Technical Support Memorandum:

Total Petroleum Hydrocarbon Fractionation

This memo supplements Fact Sheet #12 and describes the methods for determining total petroleum hydrocarbon (TPH) fractions and the development of fraction clean up levels for the VRP.

I. Introduction

The use of risk assessment for hydrocarbon contamination is made more difficult because of the extremely complex composition of most hydrocarbon-based products. These are mixtures of hundreds or thousands of different chemical compounds each of which will have its own toxicology. At present, reliable analysis of all the different components present is impossible for most fuels and there is not a sufficiently large database of risk factors available even if the analysis could be performed.

For this reason the approach which has evolved is to separate the fuel into an “aliphatic” portion, an “aromatic” portion, and sometimes a “polars” portion based on general chemical similarities of these types of compounds, and using an “aggregate” risk factor for different molecular weight ranges of these fractions. Several analytical methods have evolved that allow this analysis.

This technical support memorandum will present which of the available analytical methods can be appropriately used in the State of Wyoming and the reporting and sampling requirements that will assure the data used is reliable and appropriate for the intended purpose of screening and risk assessment. A second part of the technical support memorandum is to provide generic cleanup levels that can be used for screening TPH fractions.

II. Applicability of TPH Fractionation

If all applicable contaminants of concern are below their respective soil cleanup levels , as selected in Fact Sheet #12, (assuming adequate report limits), but TPH values are not, then TPH fractional analysis could be performed to establish what risk the remaining TPH above cleanup levels may pose. The volunteer should consult with the DEQ project manager if interested in TPH fractionation.

III. TPH Fractionation Analytical Methods

The analytical methods available for use are as follows, in order of preference:

1. Massachusetts Method
2. New Jersey Method
3. State of Washington Method
4. Texas Method

Whichever analytical method is proposed, the following Quality Control is required:

1. Calibration per method
2. Extraction procedure per method
3. Surrogates per method
4. MS/MSD and LCS per method
5. Naphthalenes breakthrough test per the Massachusetts or New Jersey Methods
6. Fractionation surrogate check per the Massachusetts or New Jersey Methods
7. Chromatographic mass discrimination check per the Massachusetts or New Jersey Methods
8. Control windows for recoveries must be per the Massachusetts or New Jersey Methods, or laboratory statistical windows, whichever is narrower.
9. The carbon ranges to be reported are as follows:

Fraction	Method
C5 through C8 Aliphatic Hydrocarbons	VPH Method
C9 through C18 Aliphatic Hydrocarbons	EPH Method
C19 through C36 Aliphatic Hydrocarbons	EPH Method
C9 through C10 Aromatic Hydrocarbons	VPH Method or EPH Method
C11 through C22 Aromatic Hydrocarbons	EPH Method

The following items must be included in the report of results, in addition to the normal laboratory report of results:

1. Case Narrative, which must include any deviations from the method other than those required by Wyoming.
2. Method blank results
3. LCS recoveries
4. MS/MSD recoveries as applicable
5. Surrogate recoveries
6. Recoveries of fractionation surrogates
7. Naphthalenes breakthrough test results
8. Chromatographic mass discrimination check results
9. Chromatograms of all samples, standards, and blanks

IV. Cleanup Levels

The cleanup levels were developed using Wyoming VRP Factsheet #12 instructions and toxicological data from the 2002 Massachusetts Toxicity Values for Petroleum Hydrocarbon Fractions.

Contaminant	Residential Soil (mg/kg)	Migration to Groundwater (mg/kg)	Water Cleanup Levels (ug/L	Source of data
GRO	-	59	7300	GRO or VPH sum
DRO	2300	-	1100	DRO or EPH sum
Fractions				
Aliphatic C5-C8	3100	21	1500	VPH C5-C8 aliphatics
Aliphatic C9-C18	7800	240000	3700	EPH C9-C18 aliphatics
Aliphatic C19 - C32	160000	960000	73000	EPH C19-C36 aliphatics
Aromatic C11-C22	2300	15000[a]	1100	EPH C11-C22 aromatics
Aromatic C9-C10	2300	3400[a]	1100	VPH C9-C10 aromatics

[a] Cleanup level based on an estimated fuel-water partitioning factor (Kfw=4000) in the fate and transport evaluation.

V. Summary

Using the analytical methodology and cleanup values above, the TPH fractions for a site may be analyzed for and compared to cleanup levels, assuming TPH fractionation is applicable for the site. The volunteer should contact the VRP Project Manager for further guidance.

References

See TPH Fractionation Study – Final Report References (Appendix A)

Appendix A : TPH Fractionation Study – Final Report

GATEWAY ENTERPRISES

Technical Consulting Report
Final

Dec. 18, 2014

Report To: Ben Luckey
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Wyoming Department of Environmental Quality
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Cheyenne, WY 82002

Subject: WDEQ Project Number 05SC0205604 – TPH Fractionation Study – Final Report

Prepared by: John G. Huntington, Ph.D.
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Note: This is a revision due to an error in the value for the C5-C8 aliphatic recommended lookup table limits in the original report. No other changes have been made.

Executive Summary

This report consists of two parts. The first part is a review of appropriate TPH fractionation analytical methods, and the conclusion of that portion of the report is that Wyoming should adopt the Massachusetts method, unmodified. A set of reporting requirements is also provided that will allow DEQ to have confidence in the data.

The second part of the report is a discussion of the approach to construct risk-based soil limits (RBSLs) using the soil fractionation approach proposed. Lookup table values are calculated and provided in the report. Several issues give rise to an excessively conservative value for some of the aromatic fractions, when the standard Wyoming model is applied. Several potential ways in which this problem can be resolved are presented, and a recommendation is given.

Background and Request.

The use of risk assessment for hydrocarbon contamination is made more difficult because of the extremely complex composition of most hydrocarbon-based products. These are mixtures of hundreds or thousands of different chemical compounds each of which will have its own toxicology. At present, reliable analysis of all the different components present is impossible for most fuels and there is not a sufficiently large database of risk factors available even if the analysis could be performed.

For this reason the approach which has evolved is to separate the fuel into an "aliphatic" portion, an "aromatic" portion, and sometimes a "polars" portion based on general chemical similarities of these types of compounds, and using an "aggregate" risk factor for different molecular weight ranges of these fractions. Several analytical methods have evolved that allow this analysis.

Part of the task is to determine which of the available methods can be appropriately used in the State of Wyoming and to develop reporting and sampling requirements that will assure the data used is reliable and appropriate for the intended purpose of risk assessment. A second part of the task is to provide a guide to incorporate such analytical results into the Wyoming risk assessment strategy.

Part 1 - TPH Fractionation Analytical Methods

Summary of Methods and Method Differences

Terminology.

There is often some confusion about the different terminology in use related to "total petroleum hydrocarbons (TPH)." Different terms are used by different workers, sometimes referring to the same analytical concept and sometimes not.

TPH is actually a concept rather than a specific analyte or group of analytes. It refers to the concentration of organic material derived from petroleum sources that is measured by some "perfect" method. No such perfect method exists, and different approaches are employed for different purposes.

Regulatory agencies recognize this and have modified the terms in use to refer more to the analytical approach taken. Many of the methods here described use the term "extractable petroleum hydrocarbons" or EPH. Also in common term is "diesel range organics", or DRO, and "residual range organics", or RRO. These two terms refer to organic material that elute in what is considered to be a typical carbon number range for diesel or heavier oils, respectively. Each of these ranges are defined by carbon number and are often slightly different in different methods. In this document we will use the terms employed by the methods under discussion.

Theoretical Concepts.

It is important to understand the basic theoretical concepts behind the various methods, in order to grasp what is feasible and what is not feasible, and to understand where the methods can fail.

There are a very great number of approaches that have been used to estimate "total petroleum hydrocarbons (TPH)." These include infrared spectroscopic methods[1], liquid chromatographic separation methods[2], gas chromatographic (GC) methods using a variety of detectors[3], most commonly flame detection (FID), extraction/gravimetric methods, various colorimetric methods, immunoassay, HPLC, and a large number of others[4].

Hydrocarbons can be detected and characterized by a range of analytical techniques, which accounts in part for the great diversity of approaches for analysis. In addition, there is a long history of hydrocarbon analysis associated with the oil and gas and refining industries that were designed to characterize hydrocarbons to assist with exploration and refining.[5, 6]

All of these different approaches are presented by their advocates as having certain qualities that make them superior, or at least appropriate for certain situations. However, none are entirely satisfactory in all situations.

Complexity of the Task

Petroleum and petroleum products consist of extremely complex mixtures of organic chemicals (some of which are not hydrocarbons in the strict sense of the word[7]. This fact makes determination of TPH a daunting analytical task. This is particularly true because each one of these chemicals has its own properties, and interacts with the matrix (water, soil, air) in its own particular way.

To analyze total petroleum hydrocarbons in precisely the same manner that other individual environmental contaminants is done would require developing an analysis for each individual compound, conducting that analysis in an appropriate manner for the given matrix, and then summing the total of all the compounds detected. Since there are often many thousands of individual chemicals in fuels, distributed in different ways in the sample matrix, this is an impossible task with current technology.

For this reason, TPH methods are "aggregate" methods in which multiple organic compounds are analyzed as a group by some type of general detector. Because of this, the methods are by definition only capable of estimates, not measurements of well-defined accuracy and precision when applied to unknown mixtures.

It follows that any methods to determine additional analytical detail, such as estimating total aromatic hydrocarbon or total aliphatic hydrocarbon contributions to a given sample for which these methods have been used to estimate the TPH, will also produce estimates. This fact should always be kept in mind when using such data.

To be sure, such estimates can be rather good, depending on the specific nature of the contamination and the methods employed. For instance, there is no reason to be overly concerned about the accuracy and precision of a DRO (diesel range organics) analysis for a known diesel spill. However, if such an analysis is conducted in a location in which a large concentration of biomass is present (which can interfere), or if the original contamination is from some fuel mixture very different from diesel (such as #6 fuel oil), the estimate may not be nearly as good and can be significantly biased, or else not provide a very accurate "TPH" result.

Current Approaches

The most common approach used today for determining TPH is the use of GC/FID combined with various cleanup procedures. This approach is thought to be appropriate for hydrocarbon

mixtures from approximately C-6 to approximately C-36. Note that the carbon number range normally refers to the straight chain paraffin (n-alkane) carbon number. The carbon number of other kinds of organic molecules that appear in these ranges can be very different.

The method begins with an extraction to separate the organics from the matrix. There are two types of extraction in common use, purge and trap and solvent extraction. Purge and trap is used for volatile hydrocarbons (gasoline-range hydrocarbons, approximately C6-C10), and solvent extraction for C10+ mixtures.

Many other approaches to deal with this step have been developed, including headspace analysis, distillation, pyrolysis, and supercritical extraction methods. However, very few laboratories have the appropriate equipment or experience with such approaches and data comparability across methods has usually not been demonstrated.

For the solvent extraction step, the choice of solvent can be important, depending on the sample matrix and the nature of the contamination. The most commonly-used solvent is methylene chloride, chosen because it has a good combination of solvent properties and low boiling point so that it can be separated from the extracted organics by a distillation concentration step. Other solvents, such as hexane, pentane, chloroform, and carbon disulfide have been employed in some methods. Each has advantages and disadvantages.

The combination of GC and FID is used for analysis primarily because the FID is very linear in its response to hydrocarbons, and the GC allows the separation of molecules from one another so that a chromatographic profile can be obtained which is rich in information about the particular mixture being analyzed.

The flame ionization detector works by accepting sample and carrier gas from the column and passing it through a hydrogen-air flame. Organic molecules, particularly hydrocarbons, alcohols, and ethers, produce positively-charged ions on combustion. A polarizing voltage attracts these ions to a collector located near the flame, and an electrical current is produced. The current is amplified and digitized in order to measure the response. Because of the specific ion chemistry that occurs in the flame and on the path to the collector, it turns out that these kinds of molecules give responses that are essentially directly proportional to the amount of carbon in the molecule[8]. This is very useful for determination of aggregate concentrations when standards are not available for each compound.

In contrast, detectors like the photoionization detector (often used for field measurements and used to determine individual compounds in methods such as SW-846 8021)[9], do not work as well for aggregate analysis because their response is very different for different structures of organic molecules. Therefore, these detectors are not typically used for such measurements in the laboratory[10].

The mass spectrometer detector (MS) is also used for this purpose at times. As is well known, this detector has the ability to gather much more structural information. It is also relatively

linear with carbon number if the total ion response is used rather than individual masses. This is because it also depends on the formation of positive ions, this time generated by electron impact, which is approximately linear for many molecules (the response is proportional to the cross-sectional area of the molecule, which is in turn roughly proportional to the carbon number)[11]. This detector is not used as often as FID, in part because it is more likely to suffer performance degradation due to contamination of the analytical system and therefore requires more maintenance.

For most purposes, both of these approaches (FID and MS) should be regarded as reasonably equivalent if the laboratory has a robust and properly calibrated method that they are using.

Separation and Analysis of Structural Types in TPH

There are many approaches that have been taken to separating and quantifying structural types in hydrocarbon analysis. Historically, the petroleum industry pioneered a number of these. ASTM 1319, for example, involves the separation of aromatics from aliphatic hydrocarbons using silica gel and visualization of the result with a fluorescent indicator. ASTM D5186 is a method to determine the aromatics content of diesel fuel using supercritical fluid chromatography. It involves elution of hydrocarbons from a silica gel column using supercritical carbon dioxide with FID detection.[12] It is capable of separating the aliphatics, monoaromatics, and polynuclear aromatics as groups from one another.

For the volatile fraction of TPH obtained by purge and trap analysis, the structural complexity is sufficiently low that a reasonable estimate can be obtained using direct identification of targets, at least in the C6-C10 region. This is not the subject of this discussion.

For the C10+ range, the most common approach today is to use silica gel to separate the aromatic fraction of compounds from the aliphatic fraction (similar to the ASTM 1319) procedure, followed by separate GC/FID analysis of both fractions. GCMS is frequently used if more structural detail is desired, such as PAH speciation.

Technical Discussion of Silica Gel

Silica gel is prepared by acidification of a solution of sodium silicate, followed by isolation and drying of the precipitated silica. The product has a very high surface area due to porosity and it has properties that can be finely tuned by variations of the manufacturing process.[13]

The material is used in chemical applications primarily due to its ability to sorb organic and inorganic molecules of various types. It has been used for many years as a solid phase in liquid and gas-phase chromatography due to these properties.

It is useful for separating hydrocarbons of various types. Its ability to sorb hydrocarbons and other organic molecules depends on number of different factors, including the polarity of the molecules, but not only that factor. For example, benzene and pentane are both nonpolar molecules, but benzene is more strongly sorbed by silica gel. This is in part because benzene is

more “polarizable” and can have polar characteristics induced by proximity to the silica gel surface.

Without going into detail, the separation of molecules by silica-gel chromatography depends on the strength of sorption to the silica gel, which is reliably a function of structure, and the tendency of an eluting solvent to dissolve (or solvate) the same molecule. Thus it involves a thermodynamic balance between sorption and solvation. By progressively changing the solvent properties during the chromatographic process, different structures of organics can be eluted from the silica gel column and separation by structural type can thus be achieved.

The Massachusetts Method (MADEP-EPH-4)

General Characteristics of the Method

In the 1990’s The Massachusetts Department of Environmental Quality began developing an approach for determining aliphatic and aliphatic fractions of TPH (more precisely, EPH, or extractable organic hydrocarbons). The most recent revision of this method was issued in 2004 and is the most widely cited method for this purpose.[14]Almost all other methods designed for aliphatic/aromatic separations cite this one as their primary reference.

The Massachusetts method is well-researched and has a high level of detail to guide the laboratory in applying the method. It is generally considered one of the most developed of the available methods and is typically used as the standard to which other methods can be compared. It has specific requirements for QA/QC and specific requirements for reporting. This method has also been extended to a method specific for air-phase analysis (APH). Most environmental standards manufacturers sell standard mixtures developed specifically for this method, and equipment suppliers provide silica gel cartridges made to meet the requirements of the method.

There are a number of steps within this method and methods similar to it that can be particularly susceptible to problems and can produce biased results. A few of these are as follows:

1. The method requires that the methylene chloride extract originally produced in the extraction step be exchanged into hexane. This is an essential step, because any significant amount of methylene chloride solvent remaining will cause potentially large bias in the silica gel separation step. The laboratory must be diligent in ensuring that this exchange is done properly.
2. The separation of aliphatic and aromatic requires the silica gel to be properly activated and that it not be overloaded with excessive levels of organics. Either improper activation or excessively high levels of organics charged to the column can produce biased results due to breakthrough of the aromatic fraction into the aliphatic fraction.
3. Proper performance of the method requires that an analyst be trained in the proper technique for liquid gravity column chromatography. It is relatively easy to allow channels in the column which will have a similar impact as overloading the column, producing biased results.

4. If there are high levels of organic interferences present in the samples, these can impact column performance even though the laboratory calculates the proper loading to use based on the best data available. For example, high levels of natural materials or petroleum may be present that are outside the carbon number range of the detected TPH, but which still has an impact on the column capacity. Such issues are relatively unlikely, but can occur in certain situations.
5. Some oils of petroleum origin contain percentage levels of substances called asphaltenes. These are not typically present in refined fuels because they are converted to other substances in the refinery. However, if they are present they are likely to precipitate in the hexane exchange step. If there are sufficient levels these can occlude levels of other hydrocarbons or simply cause physical difficulty in isolating the extract properly for the silica gel column.

In short, the method can result in biased results due to a variety of potential problems. It is important that the laboratory report sufficient QC data that the data user can make an informed decision about the likelihood of such problems. Any unusual observations or notes by the laboratory are also much more important in this analysis than in simple GRO/DRO/RRO analysis.

Key Requirements of the Massachusetts Method

A summary of the key specifications of the method are listed below. These are generally designed to ensure that the results of the method are accurate, and in particular that the silica gel separation was successful.

The method also allows the use of Method 8270 to determine the PAH targets from the same extract. Further, GCMS can be used instead of GC/FID. The specifications are altered somewhat when GC/MS is used. For instance, an internal standard calibration is used and the naphthalene+2-methylnaphthalene breakthrough is performed on all samples, not just the LCS/LCSD.

Method Specification	Matrix	Requirement
Extraction	Aqueous	SW-846 methods including continuous, separatory funnel or microextraction
	Solids	Soxhlett, Pressurized fluid extraction, microwave extraction, and microscale extraction; Ultrasonic allowed only for high-level waste; Waste dilution for free products
C9-C19 aliphatics	All	Elutes between n-Nonane and n-Nonadecane
C18-C36 aliphatics	All	Elutes between n-nonadecane and hexatriacontane
C11-C22 aromatics	All	Elutes between naphthalene and benzo (g,h,i) Perylene

Method Specification	Matrix	Requirement
Calibration model	All	External standard calibration using calibration factors or linear regression, minimum 5 points, %RSD limit 25% if calibration factor used
Calibration checks	All	Every 20 samples and at end of sequence, upper limit for %D is 25%
Surrogate standards	All	Limits are 40-140% recovery. Recommended surrogates are chlorooctadecane and o-terphenyl
Fractionation Surrogate	All	Added to extract just prior to extraction to monitor effeciency of extraction. Recommended surrogate is 2-bromonaphthalene, recovery limits 40-140%
LCS/LCSD required	Aqueous	40-140%, RPD < 20
	Solids	40-140%, RPD < 30
Breakthrough of naphthalene and 2-methylnaphthalene (LCS)	All	< 5% of the sum of the two compounds
Type of calibration standard	All	Synthetic aliphatic mix and synthetic aromatic mix
GC criteria	All	n-nonane resolved from solvent front; surrogates must be resolved from any compounds in the standard mixes; baseline separation required of individual compounds in mixes except for 2 PAHs. A Mass discrimination check is required to ensure that there is no bias related to the carbon number.

Reporting Requirements

The Massachusetts method has specific reporting requirements. These include the following:

- Laboratory Method Blank Results
- Laboratory Control Sample Results
- LCS Duplicate Sample Results
- Matrix Spike Results (only if requested by data user)
- Matrix Duplicate Results (only if requested by data user)
- Fractionation Check Standard Results
- Surrogate Spike Recoveries (for all field samples and QC samples), including fractionation and extraction surrogates
- Percentage of total naphthalene and 2-methylnaphthalene concentrations detected in the aliphatic fractions of the LCS and LCS Duplicate

Comparison to Other Methods

Texas TNRCC METHOD 1006

The Texas EPH method is TNRCC Method 1005, which is in place in final form[15]. The fractionation method is Method 1006, which is still provided as a draft and has a revision date of May, 2000[16]. There are major differences between the Texas method and the Massachusetts method. These are summarized below:

1. The Texas method uses n-pentane as the extraction solvent compared with methylene chloride in the Massachusetts method.
2. Extraction is performed by vortex mixing of aqueous samples. For solid samples, hand-shaking with 3 portions of pentane is allowed.
3. The Texas method requires no solvent exchange step since the extraction solvent is an alkane.
4. The Texas method is designed to allow analysis of hydrocarbons from C-6 to C-35 (based on n-alkanes) as opposed to the Massachusetts method, which is C-9 to C-36. Therefore the Texas Method encompasses more of the gasoline range as well as the DRO and RRO ranges.
5. Recommended surrogates are trifluoromethyl benzene or 1-chlorooctane for the nC_6 to nC_{12} range, and 1-chlorooctadecane, 2-fluorobiphenyl or o-terphenyl for the $>nC_{12}$ range (this is from Method 1005, which is referenced in Method 1006).
6. An aromatic fractionation check standard is required once each batch, but an aliphatic check standard is optional. Recovery limits are 60-140% and crossover is defined as "< 10-20%."
7. LCS and matrix spike recovery limits are set at 60-140% (for the MS/MSD, an RPD upper limit is set at 20%). No LCSD is required.
8. The method indicates that surrogate recoveries should be as per Method 1005, and in that method they are specified as 70-130% or laboratory established limits.

The Texas method is attractive because of its convenience. By using the lighter solvent, results including most of the gasoline range can be generated in a single analysis. However, the method states that it is best suited to oils up to the diesel range. Heavier oils are not expected to be analyzed with similar accuracy.

The absence of a fractionation surrogate is a drawback for this method, because there is no clear sample-by-sample indicator that the fractionation was successful. The crossover requirements are also rather wide and a separation with up to 20% of aromatics breakthrough would still be considered acceptable. This is much less control than the Massachusetts method specifies.

The use of n-pentane as the extraction solvent also means that the extraction efficiency may be reduced in some matrices, since it is less efficient at extraction of certain compound types, in particular heavier aromatics and polar compounds. The extraction protocol is also not very rigorous and in some matrices the extraction could be biased low.

Washington State Method for Determination of Extractable Hydrocarbon Fractions

This method was published in 1997, and has not been modified since that time[17]. The method is based on the Massachusetts method as it existed at that time, which was in draft form.

The method uses the same extraction solvent as the Massachusetts method, methylene chloride, and employs the same exchange for hexane prior to the fractionation step. However, this method allows sonication as the extraction approach for soils and the Massachusetts method does not. It also uses pentane rather than hexane to elute the silica gel column, and pentane serves as the solvent in the rest of the procedure.

This method provides more detail on the hexane-exchange procedure than does the Massachusetts method.

1. The surrogate acceptance range is 60-140%.
2. The LCS recovery range is 70-130%.
3. The Matrix spike recovery range is 70-130%.
4. The RPD limit for duplicates is 25%.
5. Aromatic breakthrough limits are not defined.
6. The aliphatic carbon number standard is different, comprising 7 alkanes from C-8 through C-34.
7. The aromatic standard also is different, comprising 6 compounds.
8. The standard ranges for reporting includes a more detailed breakdown than the Massachusetts method. The ranges start at C-8 rather than C-9 and end at C-34 rather than C-36.

If performed properly, this method should produce equivalent results to the Massachusetts method if the carbon number ranges reported are adjusted. Since some of the Massachusetts QC checks (for example injector port mass discrimination and aromatics breakthrough checks) are not a part of this method, it would be advisable in incorporate them if the method is used.

<u>New Jersey Extractable Petroleum Hydrocarbons Methodology</u>

New Jersey has a procedure which was last updated (Version 3) in 2010[18]. The method is also based on the Massachusetts method. Some of the differences are shown below:

1. The aliphatic hydrocarbon standard is similar to that used in the Massachusetts method except that it includes C-38 and C-40 alkanes. The Massachusetts method standard ends at C36. The aromatic hydrocarbon standard appears to be identical.
2. The carbon range markers are different for the New Jersey method. For aliphatic hydrocarbons, they include C9-C12, C12-C16 and C16-C21 ranges, as well as a C21-C40 range. The ranges used for the Massachusetts method are C9-C18 and C19-C36. The aromatic ranges are similarly divided up in more detail than in the Massachusetts method.
3. Recovery windows for the method are similar to those of the Massachusetts method.
4. Calibration protocols are similar.
5. The naphthalene breakthrough criterion is also used in the method.
6. The method also allows the use of GC/MS, identical to the Massachusetts method.

Essentially, if the carbon ranges used are adjusted to be consistent, the New Jersey method should give essentially identical results to the Massachusetts method.

Utah Fractionation Approach

Utah indicates that laboratories should obtain the data using Method 8270C, but provides no detail about how this should be done. This "method" does not appear to be an appropriate choice for Wyoming unless further detail is available about the procedures to be used.

Overall Methods Evaluation Summary

The Massachusetts and New Jersey methods are superior to the others evaluated here in terms of their required QC and fundamental specifications to ensure reproducible and accurate results. Both methods recognize the primary issues surrounding the silica gel separations and the gas chromatography and have incorporated safeguards into the methods to help alert data users to any problems in these areas.

The Washington State method is nearly as good and has the advantage that the use of pentane allows samples to be analyzed starting at C-8 as opposed to C-9 for the Massachusetts and New Jersey methods. However, it lacks some of the important QC requirements of the others and if used, it would be important that the laboratory introduce similar measures as part of their QC program.

The Texas method has merit in terms of its simplicity, but an important drawback is that it has never been finished. It is still in draft form. There are questions that arise concerning extraction efficiency in some matrices, and there is not nearly enough QC control measures similar to those used in the Massachusetts method.

In my view, in the hands of a competent laboratory, the method would work well for most situations. In the hands of an inexperienced analyst, however, biases are likely because of the lack of sufficient controlling QC requirements. It should be limited to cases where the nature of the contamination is known to be middle distillates. It should not be used in cases where heavy fuel oils or whole petroleum are considered to be likely candidates.

Laboratories may have modified any of these methods to improve upon them. For example, additional QC could be incorporated into a laboratory SOP for any of these methods and this would be allowed by the method. Because of this, I would recommend not prohibiting the use of any of these methods, instead specifying that such modifications be incorporated where appropriate. This can be done by including specific reporting requirements.

Specific Recommendations

I recommend that Wyoming DEQ control the data that it receives by specifying the reporting requirements for TPH speciation, as follows:

The methods available for use are as follows, in order of preference:

1. Massachusetts Method

2. New Jersey Method
3. State of Washington Method
4. Texas Method

Whichever method is used, the following QC is required:

1. Calibration per method
2. Extraction procedure per method
3. Surrogates per method
4. MS/MSD and LCS per method
5. Naphthalenes breakthrough test per the Massachusetts or New Jersey Methods
6. Fractionation surrogate check per the Massachusetts or New Jersey Methods
7. Chromatographic mass discrimination check per the Massachusetts or New Jersey Methods
8. Control windows for recoveries must be per the Massachusetts or New Jersey Methods, or laboratory statistical windows, whichever is narrower.
9. The carbon ranges to be reported are as follows:

Method	Carbon Range
MA EPH	C9 through C18 Aliphatic Hydrocarbons
MA EPH	C19 through C36 Aliphatic Hydrocarbons
MA EPH	C11 through C22 Aromatic Hydrocarbons

The following items must be included in the report of results, in addition to the normal laboratory report of results:

1. Case Narrative, which must include any deviations from the method other than those required by Wyoming.
2. Method blank results
3. LCS recoveries
4. MS/MSD recoveries as applicable
5. Surrogate recoveries
6. Recoveries of fractionation surrogates
7. Naphthalenes breakthrough test results
8. Chromatographic mass discrimination check results
9. Chromatograms of all samples, standards, and blanks

Volatile Range

In order to obtain all the ranges used by Massachusetts for regulatory purposes, the analysis must also include the aromatic and aliphatic composition of the volatile range. The EPH report specifications for the method do not include the C9-C12 aliphatic range nor the C9-C10 aromatic

range. Instead, this method provides the C9-C18 aliphatic range and the C11-C22 aromatic range.

The aliphatic C9-C12 aliphatic range might be dealt with simply as part of the C9-C18 aliphatic range available from the EPH analysis. However, the aromatic C9-C10 window is not reported using the standard Massachusetts method. Instead, this range of aromatics is obtained from the VPH analysis (MA DEP VPH). The method involves purge and trap analysis similar to standard GRO analysis, but with a photoionization detector (PID) used to obtain an estimate of the aromatics in the GRO range. The standard Massachusetts report provides C9-C10 aromatic hydrocarbons in addition to the C9-C8 and C9-C12 aliphatics.

This is only an estimated value because the PID becomes less selective for aromatics as the carbon number increases. Such an approach can produce a high bias for the C9-C10 aromatic range when there is a high concentration of aliphatic compounds that elute in the same window. The same carbon number range of aromatics is available in the EPH analysis, and is not susceptible to this problem, but Massachusetts has elected not to obtain the data from that analysis. This is presumably because of the potential for loss of this carbon number range during the evaporation of the solvent.

From an analytical standpoint this means that the C9-C10 aromatics range is probably the least well characterized by the Massachusetts approach.

The compounds in the C9-C10 aromatics range include C-3 and C-4 substituted benzenes, indanes and methyl indanes, tetralin, and naphthalene. All of these compounds are found in fuels at various levels.

My original concept was to avoid this problem by using the existing Wyoming approach to deal with the GRO range of hydrocarbons. However, given concerns raised in the course of this work, I have decided to include it in the risk assessment explicitly. This means that the Massachusetts VPH method will need to be used in addition to the EPH method. Laboratories that perform the EPH method also perform the VPH method, so this should not be a significant problem.

The carbon numbers to be reported by this method include the following:

Method	Carbon Range
MA VPH	C_9-C_{12} Aliphatic Hydrocarbons
MA VPH	C_9-C_{10} Aromatic Hydrocarbons

Other Analytes

In addition to the aliphatic and aromatic ranges specified above, the analysis needs at a minimum to include PAH targets and BTEX/naphthalene. This provides enough data to conduct the risk assessment.

Recommendation
My recommendation is that the Massachusetts method be specified for hydrocarbon fractionation analysis, and that the Massachusetts reporting forms be adopted by Wyoming for their use. I would allow other methods only if there can be a compelling reason shown to use a different method than the Massachusetts method.

In my opinion, however, the Massachusetts method is overly restrictive in not allowing the sonication procedure for extraction of soils. This would make some sense for non-hydrocarbons, which can be very strongly sorbed to soils and require more exhaustive extraction protocols. But for hydrocarbons, sonication is commonly used with success in many methods, and I would allow this type of extraction as a modification to the Massachusetts method, so long as the laboratory practices conform to the requirements listed in SW-846 Method 3550C (sonication extraction).

Part 2 – Implementation of TPH Fractionation Analysis in Wyoming

Strategy of Implementation
The aggregate fractions needed for risk assessment include the following.

Fraction	Method
C5 through C8 Aliphatic Hydrocarbons	VPH Method
C9 through C12 Aliphatic Hydrocarbons	EPH Method
C9 through C18 Aliphatic Hydrocarbons	EPH Method
C19 through C36 Aliphatic Hydrocarbons	EPH Method
C9 through C10 Aromatic Hydrocarbons	VPH Method or EPH Method
C11 through C22 Aromatic Hydrocarbons	EPH Method

There are multiple ways in which this additional characterization data can be used. Massachusetts has 3 protocols for this in their current regulation. These reflect different types of groundwater and soil situations, based in part on the likelihood of human exposure.

Differences in Carbon Number Ranges
There are some differences between carbon number ranges cited in various technical documents and regulatory requirements, compared to those obtained by the Massachusetts methods.

For example, Fact sheet #12 provides general definitions of GRO, DRO, and crude oil ranges, as follows:

- Gasoline and Condensate Range Organics (GRO): In general, includes C4 through C9 hydrocarbons

- Diesel Range Organics (DRO): In general, includes C10 through C24 hydrocarbons
- Crude Oil: In general, includes C5 through C34 hydrocarbon

Method 8015C, the SW-846 method on which most GRO and DRO methods are based, defines these differently, citing GRO as being C6-C10 and DRO being C10-C28. However, having made this definition, it then instructs the analyst to determine the GRO range using 2-methylpentane and 1, 2, 4-trimethylbenzene. This appears to be an internal inconsistency.

Other methods define "motor oil range organics" or "residual range organics" (RRO) that span the carbon range from the upper end of DRO to various end points generally ranging from C30 to C36. Various state methods also differ.

Part of the reason that various methods result in somewhat different ranges for these TPH analyses is that diesel, motor oil, and gasoline are not made by adherence to specific compositional recipes. They are instead made to meet performance specifications, which vary depending on the grade of fuel, the climate, changing technology, and changing regulatory requirements. This results in a situation in which trying to define a clear carbon range for any particular type of fuel is not possible.

In most real cases, different DRO or GRO or RRO methods with somewhat different carbon number ranges will produce results that are very similar to one another. However, they will not be identical and these differences could be important in any given instance. I think a specific set of regulatory requirements based on the Massachusetts definitions should be used by Wyoming. In other words, the volunteer might be allowed to use other methods as long as they can demonstrate that they meet the performance criteria of the Massachusetts method, and also report the same carbon ranges that are specified by the Massachusetts method.

Another area where this issue becomes apparent arises in attempts to find toxicity factors. The Massachusetts factors are shown in Table 1, and it is clear that the ranges shown do not in fact correspond exactly to the ranges used in the Massachusetts method, or in the Massachusetts lookup tables.

Table 1. Massachusetts Toxicity Values for Petroleum Hydrocarbon Fractions.

Table 1. Oral and Inhalation Toxicity Values for Petroleum Hydrocarbon Fractions			
Exposure Route	**Carbon Range**	**1994 MA DEP**	**2002 MA DEP**
		mg/kg/d	**Recommended Values (mg/kg/d)**
Oral	**Aliphatic**		
	C_5 - C_8	0.06	0.04
	C_9-C_{18}	0.6	0.1
	C_{19} - C_{32}	6	2
	Aromatic		

	C_6 - C_8	Evaluate each chemical in the series separately		Evaluate each chemical in the series separately
	C_9-C_{32}	0.03		0.03
				(mg/m^3)
Inhalation	**Aliphatic**			
	C_5 - C_8	-		0.2
	C_9-C_{18}	-		0.2
	C_{19} - C_{32}	-		NA*
	Aromatic			
	C_6 - C_8	-		Use individual RfCs for compounds in this range
	C_9-C_{18}	-		0.05
	C_{19}-C_{32}	-		NA
NA – not applicable to inhalation exposures since compounds not volatile.				
Wyoming requirements for the C6-C8 aromatics - existing				
C6-C8 aromatics	Soil limit (ug/Kg)	Mig to water, ug/kg	Water limit (ug/L)	
Benzene	1100	1.39	5	
Toluene	5000	4.06	1000	
Ethyl benzene	5400	414	700	
m-Xylene	590000	4620	7290	
o-Xylene	690000	4240	7290	
p-Xylene	600000	4490	7290	
Total Xylenes	630000	6001	10000	

The toxicity factors are not known to a high degree of accuracy in any case, so this difference in carbon number range is a minor matter compared to the overall uncertainty surrounding these parameters.

Direct Calculation Approach using Wyoming Risk Assessment Assumptions

The State of Massachusetts is the initial developer of the hydrocarbon fractionation analytical procedures, and has done a significant amount of investigative work in preparing the tools they are using to establish regulatory limits based on those analyses. Much of the basis for the Massachusetts work is data provided in the various compendia from the "Total Petroleum Hydrocarbon Criteria Working Group Series (volumes 1-5)." Wyoming has also used this publication as the basis for much of its approach.

I have calculated the Wyoming lookup table values for the hydrocarbon fractions. These are provided in Table 1 below, and are based on the use of the identical calculation approach presented in FS#12, using the reference dose (RfDo) values provided in the Massachusetts guidance. The actual calculations are provided in the Excel spreadsheet provided with this report.

In addition to these, BTEX, naphthalene, and PAH targets would have to pass the criteria in the existing lookup tables.

It is difficult to compare these directly to the GRO and DRO limits in the existing guidance, because the Massachusetts fractions do not correspond neatly to traditional GRO and RRO windows. However, the direct soil toxicity level of 15,600 mg/kg associated with GRO in the present guidance is much higher than the values for the aliphatic fractions in the GRO range.

The development of the path to water value for DRO described in FS#12 (page 23) used weighted average values from a detailed list of representative aliphatic and aromatic compounds expected in DRO (DRO TPH Fate and Transport Evaluation Table, page 22). These produce a very high value for Koc, which in turn results in a high value for the limit in soil. Because the aggregate values of Koc is much lower for aromatics and for aliphatics in the C9-C12 carbon number window, the same calculation produces much lower soil levels for migration to groundwater when these fractions are considered.

If the value of 0.04 is used for the GRO fraction instead of 0.2, then the value of that maximum level would drop from 15,600 to 3200 mg/Kg, with all other assumptions remaining the same. My recommendation is that to ensure that the total GRO limits are sufficiently protective, that this lower value be incorporated into the existing guidance.

The calculated set of soil limits for direct ingestion, migration to groundwater, along with the current water cleanup levels, are shown in Table 1.

Table 2. Lookup Table for TPH – Direct Calculation Approach

Contaminant	Residential Soil (mg/kg)	Migration to Groundwater DAF=1 (mg/kg)	Water Cleanup Levels (ug/L	Source of data
GRO	15625 *(3200 recommended)*	28	7292	DRO or EPH sum
DRO	2344	-	1094	GRO or EPH sum
GRO Fractions				
Aliphatic C5-C8	3125	21	1458	VPH C5-C8 aliphatics
Aromatic C6-C8				
benzene	1.1	0.0139	5	8260 or 8021
toluene	5	0.406	1000	8260 or 8021
ethylbenzene	5.4	0.414	700	8260 or 8021

Contaminant	Residential Soil (mg/kg)	Migration to Groundwater DAF=1 (mg/kg)	Water Cleanup Levels (ug/L	Source of data
xylenes	630	6.01	10000	8260 or 8021
naphthalene	3.6	1.61	729	8270
DRO Fractions				
Aliphatic C_9-C_{18}	7813	240000	3646	EPH C9-C18 aliphatics
Aliphatic C_{19} - C_{32}	156250	960000	72917	EPH C19-C36 aliphatics
Aromatic C11-C22	2344	3.8	1094	EPH C11-C22 aromatics
Aromatic C9-C10	-	0.86	-	VPH C9-C10 aromatics

Comparison to Massachusetts
The Massachusetts lookup tables do not contain a separate category for the path to water limit. This is explicitly considered as part of the development of their lookup table limits, and is incorporated into the values in the tables. In other words, the choice is made for the user and the lower of the two values is the only one appearing in the table.

However, their approach to calculating the path to water values is somewhat different from that of Wyoming. Wyoming explicitly requires a DAF (dilution/attenuation factor) of 1 (although it is adjusted by the ratio of the depth to water and the contamination thickness). The values used by Massachusetts depend on whether it is a level 1, 2, or 3 scenario, with Level 1 being the most sensitive. The DAF is significantly greater than 1 in their approach. They provide a lookup table value of 100 mg/kg for the C9-C10 aromatic fraction and a value of 1000 for the C11-C22 aromatic fraction, for the most sensitive circumstances.

This difference produces similar issues with other target compounds. For example, total xylenes has a soil toxicity threshold of 630 mg/kg in the Wyoming lookup tables, but a path to water value of 6.1 mg/kg. The Massachusetts table lists only one value of 400 mg/kg (groundwater type 1), which is based on path to water calculations (leaching).

My opinion is that the use of values closer to those used by Massachusetts would be more appropriate for Wyoming. However, justifying such an approach with the current overall strategy for risk assessment is not straightforward.

Comparison to Montana
Montana has a somewhat different approach, as described previously. They define RBSLs for surface contamination (0-2 ft) and subsurface contamination (> 2 ft) for different ranges of depth to groundwater, and for commercial versus residential scenarios. They have levels set for each fraction in the Massachusetts method, and have used either the values in their tables from leaching calculations or the values from direct content, depending on which is lower (this is flagged to indicate which is used in each case).

As an example, they list the C11-C22 aromatic fraction as having an RBSL of 400 mg/kg based on their leaching calculation compared with the value of 3.8 obtained for the C9-C22 aromatics in Table 1 using the Wyoming assumptions.

Critique and Analysis of these Possible Changes

The impact of these possible changes to Wyoming guidance can be evaluated for a reasonably likely case. For example, if a site is contaminated with a relatively typical diesel fuel, with roughly 20% aromatics content, reasonably 20% of the diesel fuel would consist of C11-C22 aromatics and although the direct ingestion limit for that fraction would be 2300 mg/Kg in the soil, the path to water limit is only 3.8 mg/kg. The path to water value would drive the decision in this case, and this means that only 19 mg/kg of total DRO could be considered acceptable. In contrast, for the same fuel without fractionation the DRO-only analysis would allow 2300 mg/kg. The contradiction between the existing standard and the standard developed for TPH fractionation needs to be resolved.

Thus using the values calculated by the Wyoming approach would mean that TPH fractionation analysis would potentially be considerably more restrictive than the present GRO and DRO approach. The much higher levels used by other States suggest that the values for the aromatic fractions calculated by the Wyoming approach are too low.

In my opinion, the crux of this problem is that the model used to calculate the final allowed soil concentration based on fate and transport properties (see the Fact Sheet 25 properties) is not reflective of the physical reality *when TPH is present.* It also appears that most States use similar models, but apply a much higher DAF, depending on assumptions and the specific model used. This is not allowed in the present Wyoming policy.

The Wyoming model is specifically designed for dissolved parameters. The first step of the calculation, as shown in the spreadsheet, is to calculate the "target soil leachate concentration" from the limit for water for each parameter. This is based on a model by Connor[19], in which the soil intervening between the contaminated zone and the groundwater attenuates the concentration due to sorptive and other effects. The model assumes a simple proportionality between the ratio of the depth to water and the thickness of the contaminated zone (equation 1). This approach is taken instead of the use of the DAF as estimated by EPA[20]. In the case of the default conditions chosen for the Wyoming lookup tables, a depth to water of 65 cm is used, along with a contamination thickness of 152 cm. This very conservative assumption actually produces a lower concentration target than the regulatory limit for water. This may be overly conservative.

The next step uses another Connor equation, the leachate concentration goal calculated in the first step and certain properties of the chemical in question to estimate the soil concentration above which the groundwater concentration target might be exceeded. These include the organic carbon-water partition coefficient and the fraction organic carbon to attempt to estimate the degree of partitioning between soil and water phases. The equation can be broken into two terms, and it can easily be seen that if there is significant organic carbon content, the

first term dominates. That is the term that is controlled by the partition coefficient between the soil and the water.

However, this model is incomplete. The parameters of interest are not present by themselves, but are rather present in intimate combination with other hydrocarbons comprising the fuel matrix. In soil, fuel contamination is present as a separate phase which has been retained by the soil pores and interparticle voids. It essentially constitutes a "solvent phase" because it is largely immiscible with water. The individual components must partition between this fuel phase and the water phase in order to dissolve. The model does not include this process, which is a critical omission for the more soluble aromatics. The result is that the extent of partitioning to the water phase will be grossly overestimated for organics unless additional calculation steps are taken. *In other words, the concentration of any given TPH fraction in soil is not equivalent to the "soil leachate concentration" calculated by the model, and is in fact biased grossly high relative to what the actual leachate concentration would be.*

The problem with this entire approach is that the Connor equation was not designed to model the key physical and chemical processes associated with fuels contamination. The generic concept of fraction organic carbon assumes that dissolved constituents are being retained by partitioning into uncontaminated natural organic substances. However, in this case, the organic material is the source of contamination and the substances of concern are being leached from it. Its characteristics are such that it will inhibit partitioning more profoundly than natural soil organic matter[21]. In order to properly calculate the concentration in the water phase, the soil phase, the water phase, and the oil phase must at minimum be explicitly considered. The Connor model is not designed to do that.

If one is to attempt to use the Connor equation and also consider the TPH as a separate phase, one way to do this is to recognize that the final "soil" concentration calculated by the Wyoming approach is actually not the concentration in the soil, but rather the concentration of each hydrocarbon fraction that is present in the aqueous phase at the point of contamination (the final leachate concentration). This is the case because the Connor equation specifically considers only dissolved-phase contaminants. Thus the "regulatory levels" of 0.86 and 3.8 mg/Kg are actually properly interpreted as the "acceptable" concentration in water at that point (in mg/L). In order to obtain a concentration in soil, these values would be multiplied by the fuel/water partition coefficient since they would be part of the fuel phase in the soil. We can estimate this as being roughly 4000, which is the value obtained by Cline and Delfino, and Rao[21] for xylenes. This is a conservative estimate since the actual values for C9+ aromatics are higher (probably > 10,000).

Using this calculation for the C9-C10 and C11-C22 aromatic fraction, the values shown in Table 3 can be estimated. These values are reasonable, but are based on relatively rough estimates of the degree of partitioning. As such, they are not as defensible as would be desired. I provide a recommended approach to deal with this in the last section of this report.

Table 3. Revised Lookup Table Considering TPH as a Phase

Contaminant	Residential Soil (mg/kg)	Migration to Groundwater DAF=1 (mg/kg)	Water Cleanup Levels (ug/L	Source of data
GRO	15625 *(3200 recommended)*	28	7292	DRO or EPH sum
DRO	2344	-	1094	GRO or EPH sum
		Migration to Groundwater (mg/kg)		
GRO Fractions				
Aliphatic C5-C8	3125	21	1458	VPH C5-C8 aliphatics
Aromatic C6-C8				
benzene	1.1	0.0139	5	8260 or 8021
toluene	5	0.406	1000	8260 or 8021
ethylbenzene	5.4	0.414	700	8260 or 8021
xylenes	630	6.01	10000	8260 or 8021
naphthalene	3.6	1.61	729	8270
DRO Fractions				
Aliphatic C_9-C_{18}	7813	240000	3646	EPH C9-C18 aliphatics
Aliphatic C_{19} - C_{32}	156250	960000	72917	EPH C19-C36 aliphatics
Aromatic C11-C22	2344	15200*	1094	EPH C11-C22 aromatics
Aromatic C9-C10	-	3400*	-	VPH C9-C10 aromatics

*Values calculated ae multiplied by the estimated kfw of 4000 in the calculation

General Approach for Volunteers

The general approach to be used by volunteers in the voluntary remediation program (VRP) would be modified by the use of the hydrocarbon fraction analysis, not available previously. The volunteer would proceed by first performing the requisite site characterization. This would include TPH analysis as prescribed currently, and also would require PAH analysis and analysis for the aromatic hydrocarbons in the C6-C10 range currently listed in the cleanup table.

Once the TPH levels are known, Option 1 is to compare the values to the levels in the lookup tables for GRO and DRO, along with any other relevant targets such as BTEX and naphthalenes. If soil levels are above those in the lookup tables but pass the individual compound limits, the volunteer has several options available. Option 2 is to use the simple fate and transport calculations available in FS#12 and FS#25, using the associated spreadsheet for FS#25 to calculate site-specific cleanup levels. This allows certain site characteristics, such as depth to groundwater, to be considered and corrects the measured TPH level to account for soil attenuation. If levels are still above those calculated by this approach, then the user has option 3, to use more complex models approved by DEQ.

Acceptance of the hydrocarbon fractionation analysis approach introduces a new option 4, which is to obtain TPH fraction analysis in addition to the GRO and DRO analyses (and other required data as indicated above). With this information, the volunteer may compare directly the site levels for the additional result to the values in the table. As indicated above, this will result in a potentially higher allowed level of TPH in the soil – depending on the chemical composition of the TPH found.

If the use of option 4 still results in levels that are too high compared to the lookup table, then the user has two more options. The first option would be to use the same strategy for the fractions as is used for the TPH with the simple model. A calculation for each fraction would have to be made.

Failing that, the volunteer would have the final option of more complex modeling using models approved by DEQ and the analytical TPH fractions.

Fate and Transport Approach

Wyoming allows a simple fate and transport approach in which calculations are made using a model developed from data in the Petroleum Working Group publications. Essentially, this approach involves estimating a water leachate concentration from an analysis of the GRO or DRO and then using one of several models to calculate a new cleanup level based on the transport properties calculated by the model. This model does not incorporate any dilution into the calculations.

For the simple site-specific calculation, the existing spreadsheet provided with FS#25 cannot be used directly for TPH fraction modeling, because it will probably yield unrealistically low values for the aromatic fractions. Unless Wyoming relaxes the prohibition on the use of DAF>1, or explicitly includes an estimate of partitioning between TPH and groundwater, it seems to me that more complex fate and transport modeling using the TPH fraction results will not be successful. More complex models might work, assuming that they explicitly consider the TPH phase in the calculation as in Table 3.

Additional Issues to Consider

There are additional practical considerations that must be recognized. The sample matrix and the nature and concentration of the hydrocarbons present can have impacts on the usability of some of the recommended QC. For example, the surrogate recoveries are sometimes not usable in hydrocarbon analysis because the hydrocarbon mix interferes too strongly to allow accurate quantification of the surrogates, or because necessary high dilutions render them unquantifiable. Matrix spikes and duplicates may not be well recovered due to heterogeneity of hydrocarbon distribution in the matrix and difficulty in obtaining representative subsamples, and this may lead to inappropriate conclusions about data quality.

These kinds of issues need to be planned for and a strategy developed to mitigate them and to appropriately use the data when they occur.

Recommendation for Wyoming

A number of alternatives exist for handling the C9-C10 and C11-C22 aromatic fractions, for example:

- Use higher DAF for hydrocarbon fraction analysis only (EPA DAF values)
- Modify the model to explicitly include partitioning between hydrocarbon phase and groundwater
- Use TCLP approach (see New York State program)
- Adopt Massachusetts limits for hydrocarbon fractions only
- Adopt Montana limits for hydrocarbon fractions only

My recommendation is that Wyoming specifically use RBSLs for the aromatic petroleum hydrocarbon fractions that are provided in the Massachusetts S-1 (GW-1) tables. Specifically, the fractions required are the C9-C10 and C11-C22 aromatic hydrocarbon fractions. The Massachusetts RBSLs are the standards applicable to soil overlying groundwater used for drinking water, and are the most stringent of the lookup table values used by Massachusetts. For these two fractions, these are 100 mg/Kg for the C9-C10 aromatics and 1000 mg/Kg for the C11-C22 aromatics.

For this case, the Massachusetts path to groundwater calculation shown in the Massachusetts documentation produces values of 290 mg/Kg and 1300 mg/Kg for the C9-C10 and C11-C22 aromatics, respectively. The values of DAF that produce these concentrations are 1400 and 6300, respectively. These are roughly in the range expected for the partition coefficient between oil and water for this type of phase and these types of compounds[21].

Massachusetts does not use these values in the table. In their system, they also have a "ceiling level" which they only describe as a level obtained by taking other factors into consideration, such as odor or various other factors that are not described. In their final table, they use the ceiling level for the RBSL, because it is lower than all the other calculated levels.

My reasoning is that these RBSLS are lower than those supported by modeling work done by the State of Massachusetts[22] and are based on worst-case considerations. They use values of the DAF that are physically reasonable for these compounds in the presence of TPH. By using these as the lookup table values for these particular hydrocarbon fractions, Wyoming will have a defensible and conservative approach that will not require additional development and modeling. Furthermore, these levels are of a similar order of magnitude to those that would be obtained using the Wyoming model with a physically reasonable value for the DAF (see Table 3).

The other approaches would likely result in effectively similar limits, but would require additional development at an unknown cost. By using the Massachusetts methods for analysis, the Massachusetts reporting approach, and the Massachusetts RBSLs for these problem aromatic fractions, Wyoming would have a consistent strategy that is well-supported scientifically. The recommended levels based on the calculation approach used in this report are shown in Table 4.

Table 4 – Recommended Levels for Wyoming Lookup Tables Incorporating Hydrocarbon Fractionation

Contaminant	Residential Soil (mg/kg)	Migration to Groundwater DAF=1 (mg/kg)	Water Cleanup Levels (ug/L	Source of data
GRO	15625 *(3200 recommended)*	28	7292	DRO or EPH sum
DRO	2344	-	1094	GRO or EPH sum
		Migration to Groundwater (mg/kg)		
GRO Fractions				
Aliphatic C5-C8	3125	21	1458	VPH C5-C8 aliphatics
Aromatic C6-C8				
benzene	1.1	0.0139	5	8260 or 8021
toluene	5	0.406	1000	8260 or 8021
ethylbenzene	5.4	0.414	700	8260 or 8021
xylenes	630	6.01	10000	8260 or 8021
naphthalene	3.6	1.61	729	8270
DRO Fractions				
Aliphatic C_9-C_{18}	7813	240000	3646	EPH C9-C18 aliphatics
Aliphatic C_{19} - C_{32}	156250	960000	72917	EPH C19-C36 aliphatics
Aromatic C11-C22	2344	1000*	1094	EPH C11-C22 aromatics
Aromatic C9-C10	-	100*	-	VPH C9-C10 aromatics

* Values for these fractions are from the Massachusetts lookup tables for S-1 soils.

References

1. See EPA Method 418.1 (now no longer used due to its need for Freon solvent) or ASTM method D7678 – 11.
2. Although HPLC has been primarily focused on separation of structural types, it has also been used to determine total petroleum hydrocarbons by using various types of detectors, such as FID. See Critical Reviews in Analytical Chemistry, 00(0):00–00 (2000), "Chromatographic Techniques for Petroleum and Related Products."
3. See SW-846 Method 8015D is the most commonly-cited basis for this approach. Also see reference 2 above.

4. In addition to Reference 2, see Total Petroleum Hydrocarbon Criteria Working Group Series Volume 1, "Analysis of Petroleum Hydrocarbons in Environmental Media", March, 1998.
5. See the long list of ASTM methods directed to this purpose.
6. Also, the IP Test Methods (Energy Institute, UK) and the ISO test methods (International Organization for Standardization, Switzerland) are important resources.
7. There are many texts on the chemistry of petroleum and its products. A good summary and a number of useful references are available in "Environmental Forensics, Contaminant Specific Guide", editors Robert D. Morrison and Brian Murphy, Elsevier, New York, 2006, starting on p. 340.
8. "Ion Formation in the Flame Ionization Detector," A.J.C. Nicholson and D.L. Swingler, Combustion and Flame, 39:43-52 (1980).
9. http://www.epa.gov/waste/hazard/testmethods/sw846/online/index.htm#table
10. People have occasionally used photoionization detectors with a higher ionizing energy (11.7 ev) as substitutes for flame detectors. This is potentially workable with appropriate calibrations.
11. The Massachusetts method for EPH analysis allows the use of GC/MS, for example – see Reference 14.
12. ASTM D5186 - 03(2009); Standard Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatograph.
13. "Demystifying Silica Gel," Stephen Weintraub, Object Specialty Group Postprints (vol. 9), 2002, Washington, D.C.: American Institute for Conservation.
14. "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)" and "Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)," Massachusetts Department of Environmental Protection, Rev. 1.1, May 2004.
15. Total Petroleum Hydrocarbons TNRCC Method 1005 Revision 03, June 1, 2001, Texas Natural Resource Conservation Commission.
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17. "Analytical Methods for Petroleum Hydrocarbons," ECY -97-602, Washington State Department of Ecology, June 1997.
18. "Extractable Petroleum Hydrocarbons Methodology (Version 3.0)", New Jersey Department of Environmental Protection, August, 2010.
19. Connor, J.A., R.L. Bowers, S.M. Paquette, and C.J. Newell. 1997. Soil Attenuation Model for Derivation of Risk-Based Soil Remediation Standards, Groundwater Services, Inc., Houston, TX, sponsored by Partners in RBCA Implementation (PIRI).
20. "Determination of Groundwater Dilution Attenuation Factors for Fixed Waste Site Areas Using EPACMTP," EPA Office of Solid Waste, May 11, 1994.
21. "Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures," Patricia V. Cline, Joseph J. Delfino, and P. Suresh C. Rao, Environmental Science and Technology, 1991, 23, 914-920.

22. MADEP Policy #WSC-02-411, Background/Support Documentation, Oct. 2002. Also see http://www.mass.gov/eea/agencies/massdep/cleanup/regulations/mcp-numerical-standards.html