	0.5777
Propylcyclopentane	0.0102	0.0222	0.0224	0.0174	0.0214
112-triMeCyPentane	0.0161	0.0058	0.0024	0.0142	0.0058
113-triMeCyPentane	0.0717	0.1037	0.1050	0.0937	0.1354
1C2C3-triMeCypentane	0.0091	0.0034	0.0020	0.0035	0.0034
1C2T3-triMeCyPentane	0.0204	0.0111	0.0095	0.0110	0.0114
1T2C3-triMeCyPentane	0.0539	0.1076	0.1304	0.0856	0.1444
1C2C4-triMeCyPentane	0.0120	0.0042	0.0025	0.0038	0.0034
1T2C4-triMeCyPentane	0.0984	0.1967	0.2175	0.1432	0.2196
113-t4-tetraMeCyPent	0.0524	0.1023	0.2697	0.0681	0.1097
1Me-1EtCyclopentane	0.0449	0.0861	0.1045	0.0553	0.1186
1Me-C2EtCyclopentane	0.0282	0.0545	0.0482	0.0365	0.0602
1MeC3EtCyclopentane	0.0701	0.1601	0.1595	0.1055	0.1652
1-M-t-3-Et Cycpentane	0.0922	0.1479	0.1494	0.1058	0.1454
C-9 Naphthene A	0.0336	0.0117	0.0083	0.0130	0.0125
C-9 Naphthene B	0.0111	0.0094	0.0098	0.0087	0.0113
C-9 Naphthene I	0.0233	0.0067	0.0098	0.0192	0.0098
Cyclohexane	0.9125	1.4150	1.1131	1.6740	1.6121
Methylcyclohexane	1.0587	1.2251	1.5061	1.4362	1.7756
Ethylcyclohexane	0.0404	0.1003	0.2623	0.1212	0.2144
1,1-diMecyclohexane	0.0187	0.0281	0.0321	0.0235	0.0325
1C2-diMecyclohexane	0.0357	0.0700	0.0690	0.0391	0.0607
1T2-diMecyclohexane	0.0505	0.1314	0.1376	0.0847	0.1148
1C3-diMecyclohexane	0.0983	0.2786	0.3225	0.1703	0.2563
1T3-diMecyclohexane	0.0930	0.2265	0.1413	0.1346	0.1849
1C4-diMecyclohexane	0.0400	0.0096	0.1275	0.0304	0.0579
Propylcyclohexane	0.0208	0.0451	0.0702	0.0291	0.0484

Appendix A – Composition of Gasoline (California Air Research Board, 2004)

wt% in Liquid Gasoline Name	Berkeley 1995	Berkeley 1996	Berkeley 1999	Berkeley 2001	Sacramento 2001
iso-Bu-Cyclohexane	0.0050	0.0032	0.0043	0.0040	0.0040
sec-Bu-Cyclohexane	0.0124	0.0094	0.0302	0.0129	0.0162
1MeC3Etcyclohexane	0.0699	0.0458	0.2527	0.1264	0.1519
1MeC4EtCyclohexane	0.0195	0.0113	0.0120	0.0074	0.0115
1MeT4Etcyclohexane	0.0174	0.0305	0.0354	0.0209	0.0328
113-triMecyclohexane	0.0266	0.0494	0.0489	0.0312	0.0439
1C2C3-triMeCyhexane	0.0080	0.0000	0.0003	0.0000	0.0000
1C2T3-triMeCyhexane	0.0481	0.0296	0.0278	0.0218	0.0252
1C3T5-triMeCyhexane	0.0491	0.1665	0.1893	0.0924	0.1258
1-M-t2-PropCyHexane	0.0296	0.0494	0.0618	0.0561	0.0470
C-10 Cyclohexane AA	0.0051	0.0127	0.0294	0.0112	0.0173
C-10 Cyclohexane BB	0.0111	0.0167	0.0452	0.0174	0.0304
2MePropylCyclohexane	0.0000	0.0000	0.0523	0.0129	0.0057
Cis-hydrindane	0.0104	0.0143	0.0130	0.0102	0.0149
alkenes (olefins)					
Propene	0.0106	0.0000	0.0003	0.0022	0.0008
1-butene	0.0194	0.0102	0.0075	0.0042	0.0077
Cis-2-butene	0.0465	0.0385	0.0278	0.0156	0.0244
Trans-2-butene	0.0419	0.0607	0.0375	0.0267	0.0286
2-methylpropene	0.0220	0.0127	0.0058	0.0045	0.0118
1-pentene	0.2293	0.0585	0.0433	0.0469	0.1051
Cis-2-pentene	0.2574	0.1037	0.0794	0.0975	0.1267
trans-2-pentene	0.4604	0.2459	0.1799	0.2192	0.2560
2-methyl-1-butene	0.3289	0.1158	0.0511	0.1097	0.1745
3-methyl-1-butene	0.0684	0.0165	0.0217	0.0146	0.0308
2-methyl-2-butene	0.6411	0.3689	0.1405	0.3979	0.4083
1-hexene	0.1049	0.0248	0.0237	0.0346	0.0388
Cis-2-hexene	0.1127	0.0397	0.0460	0.0842	0.0506
Trans-2-hexene	0.2201	0.0902	0.1161	0.2183	0.1183
Cis-3-hexene	0.1415	0.0512	0.0609	0.1110	0.0668
2-Me-1-pentene	0.1402	0.0555	0.0564	0.1201	0.0770
4-methyl-1-pentene	0.0826	0.0241	0.0260	0.0509	0.0405
2-methyl-2-pentene	0.2949	0.1812	0.2331	0.4399	0.2275
C-3Me-2-pentene	0.1145	0.0412	0.0398	0.0779	0.0580
T-3Me-2-pentene	0.1795	0.0626	0.0624	0.1216	0.0876
C-4Me-2-pentene	0.0329	0.0151	0.0205	0.0466	0.0267
T-4Me-2-pentene	0.1404	0.0733	0.1167	0.3096	0.1267
2-Et-1-butene	0.0426	0.0150	0.0118	0.0277	0.0207
2,3dimethyl-1-butene	0.0444	0.0000	0.0030	0.0425	0.0016
3,3-dimethylbutene	0.0051	0.0013	0.0018	0.0019	0.0022
2,3dimethyl-2-butene	0.0545	0.0314	0.0404	0.0681	0.0390
Nonenes	0.0053	0.0026	0.0076	0.0067	0.0041
Cyclopentene	0.1159	0.0396	0.0373	0.0390	0.0568
1-Me-cyclopentene	0.2562	0.0812	0.0565	0.0982	0.0926
3-Me-cyclopentene	0.0731	0.0207	0.0132	0.0242	0.0287
23-diMe-1-pentene	0.0206	0.0080	0.0064	0.0097	0.0070
24-dime-1-pentene	0.0151	0.0054	0.0035	0.0053	0.0036
23Dimethyl-2-Pentene	0.0012	0.0000	0.0000	0.0002	0.0000
33-DiMe-1-pentene	0.0039	0.0000	0.0008	0.0018	0.0005
44-diMe-1-pentene	0.0326	0.0070	0.0052	0.0092	0.0083
23-diMe-2-pentene	0.0679	0.0288	0.0219	0.0339	0.0279
24Dimethyl-2-Pentene	0.0044	0.0000	0.0005	0.0013	0.0000
34-diMe-c2-pentene	0.0273	0.0117	0.0039	0.0060	0.0000
44-diMe-c2-pentene	0.0100	0.0030	0.0018	0.0033	0.0029
3-Et-2-pentene	0.1524	0.0583	0.0391	0.0611	0.0555
2-Me-1-hexene	0.0401	0.0159	0.0129	0.0181	0.0128
3-Me-1-hexene	0.0074	0.0025	0.0017	0.0022	0.0017
5-Me-1-hexene	0.0236	0.0088	0.0073	0.0112	0.0085
2-Me-2-hexene	0.0746	0.0305	0.0240	0.0358	0.0282
2-Me-t3-hexene	0.0451	0.0162	0.0126	0.0179	0.0123
3-Me-c3-hexene	0.0516	0.0216	0.0166	0.0255	0.0205
3-Me-t3-hexene	0.0328	0.0135	0.0102	0.0155	0.0123
1-Heptene	0.0328	0.0102	0.0115	0.0151	0.0162

Appendix A – Composition of Gasoline (California Air Research Board, 2004)



wt% in Liquid Gasoline Name	Berkeley 1995	Berkeley 1996	Berkeley 1999	Berkeley 2001	Sacramento 2001
Cis-2-heptene	0.0018	0.0000	0.0000	0.0000	0.0000
Trans-2-heptene	0.0000	0.0125	0.0114	0.0051	0.0156
T3-Heptene	0.0676	0.0219	0.0135	0.0191	0.0087
1-Octene	0.0150	0.0000	0.0003	0.0019	0.0033
C2-Octene	0.0303	0.0119	0.0111	0.0218	0.0141
C4-Octene	0.0602	0.0470	0.0224	0.0009	0.0000
4-M-1-Heptene	0.0375	0.0410	0.0411	0.0275	0.0504
t-4-M-2-Heptene	0.0154	0.0000	0.0000	0.0000	0.0000
C-2-m-3-heptene	0.0614	0.1493	0.0000	0.0904	0.1264
c-6-M-2-Heptene	0.0055	0.0015	0.0090	0.0014	0.0016
2-Methyl-2-heptene	0.0336	0.0398	0.0376	0.0290	0.0428
2235TetMethylhexane	0.0069	0.0000	0.0060	0.0000	0.0000
C-7 Olefin A	0.0122	0.0057	0.0036	0.0070	0.0053
C-7 Olefin B	0.0019	0.0000	0.0003	0.0012	0.0000
C-7 Olefin D	0.0043	0.0012	0.0005	0.0020	0.0003
Octene B	0.0070	0.0028	0.0014	0.0029	0.0042
Octene C	0.0151	0.0073	0.0038	0.0056	0.0051
Octene D	0.0195	0.0070	0.0039	0.0073	0.0063
Octene E	0.0000	0.0000	0.0000	0.0009	0.0000
Octene F	0.0038	0.0013	0.0009	0.0021	0.0005
Octene G	0.0026	0.0000	0.0000	0.0000	0.0000
Octene H	0.0146	0.0056	0.0104	0.0066	0.0067
Octene I	0.0227	0.0094	0.0076	0.0104	0.0099
C-8 Olefin K	0.0219	0.0150	0.0130	0.0099	0.0145
C-8 Olefin M	0.0168	0.0289	0.0180	0.0045	0.0166
C-7 cyclopentene A	0.0702	0.0258	0.0156	0.0313	0.0289
C-7 cyclopentene B	0.0664	0.0251	0.0152	0.0305	0.0279
1,3-butadiene	0.0000	0.0000	0.0001	0.0000	0.0000
C-1,3-pentadiene	0.0071	0.0030	0.0014	0.0017	0.0047
T-1,3-pentadiene	0.0143	0.0054	0.0028	0.0034	0.0115
1,4-pentadiene	0.0005	0.0000	0.0002	0.0001	0.0006
2-Me-1,3-butadiene	0.0125	0.0049	0.0029	0.0035	0.0123
T-1Me-1,3-pentadiene	0.0015	0.0000	0.0001	0.0000	0.0000
1,7-Octadiene	0.0020	0.0000	0.0010	0.0003	0.0000
Cyclopentadiene	0.0083	0.0072	0.0068	0.0029	0.0069
1-Me-cyclopentadiene	0.0298	0.0207	0.0110	0.0032	0.0148
Octadiene A	0.0551	0.0227	0.0153	0.0270	0.0316
T-2-T-4-hexadiene	0.0096	0.0032	0.0017	0.0027	0.0026
aromatics					
Benzene	1.9814	0.5846	0.5367	0.5402	0.5388
Toluene	9.7808	8.0011	6.3368	8.2616	7.8443
Ethylbenzene	2.1127	1.5637	1.4841	1.4930	1.5225
o-Xylene	3.0394	2.2864	2.0803	2.2625	2.3618
m-Xylene	6.8078	5.0374	4.3582	4.9076	5.0386
p-Xylene	1.5958	1.4405	1.2670	1.3417	1.4461
Cumene	0.1286	0.0898	0.1029	0.0945	0.1069
1-Me-2-Et-benzene	0.7574	0.4914	0.5349	0.5322	0.5864
1-Me-3-Et-benzene	2.2810	1.4582	1.5342	1.5624	1.7024
1-Me-4-Et-benzene	0.9865	0.6470	0.6829	0.6879	0.7503
123-triMe-benzene	0.6751	0.4580	0.4909	0.5253	0.5626
124-TriMe-benzene	3.4686	2.3502	2.4198	2.6349	2.7962
135-triMe-benzene	1.1534	0.7534	0.7929	0.8033	0.8509
Butylbenzene	0.1370	0.0535	0.1050	0.0540	0.0877
Isobutylbenzene	0.0891	0.0616	0.0882	0.0707	0.0693
Sec-butylbenzene	0.0746	0.0322	0.0591	0.0403	0.0589
o-Cymene	0.0329	0.0272	0.0270	0.0075	0.0192
m-Cymene	0.0871	0.0446	0.0709	0.0595	0.0816
p-Cymene	0.0241	0.0135	0.0221	0.0186	0.0264
1234-tetMe-benzene	0.1214	0.0640	0.0711	0.0714	0.0704
1235-tetMe-benzene	0.3969	0.1922	0.2356	0.2306	0.2274
1245-tetMe-benzene	0.3080	0.1454	0.1832	0.1785	0.1772
Pentamethylbenzene	0.0275	0.0112	0.0144	0.0135	0.0144
Propylbenzene	0.6606	0.4489	0.5650	0.4571	0.5107

Appendix A – Composition of Gasoline (California Air Research Board, 2004)

	wt% in Liquid Gasoline Name	Berkeley 1995	Berkeley 1996	Berkeley 1999	Berkeley 2001	Sacramento 2001
Aromatics	1,3-diethylbenzene	0.2058	0.0811	0.1259	0.1114	0.1260
	1-Me-3-Pr-benzene	0.5369	0.1932	0.3234	0.2777	0.3124
	1-Me-4-Pr-benzene	0.3132	0.1179	0.2082	0.1870	0.1925
	Indan	0.4156	0.1998	0.2622	0.2359	0.2820
	1,2-diethylbenzene	0.5890	0.2553	0.3707	0.3419	0.3649
	1-Me-2-Pr-benzene	0.1625	0.0659	0.1228	0.0908	0.1042
	14-diMe2Et-benzene	0.3978	0.1701	0.2358	0.2326	0.2619
	13-diMe4Et-benzene	0.3229	0.1459	0.2066	0.1981	0.2111
	12-diMe4Et-benzene	0.5428	0.2268	0.3046	0.3034	0.3299
	13-diMe2Et-benzene	0.0356	0.0213	0.0278	0.0271	0.0262
	Indene	0.0112	0.0000	0.0439	0.0335	0.0334
	12-diMe3Et-benzene	0.1576	0.0627	0.0925	0.0841	0.0938
	1-Me35diEt-benzene	0.0688	0.0170	0.0395	0.0290	0.0289
	1-Phenyl-2Me butane	0.0530	0.0244	0.0424	0.0310	0.0296
	1-Phenyl-3Me butane	0.0090	0.0149	0.0152	0.0116	0.0044
	124-triMe-5Etbenzene	0.0477	0.0174	0.0235	0.0203	0.0213
	123-triMe-5Etbenzene	0.0545	0.0132	0.0229	0.0175	0.0236
	124-triMe-3Etbenzene	0.0091	0.0010	0.0017	0.0012	0.0014
	12-diMe-3Pr-benzene	0.0969	0.0298	0.0430	0.0331	0.0368
	135-triMe-2Etbenzene	0.0207	0.0180	0.0178	0.0151	0.0134
	Naphthalene	0.4808	0.1306	0.1903	0.1376	0.1279
	Tetralin	0.0279	0.0000	0.0001	0.0096	0.0326
	cis-Decalin	0.0000	0.0000	0.0030	0.0000	0.0000
	1-Me-3Bu-benzene	0.0824	0.0371	0.0627	0.0355	0.0326
	12-diMe-4Pr-benzene	0.0424	0.0463	0.0342	0.0426	0.0304
	125-triMe-3Etbenzene	0.0700	0.0232	0.0336	0.0281	0.0308
	123-triMe4Et-benzene	0.0176	0.0060	0.0054	0.0089	0.0096
	C-11 Aromatic K	0.0277	0.0204	0.0080	0.0159	0.0138
	C-10 Alkenylbenzenes	0.0165	0.0000	0.0488	0.0011	0.0058
	C-11 Aromatic L	0.0000	0.0000	0.0071	0.0005	0.0000
	1-Methylnaphthalene	0.1513	0.0276	0.0758	0.0423	0.0401
	2-Methylnaphthalene	0.3304	0.0698	0.1668	0.0900	0.0860
	C-11 Aromatic E	0.1243	0.0381	0.0614	0.0497	0.0553
	C-12 Aromatic A	0.0068	0.0000	0.0015	0.0009	0.0000
	C-12 Aromatic F	0.0130	0.0035	0.0057	0.0029	0.0031
	1-Methylindane	0.2248	0.0700	0.1020	0.0816	0.0962
	2-Methylindane	0.3631	0.1116	0.1594	0.1262	0.1472
	Dimethylindane A	0.0269	0.0134	0.0091	0.0080	0.0112
	Dimethylindane B	0.0660	0.0224	0.0183	0.0164	0.0269
	Dimethylindane C	0.0353	0.0119	0.0113	0.0102	0.0151
	Dimethylindane E	0.0460	0.0138	0.0127	0.0127	0.0189
	Dimethylindane F	0.0727	0.0223	0.0334	0.0220	0.0250
	Dimethylindane G	0.0477	0.0104	0.0218	0.0124	0.0198
	C-11 Indane H	0.0364	0.0086	0.0161	0.0081	0.0116
	Biphenyl	0.0000	0.0000	0.0055	0.0000	0.0000
	12-DiMe-naphthalene	0.0080	0.0006	0.0053	0.0032	0.0029
	13-DiMe-naphthalene	0.0407	0.0083	0.0299	0.0153	0.0129
	15-DiMe-naphthalene	0.0000	0.0000	0.0000	0.0005	0.0000
	16-DiMe-naphthalene	0.0190	0.0047	0.0147	0.0078	0.0060
	23-DiMe-naphthalene	0.0183	0.0043	0.0140	0.0076	0.0057
	26-DiMe-naphthalene	0.0000	0.0000	0.0012	0.0031	0.0019
	27-DiMe-naphthalene	0.0000	0.0000	0.0001	0.0000	0.0000
	1-Ethylnaphthalene	0.0128	0.0022	0.0112	0.0054	0.0032
	2-Ethylnaphthalene	0.0000	0.0000	0.0000	0.0023	0.0017
	235-TriMeNaphthalene	0.0000	0.0000	0.0028	0.0006	0.0000
	oxygenates					
	Ethanol	0.0000	0.0000	0.0000	1.2526	0.8622
	2-methyl-2-propanol	0.0000	0.0000	0.0071	0.0039	0.0046
	2-methyl-2-butanol	0.0000	0.0000	0.0023	0.0037	0.0000
	MTBE	0.9939	10.9139	8.5808	3.8286	10.5669
	TAME	0.0393	0.0170	1.0652	0.6054	0.4164
	3-Me-3-methoxypentane	0.0000	0.0000	0.0002	0.0000	0.0000
	1-Me-1methoxycyclpen	0.0000	0.0000	0.0037	0.0000	0.0000
	2-Methoxybutane	0.0000	0.0000	0.0021	0.0013	0.0040
	unclassified	1.5416	1.3297	1.8381	1.2557	1.3293

Appendix B – Preparation of Round Robin Water and Soil Samples

WATER

On June 1st, 2012, groundwater samples were obtained from a Shell station at 586 Main Street in Wilmington, MA (DEP 3-12586), from wells MW-8 and MW-405. Access to the wells was provided by Sovereign Consulting Inc. PID headspace at the top of the riser in MW-8 was 1 ppmV; in MW-405 it was 0.1 ppmV. Samples from both wells were obtained in HDPE containers using a peristaltic pump, following the initial evacuation of about 1 liter of water.

The samples were immediately transported to the MassDEP Wilmington Office, and passed through a 0.45 micron filter (Waterra). The MW-8 sample had turned rust colored (presumably from oxidation of ferrous iron). The MW-405 sample was not as discolored.

Samples were screened on a HAPSITE GC/MS, and were mostly BTEX, with high concentrations in MW-8, and somewhat lower concentrations in MW-405. The concentration of benzene in MW-8 was 130 ug/L, with Ethylbenzene at 700 ug/L.

The MW-8 sample was diluted 50% with DI water, and 2 µL of gasoline was added (to try to boost concentrations of non-BTEX contaminants). The solution was mixed via a magnetic stirrer at 700 RPMs for 30 minutes, and re-filtered via a 0.45 micron filter using a peristaltic pump setup. The filtrate was captured in a 1 liter amber bottle.

The resultant sample was analyzed on the HAPSITE GC/MS, and contaminant levels were substantially decreased, much beyond the 50% dilution. It is not clear whether the filter was removing dissolved contaminants, or if there was off-gassing via use of the peristaltic pump.

At the end of the day on 6/1/12, the filtered sample (in the 1-Liter amber bottle) was acidified with 5 mL of 1:1 HCl, and placed in storage in a refrigerator at 4°C.

Additional attempts were subsequently made to produce a water sample with more non-BTEX compounds, by (a) adding 5 µL of gasoline to another stock of the MW-8 sample, and (b) by adding 1 mL of gasoline to 1 Liter of tap water. In both cases, after filtering, the sample was almost completely BTEX, with Toluene the primary peak in the gasoline/tap water sample.

Accordingly, a decision was made to stay with the original acidified sample stock (i.e,. the MW-8 sample with 2 µL of added gasoline and post-preparation filtering).

On the afternoon of 6/5/12, the acidified stock was poured into 18 40-mL VOA vials. Care was exercised to ensure vials were full with no bubbles, and that the cap was tightly applied. Pre-printed labels were applied to each vial. Triplicate vials were then placed in a Ziploc bag, and stored at 4°C until they were picked up by couriers from each participating laboratory.

SOIL

Quikrete Premium Play Sand was obtained from Home Depot. On June 1st, 2012, a "fresh" gasoline sample ("regular" grade) was obtained from the Shell Station at 486 Main Street in Wilmington, MA (the same station where the groundwater samples were obtained earlier that day). This sample was collected in a 40 mL VOA vial (with aluminum foil inner seal).

A sample of the sand was tested for moisture content, yielding a percent moisture of 0.12 by weight.

A total of twenty 40 mL VOA vials were filled with sand on the morning of 6/5/12, by pouring 9.6 mL (15 grams) of soil into each vial.

A gasoline spiking solution was prepared in the afternoon of 6/5/12:

- 350 mL of Purge-and-Trap grade Methanol were poured into a 1 Liter glass bottle
- 1.4 mL of gasoline were then added to the 1-Liter bottle
- The 1-Liter bottled was inverted 3 times, and after 15 minutes, was inverted 3 times again

A repeating pipette was then used to dispense 15 mL of the spiking solution into each vial, resulting in a gasoline concentration of approximately 3000 μg/g (the same value used in the 1997 Round Robin program for the GC/PID/FID VPH method).

Pre-printed labels were applied to each vial, and pairs were placed in double Ziploc bags with lab names indicated.

Each package contained a note to the labs indicating that they should assume a moisture content of 0.12%, 15 gram sand sample, and 15 mL of Methanol in their calculations. All samples were stored overnight in a laboratory refrigerator at 4°C.

PICKUP

All samples were picked up at the DEP Wilmington office by lab couriers on 6/6/12.

Each courier used a chain of custody, and placed the sample package into a cooler.