

Atlantic RBCA

Guidelines for Laboratories

**Tier 1 and Tier 2 Petroleum Hydrocarbon
Methods**

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Disclaimer

This document provides guidelines for the analysis of Petroleum Hydrocarbons in water and soil as part of Atlantic RBCA site remediation methodology. It is not intended to be a detailed laboratory procedure, but rather to outline required and performance-based elements of any method used.

This document was created by the PIRI Analytical Laboratory Sub-committee in response to terms of reference outlined by the Atlantic PIRI committee. The document is still under peer-review, and as such is will be a continually evolving document as experience with the method and various sample types increases.

A detailed method with specific laboratory procedures that can be used to meet these guidelines will be available in the near future.

Atlantic RBCA Guidelines for Laboratories - Tier 1 and Tier 2 Petroleum Hydrocarbon Methods

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1.0 Method Overview

The Atlantic RBCA petroleum hydrocarbon methods consist of two procedures:

- 1) An initial evaluation method that assesses whether the total petroleum hydrocarbon (TPH) concentration minus BTEX has exceeded a *generic* risk-based screening level (known as a "Tier 1 RBSL").
- 2) An aromatic/aliphatic fractionation method that provides additional information on the nature of the total petroleum hydrocarbons within various carbon number ranges.

Note: Carbon number ranges are established based on gas chromatographic elution times of straight chain n-alkane standards. The elution time for an n-alkane is largely dependent on its boiling point (with the GC columns specified by this method). A C12 substituted aromatic may elute later than the n-C12 alkane due to boiling point and structural differences. Consequently, this compound would not be quantified in the same range as the alkanes having twelve carbon atoms, but rather within the >C12 - C16 range.

These methods will be referred to as "Tier 1" and "Tier 2" methods respectively and this document provides required elements for both methods, thereby helping to ensure inter-laboratory comparability. The methods are as closely aligned as possible to ensure the best possible data comparability and to enhance the efficiency of the sample preparation steps.

The Tier 1 and Tier 2 methods share the feature that they are each divided into two separate procedures, namely volatile (VPH) and extractable (EPH) petroleum hydrocarbon analyses. For water samples, the VPH is obtained by direct purge and trap GC/MS or headspace GC-PID/FID analysis of the sample. The EPH is measured by hexane extraction with a GC-FID analysis. For soil samples, the VPH is measured using a purge and trap GC/MS or headspace GC-PID/FID analysis of a methanol extract of the soil. The EPH is obtained by acetone:hexane extraction and GC-FID analysis. Because different Tier 1 criteria exist for potable and non-potable ground water usage, laboratories may need to develop two Tier 1 methods: i) a "low level" method for BTEX and ii) a "standard" method.

The Tier 2 method differs from the Tier 1 method in that separate concentrations are reported for aromatic and aliphatic compounds. This is accomplished through changes in the particulars of the data treatment for VPH if a GC/MS was used initially or through reanalysing the sample by GC/MS if a GC-PID/FID was used. The EPH analysis for Tier 2 differs from Tier 1 in the processing of the hexane extract prior to GC-FID analysis. These differences will be elaborated in the text.

1.1 Alternative Techniques

Note that a headspace inlet may be used as an alternative to purge and trap for VPH analysis in both Tiers 1 and 2 providing QC criteria are met (Section 6). As well, a combination photoionization/flame ionization detector (PID/FID) may be used as an alternative to GC/MS in Tier 1 VPH only. Use of GC-PID/FID for Tier 2 VPH analyses may be allowed in future if it can be demonstrated that the ability to provide an optimum combination of sensitivity and selectivity

against aliphatic responses is not a limiting factor. At present, these guidelines do not permit the use of GC-PID/FID for Tier 2 evaluations.

1.2 Calibration Standards

In order to maximize inter-laboratory data comparability, two defined mixtures of compounds are used as the primary calibration standards. The Atlantic RBCA VPH and EPH standards contain the aliphatic and aromatic compounds listed in Appendix 1.

These mixtures can also be used as retention time window-setting standards.

1.3 Surrogate Standards

The VPH analysis is monitored by addition of iso-butylbenzene as a surrogate, which also serves as a retention time marker. Iso-butylbenzene and dotriacontane are used as surrogates and retention time markers for the EPH analysis. Surrogate percent recoveries should be in the 70-130 % range and if outside this range, re-analysis is required.

1.4 Quality Control Standards

The Atlantic RBCA EPH standard is to be used to verify the quality control of the EPH fractionation procedure (i.e. column separation check mixture). Restek gasoline (or equivalent) is used as a QC standard for the VPH analysis and Restek diluent transformer oil (or equivalent) is used for the EPH analysis. See Section 6 for additional details.

2.0 Volatile Petroleum Hydrocarbons (VPH)

2.1 VPH Sample Preparation

Soil: Samples should be collected in glass jars with Teflon lined lids and kept cold. A representative portion of soil (e.g. 10 g) is placed into a 40 mL P&T vial and a known volume (e.g. 10 mL) methanol is added by the laboratory within 72 hours of receipt. A known volume of iso-butylbenzene surrogate (dissolved in methanol) is also added. The samples are then sonicated and/or mixed by shaking to ensure complete dispersion of the soil into the methanol.

Water: Samples should be collected in 40 mL purge and trap vials and preserved in the field (e.g. pH < 2 or equivalent) if desired. No air space should remain in the vials. Sampling in duplicate is advised to allow for dilutions if needed. A known volume of iso-butylbenzene surrogate (dissolved in methanol) is added prior to analysis.

2.2 Purge and Trap and Headspace

Laboratories are free to establish the operating conditions for their purge and trap and headspace methods, providing that they can meet quality assurance criteria (Section 6). Specific conditions have not been set for parameters related to the purge and trap concentrator. A Supelco J trap (or equivalent) is probably the most suitable type of trap, as it allows the use of large amounts of methanol (up to approximately 2 mL in 40 mL of water).

2.3 GC Conditions

Only DB-1, DB-5, or DB-624 (or other manufacturers' equivalent) capillary columns are permitted for VPH analysis. Note that elution order differences exist between the phases, but these have no effect when the iso-butylbenzene surrogate is used as a retention time marker.

Specifically, DB-624 and thick film DB-5 columns exhibit the retention order n-C10 < 1,2,4-trimethyl benzene < iso-butylbenzene, while DB-1 and thin film DB-5 columns have the elution order 1,2,4-trimethyl benzene < n-C10 < iso-butylbenzene. Integration to just before the start of the iso-butylbenzene surrogate peak ensures that 1,2,4-trimethyl benzene is included in the same range as n-C10 in all cases.

2.4 MS Conditions

A scan range of m/z 40 to approximately m/z 200 must be used to ensure that total RFs (and Tier 1 total purgeable RFs) are representative. This is because the single component total ion current (TIC) responses for aliphatics are much more similar to the TIC responses for aromatics when the m/z 41, 43 aliphatic ions are included in the scan.

Typical VOC analytical procedures have scans to m/z 45 in order to exclude carbon dioxide (m/z 44) and argon (m/z 40) background. Scanning to m/z 40 causes these background ions to be detected, raising the chromatographic baseline, but the advantages outweigh this disadvantage.

2.5 Analysis with GC-PID-FID

As an alternative to GC/MS, GC-PID-FID may be used to measure VPH for Tier 1 assessments, where the PID is used to measure the concentrations of BTEX. PIDs are prone to interference from aliphatic compounds. A 9.6 eV lamp can be used to reduce the interference but a great deal of sensitivity is lost compared to the more common 10.0 to 10.6 eV lamps. Therefore, GC/MS must be used for Tier 2 VPH analyses until such time that data can be provided to the Analytical Sub-Committee demonstrating equivalent results with a PID.

2.6 Definitions of VPH Target Analytes

The following compounds and ranges are determined as part of VPH analyses:

Tier 1	Tier 2
Benzene Toluene Ethylbenzene Xylenes	Benzene Toluene Ethylbenzene Xylenes
C6 - C10 Hydrocarbons	Aromatic >C8 - C10 Aliphatic C6 - C8 Aliphatic >C8 - C10

Ranges quoted refer to all compounds of a given type which have retention times within the boundaries given. Descriptors such as C6, C8, etc. refer to the retention times of the normal

hydrocarbons n-hexane, n-octane, etc. Descriptors such as >C8 refer to all compounds eluting after, but not including, C8. If a descriptor does not have a > or < sign, then that n-alkane is included in the range.

The starting point of the iso-butylbenzene surrogate peak defines the limits of all retention time ranges ending in C10. For all practical purposes the end point of the C10 or 1,2,4-trimethylbenzene peak (depending on the GC column being used) is the starting point of the iso-butyl benzene peak and the C6 - C10 range is measured accurately using this approach.

2.7 Integration and Calibration of VPH Target Compounds

The BTEX compounds are calibrated as target compounds with an expected retention time (plus or minus an acceptance range). For GC/MS analysis, a quantification ion and two qualifying ions (which must fall within an acceptable relative abundance range) or >80% match to calibration reference spectra are used to confirm identity. For GC/PID/FID, BTEX concentrations are measured using the PID trace.

The Atlantic RBCA VPH standard is used as primary calibration standard for all BTEX compounds. Thus all BTEX calibration curves may be derived from one standard.

For GC/MS, quantification and qualifier ions are as follows:

Compound	Quant. Ion, m/z	Qual. 1, m/z	Qual. 2, m/z
Benzene	78	77	50
Toluene	91	92	65
Ethylbenzene	91	106	65
Xylene(s)	91	106	105

Note 1: For compound identification, the relative abundance acceptance range for each qualifying ion should be set at ± 20 % relative deviation (or less) from the expected relative abundance. Each laboratory should determine the expected relative abundance of the qualifying ions, as mass spectrometer temperature and scan parameters can influence them. Relative abundance values from reference spectra (such as NIST or Wiley library spectra) should be considered as approximate only.

Note 2: The retention time of a peak must not be more than $\pm 2\%$ relative deviation from the expected retention time in order for the response to be assigned to the target compound. Retention times must be verified at least once each day that analysis is performed and updated as necessary.

Note 3: Xylene(s) refers to the sum of all three isomers (note Atlantic RBCA VPH standard contains only o- and p- isomers).

2.8 Integration and Calibration of VPH Hydrocarbon Ranges

2.8.1 VPH - Tier 1 C6 - C10 Range (GC/MS)

Determine the Response Factor (RF) for the Total Purgeable C6 - C10 Hydrocarbons by integration of the TIC of all 12 components in the Atlantic RBCA VPH standard (4 n-alkanes +

BTEXX + 3 other aromatics). Begin integrating from just before the start of the n-C6 peak and ending just before the start of the iso-butylbenzene surrogate peak. (Note the restrictions on scan range outlined in **2.4 MS Conditions**). To obtain the RF, divide the sum of the concentrations of all 12 components by the TIC area.

For samples, calculate the C6-C10 Hydrocarbon concentration using the formulas in Section 4.3.

2.8.2 VPH - Tier 1 C6 - C10 Range (GC/PID/FID)

Determine the Response Factor (RF) for the Total Purgeable C6 - C10 Hydrocarbons by integrating (using baseline hold) the FID chromatogram of all 12 components in the Atlantic RBCA VPH standard (4 n-alkanes + BTEXX + 3 other aromatics). Begin integrating from just before the start of the n-C6 peak and ending just before the start of the iso-butylbenzene surrogate peak. To obtain the RF, divide the sum of the concentrations of all 12 components by the FID area.

For samples, calculate the C6-C10 Hydrocarbon concentration using the formulas in Section 4.3.

2.8.3 VPH - Tier 2 Aromatic >C8 - C10 Range

Integrate m/z 78, 91, 104, 105, 106, and 120 extracted ion chromatograms beginning just after the end of the n-C8 peak and ending just before the start of the iso-butylbenzene surrogate peak. Sum all of these areas. Determine an average RF by dividing the total concentration of the standard aromatic components in this range (sum of ethyl benzene, p-xylene, o-xylene, 1-methyl-3-ethyl benzene, 1,3,5-trimethyl benzene, and 1,2,4-trimethyl benzene concentrations) by the area sum.

For samples, calculate the Aromatic >C8 - C10 concentration using the formulas in Section 4.3.

2.8.4 VPH - Tier 2 Aliphatic Ranges

Because there are too many selected ions that are needed to adequately capture all possible aliphatic compounds, the aliphatic ranges are calculated either from TIC areas that exclude aromatic components, or from total hydrocarbon concentration less the applicable aromatic concentrations.

For Tier 2 analysis, determine two separate Response Factors (RF) for the Total Purgeable C6 - C8 and >C8 - C10 Hydrocarbons. For the first range, begin integrating the TIC of the Atlantic RBCA VPH standard just before the start of the n-C6 peak and end just after the n-C8 peak. For the second range, integrate the TIC of the components from just after the n-C8 peak to just before the start of the iso-butylbenzene surrogate peak. To obtain the RFs, divide the sum of the concentrations of the components in each range by the TIC areas.

These RFs are used differently in the C6 - C8 and >C8 - C10 ranges. In the first case, the C6-C8 Aliphatic concentration is obtained by multiplying the C6 - C8 Total RF by the TIC area of all peaks in the range excluding benzene and toluene. (Note, however, that benzene and toluene are included in the calculation of the C6 - C8 RF).

In the second case, due to the larger number of aromatic peaks in the >C8 - C10 range, the approach of using TIC areas with selected components excluded is not practical. Thus, the >C8 - C10 Aliphatic concentration is obtained by calculating an intermediate Total >C8 - C10 Hydrocarbon concentration (TIC area of the range multiplied by the >C8 - C10 Total RF) and subtracting the sum of the concentrations of all >C8 - C10 Aromatics. (See Section 4.3 for details of the calculations).

3.0 Extractable Petroleum Hydrocarbons (EPH)

3.1 EPH Sample Preparation

Soil: Soil samples should be collected in glass jars with Teflon lined lids and kept cold. A well-mixed portion of soil (e.g. 5 to 10 g) is placed into a 40 mL P&T vial and a known volume of iso-butylbenzene/dotriacontane surrogate (dissolved in dichloromethane) is added. Then a known volume (e.g. 10 to 15 mL) of 50:50 (v/v) acetone:hexane is added and the sample is mixed by vigorous shaking. Extraction times must be evaluated to ensure full recovery of the EPH with actual samples from the field.

The sample must be fully dispersed after the shaking period. Samples that are not fully dispersed using this procedure (i.e. hard clays) should be extracted first by vigorous shaking with acetone only. The hexane is then added and the samples are vigorously shaken once again.

A portion of the extract is then washed with deionized water to remove the acetone and concentrate the organics in the hexane layer. The volume of water used should be at least 5 times the volume of acetone being removed.

Water: Water samples should be collected in 250 mL or 1 L glass bottles fitted with Teflon lined caps. Unless the client specifies otherwise, if the sample contains more than 5% (v/v) sediment (visual examination), the sample should be decanted prior to extraction and a comment flag added to the report.

The water is acidified to pH<2 (optional), spiked with a small volume (e.g. <100 µL) of iso-butylbenzene/dotriacontane surrogate standard (dissolved in dichloromethane) and extracted by mixing with n-hexane. Extraction conditions must be validated to ensure quantitative recovery of the EPH. The extract may be concentrated under nitrogen at room temperature to a known volume in order to achieve detection limit criteria.

3.2 EPH Aromatic/Aliphatic Fractionation

The primary acceptance criterion for column separation of the aromatic and aliphatic EPH fractions is demonstration of separation of the components of the Atlantic RBCA EPH standard (plus iso-butylbenzene added) with less than 20 % carryover of any compound into the alternate fraction. This should be demonstrated on a once per batch basis as part of method QC. Note that since the Atlantic RBCA EPH standard contains a significant fraction of dichloromethane in the solvent, a 1 in 100 dilution of this standard in hexane (i.e. 10 µg/mL in each component) is recommended for use.

Laboratories may use silica gel or alumina to perform the column separation method provided QC criteria are met. An example method using silica gel is provided here:

- Prepare silica gel columns by placing a glass wool plug and 7 mL of activated silica gel into a glass chromatography column. Add 1 mL of sodium sulphate to the top of the column. (Note: commercially available columns may also be used).
- Wash the prepared silica gel column twice with n-hexane and transfer 1 mL of sample extract onto the silica gel column. Elute the sample with small volumes of hexane and collect the

eluent from the column. Add the minimum volume of hexane required to elute all of the aliphatic components.

- Remove the sample collection tube and replace it with a new tube. Elute the column with small volumes of 50/50 (v/v) dichloromethane/acetone until all of the aromatic components have been removed from the column.
- Concentrate the aromatic and aliphatic extracts under nitrogen at room temperature to a known volume sufficient to achieve the required detection limit criteria. Analyse the extracts separately by capillary column GC-FID.

3.3 EPH GC Conditions

Only DB-1 and DB-5 (or other manufacturers' equivalent) capillary columns are permitted for this analysis. A flame ionization detector (FID) is used to detect and quantify the components.

3.4 Definitions of EPH Target Analytes

The following ranges are determined as part of EPH analyses:

Tier 1	Tier 2
<p>>C10 - C21 Hydrocarbons >C21 - <C32 Hydrocarbons</p>	<p>Aromatic >C10 - C12 Aromatic >C12 - C16 Aromatic >C16 - C21 Aromatic >C21 - <C32</p> <p>Aliphatic >C10 - C12 Aliphatic >C12 - C16 Aliphatic >C16 - C21 Aliphatic >C21 - <C32</p>

Ranges quoted refer to all compounds of a given type which have retention times within the boundaries given. Descriptors such as C12, C16, etc. refer to the retention times of the normal hydrocarbons n-dodecane, n-hexadecane, etc. Descriptors such as >C21 refer to all compounds eluting after, but not including, C21. If a descriptor does not have a > or < sign, then that n-alkane is included in the range.

The integration of >C10 begins just after the end of the iso-butylbenzene surrogate peak. This component elutes just after decane and is not included in the >C10 - <C32 ranges. The C10 descriptor is retained for simplicity.

Similarly, the integration of the >C21 - <C32 ends just prior to the start of the C32 peak. This single component is also used as a surrogate and it is not included in the >C21 - <C32 range. Again, the C32 descriptor is retained for simplicity.

3.5 Integration and Calibration of EPH Tier 1 Ranges

Determine the Response Factor (RF) by integrating (using baseline hold) the FID chromatogram of the components in the Atlantic RBCA EPH standard (mixture of n-alkanes + PAHs - see Appendix). Begin integrating just after the end of the iso-butylbenzene peak until just after the end of the C21 peak. Divide the sum of the concentrations of the 6 components in the >C10 - C21 range by the FID area to obtain the >C10 - C21 extractable RF.

Then integrate from just after the end of the C21 peak to just before the start of the C32 peak. Divide the sum of the concentrations of all components in the >C21 - <C32 range by the FID area to obtain the >C21 - <C32 extractable RF.

To calculate total hydrocarbon concentration for a specific range, determine the total area of the FID chromatogram for the carbon number range and multiply it by the RF for that range.

3.6 Integration and Calibration of EPH Tier 2 Aromatic and Aliphatic Ranges

Integrate the FID chromatograms for the aromatic fractions beginning just after the end of the iso-butylbenzene surrogate peak to just after the end of the C12 peak, (>C10 - C12). Then integrate from that point to just after the end of the C16 peak (>C12 - C16) and similarly for the C21 (>C16 - C21) and C32 peaks (>C21 - <C32). Determine an average RF within each aromatic range by dividing the total concentration of the standard aromatic components within each range by the area. To calculate the total aromatic concentration for any given range, determine the total area of the FID chromatogram for the retention time range of interest and multiply it by the RF established for the range.

Repeat the above procedure for the aliphatic fractions using the aliphatic standard components within each range. (Alternatively, response factors may be derived from the average of aromatic and aliphatic compounds in each range, and the same RF used for calculation of both fractions, provided that the instrument response factors for aromatics and aliphatics are quite similar.)

4.0 Calculations and Reporting

4.1 Tier 1 Reporting Format

Report the following analytes and surrogates for Tier 1 analyses (mg/L for waters; mg/kg (dry weight basis) for soils, and state % moisture).

Benzene
Toluene
Ethylbenzene
Xylenes
C6 - C10 Hydrocarbons
>C10 - C21 Hydrocarbons
>C21 - <C32 Hydrocarbons
Modified TPH (Tier 1)
% Rec. iso-butylbenzene – Volatile
% Rec. iso-butylbenzene – Extractable
% Rec. n-dotriacontane – Extractable

- Notes:
1. Xylenes refers to the total of o-, m-, and p- isomers
 2. C6 - C10 Hydrocarbons does not include BTEX
 3. Modified TPH (Tier 1) = (C6 - C10) + (>C10 - C21) + (>C21 - <C32)
(does not include BTEX)

4.2 Tier 2 Reporting Format

Report the following analytes and surrogates for Tier 2 analyses (mg/L for waters; mg/kg (dry weight basis) for soils, and state % moisture).

Benzene
Toluene
Ethylbenzene
Xylenes
Aromatic >C8 - C10
Aromatic >C10 - C12
Aromatic >C12 - C16
Aromatic >C16 - C21
Aromatic >C21 - <C32
Aliphatic C6 - C8
Aliphatic >C8 - C10
Aliphatic >C10 - C12
Aliphatic >C12 - C16
Aliphatic >C16 - C21
Aliphatic >C21 - <C32
Modified TPH (Tier 2)
% Rec. iso-butylbenzene – Volatile
% Rec. iso-butylbenzene –
Extractable
% Rec. n-dotriacontane –
Extractable

Notes:

1. Xylenes refers to the total of o-, m-, and p- isomers
2. Aromatic >C8 - C10 does not include ethylbenzene or xylenes
3. Modified TPH (Tier 2) = sum of all aliphatic + aromatic ranges (does not include BTEX)

4.3 Calculations

4.3.1 VPH in Water

For all individual compounds and ranges, calculate the concentration in the water sample as follows:

$$\text{Conc. (mg/L)} = \text{Area} * \text{RF} * \text{DF}$$

Where: **Area** is the appropriate integrated area of the peak or range (see 2.7 or 2.8)
RF is the appropriate response factor of the peak or range (see 2.7 or 2.8)

DF is the dilution factor, if required.

Note that standard concentrations must be expressed in mg/L of water.

In the case of the Tier 1 and Tier 2 >C8-C10 ranges, this calculation results in intermediate concentrations only (not reported). To obtain the reported concentrations, the following calculations must be performed (subtract concentrations indicated):

$$\text{C6 - C10 Hydrocarbons} = [\text{Total Purgeables}] - [\text{BTEX}]$$

$$\text{Aromatic >C8 - C10} = [\text{Total Aromatic >C8 - C10}] - [\text{E}] - [\text{X}]$$

$$\begin{aligned} \text{Aliphatic >C8 - C10} &= [\text{Total >C8 - C10}] - [\text{Total Aromatic >C8 - C10}] \\ &= [\text{Total >C8 - C10}] - [\text{Aromatic >C8 - C10}] - [\text{E}] - [\text{X}] \end{aligned}$$

4.3.2 VPH in Soil

In the case of soil samples, results must be expressed on a dry weight basis. The measured instrumental concentration must be converted to a soil concentration. Factors to be considered include the wet weight of soil analysed, the percent moisture, the volume of methanol used for extraction and analysis and the dilution effect caused by moisture in the soil mixing with the methanol used for extraction. Calculate concentrations in dry soil as follows:

$$\text{Conc. (mg/kg)} = \frac{\text{Area} * \text{RF} * \text{Vol (water)} * \text{Vol (total)}}{\text{Vol (aliquot)} * \text{Ww} * (100 - \%M)/100}$$

Where: **Area** is the appropriate integrated area of the peak or range (see 2.7 or 2.8)

RF is the appropriate response factor of the peak or range (see 2.7 or 2.8)

Vol (water) is the volume of water solution (mL) which contains the extract aliquot (after dilution for analysis)

Vol (total) is the Total Extract Volume in mL (= Methanol added to soil + water extracted). Calculate this as:

$$\text{Vol (total)} = \text{Vol (methanol)} + [\text{Ww} * \%M/100 \div 1 \text{ g/mL}]$$

Vol (methanol) is the volume of methanol added to the soil sample

%M is the percent moisture determined from a separate aliquot of soil

Vol (aliquot) is the volume of extract (methanol + entrained water, mL) taken for dilution and analysis

Ww is the *wet weight* (g) of sample extracted (the term **(100-%M)/100** corrects this to equivalent dry weight)

Note that standard concentrations must be expressed in mg/L of water.

In the case of the Tier 1 and Tier 2 >C8-C10 ranges, this calculation results in intermediate concentrations only (not reported). To obtain the reported concentrations, the following calculations must be performed (subtract concentrations indicated):

$$\text{C6 - C10 Hydrocarbons} = [\text{Total Purgeables}] - [\text{BTEX}]$$

$$\text{Aromatic } >\text{C8} - \text{C10} = [\text{Total Aromatic } >\text{C8} - \text{C10}] - [\text{E}] - [\text{X}]$$

$$\begin{aligned} \text{Aliphatic } >\text{C8} - \text{C10} &= [\text{Total } >\text{C8} - \text{C10}] - [\text{Total Aromatic } >\text{C8} - \text{C10}] \\ &= [\text{Total } >\text{C8} - \text{C10}] - [\text{Aromatic } >\text{C8} - \text{C10}] - [\text{E}] - [\text{X}] \end{aligned}$$

4.3.3 EPH in Water

For all ranges, calculate the concentration in the water sample as follows:

$$\text{Conc. (mg/L)} = \frac{\text{Area} * \text{RF} * \text{Vol (final)} * \text{DF}}{\text{Vol (sample)}}$$

Where: **Area** is the appropriate integrated area of the range (see 3.5 or 3.6)

RF is the appropriate response factor of the range (see 3.5 or 3.6)

Vol (final) is the final volume of extract (mL)

DF is the dilution factor, if required.

Vol (sample) is the volume of water extracted (mL)

Note that standard concentrations must be expressed in µg/mL of hexane.

4.3.4 EPH in Soil

In the case of soil samples, results must be expressed on a dry weight basis. The measured instrumental concentration must be converted to a soil concentration. Factors to be considered include the wet weight of soil analysed, the percent moisture and the volume of hexane (the acetone is removed by water washing) used for extraction. Calculate concentrations in dry soil as follows:

$$\text{Conc. (mg/kg)} = \frac{\text{Area} * \text{RF} * \text{Vol (hexane)} * \text{DF}}{\text{Ww} * (100 - \%M) / 100 * \text{CF}}$$

Where: **Area** is the appropriate integrated area of the range (see 3.5 or 3.6)

RF is the appropriate response factor of the range (see 3.5 or 3.6)

Vol (hexane) is the volume (mL) of *hexane* added to the soil (*not* volume of hexane:acetone)

DF is the dilution factor, if required.

Ww is the *wet weight* (g) of sample extracted (the term **(100-%M)/100** corrects this to equivalent dry weight)

%M is the percent moisture determined from a separate aliquot of soil

CF is the concentration factor from volume reduction of the extract, if required

Note that standard concentrations must be expressed in µg/mL of hexane.

4.3.5 Modified TPH

In order to compare analysis results with the Atlantic RBCA lookup tables, Total Petroleum Hydrocarbons must be reported as “Modified TPH”, that is, TPH less BTEX. Thus,

$$\text{Tier 1 Modified TPH} = (\text{C6} - \text{C10}) + (>\text{C10} - \text{C21}) + (>\text{C21} - <\text{C32})$$

(note that the C6 - C10 range does not include BTEX)

$$\text{Tier 2 Modified TPH} = \text{sum of all aliphatic} + \text{aromatic ranges}$$

(does not include BTEX)

4.3.6 Surrogate Recovery

Percent recoveries of surrogates are to be calculated and included on the final report.

5.0 Petroleum Hydrocarbon Resemblance Comments

The terms "Gas", "Diesel / #2" and "#6 Oil" appear along with corresponding modified TPH values in the Tier 1 look up table. The modified TPH (C6 - <C32 less BTEX) concentration in the sample is compared to the values found in this table and the nature of the contaminant on the site determines whether the Gas, Diesel / #2 or #6 Oil value is used. For example, if the principal product contaminating the site is gasoline, then the Gas criteria are used. Analytical reports from laboratories must accurately specify the nature of the detected contaminants.

To ensure data comparability between laboratories, the following resemblance comments should be used to describe the type(s) of petroleum contamination detected. It should be noted that this process of assigning a petroleum source type to the observed contamination is subjective and the identification is not always definitive.

5.1 Gasoline

Characteristics of gasoline include a boiling range that ends at approximately C10 - C12, with most of the mass fraction being in the C6 - C10 range; the presence of the BTEX compounds; the presence of C3- and C4- alkyl substituted benzenes and the presence of additives such as methyl-tertiary-butyl ether (MTBE, detectable by purge and trap analysis of water). If gasoline contamination is suspected, the sample chromatogram should be directly compared to a solution of gasoline analysed under the same conditions as the sample. Based on this comparison, the following resemblance comments could be made:

GASOLINE FRACTION. This indicates close similarity to the gasoline standard both in terms of the constituent compounds and their approximate relative ratios. Note, however, that significant differences exist between manufacturers, grades, and seasons of production, so this comment should be applied in a very general way.

WEATHERED GASOLINE. This indicates that some of the gasoline constituents have been partially or entirely removed relative to the fresh gasoline standard. Typical weathering patterns include relatively low (or absent) volatile constituents (i.e. an apparent increase in the relative amount of the heavier compounds) due to evaporation; selective removal of the more water-soluble (BTEX) constituents by water washing or microbial action, etc.

UNIDENTIFIED PRODUCT IN THE GAS RANGE. This indicates that the contamination corresponds approximately to the C6 - C10 range, but that it contains considerably different constituents from gasoline or very unusual relative ratios. Examples of this type of contamination would be petroleum-based cleaning solvents, aviation gas and refinery process streams.

5.2 Diesel Fuel/Furnace Oil

Diesel fuel, in this context, refers to a general class of petroleum distillate fuels. In fact, a large number of variations exist (diesel #1, diesel #2, home heating oil, marine diesel, etc.) which are not treated separately here.

In general, diesel fuel corresponds to a boiling range of approximately C8 to C24, or higher, with most of the mass fraction in the C10 - C21 range (note that some BTEX may also be present). It is characterized in the GC-FID analysis by a prominent “hump” of unresolved compounds underlying a series of individually resolved compounds that includes the n-alkanes and some highly specific branched alkanes. These “biomarkers” include pristane (prominent peak just after n-C17), phytane (peak just after n-C18), nor-pristane (elutes between n-C16 and n-C17) and farnesane (elutes between n-C14 and n-C15). These biomarkers are excellent indicators of the presence of petroleum-derived products, even if other features are not present.

Following direct comparison of sample contamination to a reference chromatogram of diesel analysed under the same conditions, the following comments may be applied:

FUEL OIL FRACTION. This indicates close similarity to the diesel standard both in terms of the constituent compounds and their approximate relative ratios. Note, however, that the different types of distillate fuels have different boiling ranges (i.e., n-alkane at beginning and end), different maximum points for the “hump” of unresolved compounds, and differences in the most abundant n-alkane. As a result, this comment should be applied in a very general fashion.

WEATHERED FUEL OIL FRACTION. This indicates that some of the fuel oil constituents have been partially or entirely removed relative to the fresh fuel oil standard. Typical weathering patterns include relatively low (or absent) volatile constituents (i.e. an apparent narrowing and shift of the maximum point of the “hump” towards the heavier compounds) due to evaporation; selective removal of the n-alkanes by microbial action, etc

UNIDENTIFIED PRODUCT IN THE FUEL RANGE. This indicates that the contamination corresponds principally to the C10 - C21 range, but that it contains considerably different constituents from diesel or very unusual relative ratios. An example of this type of contamination would be very heavily weathered diesel fuel that has lost all identifying features or a relatively low boiling mineral oil.

5.3 #6 Fuel Oil/Lubricating Oil

In general, these oils are distillate products with heavier boiling ranges than diesel fuel (mainly in the C21 - C32 range). The heavy fuel oils generally exhibit an unresolved “hump” of a large number of compounds, which may begin well before C21 and end after C32. They also have resolved features such as n-alkanes, but pattern matching of these oils can be very difficult due to relatively wide boiling ranges.

Lubricating Oils, in contrast to heavy fuel oils, have few or no individually resolved peaks (n-alkanes are partially or totally removed), and may have relatively narrow boiling ranges. A large number of possible products exist (motor oils, gear oils, mineral oils, etc.) and these can have considerably different boiling ranges.

Because specific identification of heavy oils is very difficult, and because no additional information is needed to apply the look up tables, the following comment should be applied in all cases:

LUBE OIL FRACTION.

5.4 Unidentified Peaks

In some cases, a relatively small number of peaks may be observed which do not appear to be similar to distillate products (no “hump”, n-alkanes or biomarkers) or other known petroleum products. The following comment should be used:

UNIDENTIFIED PEAKS IN THE C6 - C10 (or C10 - C21 or C21 - C32) RANGE(S). This comment indicates that the contamination observed could not be clearly attributed to a petroleum product. An example of the use of this comment would be the presence of fatty acids derived from vegetation or other chemical contaminants such as plasticizers or PAHs.

If the unidentified peaks are not included in the calculated results, this should be clearly stated in the comment, otherwise it is assumed that they are included. An example would be:

UNIDENTIFIED PEAKS IN THE C10 - C21 RANGE (NOT QUANTIFIED)

5.5 Mixtures

In the case where more than one type of contamination is present, the best estimate of its composition should be given in the comment, for example:

WEATHERED FUEL OIL FRACTION, LUBE OIL FRACTION

Mixtures are sometimes difficult to evaluate and, as a consequence, can be the cause of differences of opinion between analysts.

6.0 Quality Assurance and Quality Control

- 6.0.1** All response factors from initial calibration curves for individual components and ranges must have a relative standard deviation of $\pm 15\%$. Alternatively, a correlation coefficient criterion (e.g. 0.995 or better) may be established. Five-point curves are recommended.
- 6.0.2** Calibration curves must be verified when prepared through the use of second source standards. Commercially available BTEX and PAH mixtures can be used in this application.
- 6.0.3** Continuing calibration standards must be run at least every 12 hours of GC run time. The responses of individual components and ranges must be within $\pm 30\%$ of the calibration curves.
- 6.0.4** Method blanks should be prepared on a once-per batch basis (up to 20 samples per batch) for all analyses. Blank levels must be less than reporting limits, otherwise the analysis must be repeated or the reporting limit raised to the blank level.

- 6.0.5** GC sequences should contain a method blank or solvent blank for every 5 to 10 sample injections.
- 6.0.6** Because individual component standards are used for calibration, the linear ranges determined for the standard concentrations are not directly applicable to petroleum product concentrations. As a result, a sample response should be considered outside the linear range when the height of any peak in the sample is greater than the height of the highest standard. In these cases, the sample should be diluted and reanalysed.
- 6.0.7** Method detection limits for ranges should be determined as part of initial method validation using low concentrations of petroleum products, not the individual component standards used for calibration.
- 6.0.8** Each laboratory shall maintain a standard operating procedure with detailed descriptions of the particulars of the method as routinely applied. This documentation must also include method validation data, including statements of linearity, precision, accuracy, and method detection limits.
- 6.0.9** Matrix Spikes or Blank Spikes (Process Spikes) should be prepared on a once per batch basis (up to 20 samples per batch) using the gasoline or transformer oil QC standards. Recovery of the products must be in the range of 70 to 130 %.
- 6.0.10** For all samples, recovery of the iso-butylbenzene and n-dotriacontane surrogates should be in the range of 70% to 130%. Otherwise the sample should be prepared once again and reanalysed.

6.1 Tier 2 EPH Column Fractionation

- 6.1.1** Prepare a 1 in 100 dilution of the Atlantic RBCA EPH standard (i.e. 10 µg/mL in each component) in hexane as a column fractionation check standard. In addition, include iso-butylbenzene in this solution, as under certain conditions the separation efficiency of alkylbenzenes may be significantly different from those of the PAH compounds in the Atlantic RBCA EPH standard.
- 6.1.2** On a once-per batch basis, verify that all of the aliphatic and aromatic components of the column fractionation check standard (diluted Atlantic RBCA EPH standard plus iso-butylbenzene) are separated in to their respective fractions with no more than 20% carryover into the opposite fraction.
- 6.1.3** All of the aliphatic and aromatic components of the column fractionation check standard should be recovered in the range of 70% to 130% of the expected concentration.
- 6.1.4** For all samples, recovery of the iso-butylbenzene and n-dotriacontane surrogates should be in the range of 70% to 130% in the aromatic and aliphatic fractions, respectively.

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Appendix 1**Atlantic RBCA Standards**

Volatiles (in methanol)		Extractables (in hexane/DCM - 85%/15%)	
Aromatic	Aliphatic	Aromatic	Aliphatic
Benzene	Hexane (C ₆)	Naphthalene	Decane (C ₁₀)
Toluene	Heptane (C ₇)	Acenaphthene	Dodecane (C ₁₂)
Ethylbenzene	Octane (C ₈)	Anthracene	Hexadecane (C ₁₆)
o-Xylene	Decane (C ₁₀)	Chrysene	Heneicosane (C ₂₁)
p-Xylene		Benzo(a)Pyrene	Octacosane (C ₂₈)
1-methyl-3-ethylbenzene			Dotriacontane (C ₃₂)
1,2,4-Trimethylbenzene			
1,3,5-Trimethylbenzene			