

**POTENTIAL FALSE POSITIVES IN THE VOLATILE PETROLEUM
HYDROCARBON (VPH) ANALYTICAL METHOD: THE EFFECT OF
NON-TARGET COMPOUNDS ON MCP DECISION-MAKING**

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POTENTIAL FALSE POSITIVES IN THE VOLATILE PETROLEUM HYDROCARBON (VPH) ANALYTICAL METHOD: THE EFFECT OF NON-TARGET COMPOUNDS ON MCP DECISION-MAKING

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Regulatory Framework

Releases of petroleum products comprise a major source of environmental contamination. Although petroleum products may contain complex and variable mixtures of hydrocarbons, some states and regulatory programs still rely on traditional, inexact analytical approaches for petroleum identification and quantitation, such as using indicator compounds (i.e., benzene, toluene, ethylbenzene, xylenes (BTEX)) or the “Total Petroleum Hydrocarbon” (TPH) concentration. These analyses (BTEX and TPH) provide little or no information on the specific hydrocarbon composition or toxicity of various petroleum products.

To better assess the impact of petroleum-related compounds in the environment, MassDEP developed methods of analysis for petroleum hydrocarbons that expand beyond the traditional BTEX target compounds and TPH and include “ranges” of aromatic and aliphatic compounds. The initial Volatile Petroleum Hydrocarbon (VPH) and Extractable Petroleum Hydrocarbon (EPH) methods developed in Massachusetts were described in the “Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter” (MassDEP, 1994). After their release as draft methods in 1995, a formal rollout was implemented in a MassDEP letter to Massachusetts Licensed Site Professionals (LSPs) in 1997. The final policy was published in 2002 as #WSC-02-411, “Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach Final Policy.”

VPH and EPH are gas chromatography (GC) methods that were developed to provide a toxicological-based approach to characterizing and evaluating the risks posed by petroleum sites. These methods also include an analysis for target VPH- or EPH-associated compounds with fractionation of petroleum into collective aliphatic and aromatic carbon ranges. The methods have been twice updated since they were initially published, first in May 2004 and again in the MassDEP Compendium of Analytical Methods in July 2010. The present article focuses on the current VPH methodology.

Approach to the Study

The VPH method uses GC and two detectors in series to quantify the volatile hydrocarbons present into either an aromatic fraction utilizing the photoionization detector (PID) or an

aliphatic fraction utilizing the flame ionization detector (FID). The PID is considered the more selective detector and is particularly sensitive to aromatic compounds, while the FID responds to a much wider range of hydrocarbons in general. The method further defines the aliphatic fraction by reporting two distinct ranges of compounds, the C5-C8 and the C9-C12 aliphatic hydrocarbons. Only one range is reported for the aromatic fraction, the C9-C10 aromatic hydrocarbons, along with the following target compounds: benzene, toluene, ethylbenzene, o-xylene, m/p-xylenes (collectively, BTEX), methyl tert-butyl ether (MTBE), and naphthalene.

The VPH Method includes language that recognizes that the method is subject to a "false positive" bias from non-targeted hydrocarbon compounds, and recommends confirmatory analysis if an applicable reporting or cleanup standard is exceeded and if co-elution of a non-targeted hydrocarbon compound is suspected. Method-described interferences also reference that all compounds eluting on the PID chromatogram after o-xylene are identified by the method as aromatic hydrocarbons, thus resulting in the potential for overestimation of levels of aromatic hydrocarbons if late-eluting aliphatic compounds are present that also respond to the PID.

To examine the potential bias of common non-petroleum compounds and VPH method adjustments, two different studies of the VPH method were conducted. Each study was done twice, once in 2000 (five laboratories) and again in 2011 (four laboratories). One blind study included the analysis of aqueous control samples spiked only with halogenated ethanes (which included the common chlorinated solvents), while the other included the analysis of aqueous control samples spiked only with aromatic hydrocarbons (which included the CAM Method 8260 target mono- and alkyl-substituted aromatic compounds).

The primary purpose of these halogenated ethane studies was to evaluate whether halogenated ethanes are reported as VPH carbon ranges, such as C5-C8 aliphatics and/or C9-C12 aliphatics, and if so, to assess what approximate concentration of these common halogenated ethanes would trigger a "false" regulatory response requirement for VPH. The primary purpose of the aromatic studies was to evaluate whether method adjustment calculations result in aromatic hydrocarbons also being reported as VPH aliphatic carbon ranges, and if so, to assess what approximate concentration of these common aromatic hydrocarbons would trigger a "false" regulatory response requirement for VPH compounds other than aromatics. A secondary purpose of both of these studies was to observe whether the laboratories involved would be inclined to advise the data user that the GC chromatography for these samples did not qualitatively resemble typical 'petroleum hydrocarbon peak patterns' for which qualified laboratory environmental chemists would be expected to be quite familiar.

For the study of the VPH method with halogenated ethane compounds, aqueous control samples were prepared from a certified halogenated ethane reference standard mixture (Ultra Scientific DWM-520). Two levels of "unknown" were prepared which included distilled water spikes at the 50 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$ level with each of the following 14 compounds: chloroethane, 1,1,1,2-tetrachloroethane, 1,2-dibromoethane, 1,1,2,2-tetrachloroethane, 1,1-dichloroethane, tetrachloroethene, 1,2-dichloroethane, 1,1,1-trichloroethane,

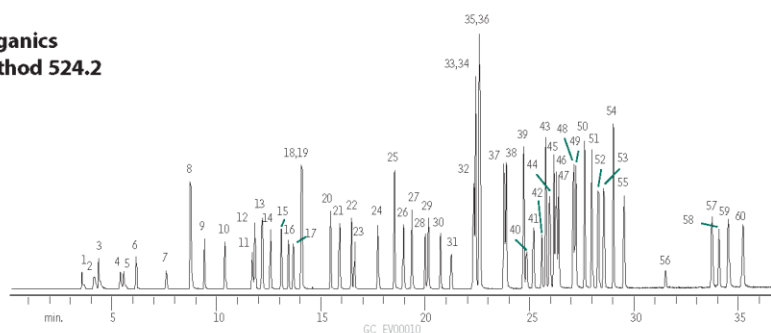
1,1-dichloroethene, 1,1,2-trichloroethane, cis-1,2-dichloroethene, trichloroethene, trans-1,2-dichloroethene, and vinyl chloride.

For the study of the VPH method with aromatic compounds, aqueous control samples were prepared from a certified aromatic reference standard mixture (Ultra Scientific DWM-550). Two levels of “unknown” were prepared which included distilled water spikes at the 24 µg/L and 300 µg/L level with each of the following 16 compounds: benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, sec-butylbenzene, tert-butylbenzene, isopropylbenzene, 4-isopropyltoluene, n-propylbenzene, 1,2,4-trimethylbenzene, styrene, 1,3,5-trimethylbenzene, n-butylbenzene, and naphthalene.

Since the VPH method had not yet been finalized at the time of the 2000 study, each of the participating analytical laboratories incorporated varying GC method parameters. For the VPH analysis conducted in 2011, each participating analytical laboratory used the Restek RTX-502.2 GC column specified in the finalized VPH analytical methodology (column specifications: 105 meter; 0.53 mm ID; 3.0 µm film; diphenyl/dimethyl polysiloxane phase). Restek RTX-502.2 column relative retention times and elution order for common volatile organic compounds (VOCs) are shown on Exhibit 1 below:

Permission for use provided by Restek; 9/13/2013.

**Volatile Organics
US EPA Method 524.2
Rtx®-502.2**



40m, 0.18mm ID, 1.0µm Rtx®-502.2 (cat.# 40915)
Conc.: Reference Standard 524 Volatiles Kit (cat.# 30052)
200ppb VOA standards in 5mL RO water.
Purge & trap: Tekmar LCS 2000
Trap: Vocab 4000
Purge: 11 min.
Desorb preheat: 250°C
Desorb time: 2 min.

Desorb flow rate: 30ml/min.
Oven temp.: 35°C (hold 4 min.) to 150°C @ 6°C/min. to 220°C @ 8°C/min. (hold 8 min.).
Inj. / det. temp.: 200°C / 250°C
Detector: MS
Linear velocity: 21cm/sec. set @ 35°C
Split ratio: 30:1

1. dichlorodifluoromethane	14. chloroform	27. 1,1,2-trichloroethane	40. bromoform	53. 1,4-dichlorobenzene
2. chloromethane	15. 1,1,1-trichloroethane	28. 1,3-dichloropropane	41. 1,1,2,2-tetrachloroethane	54. n-butylbenzene
3. vinyl chloride	16. 1,1-dichloropropane	29. tetrachloroethene	42. 1,2,3-trichloropropane	55. 1,2-dichlorobenzene
4. bromomethane	17. carbon tetrachloride	30. dibromochloromethane	43. propylbenzene	56. 1,2-dibromo-3-chloropropane
5. chloroethane	18. benzene	31. ethylene dibromide	44. bromobenzene	57. 1,3,5-trimethylbenzene
6. trichlorofluoromethane	19. 1,2-dichloroethane	32. chlorobenzene	45. 1,3,5-trimethylbenzene	58. hexachlorobutadiene
7. 1,1-dichloroethene	20. trichloroethene	33. ethylbenzene	46. 2-chlorotoluene	59. naphthalene
8. methylene chloride	21. 1,2-dichloropropane	34. 1,1,1,2-tetrachloroethane	47. 4-chlorotoluene	60. 1,2,3-trichlorobenzene
9. trans-1,2-dichloroethene	22. bromodichloromethane	35. m-xylene	48. tert-butylbenzene	
10. 1,1-dichloroethane	23. dibromomethane	36. p-xylene	49. 1,2,4-trimethylbenzene	
11. 2,2-dichloropropane	24. cis-1,3-dichloropropene	37. o-xylene	50. sec-butylbenzene	
12. cis-1,2-dichloroethene	25. toluene	38. styrene	51. p-isopropyltoluene	
13. bromochloromethane	26. trans-1,3-dichloropropene	39. isopropylbenzene	52. 1,3-dichlorobenzene	

Restek Corporation 110 Benner Circle Bellefonte, PA 16823
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Exhibit 1: Restek RTX-502.2 column relative retention times and elution order for common volatile organic compounds

Each laboratory's method included differing GC chromatographic conditions (such as oven temperature programs and carrier gas flow rates) as demonstrated by the method-specified surrogate 2,5-dibromotoluene elution times, which ranged from approximately 25 minutes to 42 minutes. One laboratory also included 2,3,4-trifluorotoluene as an additional surrogate compound.

Results of Halogenated Ethane Studies

In the 2000 halogenated ethane study, C5-C8 aliphatic hydrocarbons were detected at concentrations ranging from 99 to 310 $\mu\text{g/L}$ in samples spiked at the 50 $\mu\text{g/L}$ level and from 290 to 1,000 $\mu\text{g/L}$ in samples spiked at the 100 $\mu\text{g/L}$ level. The C9-C12 aliphatic hydrocarbons were detected at concentrations ranging from 28.2 to 37 $\mu\text{g/L}$ in samples spiked at the 50 $\mu\text{g/L}$ level and from 82.7 to 110 $\mu\text{g/L}$ in samples spiked at the 100 $\mu\text{g/L}$ level. A summary of the 2000 halogenated ethane study results is presented in Table I below:

TABLE I
SUMMARY OF WATER QUALITY DATA

LABORATORY		A	A	B	B	C	C	D	D	E	E
SAMPLE DESIGNATION	MCP	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)
PREPARATION DATE	Reportable Concentration RCGW-1	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00
HALOETHANE MIXTURE											
VPH ($\mu\text{g/L}$)											
C5-C8 Aliphatics	300	240	760	231	754	130	290	99.0	324	310	1000
C9-C12 Aliphatics	700	34	140	ND (100)	ND (100)	ND (50)	ND (50)	28.2	82.7	37	110
C9-C10 Aromatics	200	ND (20)	ND (40)	ND (100)	ND (100)	ND (50)	ND (50)	ND (20)	ND (20)	ND (5)	ND (5)
Methyl tert-butyl ether	70	ND (5)	ND (10)	ND (5)	ND (5)	ND (5)	ND (5)	ND (2)	ND (2)	ND (5)	ND (5)
Benzene	5	ND (1)	ND (2)	ND (5)	ND (5)	ND (5)	ND (5)	ND (2)	ND (2)	ND (5)	ND (5)
Toluene	1,000	ND (5)	ND (10)	ND (5)	ND (5)	ND (5)	ND (5)	ND (2)	ND (2)	ND (5)	ND (5)
Ethylbenzene	700	ND (5)	ND (10)	ND (5)	ND (5)	ND (5)	ND (5)	ND (2)	ND (2)	ND (5)	ND (5)
Xylenes, mixture	5,000	ND (5)	ND (10)	ND (5)	ND (5)	ND (5)	ND (5)	ND (2)	ND (2)	ND (5)	ND (5)
Naphthalene	140	ND (5)	ND (10)	ND (5)	ND (5)	ND (5)	ND (5)	ND (20)	ND (20)	ND (5)	ND (5)

NOTES AND ABBREVIATIONS:

1. Bold values indicate an exceedance of Method 1 (ALIPHATIC) criteria.
 2. ND(2.5): Not detected; number in parentheses is the laboratory reporting limit.
 3. VPH: Volatile Petroleum Hydrocarbons
 4. Low level and high level spikes were prepared at 50 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$, respectively, with each of the following 14 compounds: chloroethane, 1,1,1,2-tetrachloroethane, 1,2-dibromoethane, 1,1,2,2-tetrachloroethane, 1,1-dichloroethane, tetrachloroethene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethene, 1,1,2-trichloroethane, cis-1,2-dichloroethene, trichloroethene, trans-1,2-dichloroethene, and vinyl chloride.
- Haley & Aldrich, Inc.

In the 2011 halogenated ethane study, C5-C8 aliphatic hydrocarbons were detected at concentrations ranging from 120 to 230 $\mu\text{g/L}$ in samples spiked at the 50 $\mu\text{g/L}$ level and from 260 to 440 $\mu\text{g/L}$ in samples spiked at the 100 $\mu\text{g/L}$ level. C9-C12 aliphatic hydrocarbons were not detected in samples spiked at the 50 $\mu\text{g/L}$ level, and were detected at concentrations ranging from 66.8 to 110 $\mu\text{g/L}$ in samples spiked at the 100 $\mu\text{g/L}$ level. One of the four participating laboratories provided a narrative with the VPH data package which indicated that ‘chlorinated ethylenes were present in the sample matrix.’ A summary of the 2011 halogenated ethane study results is presented in Table II below:

TABLE II
SUMMARY OF WATER QUALITY DATA

LABORATORY		F	F	G	G	H	H	J	J
SAMPLE DESIGNATION	MCP	HA-101 (OW)	HA-102 (OW)	HA-101 (OW)	HA-102 (OW)	HA-101 (OW)	HA-102 (OW)	HA-101 (OW)	HA-102 (OW)
PREPARATION DATE	Reportable Concentration RCGW-1	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11
HALOETHANE MIXTURE									
VPH ($\mu\text{g/L}$)									
C5-C8 Aliphatics	300	155	346	120	260	230	440	146 a	292 a
C9-C12 Aliphatics	700	ND (50)	66.8	ND (50)	ND (50)	ND (100)	110	ND (50)	ND (50)
C9-C10 Aromatics	200	ND (50)	ND (50)	ND (50)	ND (50)	ND (100)	ND (100)	ND (50)	ND (50)
Methyl tert-butyl ether	70	ND (3)	ND (3)	ND (1)	ND (1)	ND (1)	ND (1)	ND (1)	ND (1)
Benzene	5	ND (2)	ND (2)	ND (1)	ND (1)	ND (1)	ND (1)	ND (2)	ND (2)
Toluene	1,000	ND (2)	ND (2)	ND (1)	ND (1)	ND (1)	ND (1)	ND (2)	ND (2)
Ethylbenzene	700	ND (2)	ND (2)	ND (1)	ND (1)	ND (1)	ND (1)	ND (2)	ND (2)
Xylenes, mixture	5,000	ND (4)	ND (4)	ND (3)	ND (3)	ND (3)	ND (3)	ND (4)	ND (4)
Naphthalene	140	ND (4)	ND (4)	ND (5)	ND (5)	ND (5)	ND (5)	ND (3)	ND (3)

a Value includes chlorinated ethylenes which are present in sample matrix.

NOTES AND ABBREVIATIONS:

1. Bold values indicate an exceedance of Method 1 (ALIPHATIC) criteria.
2. ND(2.5): Not detected; number in parentheses is the laboratory reporting limit.
3. VPH: Volatile Petroleum Hydrocarbons
4. Low level and high level spikes were prepared at 50 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$, respectively, with each of the following 14 compounds: chloroethane, 1,1,1,2-tetrachloroethane, 1,2-dibromoethane, 1,1,2,2-tetrachloroethane, 1,1-dichloroethane, tetrachloroethene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethene, 1,1,2-trichloroethane, cis-1,2-dichloroethene, trichloroethene, trans-1,2-dichloroethene, and vinyl chloride. Haley & Aldrich, Inc.

The results of the study with halogenated ethane-spiked samples confirm that common halogenated ethanes are reported as VPH aliphatic hydrocarbons. In general, approximately 1 mg/L total halogenated ethanes (comprised of the common chlorinated solvents such as 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and ‘daughter products’) may result in reported C5-C8 aliphatic values that exceed one or more MassDEP Method 1 risk criteria. Chromatograms suggest that low boiling halogenated ethanes (such as vinyl chloride) do not interfere and that less common, higher boiling halogenated ethanes (such as 1,1,2,2-tetrachloroethane) elute in the C9-C12 aliphatic hydrocarbon range. An example VPH chromatogram of the haloethane reference material mixture is shown in Exhibit 2:

Report Date: 11-Aug-2011 11:37:00 Chrom Revision: 1.2 13-Jul-2011 10:43:06
Data File: \\wessvr06\chromdata\InstG.i\20110810-6376.b\G27337.D
Injection Date: 10-Aug-2011 18:21:30 Limit Group: GC MA VPH
Client ID: HA-1(OW) Instrument ID: Inst. G
Lims Batch ID: 78245 Lims Sample ID: 12
Operator ID: SS
Y Scaling:

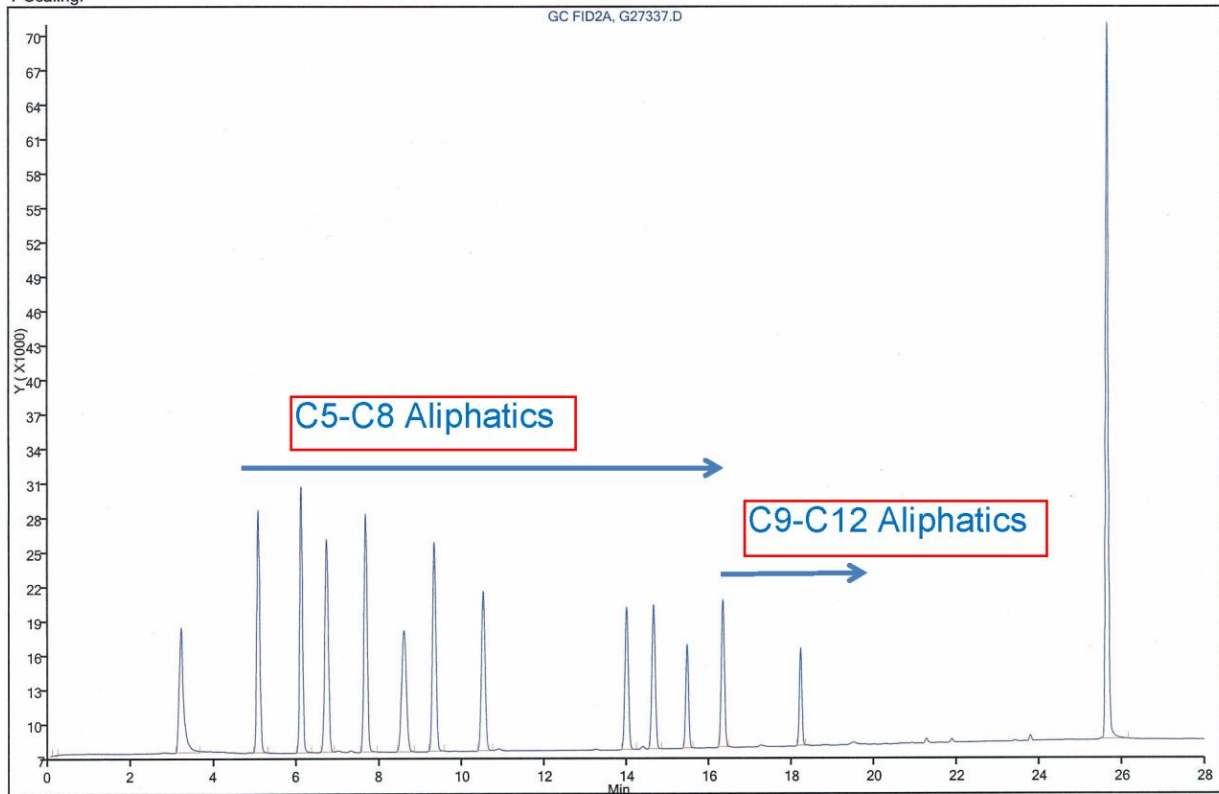


Exhibit 2: Example VPH chromatogram of haloethane reference material mixture.

Results of Aromatic Hydrocarbon Studies

In the 2000 aromatic hydrocarbon study, adjusted C5-C8 aliphatic hydrocarbons ranged from “not detected” to 34 $\mu\text{g/L}$ in samples spiked at the 24 $\mu\text{g/L}$ level, and were detected at concentrations ranging from 168 to 510 $\mu\text{g/L}$ in samples spiked at the 300 $\mu\text{g/L}$ level. The adjusted C9-C12 aliphatic hydrocarbons were detected at concentrations ranging from 40.7 to 230 $\mu\text{g/L}$ in samples spiked at the 24 $\mu\text{g/L}$ level, and from 365 to 2,300 $\mu\text{g/L}$ in samples spiked at the 300 $\mu\text{g/L}$ level. A summary of the 2000 aromatic study results is presented in Table III below:

TABLE III
SUMMARY OF WATER QUALITY DATA

LABORATORY		A		B		C		D		E	
SAMPLE DESIGNATION	MCP	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)	HA-2(OW)	HA-3(OW)
PREPARATION DATE	Reportable Concentration RCGW-1	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00	14-Apr-00
AROMATICS MIXTURE											
VPH ($\mu\text{g/L}$)											
C5-C8 Aliphatics, Adjusted	300	34	350	ND (100)	486	ND (50)	320	ND (20)	168	ND (50)	510
C9-C12 Aliphatics, Adjusted	700	230	2300	ND (100)	365	130	1300	40.7	ND (100)	66	850
C9-C10 Aromatics	200	190	1900	213	2140	150	1800	160	2560	210	2400
Methyl tert-butyl ether	70	ND (5)	ND (10)	ND (5)	ND (5)	ND (5)	ND (25)	ND (20)	ND (100)	ND (5)	ND (5)
Benzene	5	26	260	21.6	272	20	250	22.2	284	24	290
Toluene	1,000	27	270	23.9	302	22	270	21.8	277	24	300
Ethylbenzene	700	25	240	23.5	287	20	250	19.2	248	25	290
Xylenes, mixture	5,000	111	1150	77.4	811	91	1100	92.8	1144	69	860
Naphthalene	140	23	280	21.2	272	17	260	23.7	353	25	300

NOTES AND ABBREVIATIONS:

1. Bold values indicate an exceedance of Method 1 (ALIPHATIC) criteria.
 2. ND(2.5): Not detected; number in parentheses is the laboratory reporting limit.
 3. VPH: Volatile Petroleum Hydrocarbons
 4. Low level and high level spikes were prepared at 24 $\mu\text{g/L}$ and 300 $\mu\text{g/L}$, respectively, with each of the following 16 compounds: benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, sec-butylbenzene, tert-butylbenzene, isopropylbenzene, 4-isopropyltoluene, n-propylbenzene, 1,2,4-trimethylbenzene, styrene, 1,3,5-trimethylbenzene, n-butylbenzene, and naphthalene.
- Haley & Aldrich, Inc.

In the 2011 aromatic hydrocarbon study, adjusted C5-C8 aliphatic hydrocarbons were not detected in samples spiked at the 24 $\mu\text{g/L}$ level, and were detected at concentrations ranging from 295 to 620 $\mu\text{g/L}$ in samples spiked at the 300 $\mu\text{g/L}$ level. The C9-C12 aliphatic hydrocarbons were detected at concentrations ranging from 65 to 198 $\mu\text{g/L}$ in samples spiked at the 24 $\mu\text{g/L}$ level, and from 243 to 1,700 $\mu\text{g/L}$ in samples spiked at the 300 $\mu\text{g/L}$ level. A summary of the 2011 aromatic study results is presented in Table IV below:

TABLE IV
SUMMARY OF WATER QUALITY DATA

LABORATORY		F	F	G	G	H	H	J	J
SAMPLE DESIGNATION	MCP	HA-1 (OW)	HA-2 (OW)	HA-1 (OW)	HA-2 (OW)	HA-1 (OW)	HA-2 (OW)	HA-1 (OW)	HA-2 (OW)
PREPARATION DATE	Reportable Concentration RCGW-1	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11	04-Aug-11
AROMATICS MIXTURE									
VPH ($\mu\text{g/L}$)									
C5-C8 Aliphatics, Adjusted	300	ND (50)	295	ND (50)	ND (500)	ND (100)	620	ND (50)	374
C9-C12 Aliphatics, Adjusted	700	198	415	65	660	180	1700	ND (50)	243
C9-C10 Aromatics	200	196	330	170	1900	150	1600	189	1830
Methyl tert-butyl ether	70	ND (3)	ND (15)	ND (1)	ND (10)	ND (1)	ND (1)	ND (1)	ND (1)
Benzene	5	23.3	136	24	270	22	270	26.2	292
Toluene	1,000	23.6	88.1	24	280	22	270	26.1	292
Ethylbenzene	700	23.9	95.7	23	270	22	260	26	287
Xylenes, mixture	5,000	69.4	277.5	117	1380	66	770	107.8	1174
Naphthalene	140	19.7	158	24	290	22	270	21.1	271

NOTES AND ABBREVIATIONS:

1. Bold values indicate an exceedance of Method 1 (ALIPHATIC) criteria.
2. ND(2.5): Not detected; number in parentheses is the laboratory reporting limit.
3. VPH: Volatile Petroleum Hydrocarbons
4. Low level and high level spikes were prepared at 24 $\mu\text{g/L}$ and 300 $\mu\text{g/L}$, respectively, with each of the following 16 compounds: benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, sec-butylbenzene, tert-butylbenzene, isopropylbenzene, 4-isopropyltoluene, n-propylbenzene, 1,2,4-trimethylbenzene, styrene, 1,3,5-trimethylbenzene, n-butylbenzene, and naphthalene.
Haley & Aldrich, Inc.

The results of the study with aromatic hydrocarbon-spiked samples confirm that common aromatic volatile organic compounds are also reported as VPH aliphatic hydrocarbons. In general, approximately 2.7 mg/L of total target and non-target aromatic hydrocarbons may result in reported C5-C8 and C9-C12 aliphatic hydrocarbons that exceed one or more MassDEP Method 1 risk criteria. The data also indicate that of the 16 compounds spiked, only benzene and toluene elute in the C5-C8 aliphatic hydrocarbon retention time range, yet even the method adjustment to remove these two target compounds from this range often resulted in a remainder that is reported as C5-C8 aliphatics. The target compounds ethylbenzene and xylenes, as well as the alkylated benzenes, elute in the C9-C12 aliphatics retention time range. The method adjustment to remove these target compounds and non-target compounds from this range often resulted in a remainder that is reported as C9-C12 aliphatics. In addition, it appeared that styrene coelutes with o-xylene for several of the laboratories in each of the two studies, such that the o-xylene (and total xylenes) concentration may be overestimated if styrene is present. Example VPH chromatograms of the aromatic reference material mixture are shown on Exhibit 3 below:

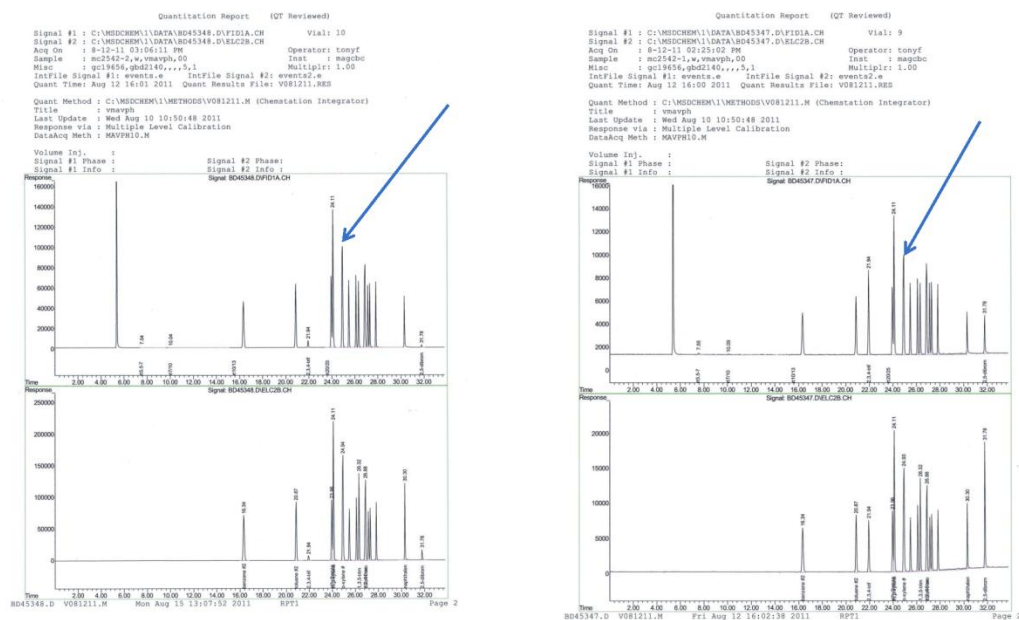


Exhibit 3: Example VPH chromatograms of the aromatic reference material mixture. Peaks highlighted by arrows suggest possible coelution of styrene with o-xylene.

The most probable explanation for this “remainder effect” after adjustment is that the target compounds are calibrated on the PID from a calibration standard that is comprised of the actual target compounds themselves. The response factors that are used to calculate target compound concentrations are compound-specific on the PID. Although the FID responds to these target compounds as well, their contribution to the aliphatic range concentration is based on the general aliphatic range response factor and not on the compound-specific response factor used on the PID. It is this difference in the response factors utilized between the two detectors that can account for a residual contribution to the aliphatic range concentration.

Case Study

While environmental professionals and LSPs conducting comprehensive reviews of analytical data for VPH and VOCs have previously identified and corrected some of the instances when false positives were reported, the findings of these studies were more dramatically confirmed in a recent Massachusetts case study. During MCP response actions, concentrations of 1,2-dichloroethane were detected in a monitoring well in excess of 500,000 $\mu\text{g/L}$, which exceeds the 100,000 $\mu\text{g/L}$ MCP Upper Concentration Limit (UCL) for this compound. VPH analysis of the same sample indicated the presence of C5-C8 aliphatics in excess of 175,000 $\mu\text{g/L}$, which exceeds the 100,000 $\mu\text{g/L}$ UCL for this aliphatic range. The laboratory data were CAM Compliant with acceptable QC, and non-conformances were not reported. Additional comprehensive review of the data indicated that the detection of (and UCL exceedance for) C5-C8 aliphatic hydrocarbons in the VPH analysis was solely due to the presence of 1,2-dichloroethane. Case Study chromatograms for CAM Method 8260 and VPH are shown on Exhibit 4-6 below:

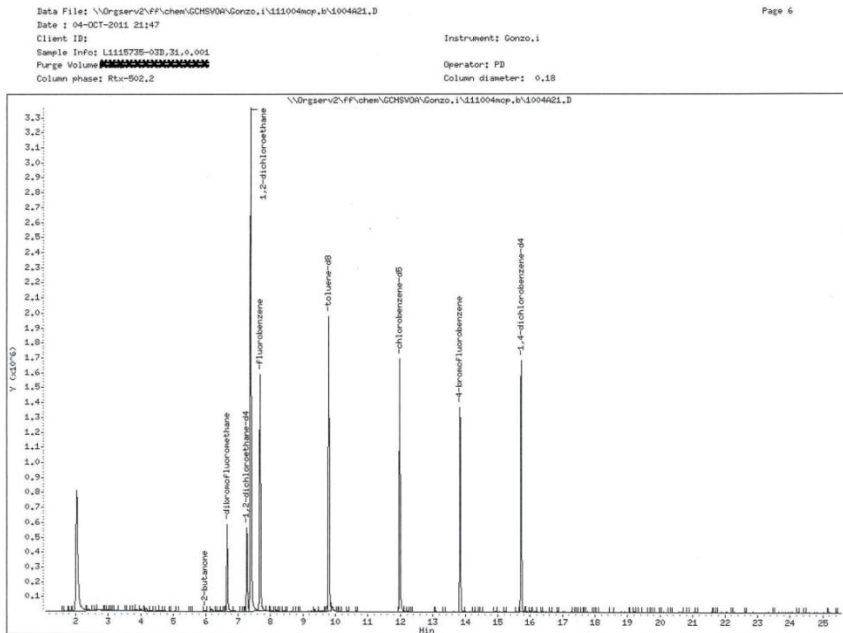
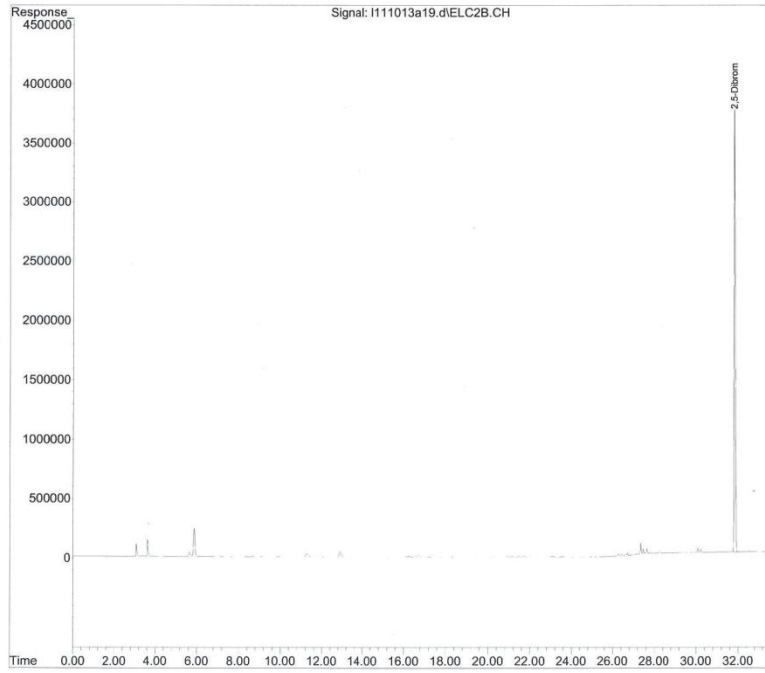


Exhibit 4: Case Study chromatogram for CAM Method 8260.



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Exhibit 5: Case Study PID chromatogram for VPH.

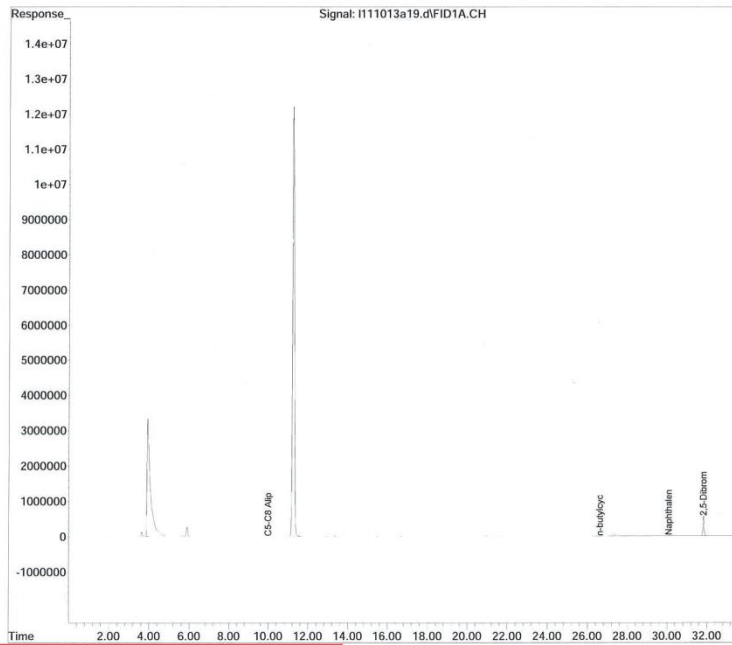


Exhibit 6: Case Study FID chromatogram for VPH.

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As a result of this review, the laboratory reissued the report and adjusted the C5-C8 aliphatic data for VPH by subtracting the native sample Method 8260 result for 1,2-dichloroethane, resulting in an updated C5-C8 aliphatics VPH result that was appropriately “Not Detected.” The laboratory also documented and narrated these data adjustments in its revised report. The LSP was technically justified in instructing the laboratory to do this, as described in more detail below.

Strategies for Managing VPH Data When Interferences are Suspected

MassDEP has long been aware of the interferences identified in these studies, there are regulatory provisions that justify data adjustments (including subtraction) if these interferences are appropriately demonstrated. For example, the MCP specifically defines the VPH aliphatic carbon ranges as shown below (bold emphasis added):

***C₅ through C₈ Aliphatic Hydrocarbons** means the cumulative concentration of all aliphatic hydrocarbon compounds with boiling points greater than 36EC and less than 150EC, as measured by chromatographic methods approved by the Department or equivalent procedures, excluding the individual compounds listed at 310 CMR 40.0974(2).*

***C₉ through C₁₂ Aliphatic Hydrocarbons** means the cumulative concentration of all aliphatic hydrocarbon compounds with boiling points equal to or greater than 150EC and less than 217EC, as measured by chromatographic methods approved by the Department or equivalent procedures, excluding the individual compounds listed at 310 CMR 40.0974(2).*

Therefore, if the individual compounds listed at 310 CMR 40.0974(2), such as 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, or for example, methyl ethyl ketone, were detected by CAM Method 8260 and demonstrated to interfere with VPH carbon range results, the concentrations of these compounds could be subtracted from the appropriate C5-C8 or C9-C12 aliphatic carbon range results.

The MCP specifically defines the C9-C10 aromatics range as shown below (bold emphasis added):

***C₉ through C₁₀ Aromatic Hydrocarbons** means the cumulative concentration of all aromatic hydrocarbon compounds with boiling points greater than 169EC and equal to or less than 218EC, as measured by chromatographic methods approved by the Department or equivalent procedures, excluding the individual compounds listed at 310 CMR 40.0974(2).*

The subtraction allowance does not apply to the VPH C9-C10 aromatics. The CAM Method 8260 individual target compounds sec-butylbenzene, tert-butylbenzene, isopropylbenzene, 4-isopropyltoluene, n-propylbenzene, 1,2,4-trimethylbenzene, styrene, 1,3,5-trimethylbenzene, and n-butylbenzene are not listed among the MCP Method 1 standards listed at 310 CMR 40.0974(2). Simply stated, it would not be acceptable for an LSP to subtract the individual concentrations of these specific Method 8260 target compounds from the collective VPH result

for C9-C10 aromatics, since they are themselves alkylated benzenes and are therefore C9-C10 aromatic compounds.

Alternative Method

As described above, the current VPH methodology is a GC method that differentiates the aromatic and aliphatic fractions by their differing responses to the FID and PID. The identification of specific compounds and carbon ranges in the analytical method is determined by the retention time on the GC column, such that non-petroleum compounds with the “right” retention times can be reported as petroleum-related constituents. To address this potential confounding of VPH analytical results, an alternative VPH methodology has been proposed by MassDEP. The alternative method is currently under review and is based on GC/MS, similar to the MassDEP Air-Phase Petroleum Hydrocarbon (APH) analytical method.

The GC/MS method for analysis of VPH is capable of better distinguishing non-petroleum compounds. As with APH, it is expected that this method would specify that all peaks eluting in a given range, petroleum hydrocarbon-related or not, be summed and reported. Also consistent with the APH practice, the user could direct the analytical laboratory to review and separate out peaks that are not petroleum-related compounds and reduce the corresponding reported data values to account for these non-target compounds. The excluded compounds would be categorized as tentatively identified compounds and noted in the report narrative.

Summary

The results of the study with halogenated ethane-spiked samples confirm that common halogenated ethanes are reported as VPH aliphatic hydrocarbons. Approximately 1 mg/L total halogenated ethanes (comprised of the common chlorinated solvents such as 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and ‘daughter products’) may result in reported C5-C8 aliphatic values that exceed one or more MassDEP MCP Method 1 risk criteria. Our review of the chromatograms suggests that low boiling halogenated ethanes (such as vinyl chloride) are not expected to interfere with the VPH analysis and that less common, higher boiling halogenated ethanes (such as 1,1,2,2-tetrachloroethane) will elute in the higher boiling point C9-C12 aliphatic hydrocarbon range.

The results of the study with aromatic hydrocarbon-spiked samples confirm that common aromatic volatile organic compounds (BTEX and alkylated benzenes) are also reported as VPH aliphatic hydrocarbons. Approximately 2.7 mg/L of total target and non-target aromatic hydrocarbons may result in reported C5-C8 and C9-C12 aliphatic hydrocarbons that exceed one or more MassDEP MCP Method 1 risk criteria. Although benzene and toluene were the only compounds that elute in the C5-C8 aliphatic hydrocarbon retention time range, even the method adjustment to remove these two target compounds from this range often resulted in a remainder that is reported as C5-C8 aliphatics. The target compounds ethylbenzene and xylenes as well as the non-target alkylated benzenes elute in the C9-C12 aliphatics retention time range and the method adjustment to remove these target compounds and non-target compounds from this range often resulted in a remainder that is reported as C9-C12 aliphatics.

In addition, styrene may coelute with o-xylene. The results for o-xylene (and therefore, total xylenes) may be biased high by the concentration of styrene, if present.

Based on the results of these studies, the authors conclude that VPH analysis can result in “false positive” results under certain conditions, such as when common chlorinated solvents are present. By inference, the presence of other non-target VOCs (e.g., methyl ethyl ketone) could also result in false positive VPH results. This interference may even be great enough to trigger a reporting condition or other MCP response actions for VPH. Since the VPH analytical method does not include a requirement to narrate “qualitative” matters such as peak patterns, environmental professionals can opt to review GC chromatograms and supporting data with their laboratories when VPH interference is suspected in environmental samples. Environmental professionals can also employ Method 8260 in instances where VPH interference is suspected. Although this hypothesis was not tested as part of our 2000 and 2011 studies, the authors believe that the EPH method may be similarly susceptible to false positives. Accordingly, EPH data should also be reviewed by environmental professionals and their laboratories when interferences are suspected.

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James Occhialini serves as an Alpha Analytical Vice President of Technical Sales and the National Account Manager for ecological/human health risk assessment and dredging project applications. Jim has almost 35 years of environmental analytical and consulting experience working on a wide range of project applications including ecological and human health risk assessment; dredging; site characterization and remediation; analytical method development; and data usability evaluation. Jim is very active with a number of regulatory workgroups and industry associations and frequently participates in Alpha Analytical webinars and as a presenter or trainer on numerous technical topics. Jim provides extensive project-level technical support in the areas of sediment and tissue analysis; data interpretation and usability; sampling and analytical method selection; and quality assurance/quality control.