COMMONWEALTH OF MASSACHUSETTS
EXECUTIVE OFFICE OF ENVIRONMENTAL AFFAIRS
DEPARTMENT OF ENVIRONMENTAL PROTECTION
ONE WINTER STREET, BOSTON, MA 02108 617-292-5500

ARGEO PAUL CELLUCCI
Governor

TRUDY COXE
Secretary

DAVID B. STRUHS
Commissioner

Report on Results of the

Fall 1997 VPH/EPH Round Robin

Testing Program

January 12, 1998

Executive Summary

In the Fall of 1997, a second interlaboratory "Round Robin" evaluation was conducted of two new analytical methods developed by the Massachusetts Department of Environmental Protection (MADEP) to quantitate Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH). In total, data was provided by 27 participating laboratories and the MADEP Wall Experiment Station (WES).

Each laboratory was provided a soil and water sample for analyses by the VPH method, and a soil and water sample for analyses by the EPH method. The soil samples consisted of a dry sand spiked with measured quantities of gasoline (VPH) and #2 Fuel oil (EPH). The water samples were "real world" groundwater samples obtained from gasoline (VPH) and fuel oil (EPH) contaminated sites. All samples were prepared, packaged, and shipped cold from WES.

Data from use of an unmodified VPH method was provided by 21 labs and WES; data from the use of an unmodified EPH method was provided by 23 labs and WES. Laboratory proficiency was determined based upon the evaluation of Z-scores calculated for each method and each matrix. A summary of laboratory proficiency, and method performance by proficient labs, is tabulated below:

Summary of Method Performance by Laboratories Meeting Proficiency Criteria

				Data from Proficient Laboratories			
Method	**Matrix**	**# Labs Proficient**	**% Labs Proficient**	**Fraction**	**%RSD**	**% labs within +/- 30% mean VPH value**	**% labs within +/- 40% mean EPH value**
VPH	**soil**	**20**	**95**	**C5-C8 Aliphatics**	**28**	**80**	
				C9-C12 Aliphatics	**52**	**50**	
				Total GC/FID	**31**	**70**	
				C9-C10 Aromatics	**24**	**80**	
	water	**17**	**81**	**C5-C8 Aliphatics**	**31**	**71**	
				C9-C12 Aliphatics	**44**	**47**	
				Total GC/FID	**24**	**76**	
				C9-C10 Aromatics	**20**	**82**	
EPH	**soil**	**19**	**83**	**C9-C18 Aliphatics**	**23**		**95**
				C19-C36 Aliphatics	**30**		**89**
				C11-C22 Aromatics	**19**		**100**
				Total All Fractions	**17**		**100**
	water	**20**	**87**	**C9-C18 Aliphatics**	**84**		**22**
				C19-C36 Aliphatics	**192**		**94**
				C11-C22 Aromatics	**47**		**72**
				Total All Fractions	**35**		**83**

In total, 17 laboratories were deemed proficient in both VPH matrices, and 16 labs were deemed proficient in both EPH matrices. Of the 20 labs who performed both method unmodified, 11 were deemed proficient in all matrices.

On the basis of an evaluation of data received on the unmodified methods, two significant methodological issues were noted:

- *The choice of chromatographic column used for the VPH method can significantly effect whether hydrocarbons present in a sample will be quantitated in the C5-C8 or C9-C12 Aliphatic range. As such, the final VPH method should be more specific on which columns are permissible.*

- *During the EPH fractionation process, stripping of aromatics into the aliphatic fraction is more common and problematic than stripping of aliphatics into the aromatic fraction. Because of their weakly polar properties, naphthalene and substituted naphthalenes are prone to leach into the aliphatic fraction if excessive volumes of hexane are used to elute the silica gel fractionation cartridge/column; differences as small as 0.5 mL of hexane may be significant. Although these compounds comprise a relatively small percentage of the total hydrocarbon content of petroleum products, they can comprise up to 50% or more of the water soluble fraction of fuel oils. For this reason, fractionation difficulties of this nature are more likely to significantly impact results of water analyses, as compared to soil analyses. This is reflected in the substantially better method performance seen for soil samples during this interlaboratory study. To better monitor this problem on a sample-by-sample basis, and allow for the institution of corrective measures, where needed, the final EPH method should require the use of one or more fractionation surrogate compounds. This surrogate, with properties similar to naphthalene, should be added to the EPH sample extract immediately prior to fractionation.*

Even with the problems noted above, MADEP is of the opinion that data received from laboratories deemed proficient in the unmodified methods is of a level of precision and accuracy commensurate with other environmental analyses, and is suitable for use in the agency's risk-based approach to characterize petroleum contaminated media. Moreover, with the institution of the procedural refinements noted above, and as laboratories continue to gain experience in the use of these new techniques, MADEP is confident that data quality will only continue to improve.

Data received from laboratories using modifications of the VPH and EPH methods show mixed results. Additional information and evaluation is required before more definitive conclusions can be made on method and laboratory performance.

BACKGROUND

In August, 1995, the Massachusetts Department of Environmental Protection (MADEP) issued the draft VPH and EPH analytical methodologies. Both methods are designed to fractionate complex hydrocarbon mixtures into collective ranges of aliphatic and aromatic compounds, and provide necessary data to support a new toxicological approach developed by the agency to characterize petroleum contaminated media.

The VPH method is a single-analysis purge and trap gas chromatography (GC) procedure with PID/FID "in series" detectors, employing the selectivity of PID response to differentiate aliphatic from aromatic compounds. The EPH method is a solvent-extraction GC/FID procedure which employs a post-extraction, pre-analysis silica gel/differential solvent fractionation process to differentiate aliphatic from aromatic compounds prior to two separate injections into the GC.

In the Spring of 1997, an interlaboratory "Round Robin" evaluation of the VPH and EPH methods was conducted, involving 28 laboratories and the MADEP Wall Experiment Station (WES). The primary purpose of this effort was to establish method detection/reporting limits, evaluate method ruggedness, and identify problem areas. This initial effort revealed problems with the way the study was conducted, with the way certain laboratories were conducting the analyses, and with the methods themselves. A complete report on the results of the first Round Robin study was released by the agency under cover letter dated June 30, 1997.

The VPH and EPH methods, supporting and associated toxicological and regulatory documents, and the June 1997 report on the first Round Robin study are available on the World Wide Web at http://www.magnet.state.ma/us/bwsc/pubs.htm.

OBJECTIVES AND SCOPE OF SECOND ROUND ROBIN STUDY

The objective of the Second Round Robin program was to build and expand upon the goals and outcomes of the first study, better evaluate method and laboratory performance at contaminant concentrations of regulatory significance, and determine any additional procedural refinements needed prior to finalization of the test methods.

While the first Round Robin effort yielded useful information on method detection limits and ruggedness, it failed to adequately characterize method (and laboratory) performance on matrices and concentrations more relevant to the MADEP Waste Site Cleanup program. Moreover, because of difficulties experiences by a sample preparation vendor in attempting to spike (sparingly soluble) neat petroleum products into reagent water, none of the water sample data were deemed to be reliable. Accordingly, soil samples evaluated during the Second Round Robin study were spiked at higher concentrations closer to MADEP "Reportable Concentration" values, and contaminated water samples were obtained from actual field sites, to ensure the dissemination of stable and meaningful "real world" samples.

The scope of the second study was more limited than the first Round Robin effort. Each participating laboratory submitted data on only 4 samples: a water sample contaminated with gasoline, a sand sample spiked with gasoline, a water sample contaminated with fuel oil, and a sand sample spiked with diesel fuel. In order to address problems experienced by laboratories in the first effort, a meeting was held in September 1997 with participating laboratories to discuss the results of the first study, point out problem areas with each method, clarify areas of confusion, and delineate methodological changes.

As with the first study, the second Round Robin program was designed and implemented in a way that would best achieve its primary objective: the evaluation of the draft VPH and EPH test methods. The assessment of laboratory proficiency was once again a secondary and ancillary objective. ***The results of this study should not be presented or construed as a MADEP laboratory "certification" program.***

DESIGN AND EXECUTION OF SECOND ROUND ROBIN STUDY

All laboratories who participated in the First Round Robin study were offered the opportunity to participate in the second effort. In total, 27 of the 28 laboratories submitting data for the first round also provided data for the second round. As in the first study, participating laboratories were offered the opportunity to receive a "Certificate of Proficiency" if submitted data was within acceptable limits.

Sample Preparation and Distribution

All samples were prepared and packaged at the MADEP Wall Experiment Station (WES) in Lawrence, Massachusetts.

VPH Water Samples

The source for the VPH water samples was a groundwater recovery well at a gasoline service station in Lynnfield, Massachusetts. The site in question has been contaminated by a release of gasoline, and the recovery well is being used to provide hydraulic containment of a dissolved plume of gasoline contaminants. It is important to note that the recovery well chosen was downgradient from known areas of Non Aqueous Phase Liquids (NAPL), and has never displayed visual or analytical evidence of NAPL.

Two one-gallon jugs of contaminated water were obtained by agency staff on September 4, 1997, acidified with 1:1 hydrochloric acid to a pH of less than 2, and refrigerated. In addition, triplicate samples of this source were obtained in 40 mL vials, to determine the concentration of VPH fractional ranges. The source water was clear, with a discernible petroleum odor.

Analysis of the 40 mL vial samples revealed gasoline contamination higher than desired levels, dictating the need for a dilution of the source water. Accordingly, on September 10, 1997, a peristaltic pump was used to transfer 2 liters of the Lynnfield source water into a 6 liter glass jug with a glass/Teflon stopcock. To ensure that this sample was free of NAPL suspensions, this 2 liter volume was passed through an in-line 0.45 micron filter. The 6 liter jug was then filled to volume with reagent (organic-free) water, acidified by the addition of 20 mL of 1:1 hydrochloric acid, stoppered, inverted 15 times, allowed to stand for 30 minutes, then again inverted 15 times. The pH of this solution was confirmed to be less than 2.

Water samples were then immediately withdrawn through the glass/Teflon stopcock at the base of the 6 L jug and dispensed into 40 mL vials, through a Teflon tube inserted into the stopcock to minimize turbulence. Each vial was filled to overflowing, tightly capped, and inspected for the presence of air bubbles. In total, 72 vials were filled in this manner over a 1 hour period, then stored at 4°C.

VPH Soil Samples

The VPH soil samples were prepared by spiking a dry sand sample with a gasoline/methanol solution.

Initially, 4 mL of gasoline were dispensed into a 1 L bottle of purge-and-trap grade methanol. A repeating pipette was then used to dispense 10.1 mL of this solution onto 10 grams of a dry sand that had been added to a 20 mL vial. This provided the 1 gram soil/1 mL methanol ratio required in the VPH method for soil preservation, while at the same time spiking the soil sample with 3050 ug/g of gasoline. In total, 72 vials were spiked in this manner over a 2 hour period, then stored at 4°C.

EPH Water Samples

The source for the EPH water samples was a groundwater/NAPL recovery well in a residential neighborhood in Lawrence, Massachusetts. The site in question was contaminated by the presumed release of a large quantity of #2 fuel oil from a former bakery, located several hundred feet upgradient of the recovery well. This release was thought to have occurred in the 1960s, and so this product, which is present as a NAPL throughout a large area, is heavily weathered. The recovery well is equipped with two pumps; a groundwater depression pump, and a NAPL recovery pump.

On September 9, 1997, 20 one-gallon jugs of contaminated water were obtained from the groundwater depression pump at the Lawrence site. Although designed and operated in a manner to prevent the entrainment of NAPL into the groundwater depression system, as an added precaution, the water was passed through an in-line 0.45 micron filter during collection. The 20 one-gallon jugs were transported to the Wall Experiment Station (WES) in 5 cases containing 4 gallons each. At WES, 3 jugs from each case were dispensed into a 50 L glass vessel, and the remaining jug was dispensed into a separate 20 L glass vessel. In this manner, an attempt was made to make the two vessels as homogeneous as possible (the use of two vessels was necessary due to the large number of samples needed to provide duplicate 1 liter samples to the 27 participating laboratories). Each vessel was then acidified by adding 5 mL/L of 1:1 hydrochloric acid, stoppered, and allowed to stand overnight. The source water was clear, with a discernible petroleum odor; the 50L vessel also contained an odor resultant from its earlier cleaning with MtBE.

On September 10, 1997, the contents of both vessels were thoroughly mixed with glass/Teflon rods. The source water was then dispensed into individual 1 liter sample containers via a peristaltic pump and/or Teflon siphon. To ensure uniform samples, each 1 liter sample container was filled with 700 mL of water from the 50L vessel, and 300 mL of water from the 20L vessel. Graduated cylinders were used to ensure precise proportionment. In total, 70 one-liter sample containers were filled in this manner, capped, and stored at 4°C.

EPH Soil Samples

Initially, 10 grams of dry sand were dispensed into 1 case (72) of 20-mL vials. Subsequently, 1 mL of a spiking solution was added to each vial. The spiking solution consisted of a #2 fuel oil dissolved in hexane, at a concentration that resulted in a soil concentration of 6000 ug/g total fuel oil. The vials were tightly capped and stored at 4°C.

Sample Shipment

All samples were labeled, packed, and shipped from the Wall Experiment Station on September 15, 1997. Each of the 27 participating laboratories received the following:

- duplicate 40 mL VPH water samples
- duplicate 20 mL VPH soil samples
- duplicate 40 mL methanol blanks
- duplicate 1 liter EPH water samples
- duplicate 20 mL EPH soil samples

To avoid contaminating the VPH samples with the hexane solvent in the EPH samples, the VPH and EPH samples were placed in separate Styrofoam shipping containers (with ice packs). All samples were shipped cold by overnight express. In subsequent days, 3 labs reported receiving shipments with one broken (duplicate) EPH water sample, and one lab reported a broken (duplicate) EPH soil sample. In addition, the shipment to two laboratories in the same community were initially mis-routed by the overnight carrier.

Quality Control

To ensure and document the homogeneity and stability of samples prepared and shipped from the Wall Experiment Station, duplicate samples were obtained from the production line at the beginning, middle, and end of the sample preparation process. One sample each from the beginning, middle, and end were then analyzed at WES on "Day Zero" (September 10th) and "Day 7" (September 17th). An additional 3 samples of the VPH "end" water were also analyzed. The results of these analyses are presented in Table 1. Based upon these data, no problems were noted with sample consistency or stability.

Certificate of Proficiency

As in the first study, MADEP offered to provide a "Certificate of Proficiency" to participating laboratory that performed well during the second Round Robin effort. In a letter from MADEP dated September 15, 1997, the parameters of this proficiency evaluation were delineated, and involved meeting acceptance limits for each aliphatic/aromatic faction based upon the mean and standard deviation of replicate analyses performed at the Wall Experiment Station. However, the agency also reserved the right to use other statistical evaluation methodologies, depending upon a review of the data received.

Based upon a number of considerations, MADEP has now determined that the use of a Z-score approach appears to be the most objective and relevant means to evaluate laboratory performance during the second Round Robin effort. Chief among these considerations are the following:

- unlike the first study, it is not possible to know the total spike concentrations of the "real world" groundwater samples, to provide some level of verification of the data obtained by WES chemists;

- unlike the first study, problems were experienced by WES in the fractionation of the EPH soil and water samples, calling into question the appropriateness of using these data as benchmark values;

- unlike the first study, it is now clear that the chromatographic column used at WES for the VPH analyses results in a substantially different apportionment of hydrocarbons among the C5-C8 and C9-C12 Aliphatic fractions, relative to the columns used by most other laboratories, calling into question the appropriateness of using these data as benchmark values.

To judge proficiency in the second Round Robin, MADEP has adopted the procedures and criteria employed by the US EPA in evaluating interlaboratory performance: the use of biweight mean and standard deviation data, and computation of Z-scores for each method, matrix, and analyte. In order to eliminate from consideration non-methodological variables, such as the choice of methods/detectors in determining the concentrations of the BTEX/PAH Target Analytes, proficiency was evaluated on the basis of unadjusted aliphatic/aromatic range data. Participating labs were also asked to provide concentration data on the Target Analytes, however, to enable an evaluation of the variability and sensitivity of data adjustments of this nature, and to identify problems experienced by laboratories in conducting the data manipulations required or allowed by the methods.

RESULTS OF THE SECOND ROUND ROBIN STUDY

Wall Experiment Station

Data from the replicate analyses performed at the Wall Experiment Station are provided in Table 1.

Table 1
Results of VPH/EPH analysis at the MADEP Wall Experiment Station

Method	Matrix	Fraction	Concentration [ug/g for soil, ug/L for water]								
			Begin Day 0	Mid Day 0	End Day 0	Begin Day 7	Mid Day 7	End Day 7	End Day 7	End Day 7	End Day 7
VPH	Soil	C5-C8 Aliphatics	2830	2773	2682	2995	3000	2892			
		C9-C12 Aliphatics	824	751	787	844	859	851			
		C9-C10 Aromatics	441	442	442	501	497	560			
		Total GC/FID	3654	3524	3469	3839	3859	3743			
	Water	C5-C8 Aliphatics	3142	3152	3315	3282	3505	3327	3187	3382	3245
		C9-C12 Aliphatics	1315	1353	1408	1390	1477	1416	1360	1432	1386
		C9-C10 Aromatics	861	840	951	1012	1243	1089	975	1072	1117
		Total GC/FID	4457	4505	4723	4672	4982	4743	4547	4814	4631
EPH	Soil	C9-C18 Aliphatics	2885	2385	2140	1635	1817	2435			
		C19-C36 Aliphatics	668	490	486	323	419	528			
		C11-C22 Aromatics	305	489	581	1235	1296	1320			
		Total All Fractions	3858	3364	3207	3193	3532	4283			
	Water	C9-C18 Aliphatics	188	157	164	473	490	590			
		C19-C36 Aliphatics	38	68	49	56	49	64			
		C11-C22 Aromatics	1429	829	984	944	1000	698			
		Total All Fractions	1655	1054	1197	1473	1539	1352			

Note that the data displayed in Table 1 was obtained for 3 reasons:

- the "Day 0" analyses were undertaken prior to shipment of the samples to ensure that all samples from the production line were sufficiently homogeneous;

- the "Day 7" analyses were undertaken subsequent to the shipment of the samples to determine the analyte concentrations on or near the day that samples were received by participating laboratories; and

- the replicate analyses were otherwise used to evaluate single laboratory (WES) precision and accuracy, and provide data for evaluation in the Round Robin effort.

Based upon the data presented in Table 1, the following conclusions were made:

◊ There were no significant differences or trends noted in the quality or chemistry of samples at the beginning, middle, or end of the sample preparation and packaging process;

◊ There were no significant differences in the concentration of total hydrocarbons between the day the samples were prepared (Day 0) and the day they were received by participating laboratories (Day 7);

◊ The single laboratory/analyst precision of the 6 to 9 replicate VPH sand and water samples was very good, with the RSD of each VPH soil fraction less than 10%, and the RSD of each VPH water fraction less than 13%;

◊ The single laboratory/analyst precision of the combined EPH fractions was relatively good, with an RSD of 29% for the sand samples, and 15% for the water samples. However, difficulties in fractionation were evident, based upon an RSD of 53% for the C11-C22 Aromatic fraction in sand, and RSD value of 52% for the C9-C18 Aliphatic fraction in the water samples. It has become clear that aromatics were stripped into the aliphatic fractionation solution for the Day 0 sand samples, and Day 7 water samples. This issue is addressed in more detail in later sections, and has prompted modifications to the EPH methodology.

Data Received from Participating Laboratories

Data submittals were received from 27 laboratories, who, along with the Wall Experiment Station, were assigned identification numbers of 1 to 28.

Because the VPH and EPH methods are "performance based", modifications are permissible, and laboratories were free to incorporate minor or major changes to the MADEP procedures during the Round Robin study. To enable meaningful evaluation of the data, the draft methods, and any method modifications, participating laboratories were required to identify and document key operational elements (e.g., type of chromatographic column) and any changes made to the draft procedures (e.g., use of MS detector).

Of the 27 laboratories submitting VPH data:

- 21 labs used the draft MADEP VPH method with little or no modification;
- 5 labs used a GC/MS technique; and
- 1 lab used a combined VPH/EPH technique.

Of the 27 laboratories submitting EPH data:

- 23 labs used the draft MADEP EPH method with little or no modification;
- 2 labs used a GC/MS to analyze the aliphatic and aromatic fractions;
- 1 lab used a GC/MS technique in lieu of silica gel fractionation; and
- 1 lab used a high temperature PID/FID technique

One laboratory (Lab # 18) requested and received two complete sets of (duplicate) samples, and provided two complete data submittal packages, in which a high temperature PID/FID unit was used to quantitate VPH and EPH aliphatic and aromatic fractions, using (1) a 10.2 eV PID lamp, and (2) a 9.6 eV PID lamp. In total, 29 sets of data have been tabulated and evaluated (1 data set from 26 participating labs, 2 sets of data from Lab #18, and the data generated by the MADEP Wall Experiment Station). A summary of the data provided by laboratories using the VPH and EPH methods with little or no modification is presented in Tables 2 through 5. A summary of the data provided by laboratories who substantially modified these methods are presented in Tables 6 through 9.

Table 2
VPH Soil Data
Unmodified VPH Method
ug/g

	Unadjusted Range Data				Target Analytes						Target Analytes						Detector	Adjusted Range Data		
	C5-C8	C9-C12	C9-C10	Total	Detected in C5-C8 Aliphatic Range						Detected in C9-C12 Aliphatic Range						for Target	C5-C8	C9-C12	C9-C10
Lab#	Aliphatics	Aliphatics	Aromatics	GC/FID	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	EB	Naph	Tol	mp-XYL	o-XYL	TMB	Analytes	Aliphatics	Aliphatics	Aromatics
1	367	133	44	500	48	224	260	107	210			F			101	100	PID	N.D.	N.D.	N.D.
2	880	961	301	1841	47	253	330				126	9		271	120	110	PID	250	325	182
3	1410	1420	324	2830	62	250	298				129	9		244	112	107	PID	800	819	208
4	1510	617	333	2127	53	7	268				110	8		219	100	102	PID	1182	78	223
5	1530	1250	381	2780	60	227	312				125	10		251	112	110	PID	931	642	261
6	1620	1100	573	2720	63	214	309				130	13		253	110	109	PID	1034	485	451
7	1720	757	455	2477	59	85	279	113	251			26			94	106	PID	933	531	323
8	1740	1370	351	3110	55	208	309				133	13		253	110	110	PID	1168	751	228
9	1770	1140	333	2910	851	235	312				124	10		254	104	111	PID	372	537	212
10	1780	1270	247	3050	38	87	176				79	6		164	62	53	PID	1479	906	188
11	1807	1135	499	2942	73	466	361				178	13		317	139	165	PID	907	323	321
12	1810	2750	363	4560	71	287	349				152	10		262	126	118	PID	1103	2082	235
13	2050	2520	564	4570	69	258	375				158	4		299	126	138	MS	1348	1795	422
14	2070	1710	376	3780	67	253	324				147	9		250	120	121	PID	1426	1063	246
15	2340	1050	363	3390	60	235	310	126				15		249	114	109	PID	1609	563	239
16	2370	3096	397	5466	59	<C5	301	121	235	102		22				105	PID	1552	2969	270
17	2480	1140	350	3620	70	243	400				142	10		284	121	100	MS	1767	483	240
18	2523	781	212	3304	63	210	296	130	177	98		8				103	PID	1549	670	101
19	2547	525	392	3072	67	255	410	164	333	153		11				147	MS	1165	367	234
20	2780	1810	419	4590	67	224	259				102	9		188	90	87	PID	2230	1334	323
22	3370	2673	432	6043	63	217	337				134	7		267	117	109	PID	2753	2039	316
WES	2850	819	481	3669	117	298	412	160	278	133		17				124	PID	1452	678	340
Mean	1969	1365	372	3334	99	226	318	132	247	122	131	11		252	110	111		1327	926	265
Std Dev	671	774	115	1211	169	89	55	22	54	26	24	5		38	17	21		520	725	81
%RSD	34	57	31	36	170	40	17	17	22	22	18	46		15	15	19		39	78	30
BW Mean	1982	1204	383	3288																
BW Std Dev	729	618	115	1073																
BW %RSD	37	51	30	33																

Table 3
VPH Water Data
Unmodified VPH Method
ug/L

	Unadjusted Range Data				Target Analytes						Target Analytes						Detector	Adjusted Range Data		
	C5-C8	C9-C12	C9-C10	Total	Detected in C5-C8 Aliphatic Range						Detected in C9-C12 Aliphatic Range						for Target	C5-C8	C9-C12	C9-C10
Lab#	Aliphatics	Aliphatics	Aromatics	GC/FID	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	EB	Naph	Tol	mp-XYL	o-XYL	TMB	Analytes	Aliphatics	Aliphatics	Aromatics
1	507	291	109	798	94	224	582	170	713			64			288	349	PID	0	0	0
2	1033	2071	771	3104	81	240	585				158	80		720	170	281	PID	127	662	410
3	1520	3780	859	5300	104	257	620				183	96		764	180	320	PID	539	2237	443
4	2510	1720	948	4230	102	210	605				184	82		761	176	316	PID	1593	201	550
5	1680	2930	934	4610	113	248	675				196	104		822	195	334	PID	644	1279	496
6	1440	2240	1230	3680	105	225	605				190	100		750	185	315	PID	505	700	815
7	1520	984	701	2504	67	135	410	116	571			123			122	213	PID	221	526	365
8	1550	2550	899	4100	90	192	590				172	113		730	167	313	PID	678	1055	473
9	1440	2210	805	3650	111	213	640				179	91		778	182	319	PID	476	661	395
10	3800	6910	1780	10710	123	242	736				215	141		1060	207	343	PID	2699	4944	1296
11	1619	4600	822	6219	99	261	545				170	91		640	170	316	PID	714	3213	415
12	1730	5400	830	7130	108	243	606				197	88		698	177	302	PID	773	3938	440
13	1830	6000	1630	7830	89	192	570				155	68		668	149	285	MS	979	4675	1277
14	1830	3250	677	5080	93	214	571				167	81		679	153	274	PID	952	1896	322
15	2100	2300	853	4400	100	248	600	177				100		741	176	303	PID	975	980	450
16	2670	1620	834	4290	93	<C5	547	158	664	152		104				269	PID	1056	1247	461
17	2710	2750	935	5460	113	286	572				176	112		676	167	295	MS	1739	1324	528
18	2826	1280	498	4106	99	221	579	168	519	158		85				260	PID	1082	935	153
19	3341	1453	1351	4794	120	215	850	256	1050	255		100				415	MS	595	938	836
20	2332	3455	1120	5787	130	286	682				186	91		769	187	308	PID	1234	1914	721
22	1820	2675	651	4495	89	206	517				150	68		636	146	250	PID	1008	1425	333
WES	3282	1393	920	4675	112	308	651	189	775	184		109				330	PID	1063	954	481
Mean	2050	2812	916	4861	102	232	606	176	715	187	179	95		743	178	305		936	1700	560
Std Dev	802	1669	355	1974	14	38	84	42	188	47	17	18		99	34	41		566	1362	289
%RSD	39	59	39	41	14	16	14	24	26	25	10	19		13	19	13		60	80	52
BW Mean	2006	2542	855	4605																
BW Std Dev	864	1504	177	1361																
BW %RSD	43	59	21	30																

Table 4
EPH Soil Data
Unmodified EPH Method
ug/g

	Unadjusted Range Data				Target Analytes										Detector	Adjusted	% C11-C22 Aromatics	
	C9-C18	C19-C36	C11-C22	Total All	Detected in C11-C22 Aromatics Range										for Target	C11-C22	Target	naph &
Lab#	Aliphatics	Aliphatics	Aromatics	Fractions	Acen	Acenyl	Anthra	Fluroan	Fluore	In(123)P	2-mnap	Naph	Phen	Pyrene	Analytes	Aromatics	Analytes	2-mnap
1	2630	506	1310	4446	1.30				2.21		24.00	8.00	5.00		MS	1269	3	2
2	2810	529	2340	5679	14.00	1.36	2.39	0.54	15.00		24.90	10.90	10.30	1.18	FID	2259	3	8
3	1760	313	836	2909	4.36	0.50	1.11	0.87	6.06		38.10	7.00	6.10	0.83	FID	771	8	2
4	1640	237	844	2721	1.61		1.30	0.84	2.25		35.50	8.25	5.37	1.16	FID	788	7	6
5	2120	472	1060	3652	6.14				5.89		47.40	24.00	7.33		FID	969	9	4
6	2560	417	1380	4357			0.88		5.16		54.60	19.90	7.71	0.45	MS	1291	6	21
7	1190	142	205	1537	1.41		0.80	0.14	1.22	0.03	4.57	1.23	1.79	0.01	FID	194	5	4
8	3000	486	998	4484					7.80		30.00	9.31			FID	951	5	2
9	1480	257	1310	3047	0.20	11.60	1.56	0.82	18.50		37.90	8.91		0.53	FID	1230	6	5
10	2320	396	984	3700	5.76				5.34		59.30	10.60	5.40		FID	898	9	5
11	2090	628	1268	3986	1.78	6.84	2.15		1.34		22.50	6.63	3.95	1.78	FID	1221	4	18
12	1300	373	1090	2763	55.00		76.70		34.80		128.00	97.40	46.00		?	652	40	7
13	2110	412	1010	3532	1.70				2.60		20.20	8.47	5.94		MS	971	4	9
14	1860	297	1190	3347	10.30	2.10	2.40		4.10		82.40	14.30	6.60		FID	1068	10	4
15	2370	334	1310	4014	3.04				6.34		69.20	25.60	8.29		FID	1198	9	7
16	6180	1060	1570	8810	9.95				19.10		88.70	48.70	8.86		FID	1395	11	7
17	1380	249	739	2368	1.28	0.76	0.37		2.27		31.00	16.10	4.11	0.43	MS	683	8	4
19	1680	630	1205	3515	2.00		0.95		2.60		42.30	18.00	6.40		MS	1133	6	5
20	3784	309	1334	5427	55.00	30.00			16.00		160.00	74.00	11.00		FID	988	26	5
22	2550	295	766	3611	2.10	9.20	1.20	1.30	4.00		24.00	9.00	10.20	2.00	FID	703	8	2
23	1660	391	1220	3271	8.02	10.90	1.29	8.48	9.13	0.05	53.10	11.70	7.16	1.16	FID	1109	9	3
24	1880	329	1320	3529	6.24	1.97	0.86		2.75		56.40	14.40	5.62	0.54	FID	1231	7	3
25	1724	306	921	2951	5.50	3.60	10.40		7.30		43.90	8.39	0.61	0.55	FID	841	9	5
WES	2216	486	871	3573			0.48	0.69	3.83		26.27	10.84	4.50	0.49	FID	824	5	5
Mean	2262	411	1128	3801	9	7	7	2	8	0	50	20	8	1		1026	9	6
Std Dev	1028	184	385	1397	16	9	19	3	8	0	35	23	9	1		375	8	4
%RSD	45	45	34	37	167	120	288	161	101	45	71	115	109	67		37	89	73
BW Mean	1978	374	1098													988		
BW Std Dev	652	144	310													293		
BW %RSD	33	39	28													30		

Table 5
EPH Water Data - Unmodified EPH Method
ug/L

	Unadjusted Range Data				Target Analytes										Detector	Adjusted	%C11-C22 Aromatics	
	C9-C18	C19-C36	C11-C22	Total All	Detected in C11-C22 Aromatics Range										for Target	C11-C22	Target	naph &
Lab#	Aliphatics	Aliphatics	Aromatics	Fractions	Acen	Acenyl	Anthra	Fluroan	Fluore	In(123)P	2-mnap	Naph	Phen	Pyrene	Analytes	Aromatics	Analytes	2-mnap
1	720	<500	2600	3320	5				6		172	112	5		MS	2300	12	11
2	ND	ND	2170	2170	16.1	27.4			19.8		105	150	9.38		FID	1842	15	12
3	137	11	1250	1398	10.2				9.56		196	152	6.88		FID	875	30	28
4	52.5	7	815	875	9.02				7.74		189	140	5.82		FID	463	43	40
5	128	<15	746	874	10.3				8.61		204	183	6.7		FID	333	55	52
6	49.3	<1	1900	1949	10				13.7		319	268	8.6		MS	1281	33	31
7	911	52	1210	2173	11.1	16.8	1.07	0.4	8.43	12	299	229	6.15	3.04	FID	622	49	44
8	1480	<40	550	2030					6.96		65.2	44.1			FID	434	21	20
9	285	22	1598	1905	13.1	38.2		8.81	15.6		2.04	136	12.5		FID	1367	14	9
10	<250	<250	1950	1950								340	267		FID	1343	31	17
11	466	<40	1350	1816	5.2				6.72		189	134	8.78		FID	1006	25	24
12	285	926	490	1701	15		6.28		16.2		94.9	71.6	19.6		?	266	46	34
13	1010	139	800	1949	3.43				5.25		73.6	54.2	6.17		MS	657	18	16
14	<50	<50	1130	1130	14.8				11.8		316	256			FID	531	53	51
15	2	<10	1510	1512	14.4				9.8		337	276	6.6		FID	866	43	41
16	228	139	1630	1997	15.5	20.5			16.4		391	337	7.78		FID	842	48	45
17	772	12	1030	1814	7.4				8.42		295	272	6.6		MS	441	57	55
19	288	420	1508	2216	5.9				7.3		160	110	7.1		MS	1218	19	18
20	1060	<50	2080	3140	33	33			28		455	411	11		FID	1109	47	42
22	1040	2.8	739	1782	5.8	12.4	0.6		6.3		73.8	32.7	2.8		FID	605	18	14
23	409	229	678	1316	12.1	3.87	8.18	8.27	11.5	9.32	82.4	43.1	14.7	9.59	FID	410	40	19
24	12	25.7	1100	1138	12	16.1	0.48		9.62		227	164	6.72		FID	664	40	36
25	865	488	834	2187	2.87	12.1	8.77	1.5	6.34		150	101	82		FID	392	53	30
WES	344	54	981	1379			0.49	0.52	7.65		117	64.8	6.08	0.19	FID	784	20	19
Mean	502	181	1277	1822	11	20	4	4	11	11	196	170	23	4		860	35	34
Std Dev	427	265	563	595	6	11	4	4	5	2	117	106	57	5		502	15	14
%RSD	85	147	44	33	59	55	105	109	50	18	60	62	243	113		58	43	42
BW Mean	455	49	1194													735		
BW Std Dev	459	72	610													427		
BW %RSD	101	147	51													58		

Table 6
VPH Soil Data
Modified VPH Method
ug/g

	Unadjusted Range Data				Target Analytes						Target Analytes						Detector	Adjusted Range Data			Significant
	C5-C8	C9-C12	C9-C10	Total	Detected in C5-C8 Aliphatic Range						Detected in C9-C12 Aliphatic Range						for Target	C5-C8	C9-C12	C9-C10	Method
Lab#	Aliphatics	Aliphatics	Aromatics	Gasoline	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	EB	Naph	Tol	mp-XYL	o-XYL	TMB	Analytes	Aliphatics	Aliphatics	Aromatics	Modification
18(2)	2248	766	228	3242	63	210	296	130	177	98		8				103	PID	1274	655	117	9.6 eV PID
23	1262	1920	555	3737	92	321	403				171	15		297	140	116	MS	446	1181	424	GC/MS
24	1060	229	557	1846	72		517	225	437	188		19				198	FID	988	229	357	Solvent extr
25	N/A	N/A	N/A	1035	9	11	11				3	9		25	22	18	MS	708	44	175	GC/MS
26	2800	2100	700	5600	64	215	353				146	66		285	120	118	MS	2168	1365	516	GC/MS
27	N/A	N/A	N/A	2454	83	166					70	9	198	238	106	31	MS	1164	20	369	GC/MS
28	N/A	N/A	N/A	3009	63	281	323	132				9		259	109	115	MS	1140	92	486	GC/MS
Statistics from Unmodified Method Data:																					
Mean	1969	1365	372	3334	99	226	318	132	247	122	131	11		252	110	111		1327	926	265	
Std Dev	671	774	115	1211	169	89	55	22	54	26	24	5		38	17	21		520	725	81	
%RSD	34	57	31	36	170	40	17	17	22	22	18	46		15	15	19		39	78	30	

Table 7
VPH Water Data
Modified VPH Method
ug/L

	Unadjusted Range Data				Target Analytes						Target Analytes						Detector	Adjusted Range Data			Significant
	C5-C8	C9-C12	C9-C10	Total	Detected in C5-C8 Aliphatic Range						Detected in C9-C12 Aliphatic Range						for Target	C5-C8	C9-C12	C9-C10	Method
Lab#	Aliphatics	Aliphatics	Aromatics	Gasoline	Ben	MtBE	Tol	EB	mp-XYL	o-XYL	EB	Naph	Tol	mp-XYL	o-XYL	TMB	Analytes	Aliphatics	Aliphatics	Aromatics	Modification
18(2)	2539	1257	524	4320	99	221	579	168	519	158		85				260	PID	795	912	179	9.6 eV PID
23	1194	1778	636	3608	68	233	403				118	64		449	114	187	MS	490	846	385	GC/MS
24	2010	101	338	2449	134		629	190	780	186		86				322	FID	1876	101	16	Solvent extr
25	N/A	N/A	N/A	2397	111	262	205				190	83		350	183	293	MS	279	5	436	GC/MS
26	3200	4500	1500	9200	137	296	836				249	54		982	246	390	MS	1931	2579	1056	GC/MS
27	N/A	N/A	N/A	3733	68	195					160	101	707	824	140	280	MS	153	4	1101	GC/MS
28	N/A	N/A	N/A	3745	106	286	582	199					91	717	167	303	MS	422	27.5	844	GC/MS
Statistics from Unmodified Method Data:																					
Mean	2050	2812	916	4861	102	232	606	176	715	187	179	95		743	178	305		936	1700	560	
Std Dev	802	1669	355	1974	14	38	84	42	188	47	17	18		99	34	41		566	1362	289	
%RSD	39	59	39	41	14	16	14	24	26	25	10	19		13	19	13		60	80	52	

Table 8
EPH Soil Data 6
Modified EPH Method
ug/g

	Unadjusted Range Data				Target Analytes									Detector	Adjusted	%C11-C22	Aromatic	Significant
	C9-C18	C19-C36	C11-C22	Total	Detected in C11-C22 Aromatics Range									for Target	C11-C22	Target	naph &	Method
Lab#	Aliphatics	Aliphatics	Aromatics	Fuel Oil	Acen	Acenyl	Anthra	Fluroan	Fluore	2-mnap	Naph	Phen	Pyrene	Analytes	Aromatics	Analytes	2-mnap	Modifications
18	3171	672	876	4719	2.53	5.15	1.40	1.12	3.44	41.3	20	5.37	0.63	PID	795	9	7	10.2PID/FID
18(2)	2839	677	952	4468	2.53	5.15	1.40	1.12	3.44	41.3	20	5.37	0.63	PID	871	9	7	9.6 PID/FID
18(3)	2300	779	477	3556	2.53	5.15	1.40	1.12	3.44	41.3	20	5.37	0.63	PID	436	9	6	PID/FID w/frac
26	1714	482	796	2992						18.2	6.69	6.61		MS	765	4	3	GC/MS-range
27	1330	405	N.D.	1735	4.36	0.50	1.11		0.90	16.3	6.45	1.13	0.50	MS	N.D.	N/A	N/A	GC/MS - no frac
28	991	131	2050	3172	1.09		0.94	0.2	1.6	35.8	15.4	2.78	0.5	MS	1992	3	6	GC/MS-range
Statistics from Unmodified Method Data:																		
Mean	2262	411	1128	3801	9	7	7	2	8	50	20	8	1		1026	9	6	
Std Dev	1028	184	385	1397	16	9	19	3	8	35	23	9	1		375	8	4	
%RSD	45	45	34	37	167	120	288	161	101	71	115	109	67		37	89	73	

Table 9
EPH Water Data
Modified EPH Method
ug/L

	Unadjusted Range Data				Target Analytes									Detector	Adjusted	%C11-C22	Aromatic	Significant
	C9-C18	C19-C36	C11-C22	Total	Detected in C11-C22 Aromatics Range									for Target	C11-C22	Target	naph &	Method
Lab#	Aliphatics	Aliphatics	Aromatics	Fuel Oil	Acen	Acenyl	Anthra	Fluroan	Fluore	2-mnap	Naph	Phen	Pyrene	Analytes	Aromatics	Analytes	2-mnap	Modifications
18	2882	676	981	4539	4.08	11.9	4.04	N.D.	2.7	168	146	4.01	N.D.	PID	640	35	32	10.2 PID/FID
18(2)	2753	542	1245	4540	4.08	11.9	4.04	N.D.	2.7	168	146	4.01	N.D.	PID	904	27	25	9.6 PID/FID
18(3)	1079	389	521	1989	4.07	9	N.D.	N.D.	4.7	93	68	5.3	N.D.	PID	337	35	31	PID/FID w/frac
26	631	<57	296	927					4.24	39.9	37.5	4.72	N.D.	MS	210	29	26	GC/MS-range
27	1057	49	N.D.	1106				N.D.	2.63	146	113	4.19	N.D.	MS	N.D.	N/A	N/A	GC/MS - no frac
28	24	32	1110	1166	5.93				7.21	194	160	6.25	N.D.	MS	737	34	32	GC/MS-range
Statistics from Unmodified Method Data:																		
Mean	502	181	1277	1822	11	20	4	4	11	196	170	23	4		860	35	34	
Std Dev	427	265	563	595	6	11	4	4	5	117	106	57	5		502	15	14	
%RSD	85	147	44	33	59	55	105	109	50	60	62	243	113		58	43	42	

DISCUSSION

UNMODIFIED METHODS

VPH

Reported fractional data for the VPH soil and water samples are graphically displayed in Figures 1 through 6. In order to compare "apples with apples", except as otherwise indicated, the values presented in these graphs are **unadjusted fractional concentration data**, from which the concentration of Target Analytes (e.g., BTEX) have not been subtracted. This allows for a direct evaluation of the aliphatic and aromatic fractional data, without the added element of uncertainty introduced in the generation and manipulation of Target Analyte data.

Soil Data

In Figure 1, relatively good data distribution is noted for the VPH sand (soil) sample, especially for the C9-C10 Aromatics and C5-C8 Aliphatics, with an RSD of 31% and 34%, respectively (see Table 2). Poorer performance is noted in the C9-C12 sand sample, due largely to 4 outlier labs (ID numbers 13, 22, 12, and 16), and the effects of chromatographic column selection (discussed in a later section).

Relatively good distribution is also noted for the total GC/FID data plotted in Figure 2 (the sum of the C5-C8 Aliphatics and C9-C12 Aliphatics). The percent recovery data - computed by comparing the total GC/FID value to the gravimetric total gasoline value of 3050 ug/g - show a good clustering around 100%. In the bottom graph in Figure 2, the C9-C10 Aromatics are shown to be a small percentage of the total GC/FID response.

Water Data

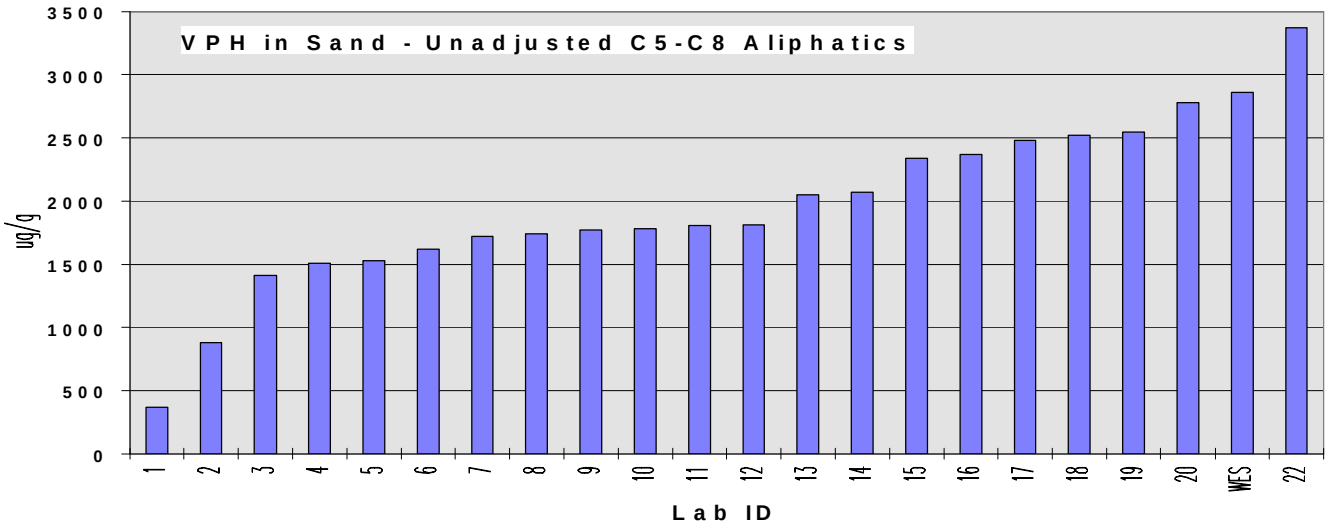
The data for the VPH water sample plotted in Figure 3 show relatively poor correlation for the individual aliphatic fractions, with better correlation for the C9-C10 Aromatics and the sum of the aliphatic fractions (total GC/FID data in Figure 4). As with the soil data, outliers are noted, especially on the high end of the C9-C10 Aromatic and Total GC/FID plots. In Figure 4, the concentrations of C9-C10 Aromatics are once again seen to be a small fraction of the Total GC/FID response, though larger than with the soil data. This finding is consistent with the use of "real world" groundwater samples, in which aromatic compounds comprise the majority of the water soluble fraction.

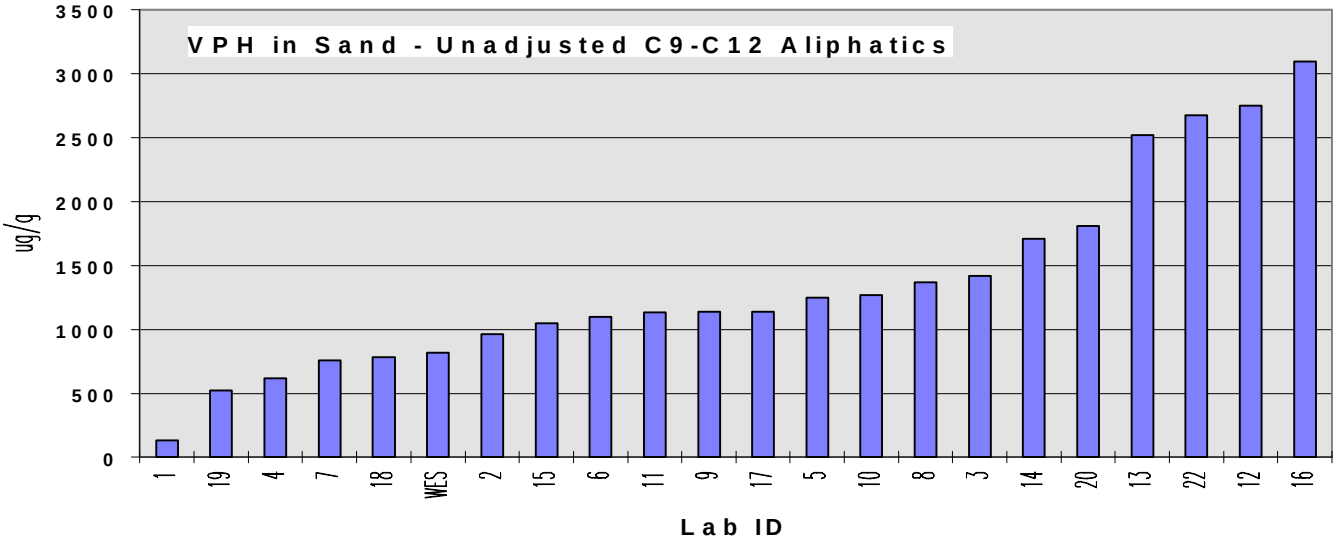
Column Effects

Although the choice of chromatographic column was known to have an impact on the elution time and/or order of VPH Target Analytes (e.g, BTEX) and range "marker" compounds (e.g., n-nonane), the significance of these impacts on the quantitation of the aliphatic ranges has not been clear. Based upon the data obtained from the Second Round Robin study, however, these variations may be significant.

In Tables 1 and 2, it can be noted that 15 of the 22 labs reported that the Target Analytes Ethylbenzene, m/p-Xylenes, and o-Xylene eluted within the C9-C12 Aliphatic FID chromatogram. For the remaining 7 labs, including the MADEP Wall Experiment Station, these compounds eluted, in whole or in part, in the earlier C5-C8 Aliphatic FID chromatogram. In addition to influencing the elution characteristics of these Target Analytes, it can also be surmised that the choice of column can also shift the elution time and order of the numerous branched and cyclic alkanes comprising the aliphatic fractions of petroleum products such as gasoline. This can have a substantial impact on where midweight aliphatic compounds end up - in the C5-C8 Aliphatic range or C9-C12 Aliphatic range - and on the adjustments made to reported VPH data when the concentration of Target Analytes are subtracted from these ranges. Moreover, the choice of column may also have a smaller, though potentially significant impact, on the starting and ending points

Figure 1 - VPH in Sand - Unadjusted Range Data





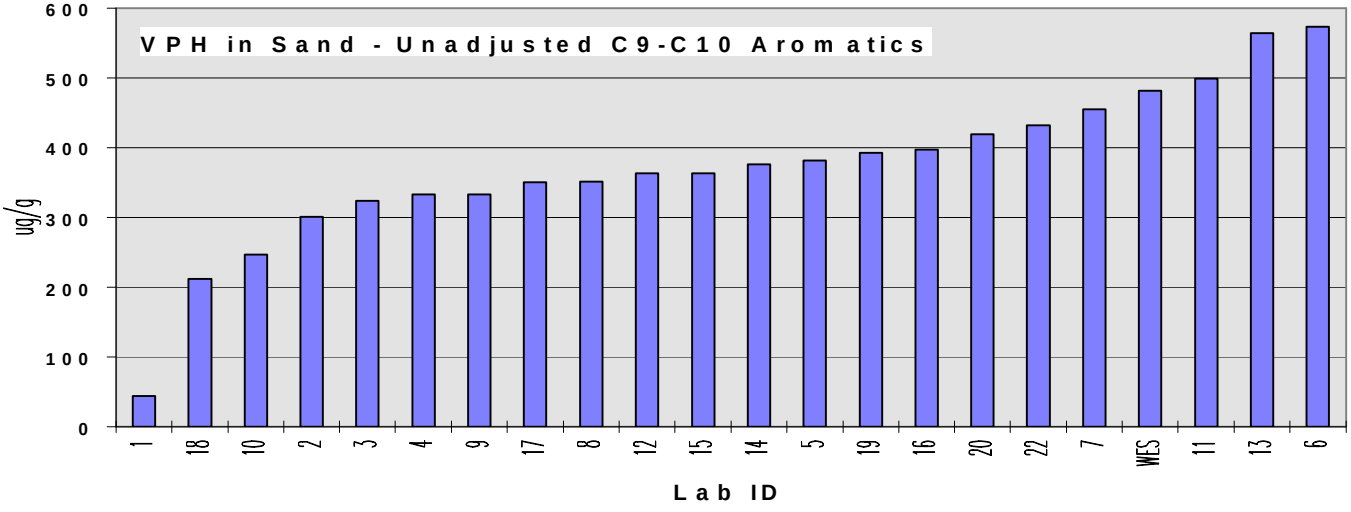
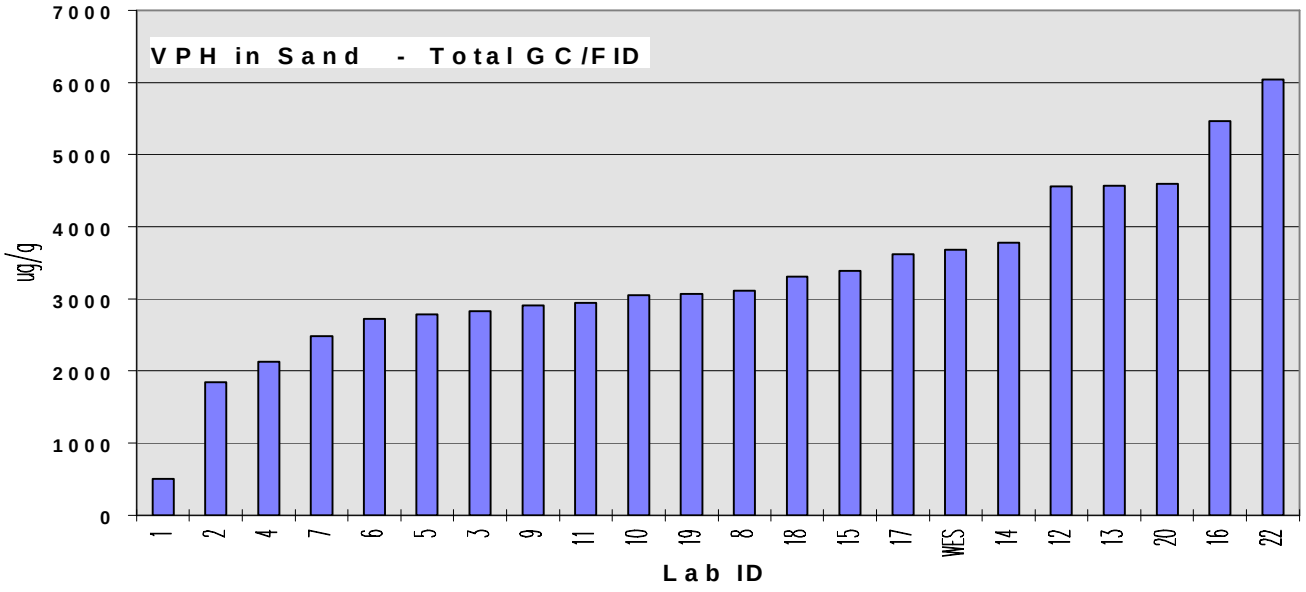
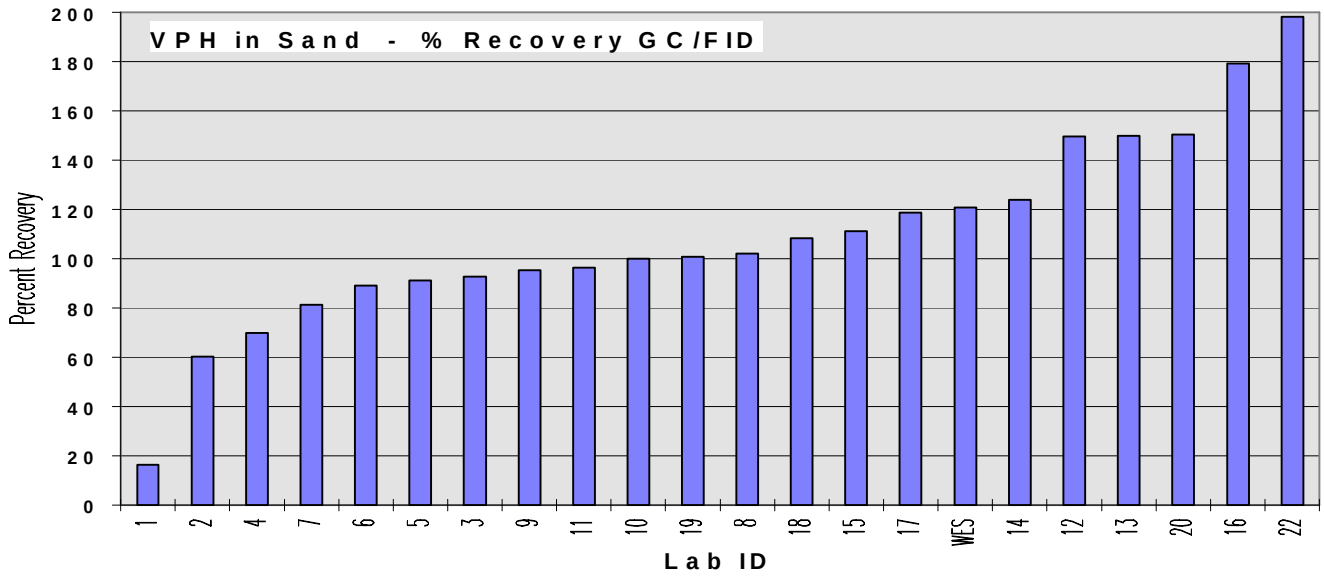


Figure 2 - VPH in Sand - Recoveries





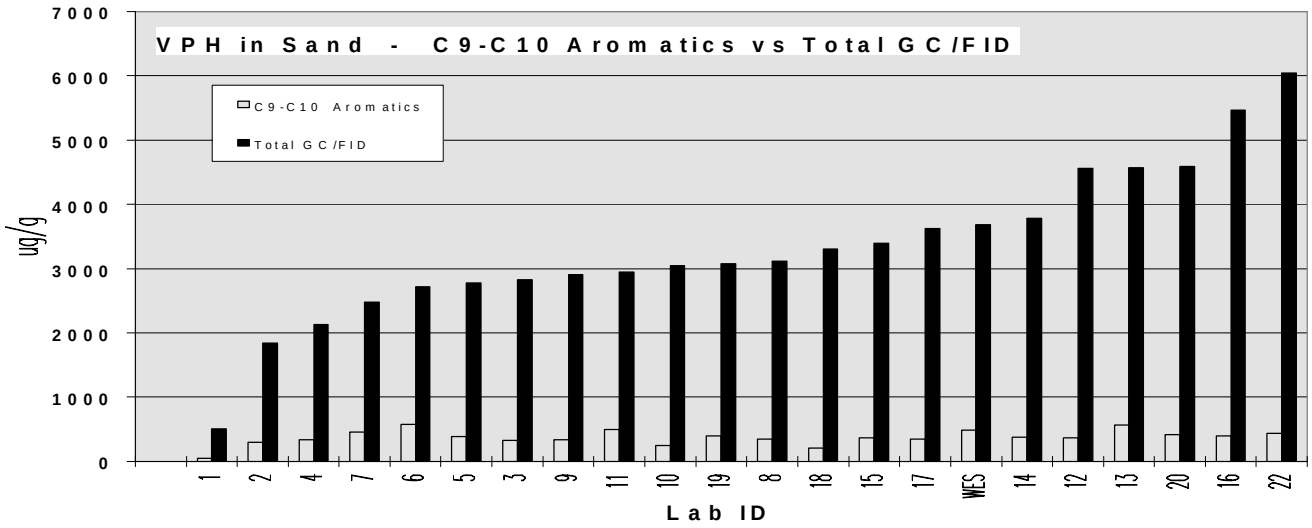
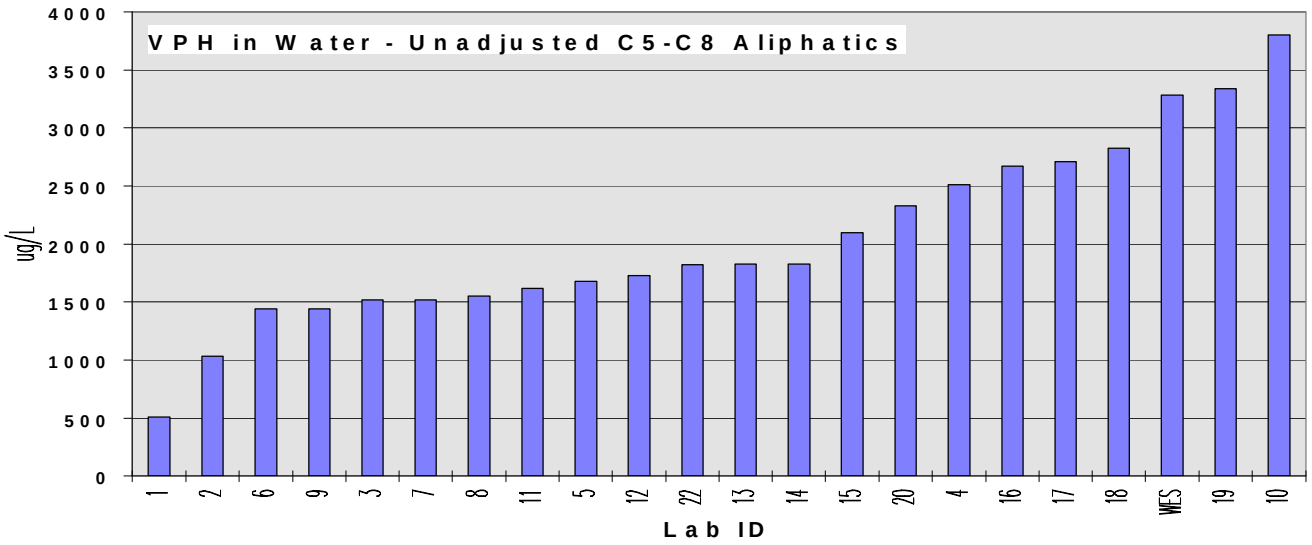
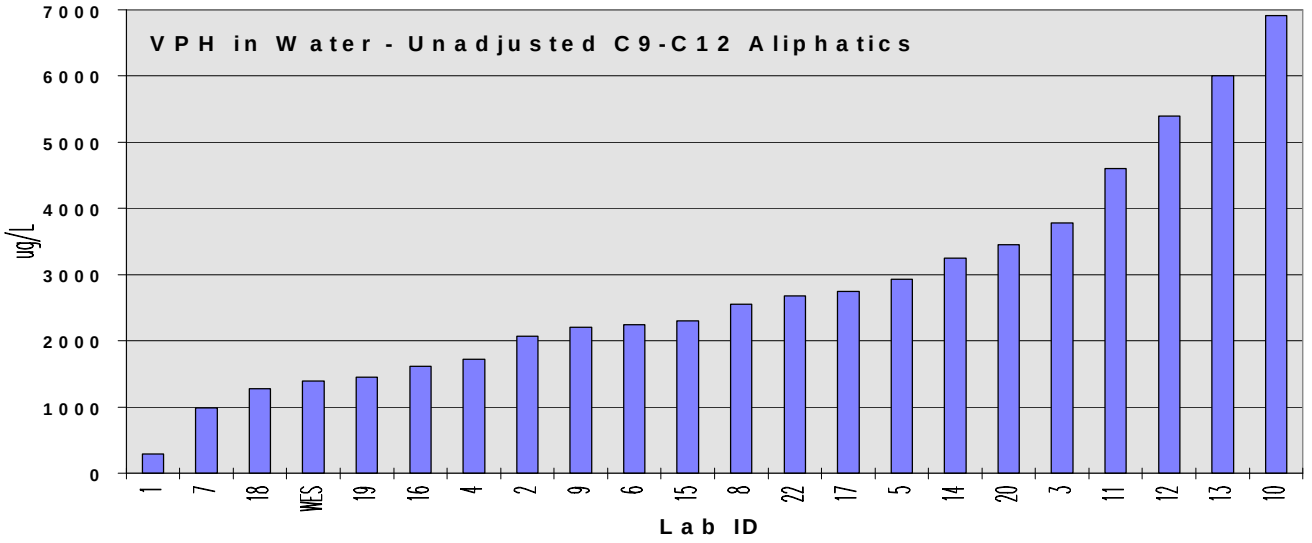


Figure 3 - VPH in Water - Unadjusted Range Data





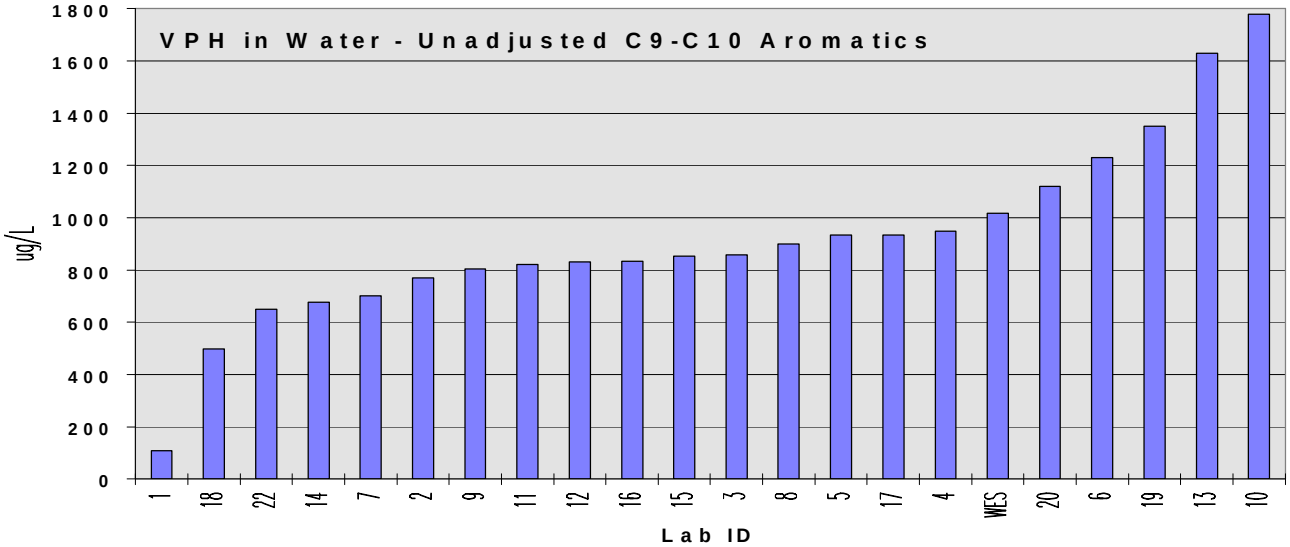
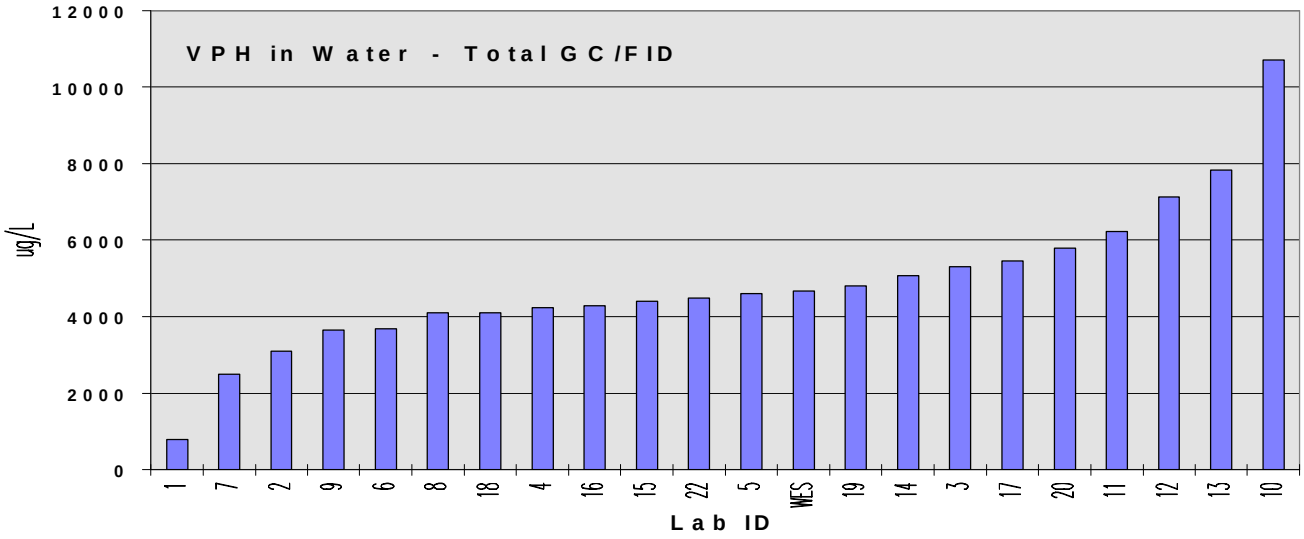
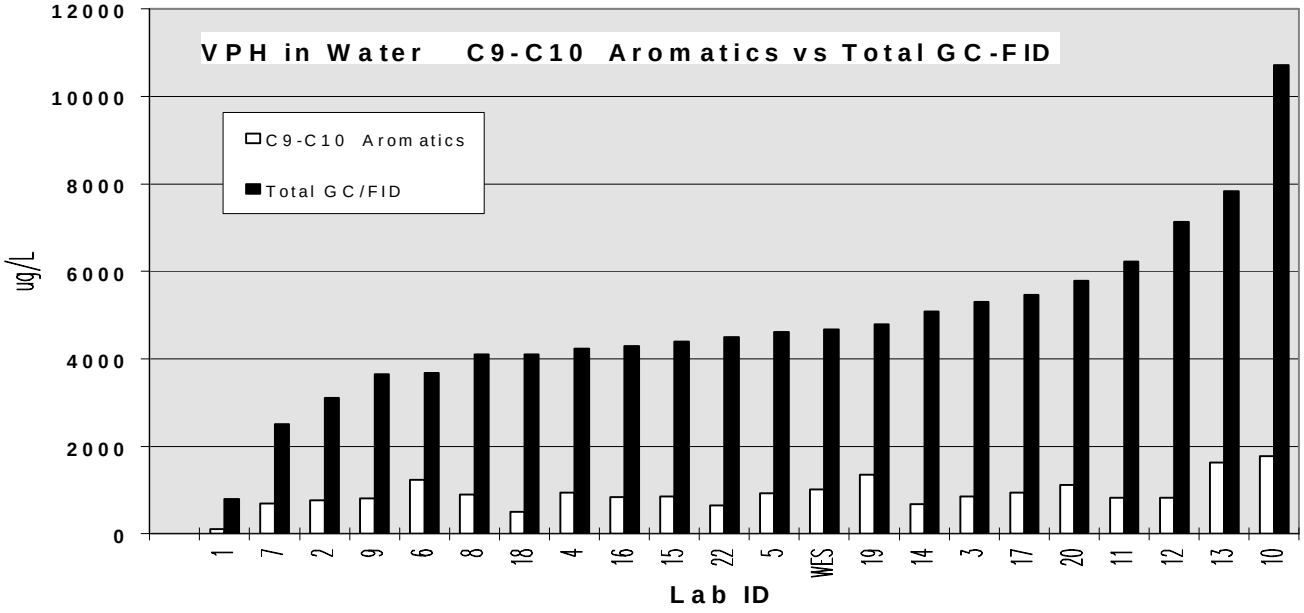


Figure 4 - VPH in Water - Recoveries





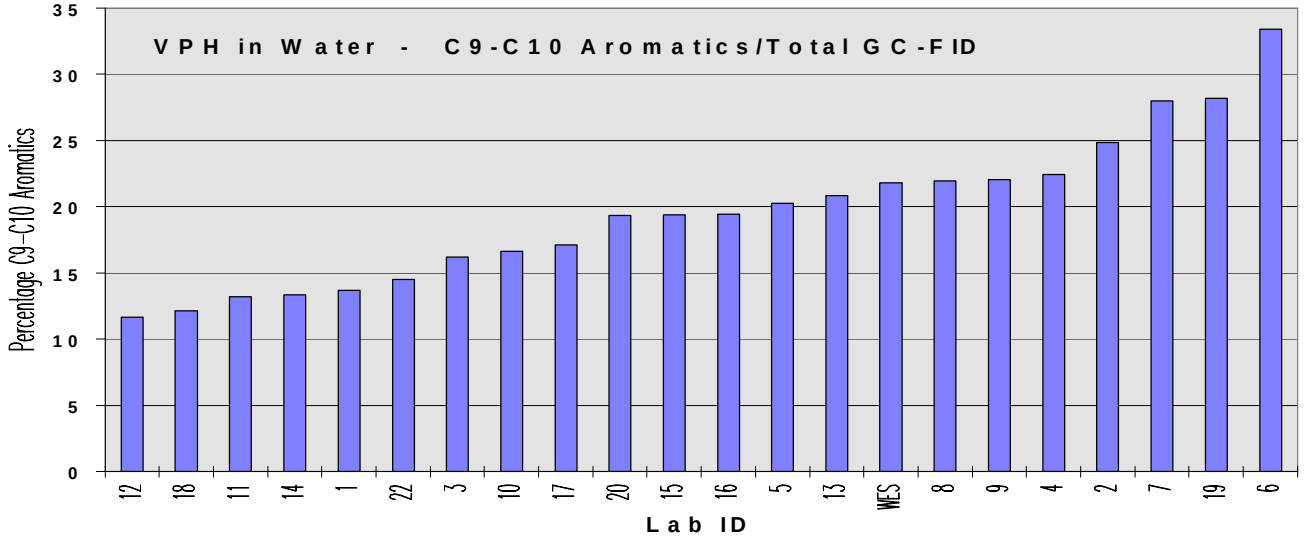
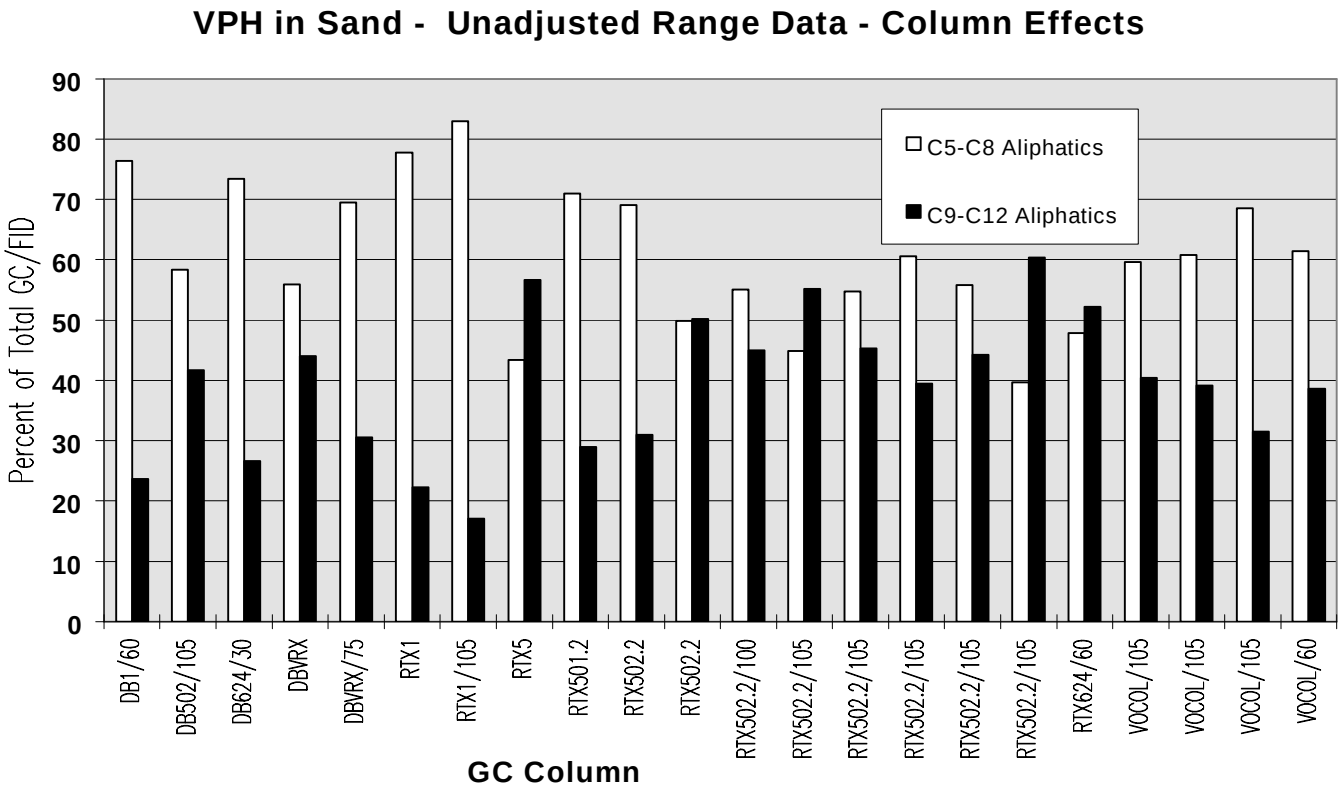


Figure 5 VPH Sand Data - Column Effects



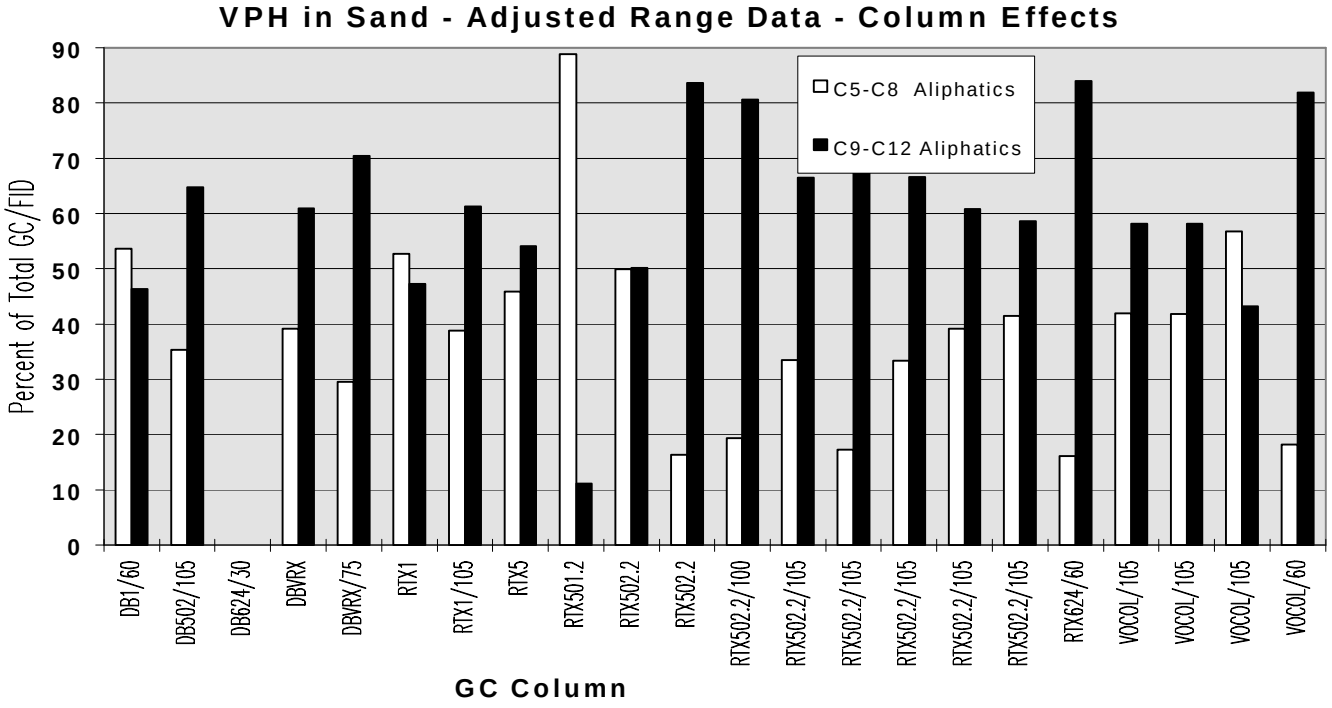
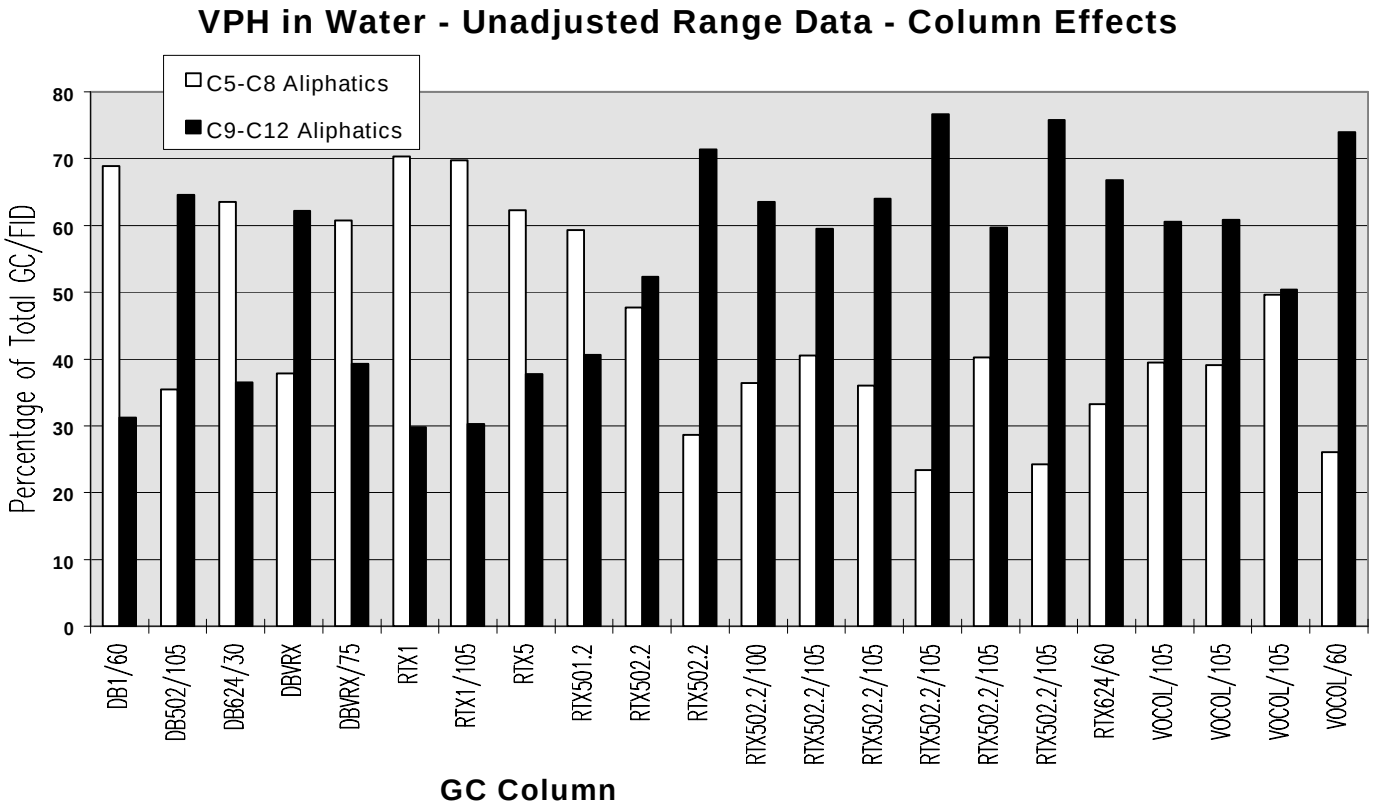
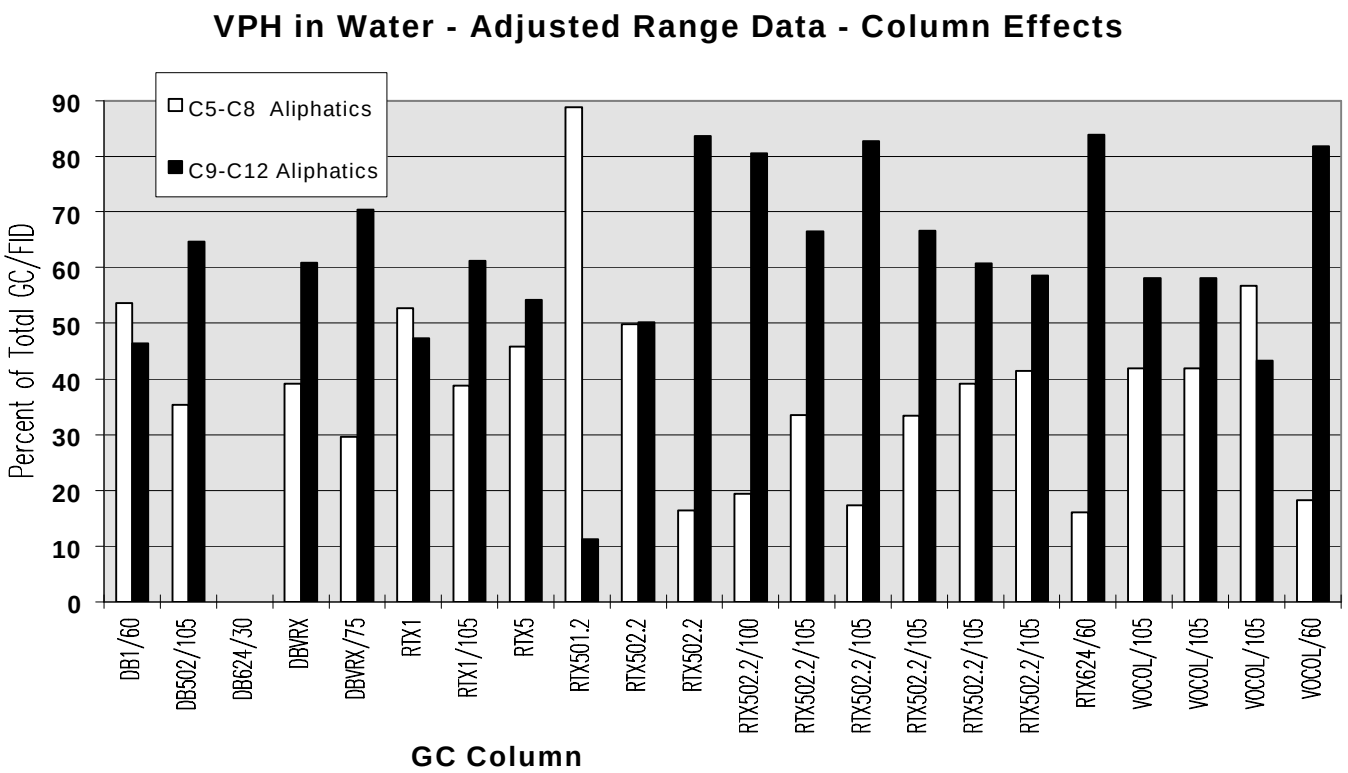


Figure 6 VPH Water Data - Column Effects





of the aliphatic ranges, and starting and ending points of the C9-C10 Aromatic fractions - with a concomitant impact on the ultimate range concentration value.

For both the VPH sand and water sample, the poorest data correlations were noted for the individual (unadjusted) aliphatic ranges, with better correlation seen for the C9-C10 Aromatic range and the Total GC/FID data. As an example, in Figure 3, WES data for C5-C8 Aliphatics is seen as a high-level outlier, while the WES data for the C9-C12 Aliphatics is seen as a low-level outlier. However, in Figure 4, the Total GC/FID WES data is shown to be near the middle of the data distribution - indicating that the column used by WES (RTX-1) was eluting most of the midweight branched and cyclic alkanes prior to the normal-alkane (C9) "marker" compound, and therefore in the C5-C8 Aliphatic range. Only one other lab, #19, used this column - with similar results.

Although all labs did not provide complete and/or clear details in this regard, it appears that 12 different chromatographic columns were used by the 22 labs who performed the unmodified MADEP VPH procedure during the second Round Robin study. Available information and data are displayed in Figures 5 and 6, plotting the percent distribution of aliphatics among the two VPH ranges. Based upon these data, significant variation in the apportionment of the aliphatics within the two ranges appears to exist:

- As indicated in Figure 5, most labs reported more C5-C8 Aliphatics in the soil sample than C9-C12 Aliphatics; this is consistent with the use of a fresh gasoline product to spike these samples. The "adjusted range" data plotted in the bottom graph in Figure 5 can perhaps provide a better means to evaluate this issue, as the BTEX/MtBE and naphthalene Target Analytes that comprise a significant percentage of the GC/FID response have been removed from consideration. Although several labs reported more C9-C12 Aliphatics than C5-C8 Aliphatics, it is not clear whether this is related to a column effect or some other variable or problem; for example, while 6 of the 9 labs using a 502.2 column reported more C5-C8 than C9-C12 Aliphatics, 3 reported the opposite. However, it does appear that the RTX 501.2 column provides a significant overquantitation of the C5-C8 Aliphatics (>90%); this is especially true given the fact that the C9-C12 "Aliphatic" range reported on the FID is likely comprised of a significant percentage of alkyl aromatic compounds (a known bias in the method).

- In Figure 6, most labs reported more C9-C12 Aliphatics than C5-C8 Aliphatics in the water sample; once again, this is consistent with the fact that these are (filtered) "real world" groundwater samples obtained from a downgradient plume area at a gasoline contaminated site. High concentrations of C5-C8 Aliphatics would not be expected; as these compounds are volatile, sparingly soluble, and unlikely to migrate significant distances in groundwater in a dissolved phase. While the heavier aliphatics are also unlikely to migrate appreciable distances, the alkyl aromatic compounds present in gasoline will, and will be quantitated on the GC/FID as C9-C12 "Aliphatics". Once again, the RTX 501.2 column would appear to be an outlier, reporting almost 90% of the "adjusted" aliphatic range data as C5-C8 Aliphatics. There is also a suggestion that the DB/RTX 1 columns are also overquantitating C5-C8 Aliphatic range data.

On the basis of this data, certain columns appear unsuitable. Moreover, in the interest of improving interlaboratory precision, the use of multiple columns should be avoided.

Ideally, the column specified by the method should ensure that all aliphatic compounds eluting prior to n-nonane are C8 or less, and all aliphatic compounds eluting after n-nonane are C9 or heavier. Absent this ideal arrangement, a conservative approach would be to ensure that any bias present in this segregation would tend to overquantitate the C5-C8 Aliphatics, since this fraction is deemed to be more toxic than the heavier aliphatics. Given this premise, columns reporting a higher percentage of C5-C8 Aliphatics would be desirable.

The draft method specified use of a 502.2 column. These columns, in general, produced data in the "middle of the pack". For this reason, and in light of their widespread use and availability, and application to analyses of BTEX compounds, the continued specification of this column is recommended. While not as conservative as some of the other columns, sufficient conservatism is deemed to exist, given the fact that, like all boiling point columns, many of the branched and cyclic alkanes will elute before the normal alkane. Thus, many of the compounds eluting prior to n-nonane and quantitated as C5-C8 Aliphatics will be branched and cyclic C9 and heavier compounds.

Data Manipulations

Note that the VPH method, unlike the EPH Method, involves no analytical fractionation step. Rather, the selectivity of detector response (PID vs FID) is used to differentiate aromatic from aliphatic compounds, and an assumption is made that all (or at least most) compounds detected by the PID are aromatics.

The VPH Target Analytes (BTEX/naphthalene/MtBE) are all detected by the FID, significantly inflating the C5-C8 and C9-C12 Aliphatic range values. Accordingly, the VPH method recommends a series of data manipulation steps to subtract out the concentration of these Target Analytes - as well as other non-aliphatic compounds such as the Trimethylbenzenes - from the aliphatic ranges. The method specifically allows, and many labs routinely employ MS detectors to better quantitate the concentrations of these Target Analytes.

As previously discussed, to eliminate this element of variability, only unadjusted range data was considered in this evaluation of submitted data, and in judging lab proficiency. However, labs were asked to report concentrations of Target Analytes, and make and provide the manipulations required by the Method. These actions and procedures were again highlighted and explained in the instructions provided to participating laboratory. Moreover, to facilitate these actions, a one page reporting format and table was provided to all participating labs, specifying a line-by-line entry of key data, with "bottom line" values for the "adjusted range data".

As part of the review of the second Round Robin data submittal, the calculated values provided by labs for the "adjusted range data" were checked against the data provided for the unadjusted ranges, and Target Analytes eluting in the ranges of interest. Inexplicably, more than 50% of labs reporting data for the unmodified VPH method made calculation errors in at least one of the 3 fractions - for both the sand (12/21) and water (13/21) data. Many labs made errors in two of the ranges; one lab made errors in all three ranges. The majority of these errors were significant. (*Note that the adjusted range data presented in Tables 2 and 3 are **corrected** data, not necessarily **reported** data*)

This indicates a need for more education and emphasis on this issue, and a requirement or recommendation that all data levels and adjustments be provided for each analytical report.

Quantitation of Target Analytes by GC or GC/MS

Based upon the data presented in Tables 2 and 3, the following conclusions have been made:

- Of the 22 labs conducting the unmodified VPH analysis, only 3 elected to use an MS detector to quantitate Target Analytes. It is noted that the data from these three labs are not significantly different from the mean values obtained for all of the labs.

- Relatively good correlation is noted for the Target Analytes quantitated in the VPH water sample (Table 3), with most RSD values less than 20%. Similar results are noted for the soil data contained in Table 2, except for benzene, MtBE, and naphthalene, with %RSD values of 170, 40, and 46, respectively. However, if the data from Lab # 9 is not considered, the benzene RSD drops to only 24%. Similarly, eliminating lab #11 from the MtBE data drops the RSD to 34%; eliminating labs #7 and #16 from the naphthalene data summary drops the RSD to 31%.

These findings suggest good comparability among these data for participating labs, and suggests the potential for good comparability for the adjusted range value data, absent mathematical errors in data manipulations.

EPH

Reported fractional data for the EPH soil and water samples are graphically displayed in Figures 7 through 16. As with the VPH data, in order to compare "apples with apples", except as otherwise indicated, the values presented in these graphs for C11-C22 Aromatics are **unadjusted fractional concentration data**, from which the concentration of Target Analytes (e.g., PAHs) have not been subtracted. (No Target Analytes elute in the aliphatic ranges, so no adjustments are needed).

Soil Data

Except for a few low and high outliers, very good correlation is noted in the data reported for all of the EPH fractional ranges. The best distribution was seen in the C11-C22 Aromatic fraction, with an overall RSD value of 34%. More data scatter is seen in the two aliphatic fractions, with RSD values of 45% each. The percent recovery data - computed

by comparing the combined concentrations reported for the 3 fractions to the gravimetric total fuel oil spiking value of 6000 ug/g - show a good clustering around 60%. Note that the low fractional outlier - Lab #1, and the high fractional outliers, Labs #2 and #16, are also outliers in the Total All Fraction and Percent Recovery graphs displayed in Figure 8. This indicates that poor performance was due to low or high recoveries/integration of the sample, as opposed to fractionation problems.

As indicated in Table 4, the mean combined concentrations of all reported (PAH) Target Analytes is less than 10% of the (unadjusted) C11-C22 Aromatic value. Two PAH Target Analytes - naphthalene and 2-methylnaphthalene - account for the majority of the Target Analyte concentrations.

Water Data

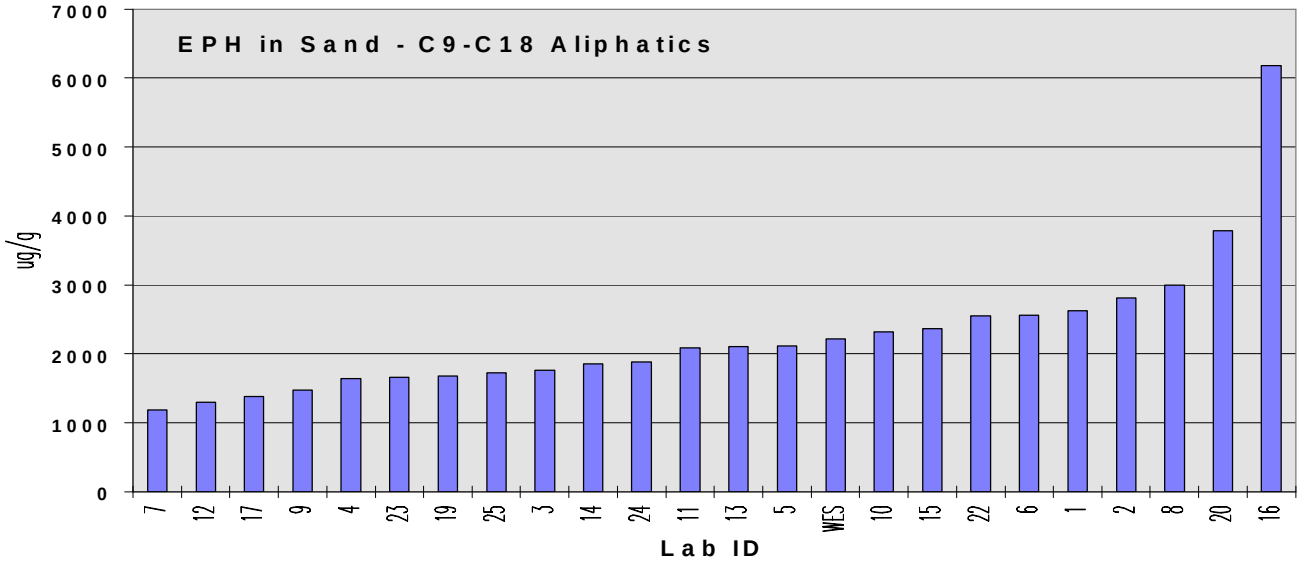
Considerably less correlation was seen in the EPH water data, and it was by far the poorest performing matrix. There are clearly fractionation problems evident from this data, especially when reviewing the data scatter on the last two graphs in Figure 10. Nevertheless, the following mitigating observations should also be considered:

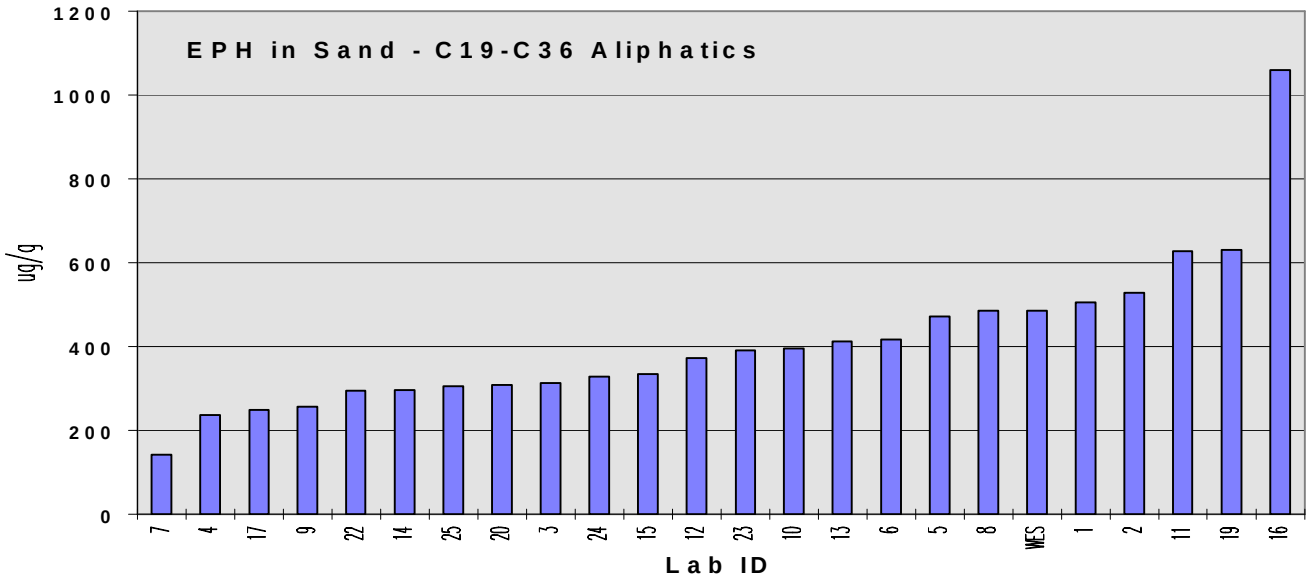
- C11-C22 Aromatics, with an overall RSD of 44%, was the best performing EPH range. This is significant, since this fraction is the most toxic, soluble, and mobile EPH range.

- The sample concentrations in the C9-C18 Aliphatic and C19-C36 Aliphatic ranges, with mean values of 502 and 181 ug/L, respectively, are below regulatory notification and cleanup limits (1000 and 5000 ug/L, respectively). While an attempt was made to disseminate samples containing hydrocarbons at levels at or above regulatory levels of concern, because the EPH water sample was a “real world” groundwater sample, only relatively low levels of these sparingly-soluble aliphatics were present, even though the C11-C22 Aromatic mean concentration value of 1277 ug/L is well above the lowest regulatory level of 200 ug/L.

It is not clear why appreciable concentrations of (essentially insoluble) C19-C36 Aliphatics were reported by some laboratories. While values under 50-75 ug/L may be below a reporting limit, and representative of baseline noise, levels reported over 100 ug/L would appear indicative of methodological/column bleed/contamination problems unrelated to the fractionation process. A preliminary review of submitted chromatograms appear to support this premise, though some of the chromatograms submitted by laboratories reporting these high values are difficult to interpret.

Figure 7 - EPH in Sand - Unadjusted Range Data





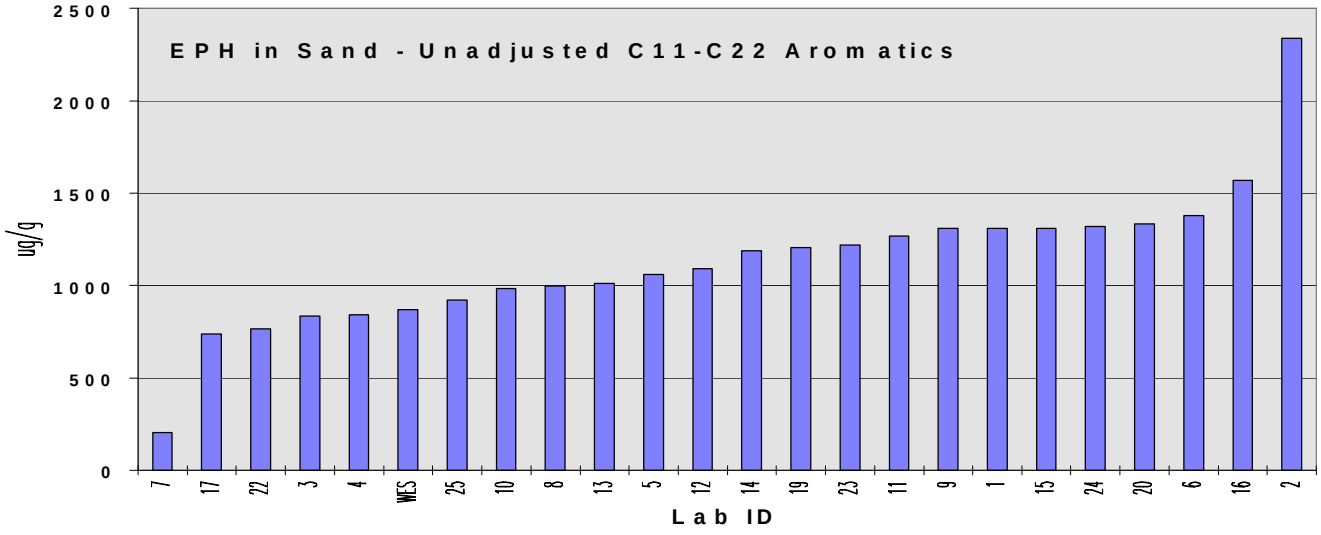
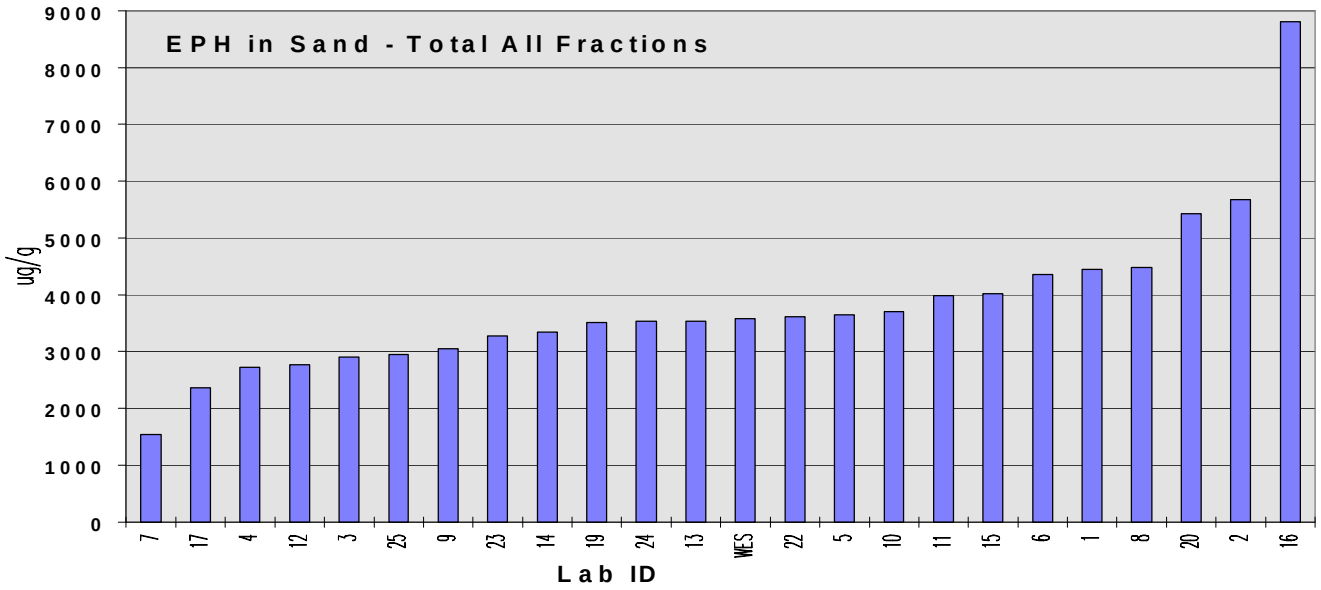
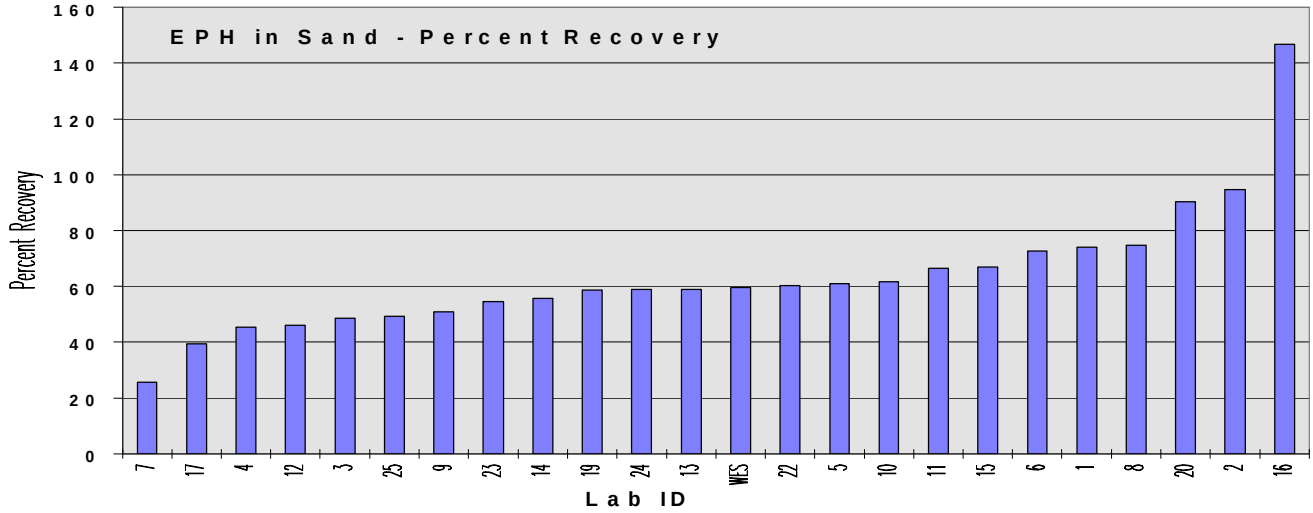


Figure 8 - EPH in Sand - Recoveries





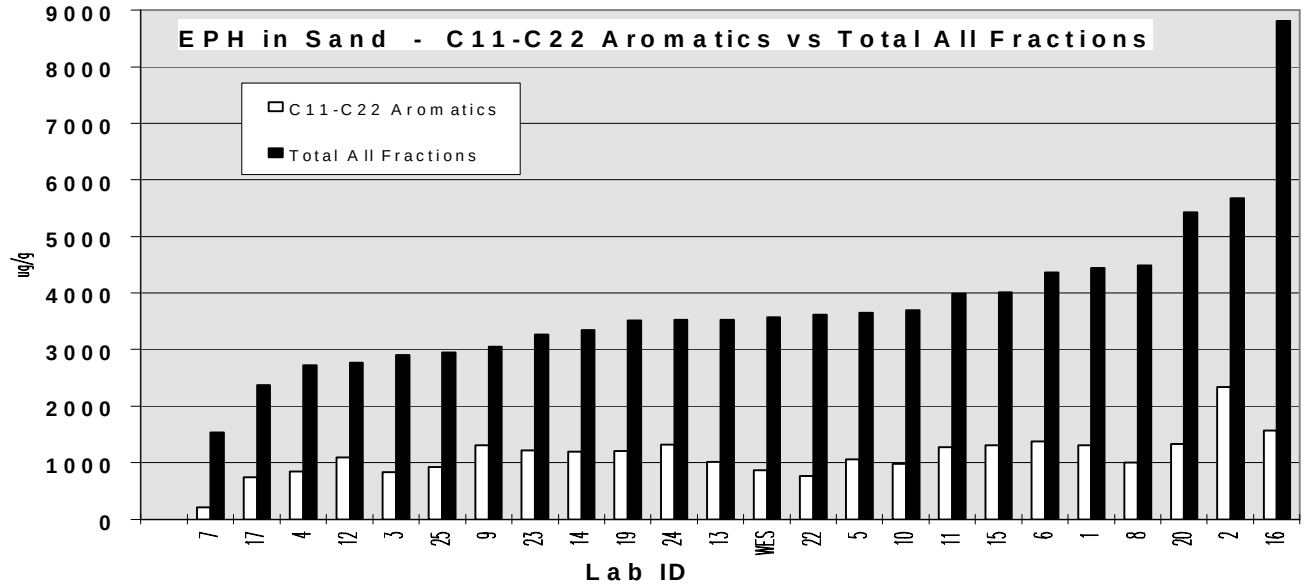


Figure 9 - EPH in Water - Unadjusted Range Data

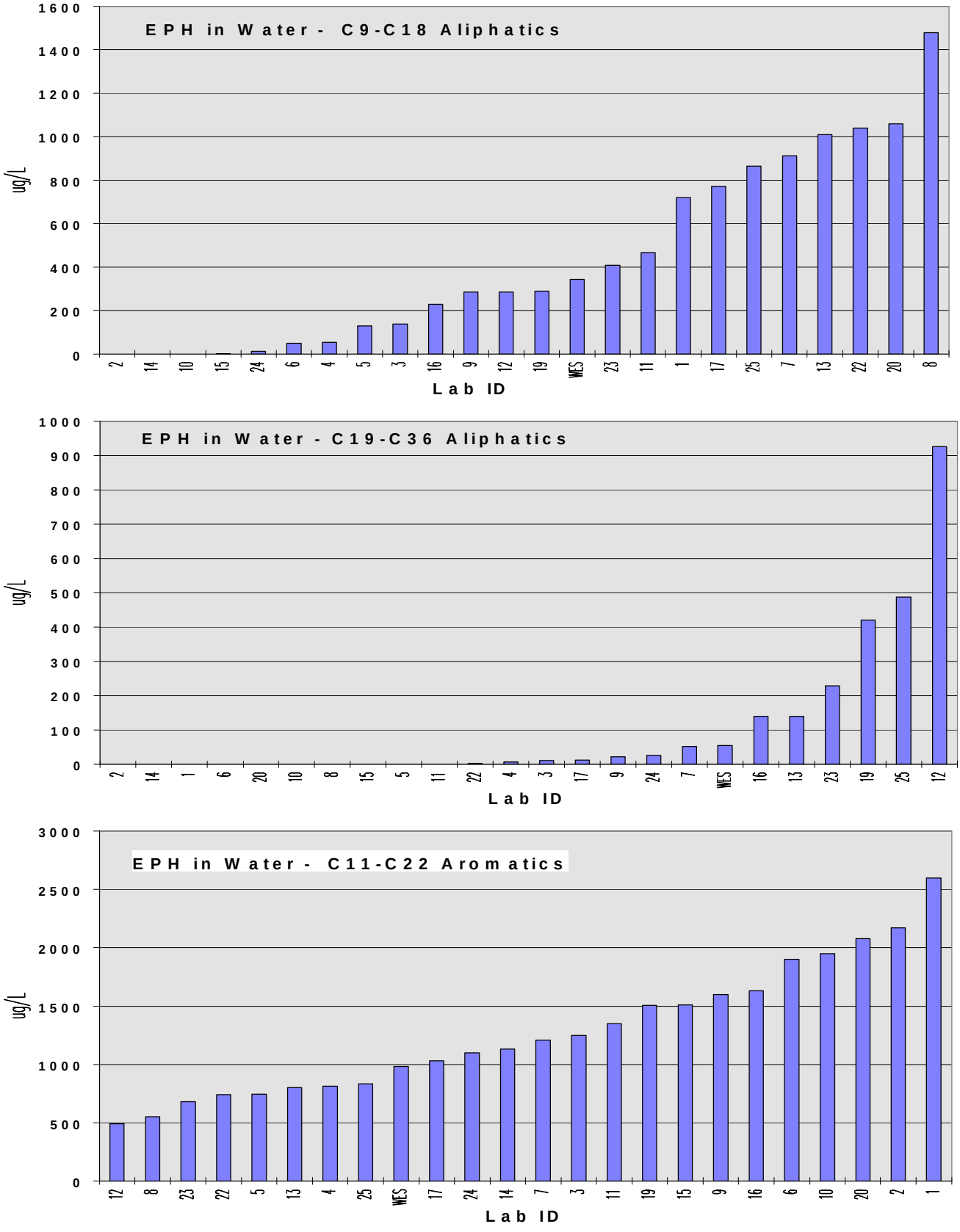
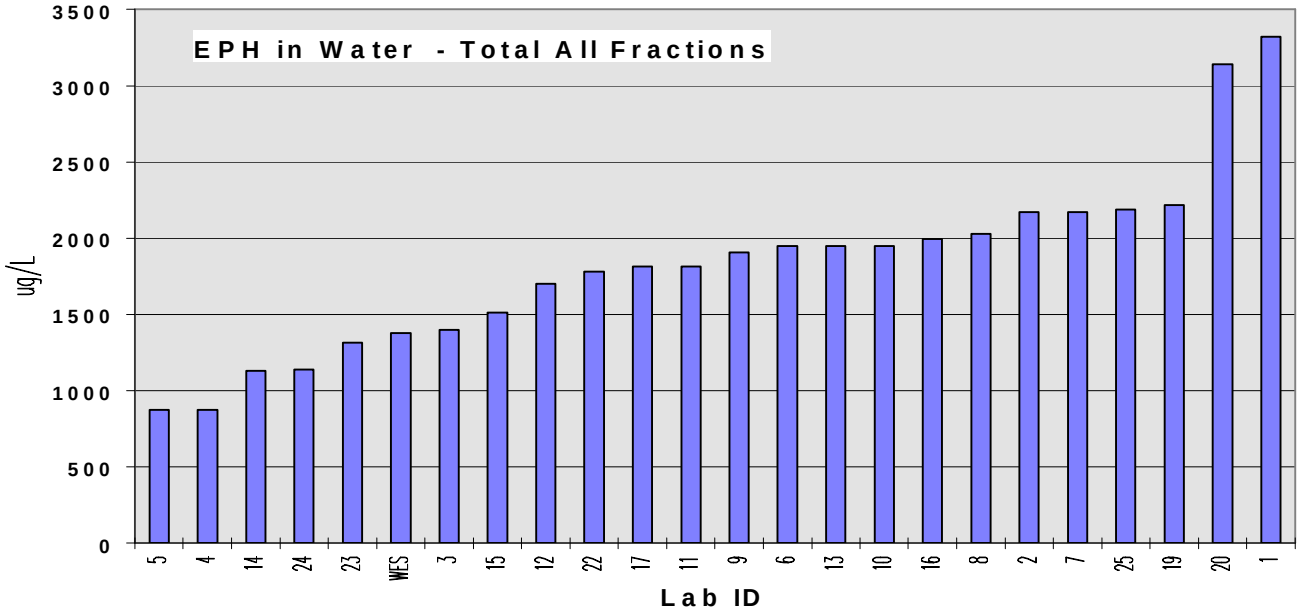
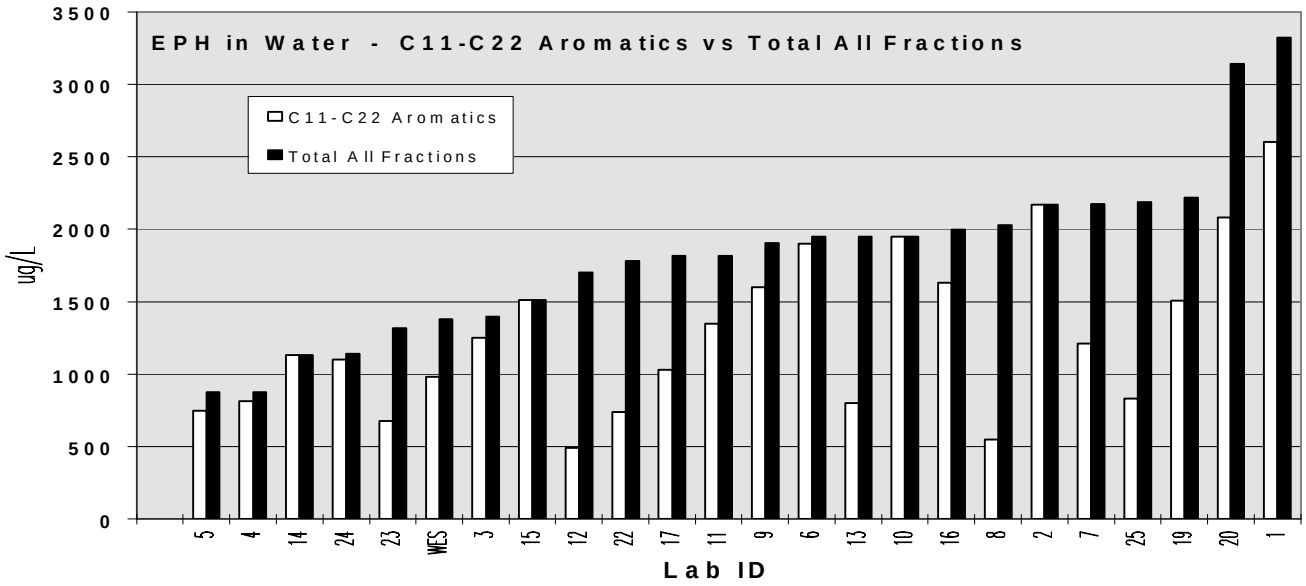


Figure 10 - EPH in Water - Recoveries





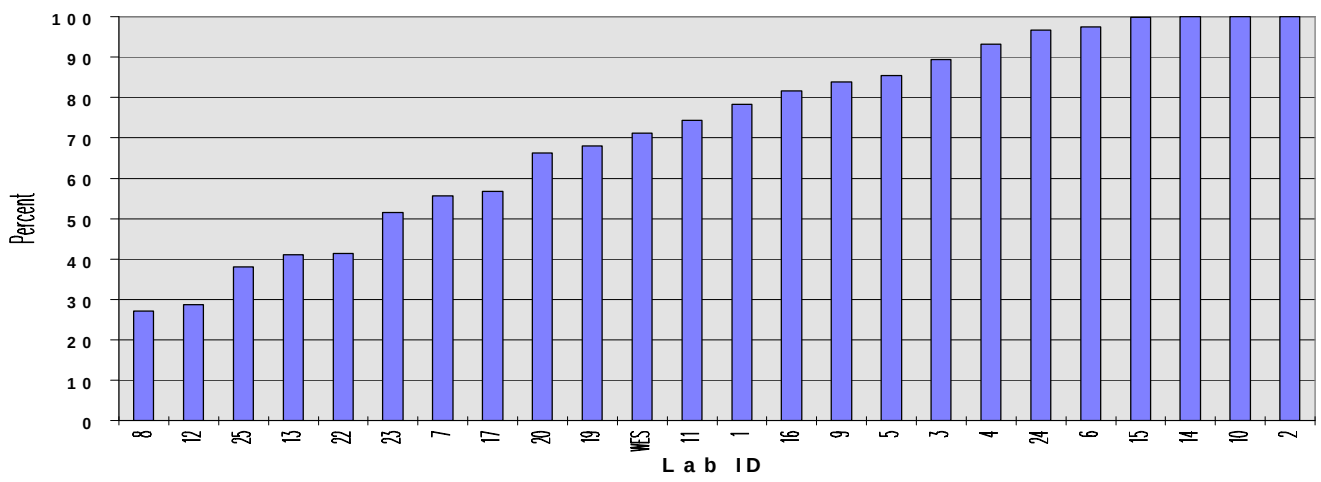
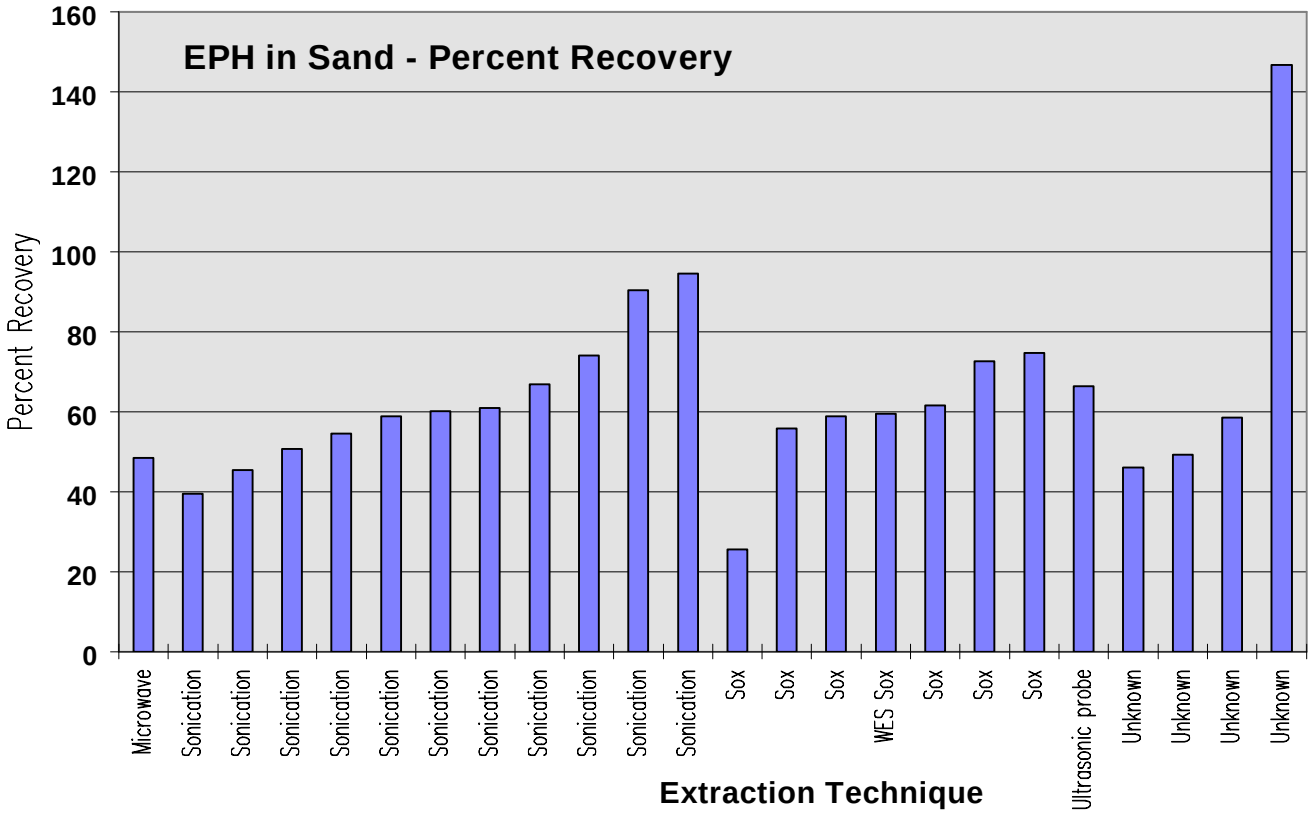


Figure 11 - EPH in Soil - Extraction Efficiencies



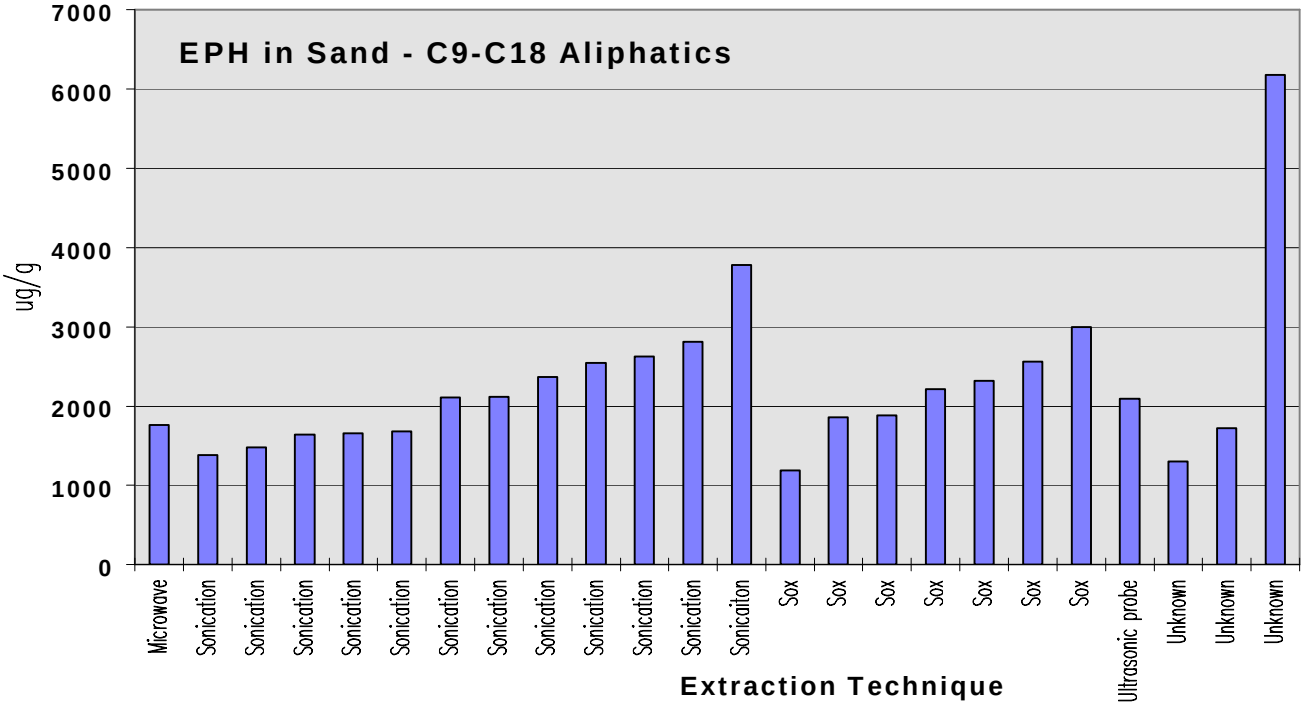
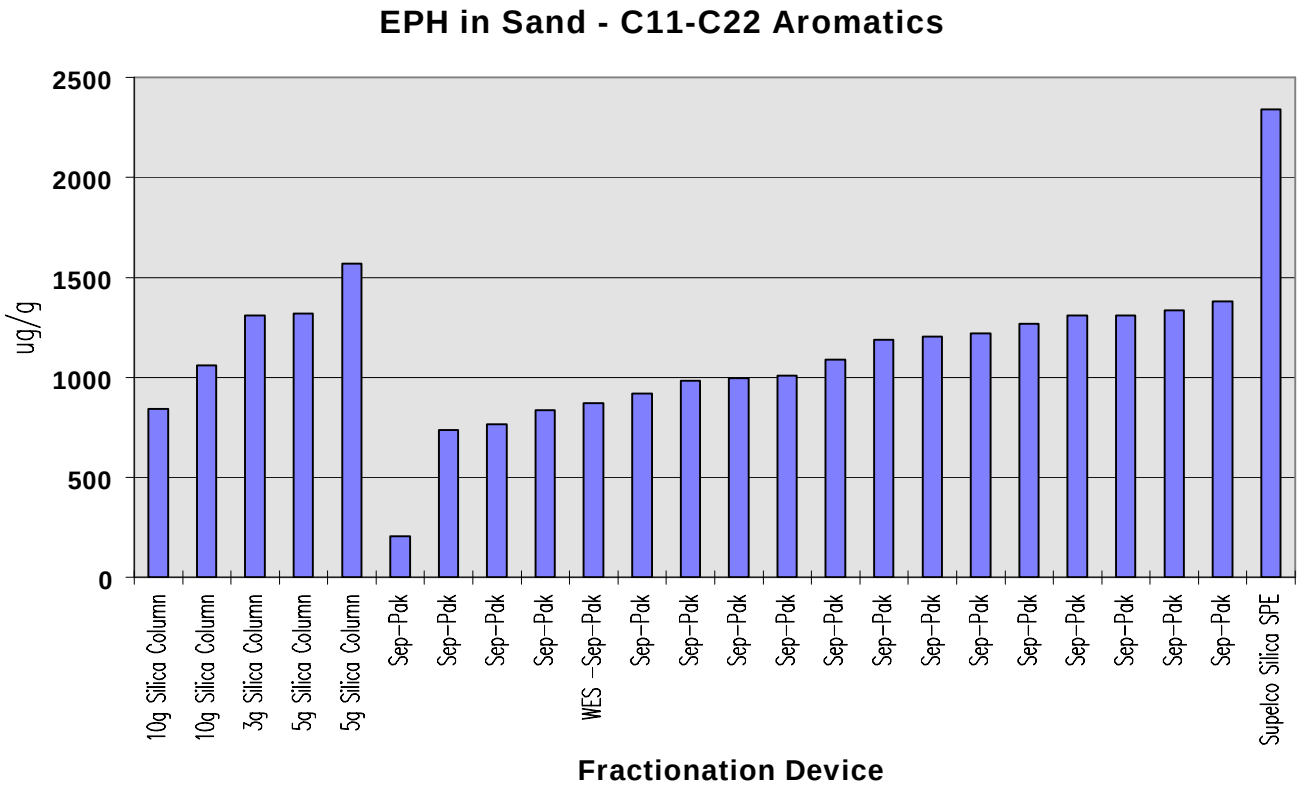


Figure 12 - EPH in Soil - Silica Gel Fractionation



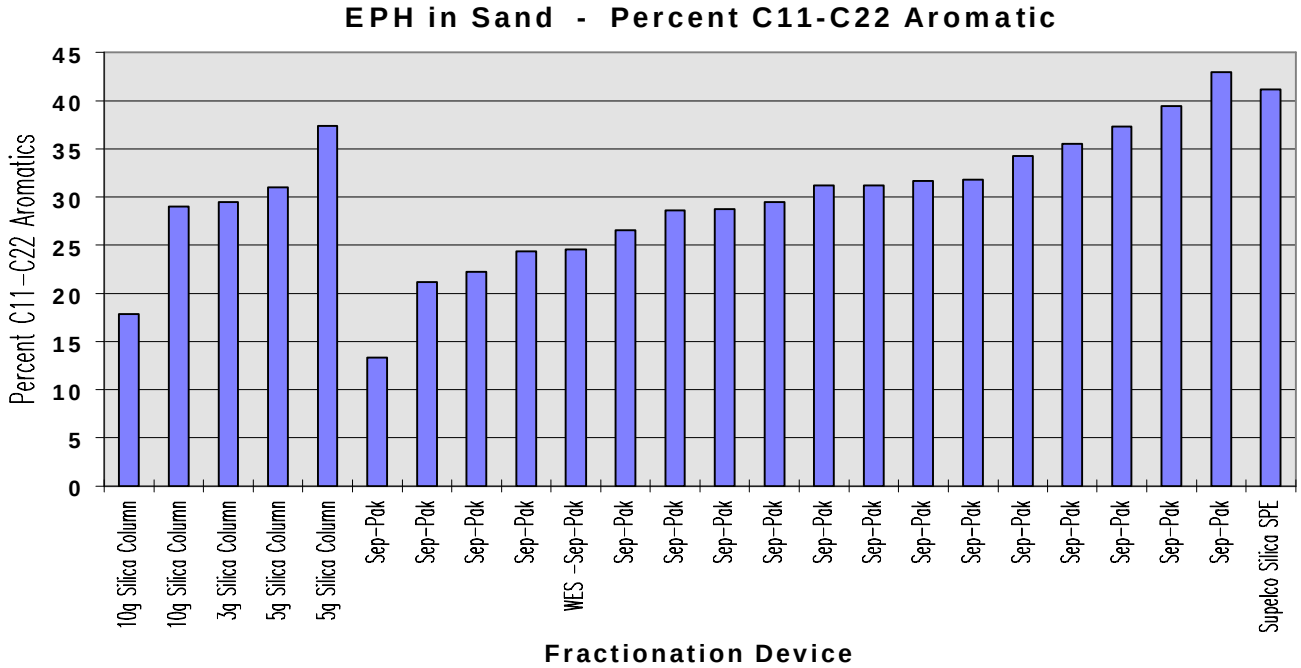
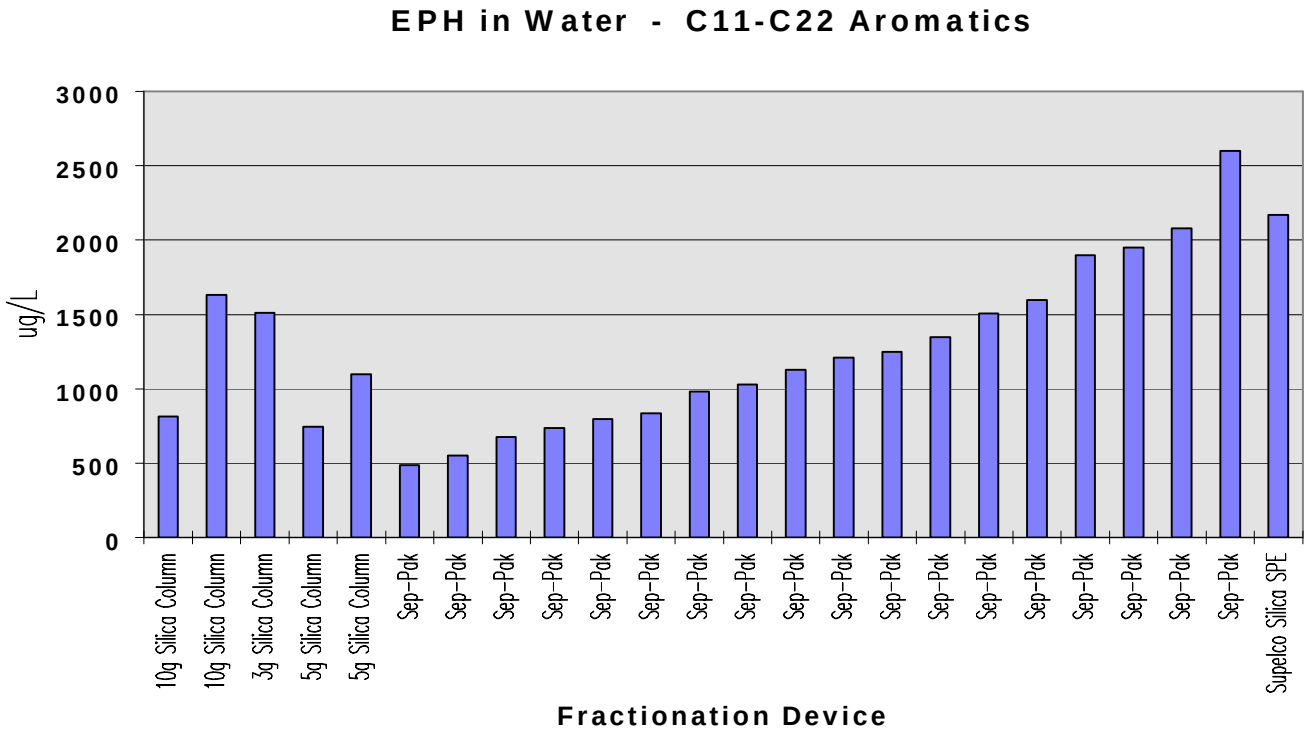


Figure 13 - EPH in Water - Silica Gel Fractionation



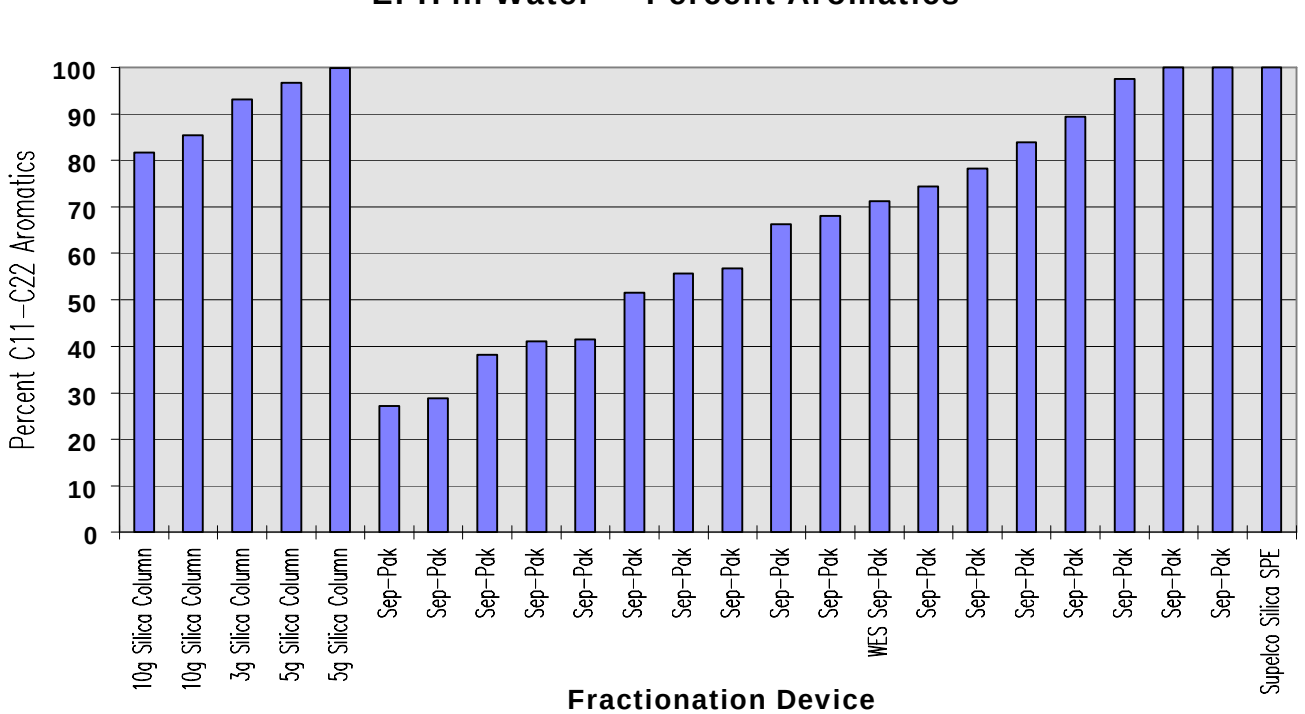
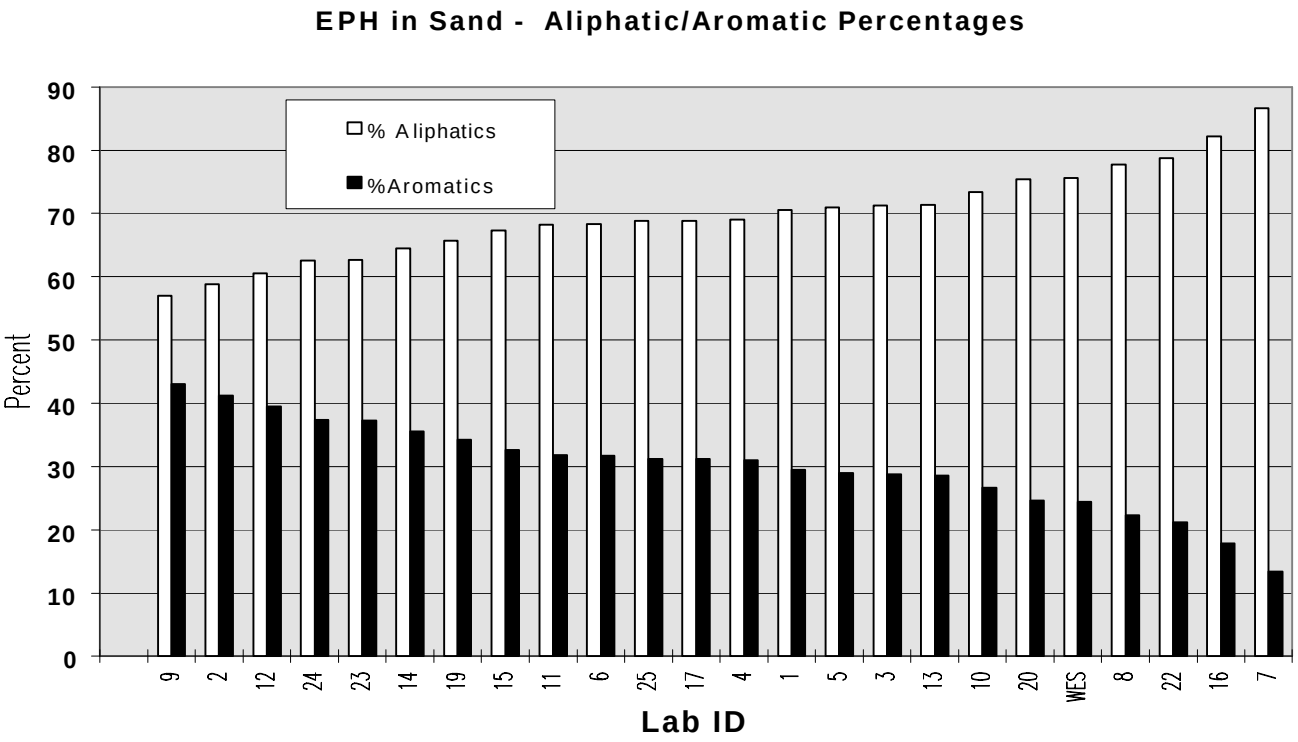


Figure 14 - EPH Fractionation



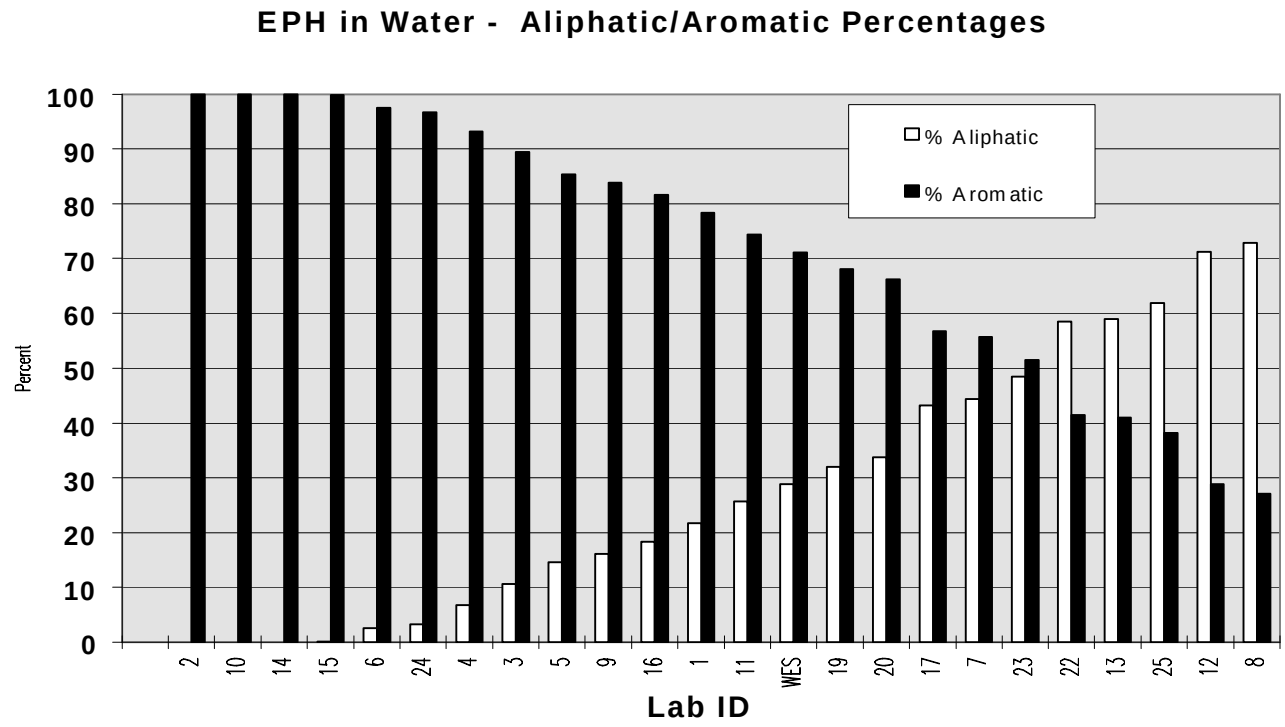
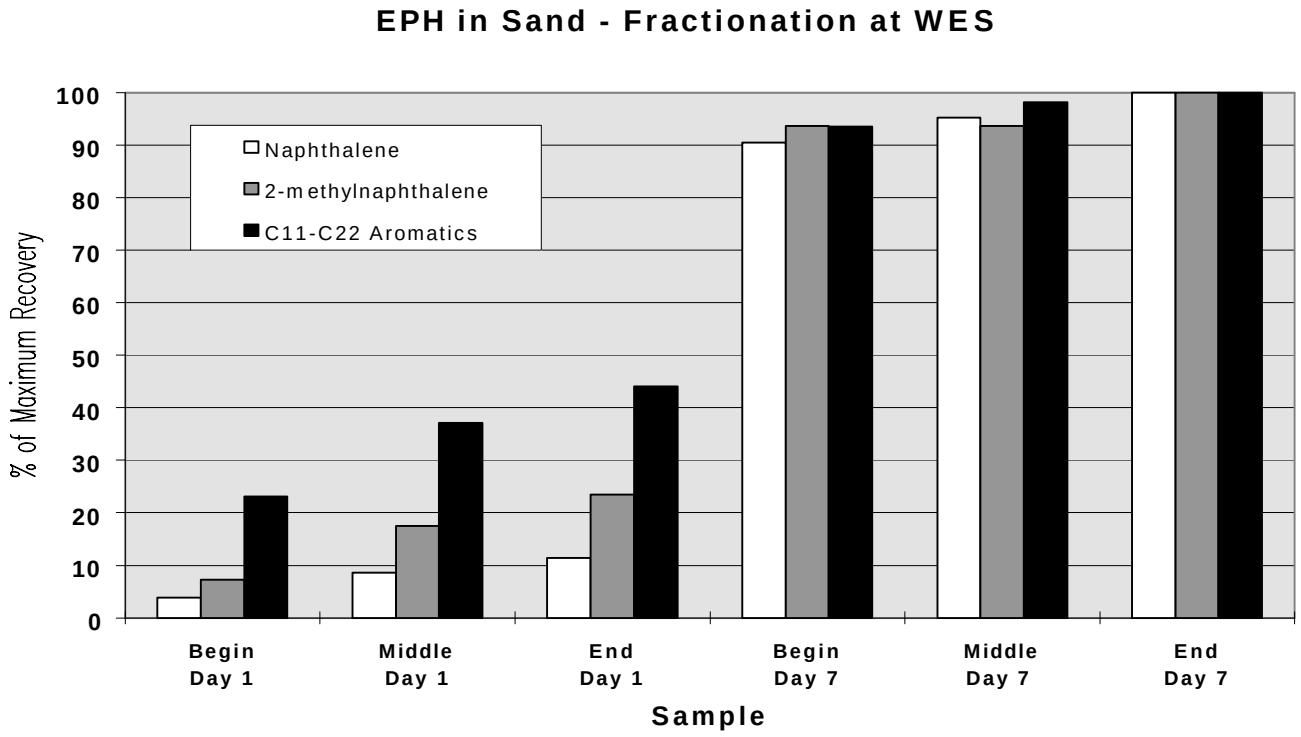


Figure 15 - EPH Fractionation at the Wall Experiment Station



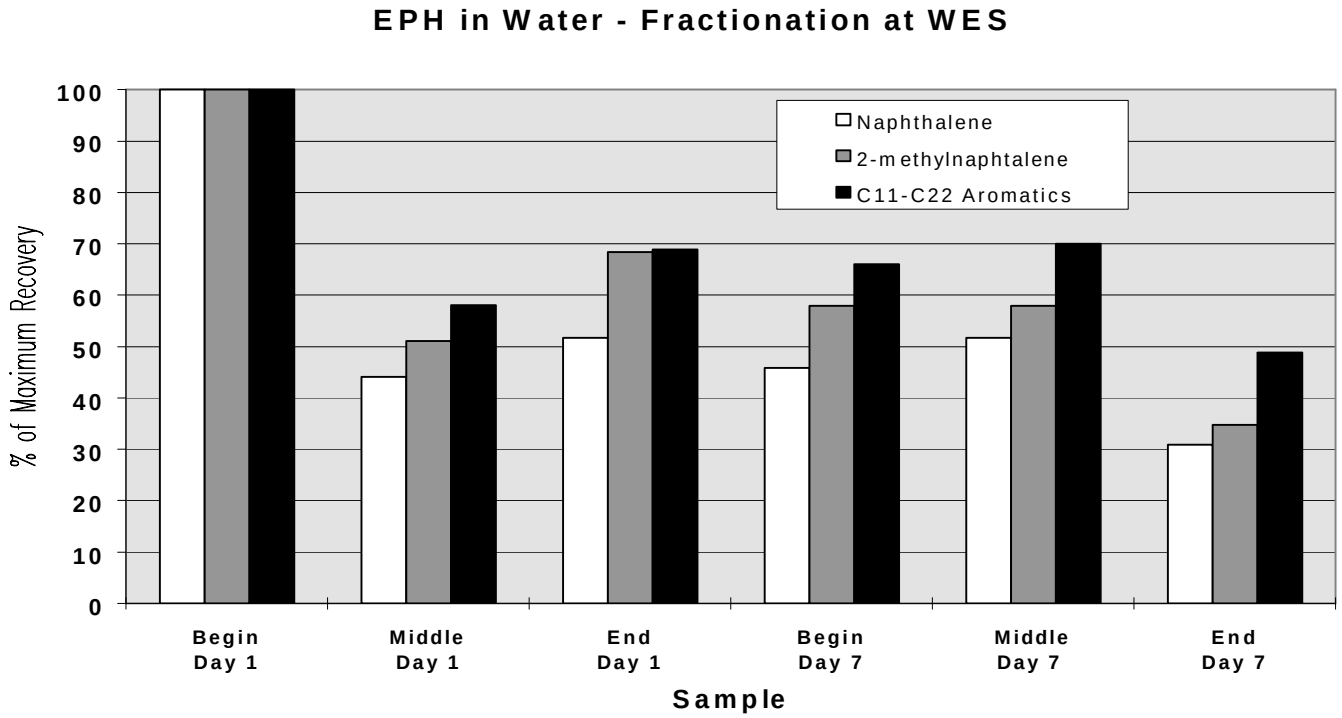
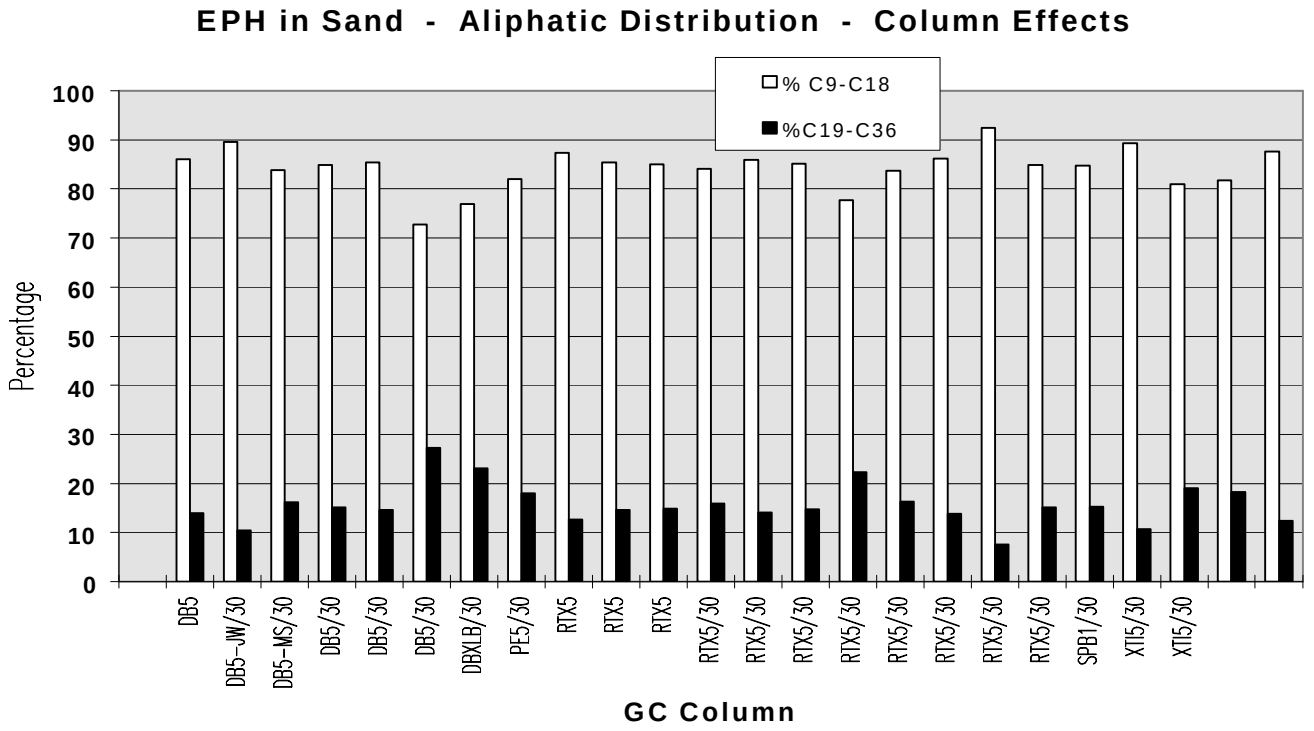
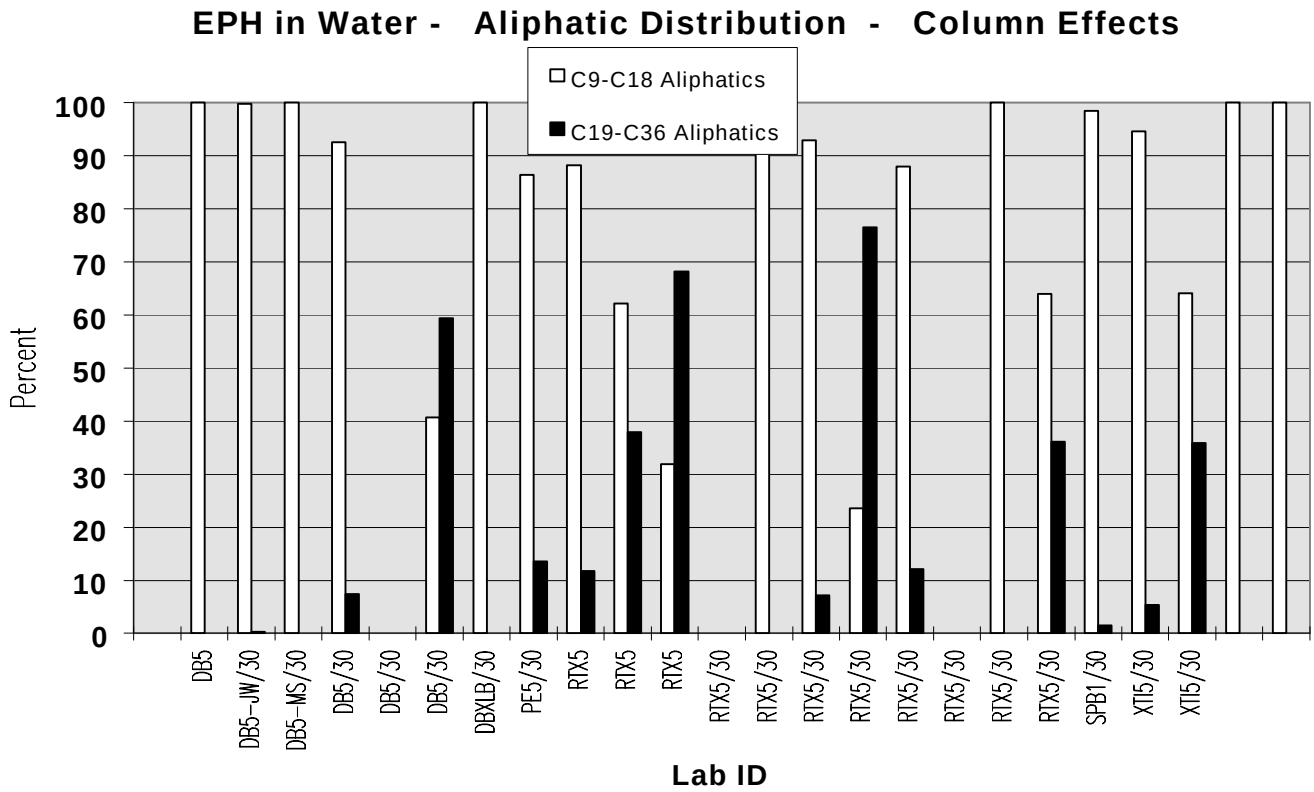


Figure 16 - EPH Column Effects





Significantly, the PAH Target Analytes comprised (on average) 35% of the (unadjusted) C11-C22 Aromatic fraction. Of more significance is the finding that just two PAH compounds - naphthalene and 2-methylnaphthalene, accounted for (on average) 34% of the (unadjusted) C11-C22 Aromatic fraction (see Table 5). The implications of this finding are further discussed below, under "Fractionation Problems".

Soil Extraction Technique/Efficiencies

Some concern has been expressed over the effectiveness of the various soil extraction techniques used by laboratories. On one hand, some parties believe that only the more rigorous and aggressive soxhlet/soxtec extraction process (recommended in the draft EPH method) is able to achieve acceptable recovery of soil hydrocarbons. On the other hand, an argument has been made that the time and solvent use inherent in the soxhlet/soxtec procedures are wasteful and unnecessary, and may even result in the volatilization of lighter (C9-C11) hydrocarbons.

Based upon the data presented in Figure 11, no significant difference was noted between the sonication and soxhlet/soxtec extraction procedures, in terms of overall percent recovery of all fractions, or in the reported concentrations of C9-C18 Aliphatics. Somewhat lower recovery was reported by the one lab using a microwave digestion procedure.

It should be noted, however, that the EPH soil sample consisted of a dry sand sample spiked with a #2 fuel oil sample. Different results may be obtained when extracting a heavier and/or more weathered/sequestered fuel oil from soils with higher organic carbon contents.

Fractionation Techniques

Although the draft EPH method recommends use of a Sep-Pak silica gel cartridge to fractionate aliphatics from aromatics, some labs have experienced problems with the leaching of compounds from the cartridge casing, and have elected to use self-packed silica gel columns to perform this function. Data relating to the performance of either device is presented for EPH soil and water samples in Figures 12 and 13.

As can be seen in Figure 12, significant differences are not apparent in the concentration or percentage of C11-C22 Aromatics reported for the soil sample. In Figure 13, the self-packed silica gel columns used to fractionate the EPH water sample appear to have resulted in data with a higher percentage of C11-C22 Aromatics. It is not clear, however, whether this is due to differences in the fractionation efficiencies of these devices, or with fractionation problems resulting from excessive hexane usage.

Fractionation Problems

Among the most significant findings of the second Round Robin study is a better characterization and understanding of the nature and extent of silica gel fractionation problems experienced by participating labs (including the MADEP Wall Experiment Station).

Based upon the data obtained, it appears that the elution of the silica gel cartridge/column with hexane is a more sensitive and critical step than initially believed, and that even small (0.5 mL) differences in the amount of hexane used can result in significant leaching of naphthalene and substituted naphthalenes into the aliphatic fraction.

Because naphthalene and substituted naphthalenes make up a substantial portion of the water-soluble-fraction of fuel oils, this problem is much more significant in water than soil. This is consistent with the relatively good correlation of soil fractional data in Figures 7 and 8, and relatively poor correlation of water fractionation data in Figures 9 and 10. This finding is even more evident in reviewing the data plotted in Figure 14.

Soil Data

The aromatic content of the fuel oil used to spike the EPH soil samples was reported to be 38% (by weight). As indicated in Table 4, and plotted in the upper graph in Figure 14, the mean aromatic recovery by labs using the unmodified EPH method was about 30%. Of the 24 labs providing data, 3 reported concentrations of C11-C22 Aromatics slightly above 38% by weight (Labs #9, #2, #12), while the remaining labs reported values less than 38%. While the mean aromatic recovery and data distribution for the soil sample is relatively good, it does suggest that excessive leaching of aromatics into the aliphatic fraction is more problematic than aliphatic breakthrough to the aromatic fraction, and that the volume of hexane used to elute the aliphatics from the silica gel column may be excessive.

It would appear that excessive use of hexane resulted in significant "stripping" of aromatics in lab data reporting less than 30% aromatics, including substantial breakthrough for Labs #8, 22, 16 and 7. Because the recommended aromatic surrogate for the EPH method (Ortho-Terphenyl) elutes mid-way through the chromatographic run (after Anthracene), the stripping of the lighter aromatics (especially naphthalenes and substituted naphthalenes) may not be evident. In fact, no problem with OTP recovery was noted by Labs #8, 22, 16, or 7, and only Lab #8 reported low recoveries for naphthalene and 2-methylnaphthalene in the Fractionation Check Solution. However, it is noted that the concentrations reported for naphthalene and 2 methylnaphthalene by 3 of these 4 facilities were significantly lower than the mean value for all labs. Only Lab #16 reported concentrations of these two PAHs higher than the mean values. Because Lab #16 also reported a relatively high aromatic content in the EPH water sample, fractionation difficulties may not have been the primary cause of the poor performance noted on the soil sample. A review of the chromatograms supplied by these labs was inconclusive.

Water Data

While the collective concentrations of naphthalene and 2-methylnaphthalene accounted for only about 6% of the total concentration of (unadjusted) C11-C22 Aromatics in the EPH soil sample, these two compounds accounted for 34% of the total concentration of the aromatics in the EPH water sample (see Tables 4 and 5). As such, problems associated with the stripping of these lighter aromatics into the aliphatic fraction would be magnified in the water sample.

This premise is confirmed when reviewing the bottom graph in Figure 14. Because this was a "real world" sample, the true aromatic content of the water sample is not known. However, because the source of the hydrocarbon contamination in this sample is thought to be a heavily weather fuel oil, and because the sample was believed to be free of NAPL suspensions, at least 80% of the water soluble fraction would be expected to be aromatic. While most labs reported an aromatic content greater than 50%, fractionation breakthrough appears to be a significant and widespread problem, as evidenced by the steadily increasing percentage of aliphatics plotted in this graph from about the center of the graph to the far right.

The lowest percentages of aromatics were reported by Labs #22, 13, 25, 12, and 8. As with the soil data, no problems with were noted by these labs with the recovery of OTP or compounds in the Fractionation Check Solution, except for Lab #8 which reported a somewhat low recovery of OTP at 55%, and low recoveries of naphthalene and 2-methylnaphthalene in the Fractionation Check Solution at 26% and 33%, respectively. However, low concentrations of naphthalene and 2-methylnaphthalene were reported by these 5 labs in the EPH water sample; on average, less than half the mean value reported by all labs (see Table 5). A review of the chromatograms supplied by these labs was inconclusive.

Wall Experiment Station Data

As can be seen in Figure 14, fractionation problems and aromatic breakthrough were also experienced at the MADEP Wall Experiment Station (WES). Unlike other participating labs, however, 6 replicate samples were run for the EPH soil and water sample, over two different days, by the same analyst. Relevant data from these analyses have been plotted in Figure 15, which shows the relationship between recoveries of naphthalene, 2-methylnaphthalene, and (unadjusted) C11-C22 Aromatics. As can be seen in these graphs, high recoveries of these lighter PAH compounds coincided with high recoveries for the collective C11-C22 Aromatics.

On the basis of the observations and findings discussed above, certain method refinements would appear necessary to monitor and mitigate fractionation problems experienced during this study:

- The amount of hexane used to rinse the silica gel fractionation cartridge/column should be kept to a minimum.

- In addition to the use of a general/matrix surrogate like OTP, an additional "Fractionation Surrogate" should be recommended by the method. This compound, which should have properties similar to naphthalene, would be added to the sample extract just prior to it being loaded onto the fractionation cartridge/column. This would enable a finding as to whether unacceptable stripping of lighter aromatics into the aliphatic fractions had occurred as a result of excessive hexane usage.

- The current method requirement to concentrate the (pre-fractionation) sample extract to 1 mL should be changed to 2-3 mLs. In this manner, if unacceptable recovery of the Fractionation Surrogate was noted, additional 1 mL aliquots could be obtained, for re-fractionation and re-analysis. While this will increase range detection limits, it should still enable detection of the lowest regulatory EPH standard: 200 ug/L for C11-C22 Aromatics in GW-1 (drinking water) areas.

Column Effects

As can be seen in Figure 16, laboratories performing the unmodified EPH method reported using 6 different types of chromatographic columns. A relatively consistent distribution among aliphatic ranges is apparent in reviewing the soil data, and no column effects are evident. While significant differences are noted in the proportion of aliphatics in the C9-C18 and C19-C36 ranges in the water data, no trends are noted, and these differences are likely due to other methodological parameters.

Data Manipulations

Unlike the VPH method, data adjustments and manipulations are not a major element of the EPH method. Only one range, C11-C22 Aromatics, requires adjustments (subtraction of the Target Analyte PAHs). Like the VPH data, however, mathematical errors were noted in the reported "adjusted" concentrations for the C11-C22 Aromatics: out of the 23 labs providing data for the unmodified method, 4 made errors with the soil data, and 11 with the water data.

Quantitation of Target Analytes by GC or GC/MS

Because of the fractionation problems discussed previously, it is not possible to make conclusions on the comparison of GC/FID and GC/MS data for the EPH Target Analytes. Overall, poor correlation among lab data was noted, especially for the EPH water samples.

MODIFIED METHODS

VPH

In total, 6 labs significantly modified the draft MADEP VPH method, and one lab (#18) submitted two data packages; one for the unmodified method, and one for a method modification. A summary of the submitted data is contained in Tables 6 and 7. Data from each type of modification is discussed briefly below.

Use of 9.6 eV PID Lamp - Lab #18(2)

This modification involved the use of a 9.6 eV PID lamp, in lieu of the 10.0 +/- lamp used by most other labs. The idea behind this modification is to reduce the degree of PID response to non-aromatic compounds, and therefore reduce or eliminate the overquantification of aromatics in the C9-C10 Aromatic range. In reviewing the data for Lab #18 obtained using a 10.2 eV PID, however, no significant differences are noted in the reported values for the C9-C10 Aromatics; in fact, the concentrations reported using the 9.6 eV lamp are actually slightly higher than the data reported using the 10.2 eV lamp.

Use of GC/MS to differentiate Aliphatics from Aromatics - Labs # 23, 25, 26, 27, 28

While the draft VPH method relies upon the selectivity of the PID response to differentiate aromatics from aliphatics, 5 labs submitted data for which a GC/MS technique was apparently used to make this determination, although complete details were either not provided or not entirely clear in most submittals.

Labs #23 and 26 provided data for the "unadjusted" ranges. For both the soil and water sample, both labs were within about one standard deviation of the mean of the unmodified lab data for the aliphatic fractions, but both were several standard deviations above the mean for the C9-C10 Aromatics in soil, and Lab #26 was several standard deviations above the mean for the C9-C10 Aromatics in water.

While the total of all unadjusted fractions in soil for Lab #23, at 3737 ug/g, is near the unmodified method GC/FID mean of 3334 ug/g (and gravimetric spike level of just over 3000 ug/g), the total value for Lab #26 at 5600 ug/g is substantially above both values. Similarly, the total of all unadjusted fractions in water for lab #23 is somewhat above the mean of the unmodified data; the total for Lab #26 is substantially elevated.

The remaining 3 labs only provided data for the Target Analytes and the "adjusted" ranges; presumably because their methodology did not result in an unadjusted range value. A comparison of these data with the adjusted range data for the unmodified VPH data yields the following:

- For the soil data, Labs #25, 27 and 28 were within about 1 standard deviation of the unmodified method mean value for C5-C8 Aliphatics and C9-C10 Aromatics, but reported much lower concentrations for the C9-C12 Aliphatics. With respect to the sum of all adjusted fractions and Target Analytes ("total gasoline"), the data from Labs #27 and 28 compares favorably with the gravimetric spiking value and mean GC/FID value from unmodified labs, while the total from Lab #25 is significantly low.

- For the water data, Labs #25, 27, and 28 reported low values for the C5-C8 Aliphatics, high values for the C9-C10 Aromatics, and much lower values for the C9-C12 Aliphatics. With respect to the sum of all adjusted fractions and Target Analytes ("total gasoline"), the data from Labs #27 and 28 is somewhat lower, but within 1 standard deviation of the mean GC/FID data from the unmodified method. Once again, Lab #25 is significantly lower.

Using a GC/MS technique, lower values would be expected for the C9-C12 Aliphatic range, especially in the water sample, as the FID value obtained in the unmodified method would be expected to contain

mainly alkyl aromatic compounds. It is not clear, however, why the water data for the C9-C10 range was so much higher than the unmodified method, given that the PID used to quantitate the C9-C10 Aromatics is inflating this value, to some degree, by picking up some aliphatics.

Use of a combined VPH/EPH Test Method - Lab #24

In this modification, Lab #24 has chosen to use a solvent extraction/fractionation technique, with separate GC/FID analyses, to quantitate C6-C36 hydrocarbons. Pentane and MtBE, however, can not be reliably quantitated by this procedure.

In the soil sample, not unexpectedly, the C5-C8 Aliphatic value was more than 1 standard deviation below the mean of the unmodified lab data, while the C9-C10 value was more than 1 standard deviation above the unmodified mean concentration. Similar to the GC/MS data, much lower values were reported for the C9-C12 Aliphatics, which are known to be overquantitated by the unmodified VPH method. In the water sample, there was excellent agreement with the C5-C8 Aliphatic values, but a low value reported for the C9-C10 Aromatics. As with the soil data, a much lower concentration was reported for the C9-C12 Aliphatics.

The total value of all hydrocarbons in soil and in water is more than 1 standard deviation lower than the mean GC/FID value from unmodified lab data.

It is difficult to judge the performance of these modified methods, given the need to compare "apples with apples". Also, given the biases in the unmodified method, data obtained from some of these techniques may in fact be closer to the true values (e.g., C9-C12 Aliphatics). A reasonable first cut may be to evaluate how close the total gasoline values compares with mean unmodified and gravimetric spiking data for the soil sample, and mean unmodified value for the water sample. In this context, total gasoline is defined as the GC/FID value obtained in the unmodified method (i.e., sum of C5-C8 and C9-C12 Aliphatics), and the summation of all unadjusted fractions from modified methods providing such data, or the summation of all adjusted fractions and target analytes from methods not providing unadjusted data.

From Table 6, it can be seen that the solvent extraction VPH/EPH method employed by Lab #24, at a total gasoline concentration of 1846 ug/g, is significantly below the spiked value of 3050 ug/g and mean unmodified lab GC/FID data of 3334 ug/g. Because this sample was spiked with fresh gasoline, and because of the solvent extraction procedure used by this lab, this low recovery is not unexpected. For the labs using a GC/MS method, mixed results were obtained. The total gasoline concentration of 1035 ug/g reported by Lab #25 is substantially lower than spiked and mean GC/FID values from unmodified lab data. Lab #26 is significantly higher. Other data via this method is consistent with unmodified method data.

EPH

In total, 4 labs significantly modified the draft MADEP EPH method, including one lab (#18) that submitted three data packages for a series of modifications involving the use of a PID/FID procedure. A summary of the submitted data is contained in Tables 8 and 9. Data from each type of modification is discussed briefly below.

EPH by High Temperature PID/FID

Lab #18 used a high temperature PID/FID detector to analyze the EPH samples, and provided three data submittals: (1) for a 10.2 eV PID/FID analysis with no silica-gel prefractionation; (2) for a 9.6 eV PID/FID analysis with no silica-gel fractionation, and (3) for a PID/FID analysis with silica gel fractionation.

To fairly evaluate the PID/FID data, adjustments were made to subtract the PID response from the appropriate aliphatic fractions. Similar to the VPH results from this lab, the data produced by the 9.6 eV

PID was once again similar to the 10.2 ev PID. The soil data was about one standard deviation higher than the unmodified lab data for both aliphatic fractions, but one standard deviation lower on the C11-C22 Aromatics. Conversely, both aliphatic fractions reported for the water sample were a number of standard deviations above data reported by the unmodified method, while the C11-C22 Aromatic data was close to the unmodified method.

In the 18(3) data, the EPH extract was fractionated with a silica gel cartridge, and then analyzed with a high temperature PID/FID detector. This data was more comparable to the unmodified method data, though the C11-C22 Aromatic concentration in soil was significantly lower than the mean value from unmodified method data.

GC/MS with Silica Gel Fractionation

Two labs, #26 and 28, used the draft EPH method, modified by use of a GC/MS to quantitate range data as well as Target Analyte data. The total fuel oil recovery by both labs in the soil samples were somewhat low, but within a standard deviation of the unmodified lab data mean value for the summation of all fractions, though the C11-C22 Aromatic concentration reported by Lab #28 is substantially elevated. For the water sample, Lab #26 reported C11-C22 Aromatics substantially below the non-modified lab mean value, and Lab #28 reported concentrations of C9-C18 well below the mean value for non-modified mean data.

Since a silica gel fractionation step was used by these lab, it is not clear why the data for some fractions is so far from that reported by other labs.

GC/MS without Silica Gel Fractionation

One Lab, #27, used a GC/MS to differentiate and quantitate aliphatic and aromatic hydrocarbons, without the use of a pre-analysis silica gel fractionation step. However, this lab reported N.D. values for the C11-C22 Aromatics in both the sand and water sample. This is a major deviation from other lab data, and inconsistent with the known aromatic content of the fuel-oil spiked soil sample, and presumed chemistry of the "real world" contaminated water sample.

On the basis of the above, the high temperature PID/FID unit appeared to perform reasonably well on the soil sample, but not the water sample. The GC/MS technique without silica-gel prefractionation did not produce reliable data. The data produced by labs using GC/MS in lieu of an FID to quantitate range data was mixed; it is not clear if this is due to the use of the MS detector, or other methodological or procedural problems.

LABORATORY PROFICIENCY

Laboratory proficiency was determined using Z-scores, as recommended by the International Standards Organization (ISO) "International Harmonized Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories", and as used and applied by the United States Environmental Protection Agency (USEPA) in their RCRA Proficiency Evaluation & Method Testing Program. Proficiency was judged for each method and matrix, based upon an analyte-by-analyte calculation of Z-scores:

$$\text{Z-score} = \frac{\text{Result - Study Mean}}{\text{Study Std. Deviation}}$$

Z scores may be positive or negative depending upon whether the value reported by the laboratory was higher or lower than the study mean, respectively. To be consistent with the data treatment used by the USEPA, Z-scores were based upon the biweight mean and standard deviation of all reported values for each aliphatic/aromatic

fractional range.[1] In order for a laboratory to be deemed proficient in a method and matrix, individual Z-scores for each fractional range had to be below 2.5.

UNMODIFIED METHODS

A tabulation of Z-scores for participating laboratories who submitted data based upon use of an unmodified VPH and/or EPH method is provided in Table 10. A summary of laboratory proficiency for all samples analyzed by the unmodified methods is presented in Table 11. This data is graphically presented in Figures 17 and 18.

Two data treatment decisions bear noting:

- Because of the problems observed with column effects in the VPH samples, laboratories with Z-scores above 2.5 in either aliphatic fractions were deemed proficient if the Z-score for Total GC/FID concentrations (i.e., the sum of C5-C8 and C9-C12 Aliphatics) was less than 2.5;

- Because the likely true values for the concentrations of C9-C18 and C19-C36 Aliphatics in the water sample are near or below reporting limits, a Z-score of 0 was assigned to labs reporting "None Detected".

As can be seen from this data, 20 of 21 labs were deemed proficient for the VPH soil sample, 17 of 21 for the VPH water sample, 19 of 23 for the EPH soil sample, and 20 of 23 for the EPH water sample.

MODIFIED METHODS

A tabulation of Z-scores for participating laboratories who submitted data based upon use of a modified VPH and/or EPH method is provided in Table 12. This data is graphically presented in Figures 19 and 20.

Three data treatment decisions bear noting:

- With the exception of Lab 18(2), which submitted a VPH data set based upon the use of a 9.6 eV PID lamp, it was not possible to calculate a "total GC/FID" value, to eliminate from consideration column effects. However, only Lab #23 in the soil data, and Lab #24 in the water data, showed possible signs of a column effect, and in both cases the Z-scores of all aliphatic fractions were less than 2.5;

- Lab #26 was assigned a Z-score of 0 for reporting N.D. for C19-C36 Aliphatics in the EPH water sample;

- For Lab data #18 and 18(2), in which a high temperature PID/FID was used exclusively to fractionate aliphatics from aliphatics, the PID response was subtracted from the appropriate aliphatic fraction.

As can be seen from this data, two of the soil submittals (Labs #18(3) and 28) contained fractional outliers with a Z score greater than 2.5. For the water samples, all of the PID/FID data from Lab #18 - including 18(3), which contained a silica gel fractionation step, had Z-scores above 2.5 for at least one aliphatic fraction. The other GC/MS methods performed acceptably.

Further detailed data-specific information and evaluation is necessary to determine whether each of these modified methods is sufficiently accurate and reproducible. On the basis of the above, certain methods and labs appear promising.

---

[1] Kafadar, K., *A Biweight Approach to the One-Sample Problem*, Journal of the American Statistical Association, Vol. 77, No. 378, June, 1982, pp. 416-424.

Table 10
Summary of Z Scores for Unmodified Methods

VPH Method										
	SAND					WATER				
	C5-C8	C9-C12	C9-C10	Total	Pass FID & C9-	C5-C8	C9-C12	C9-C10	Total	Pass FID & C9-
Lab#	Aliphatics	Aliphatics	Aromatics	GC/FID	C10 Aromatics?	Aliphatics	Aliphatics	Aromatics	GC/FID	C10 Aromatics?
1	-2.22	-1.73	-2.95	-2.60	FALSE	-1.73	-1.50	-4.21	-2.80	FALSE
2	-1.51	-0.39	-0.71	-1.35	TRUE	-1.13	-0.31	-0.47	-1.10	TRUE
3	-0.78	0.35	-0.51	-0.43	TRUE	-0.56	0.82	0.02	0.51	TRUE
4	-0.65	-0.95	-0.43	-1.08	TRUE	0.58	-0.55	0.53	-0.28	TRUE
5	-0.62	0.07	-0.02	-0.47	TRUE	-0.38	0.26	0.45	0.00	TRUE
6	-0.50	-0.17	1.65	-0.53	TRUE	-0.66	-0.20	2.12	-0.68	TRUE
7	-0.36	-0.72	0.63	-0.76	TRUE	-0.56	-1.04	-0.87	-1.54	TRUE
8	-0.33	0.27	-0.28	-0.17	TRUE	-0.53	0.01	0.25	-0.37	TRUE
9	-0.29	-0.10	-0.43	-0.35	TRUE	-0.66	-0.22	-0.28	-0.70	TRUE
10	-0.28	0.11	-1.18	-0.22	TRUE	2.08	2.90	5.23	4.49	FALSE
11	-0.24	-0.11	1.01	-0.32	TRUE	-0.45	1.37	-0.19	1.19	TRUE
12	-0.24	2.50	-0.17	1.19	TRUE	-0.32	1.90	-0.14	1.86	TRUE
13	0.09	2.13	1.57	1.19	TRUE	-0.20	2.30	4.38	2.37	FALSE
14	0.12	0.82	-0.06	0.46	TRUE	-0.20	0.47	-1.01	0.35	TRUE
15	0.49	-0.25	-0.17	0.10	TRUE	0.11	-0.16	-0.01	-0.15	TRUE
16	0.53	3.06	0.12	2.03	TRUE	0.77	-0.61	-0.12	-0.23	TRUE
17	0.68	-0.10	-0.29	0.31	TRUE	0.81	0.14	0.45	0.63	TRUE
18	0.74	-0.68	-1.49	0.01	TRUE	0.95	-0.84	-2.02	-0.37	TRUE
19	0.78	-1.10	0.08	-0.20	TRUE	1.55	-0.72	2.80	0.14	FALSE
20	1.09	0.98	0.31	1.21	TRUE	0.38	0.61	1.50	0.87	TRUE
22	1.90	2.38	0.43	2.57	TRUE	-0.22	0.09	-1.15	-0.08	TRUE
WES	1.19	-0.62	0.85	0.36	TRUE	1.48	-0.76	0.37	0.05	TRUE

EPH Method								
	SAND				WATER			
	C9-C18	C19-C36	C11-C22	Pass All	C9-C18	C19-C36	C11-C22	Pass All
Lab#	Aliphatics	Aliphatics	Aromatics	Fractions?	Aliphatics	Aliphatics	Aromatics	Fractions?
1	0.95	0.95	0.72	TRUE	0.53	0.00	2.27	TRUE
2	1.24	1.12	4.42	FALSE	0.00	0.00	1.55	TRUE
3	-0.43	-0.47	-0.99	TRUE	-0.71	-0.53	0.02	TRUE
4	-0.63	-1.03	-0.96	TRUE	-0.89	-0.58	-0.70	TRUE
5	0.14	0.70	-0.18	TRUE	-0.73	0.00	-0.82	TRUE
6	0.84	0.29	0.97	TRUE	-0.90	0.00	1.10	TRUE
7	-1.34	-1.73	-3.26	FALSE	0.93	-0.01	-0.04	TRUE
8	1.54	0.80	-0.40	TRUE	2.14	0.00	-1.14	TRUE
9	-0.88	-0.88	0.72	TRUE	-0.40	-0.39	0.60	TRUE
10	0.46	0.14	-0.45	TRUE	0.00	0.00	1.19	TRUE
11	0.09	1.85	0.57	TRUE	-0.01	0.00	0.19	TRUE
12	-1.17	-0.03	-0.07	TRUE	-0.40	10.91	-1.24	FALSE
13	0.12	0.26	-0.36	TRUE	1.14	1.08	-0.73	TRUE
14	-0.27	-0.59	0.29	TRUE	0.00	0.00	-0.18	TRUE
15	0.54	-0.32	0.72	TRUE	-1.00	0.00	0.46	TRUE
16	6.62	5.02	1.65	FALSE	-0.52	1.08	0.66	TRUE
17	-1.04	-0.94	-1.33	TRUE	0.64	-0.51	-0.34	TRUE
19	-0.56	1.86	0.34	TRUE	-0.39	4.59	0.45	FALSE
20	2.79	-0.50	0.81	FALSE	1.25	0.00	1.40	TRUE
22	0.83	-0.60	-1.24	TRUE	1.20	-0.63	-0.83	TRUE
23	-0.59	0.10	0.40	TRUE	-0.13	2.20	-0.93	TRUE
24	-0.24	-0.35	0.76	TRUE	-0.97	-0.34	-0.23	TRUE
25	-0.49	-0.52	-0.68	TRUE	0.83	5.44	-0.67	FALSE
WES	0.29	0.80	-0.86	TRUE	-0.27	0.01	-0.42	TRUE

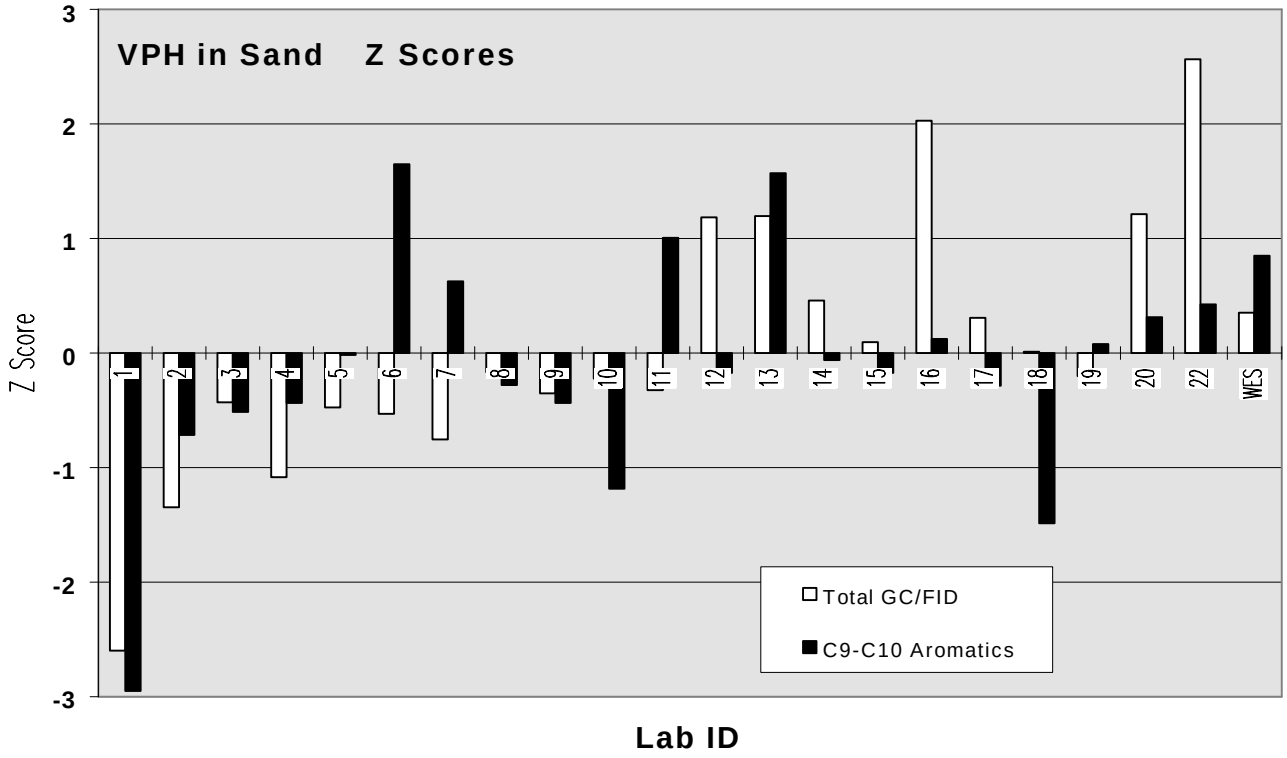
Table 11
Summary of Laboratory Proficiency for all Samples for Unmodified Methods

	VPH		EPH		VPH	EPH	EPH & VPH
Lab #	Soil	Water	Soil	Water	Soil & Water	Soil & Water	Soil & Water
1	FAIL	FAIL	PASS	PASS	FAIL	PASS	FAIL
2	PASS	PASS	FAIL	PASS	PASS	FAIL	FAIL
3	PASS	PASS	PASS	PASS	PASS	PASS	PASS
4	PASS	PASS	PASS	PASS	PASS	PASS	PASS
5	PASS	PASS	PASS	PASS	PASS	PASS	PASS
6	PASS	PASS	PASS	PASS	PASS	PASS	PASS
7	PASS	PASS	FAIL	PASS	PASS	FAIL	FAIL
8	PASS	PASS	PASS	PASS	PASS	PASS	PASS
9	PASS	PASS	PASS	PASS	PASS	PASS	PASS
10	PASS	FAIL	PASS	PASS	FAIL	PASS	FAIL
11	PASS	PASS	PASS	PASS	PASS	PASS	PASS
12	PASS	PASS	PASS	FAIL	PASS	FAIL	FAIL
13	PASS	FAIL	PASS	PASS	FAIL	PASS	FAIL
14	PASS	PASS	PASS	PASS	PASS	PASS	PASS
15	PASS	PASS	PASS	PASS	PASS	PASS	PASS
16	PASS	PASS	FAIL	PASS	PASS	FAIL	FAIL
17	PASS	PASS	PASS	PASS	PASS	PASS	PASS
18	PASS	PASS	N/A	N/A	PASS	N/A	N/A
19	PASS	FAIL	PASS	FAIL	FAIL	FAIL	FAIL
20	PASS	PASS	FAIL	PASS	PASS	FAIL	FAIL
22	PASS	PASS	PASS	PASS	PASS	PASS	PASS
23	N/A	N/A	PASS	PASS	N/A	PASS	N/A
24	N/A	N/A	PASS	PASS	N/A	PASS	N/A
25	N/A	N/A	PASS	FAIL	N/A	FAIL	N/A
WES	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Total Number of Labs Passing (excluding WES)							
	20	17	19	20	17	16	11

Table 12
Summary of Z-scores for Modified VPH and EPH Method

VPH Method - Modified									
	SAND				WATER				
Lab#	Adjusted C5-C8 Aliphatics	Adjusted C9-C12 Aliphatics	Adjusted C9-C10 Aromatics	Pass All Fractions?	Adjusted C5-C8 Aliphatic	Adjusted C9-C12 Aliphatics	Adjusted C9-C10 Aromatics	Pass All Fractions?	Method Modification
18(2)	0.12	0.03	-1.77	TRUE	-0.77	-0.22	-1.92	TRUE	9.6 eV PID
23	-1.37	1.18	2.11	TRUE	-0.63	-0.31	-0.46	TRUE	GC/MS
24	-0.39	-0.89	1.27	TRUE	2.18	-1.28	-3.06	FALSE	Solvent extr
25	-0.90	-1.29	-1.04	TRUE	-1.06	-1.40	-0.11	TRUE	GC/MS
26	1.73	1.57	3.28	FALSE	2.29	1.95	4.26	FALSE	GC/MS
27	-0.08	-1.34	1.42	TRUE	-1.31	-1.41	4.58	FALSE	GC/MS
28	-0.12	-1.19	2.90	FALSE	-0.77	-1.37	2.77	TRUE	GC/MS
EPH Method - Modified									
	SAND				WATER				
Lab#	C9-C18 Aliphatics	C19-C36 Aliphatics	C11-C22 Aromatics	Pass All Fractions?	C9-C18 Aliphatics	C19-C36 Aliphatics	C11-C22 Aromatics	Pass All Fractions?	Method Modification
18	0.61	1.51	-0.72	TRUE	3.19	8.44	-0.35	FALSE	10.2 PID/FID
18(2)	1.32	2.10	-0.47	TRUE	5.01	6.85	0.08	FALSE	9.6 PID/FID
18(3)	0.49	2.81	-2.14	FALSE	1.36	4.72	-1.10	FALSE	PID/FID w/frac
26	-0.40	0.75	-0.97	TRUE	0.38	0.00	-1.47	TRUE	GC/MS TIC
27	-0.99	0.22	N.D.	FALSE	1.31	0.00	-1.10	TRUE	GC/MS - no frac
28	-1.51	-1.69	3.07	FALSE	-0.94	-0.24	-0.14	TRUE	GC/MS TIC

Figure 17
Unmodified VPH Method - Summary of Z Scores



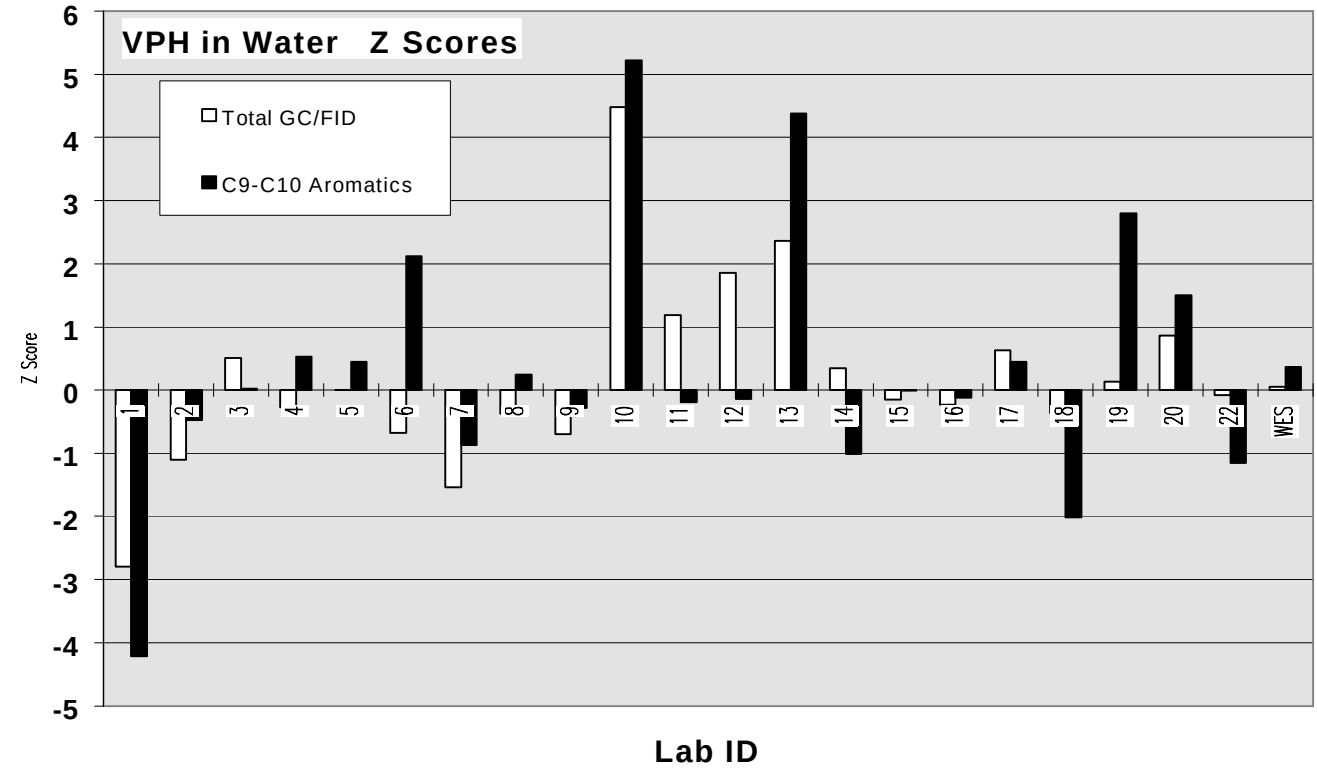
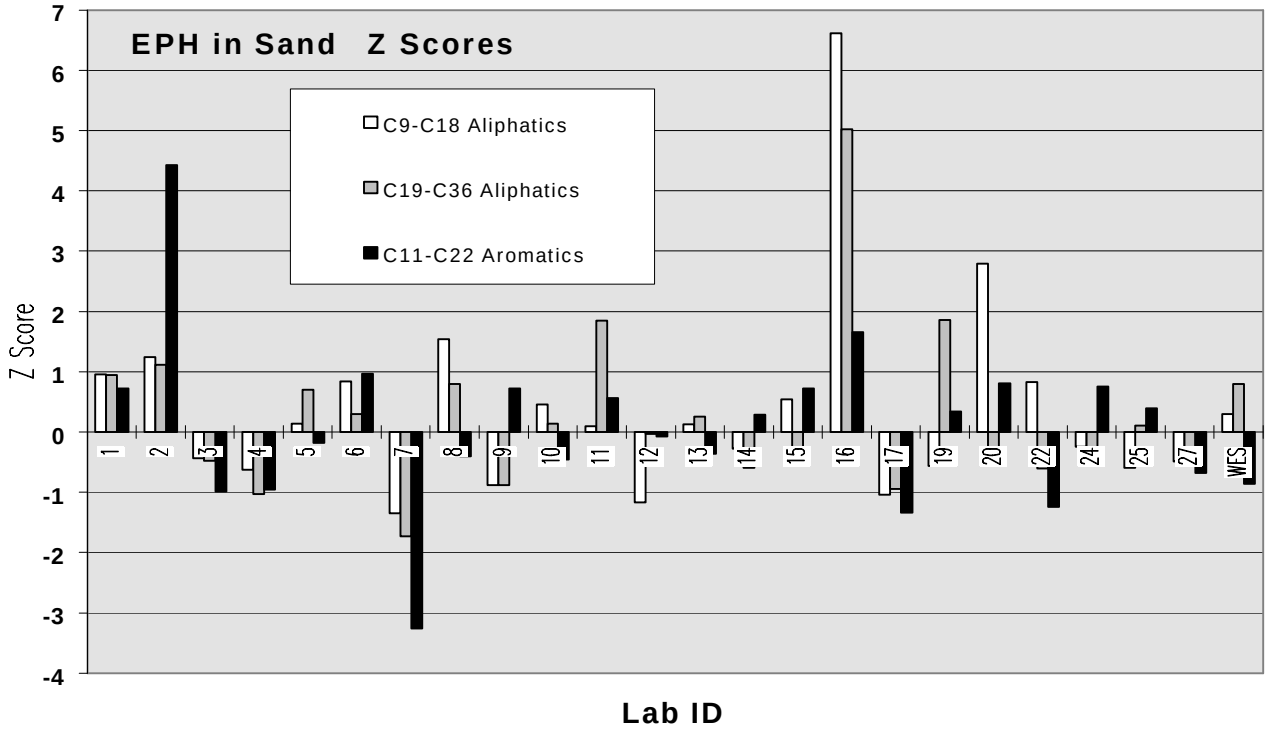


Figure 18
Unmodified EPH Method - Summary of Z Scores



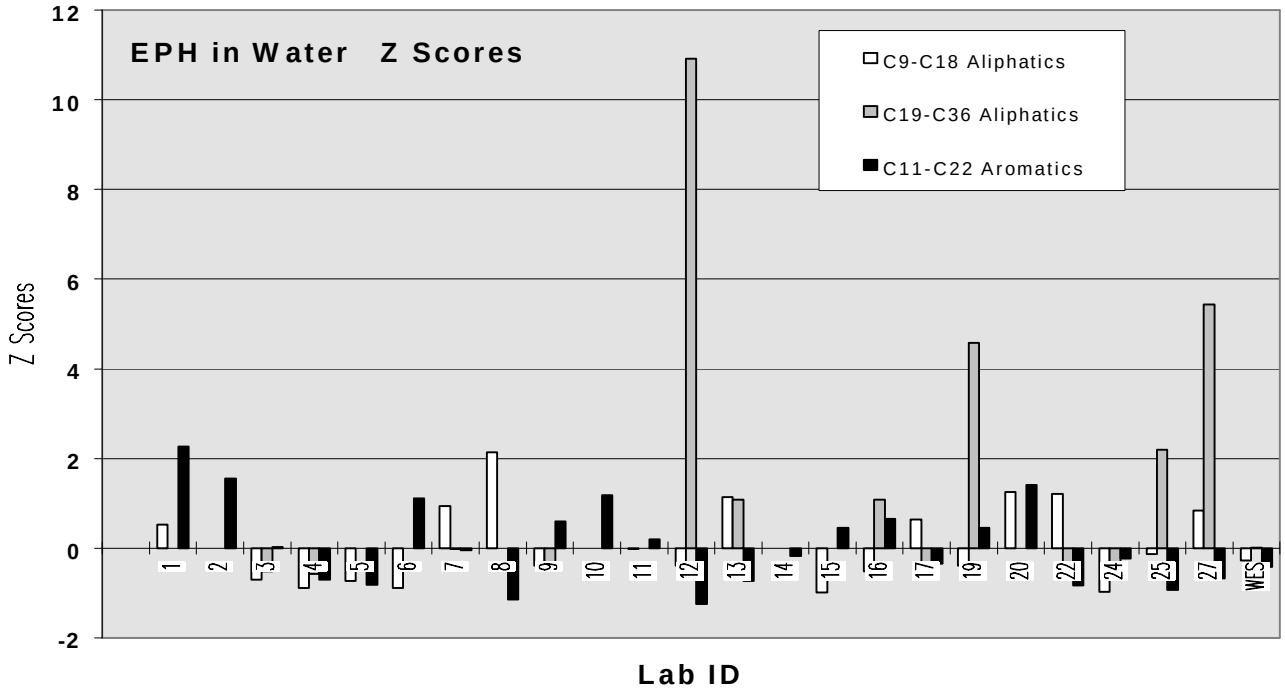
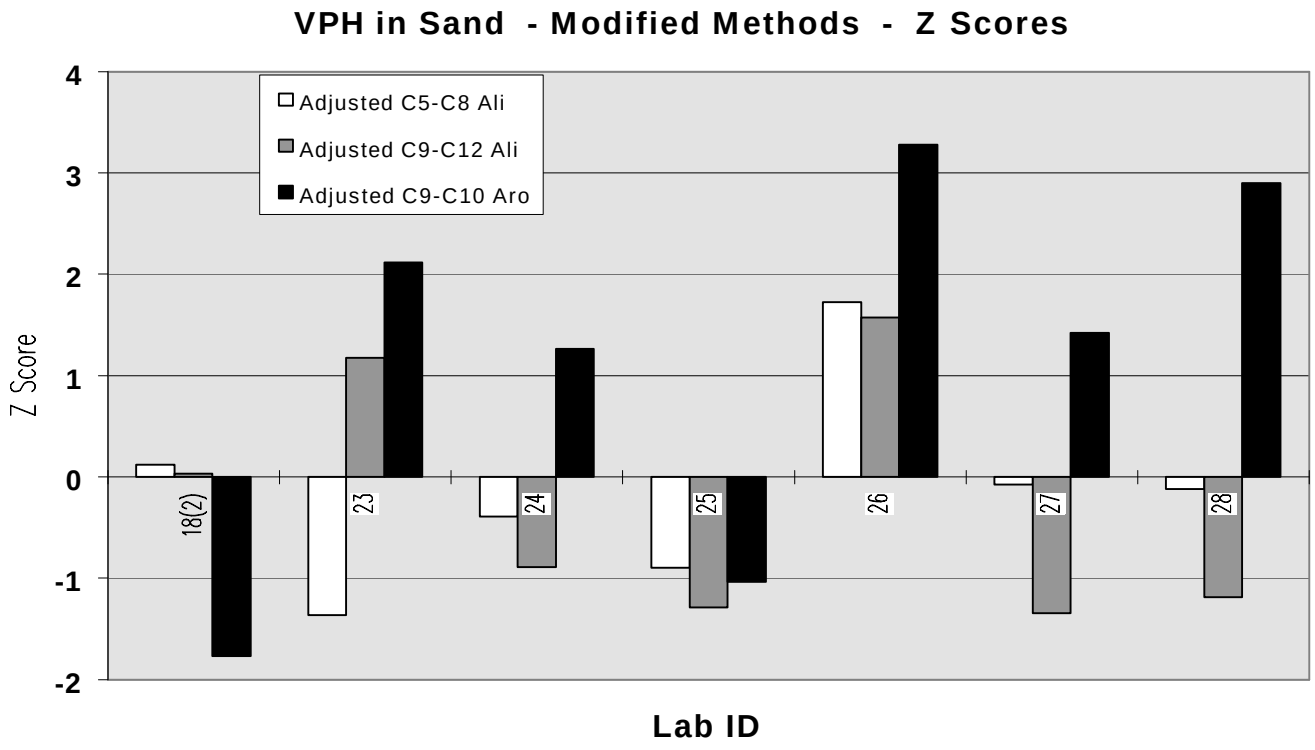


Figure 19
Modified VPH Methods Z-scores



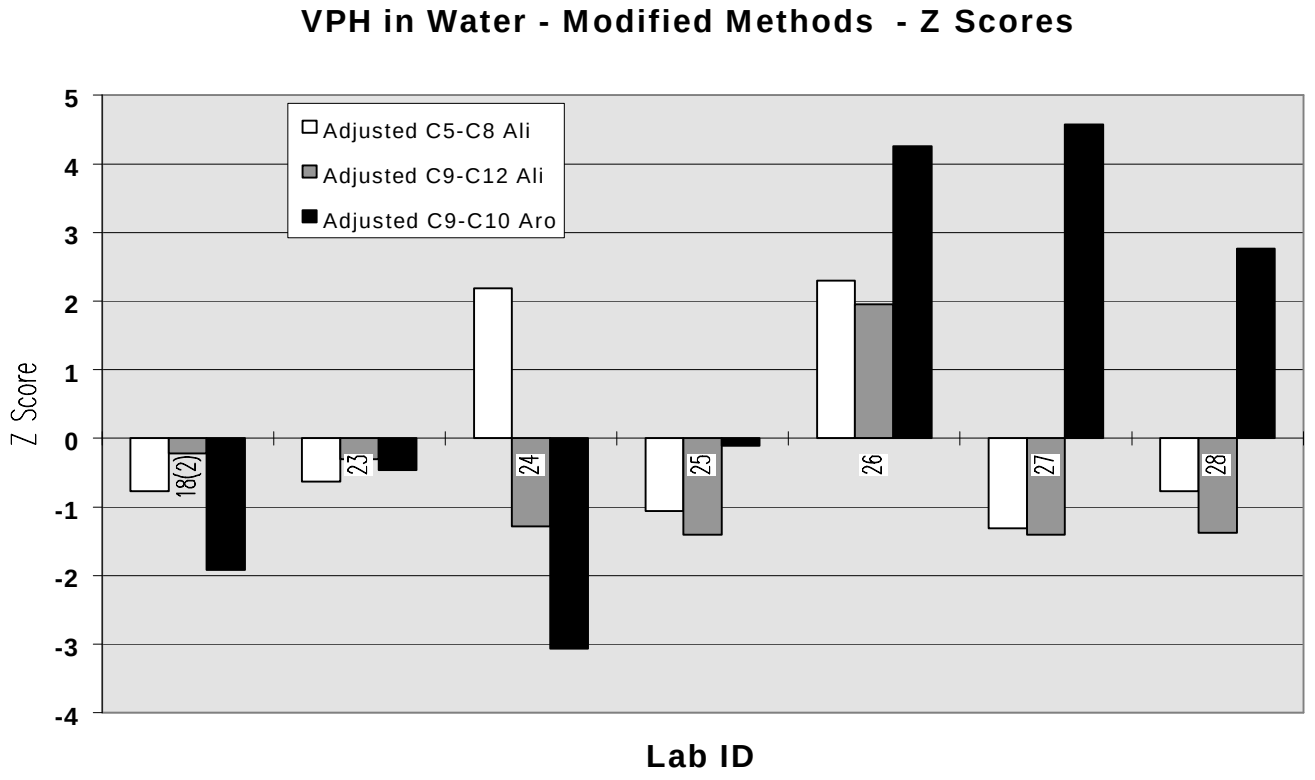
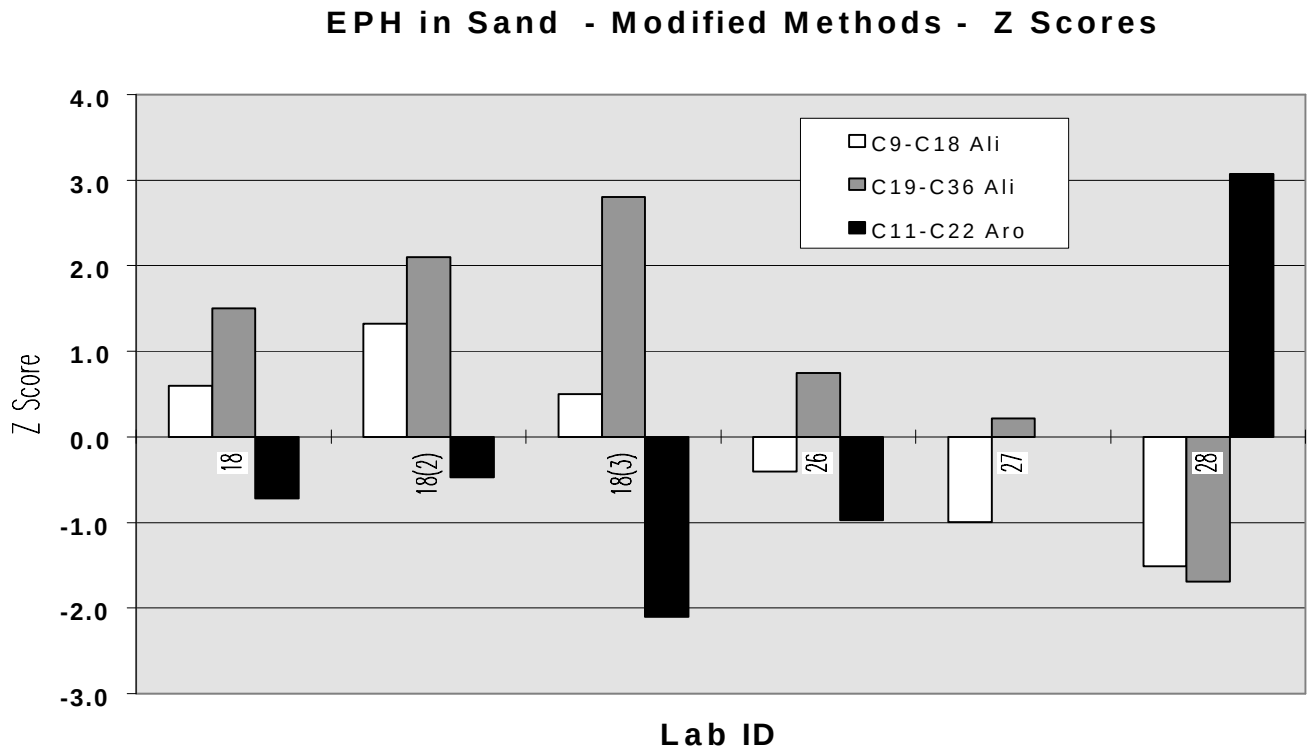
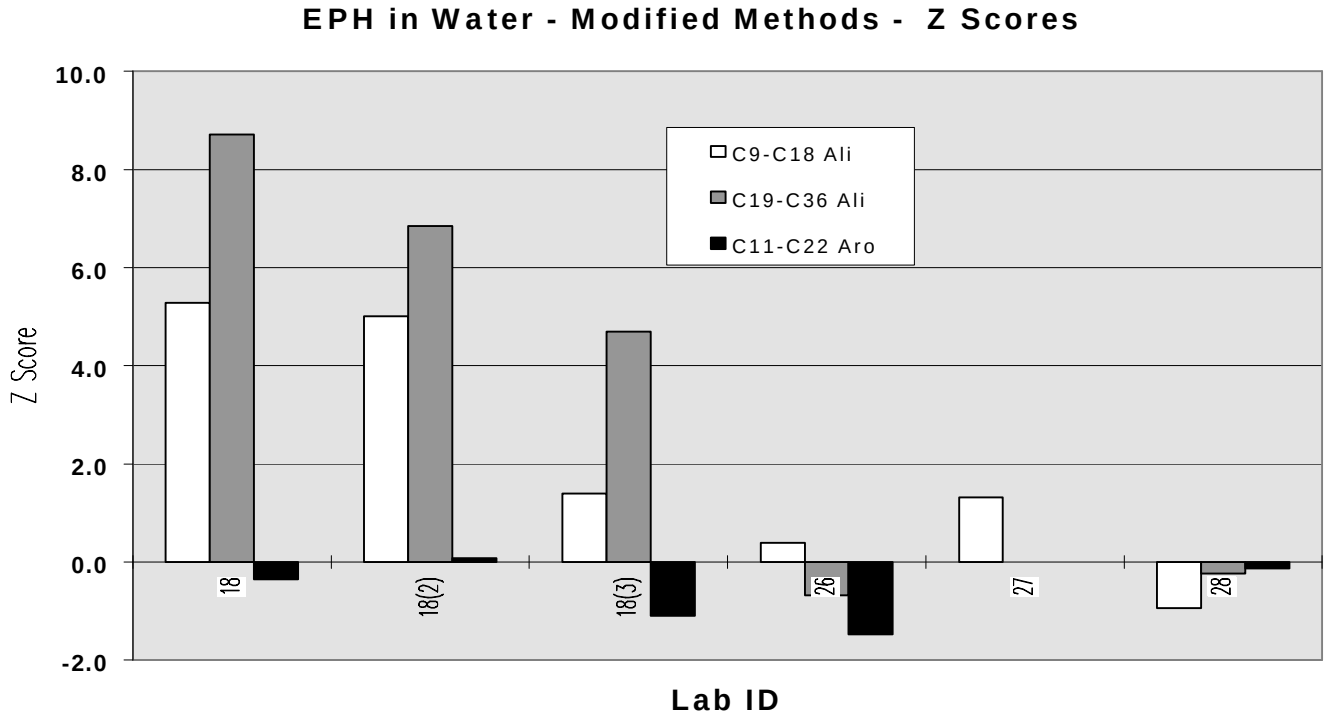


Figure 20
Modified EPH Methods Z-scores





METHOD PERFORMANCE AMONG PROFICIENT LABORATORIES

A summary of data provided by laboratories deemed to be proficient in the use of the unmodified method is presented below:

Summary of Method Performance by Laboratories Meeting Proficiency Criteria

				Data from Proficient Laboratories			
Method	**Matrix**	**# Labs Proficient**	**% Labs Proficient**	**Fraction**	**%RSD**	**% labs within +/- 30% mean VPH value**	**% labs within +/- 40% mean EPH value**
VPH	**soil**	**20**	**95**	**C5-C8 Aliphatics**	**28**	**80**	
				C9-C12 Aliphatics	**52**	**50**	
				Total GC/FID	**31**	**70**	
				C9-C10 Aromatics	**24**	**80**	
	water	**17**	**81**	**C5-C8 Aliphatics**	**31**	**71**	
				C9-C12 Aliphatics	**44**	**47**	
				Total GC/FID	**24**	**76**	
				C9-C10 Aromatics	**20**	**82**	
EPH	**soil**	**19**	**83**	**C9-C18 Aliphatics**	**23**		**95**
				C19-C36 Aliphatics	**30**		**89**
				C11-C22 Aromatics	**19**		**100**
				Total All Fractions	**17**		**100**
	water	**20**	**87**	**C9-C18 Aliphatics**	**84**		**22**
				C19-C36 Aliphatics	**192**		**94**
				C11-C22 Aromatics	**47**		**72**
				Total All Fractions	**35**		**83**

For the unmodified VPH method, about 80% of proficient labs reported a C9-C10 Aromatic value within 30% of the mean; the single-laboratory level of precision specified by the method. Somewhat lower results were reported for the aliphatic fractions, likely due, in whole or in part, to the column effects discussed previously.

For the unmodified EPH method, good interlaboratory reproducibility is seen for the EPH soil sample. Problems are evident in the water sample, due to the fractionation problems discussed previously, and due to the low concentrations of aliphatics present in the "real world" sample used.

CONCLUSIONS

On the basis of the information and data presented and discussed above, the following conclusions are offered:

- The choice of chromatographic column used in the VPH method may significantly effect the quantitation of C5-C8 Aliphatics and C9-C12 Aliphatics;

- Stripping of aromatics into the aliphatic EPH fraction is more problematic than stripping of aliphatics into the aromatic fraction. Because of their weakly polar properties, naphthalene and substituted naphthalenes appear especially susceptible to leaching from the silica gel fractionation cartridge/column due to excessive hexane use. The use of one or more fractionation surrogate compounds, with properties similar to naphthalene, is recommend to monitor aromatic breakthrough, and enable corrective actions.

- A significant number of laboratories had difficulties with range concentration adjustments, especially in the VPH methods.

- For labs using the unmodified VPH and EPH methods, based on the use of Z-scores, 95% of participating labs were deemed to be proficient in the analyses of the VPH soil sample, 81% in the analyses of the VPH water sample, 83% in the analyses of the EPH soil sample, 87% in the analyses of the EPH water sample. In total, 17 of these labs were deemed proficient in both VPH matrices; 16 were deemed proficient in both EPH matrices; 11 labs were deemed proficient in all VPH and EPH matrices.

- Additional information and evaluation is required to determine the performance of modified VPH and EPH methods, and proficiency of the labs conducting these methods.

- The interlaboratory accuracy and precision of the VPH and EPH methods, based upon data provided by laboratories determined to be proficient, is deemed to be acceptable. Moreover, significant improvements are expected, based upon the institution of the method refinements recommended in this report, as well as through the result of continued laboratory use and experience.