MA DEP/LSPA Spring Training Seminar
Understanding and Using the New VPH/EPH Approach

Introduction

Session 1: Basic Toxicology

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UNDERSTANDING &USING THE NEW VPH/EPH APPROACH

- INTRODUCTION - Hutcheson
- BASIC TOXICOLOGY - Hutcheson
- ANALYTICAL METHODS - Anastas
- SCREENING - Duggan
- METHODS 1,2 AND 3 - Locke
- IMPLEMENTATION ISSUES - Fitzgerald

BASIC TOXICOLOGY

Michael S. Hutcheson
Office of Research and Standards

ROOM FOR IMPROVEMENT

- Belief: PHC risks being incompletely characterized
- One-half of MADEP/BWSC sites are petroleum only
- Another 10% of sites have petroleum constituents

ALIPHATICS / ALICYCLICS

- **SATURATED HYDROCARBONS**: paraffins, alkanes, methanes. Straight, branched, cyclic
- **UNSATURATED HYDROCARBONS** at least 2 carbon atoms joined by 2 or more double bonds.
  - ALKENES (olefins)
  - ALKYNES

AROMATICS

- BENZENE: single aromatic ring
- ALKYLBENZENES
- POLYNUCLEAR AROMATICS

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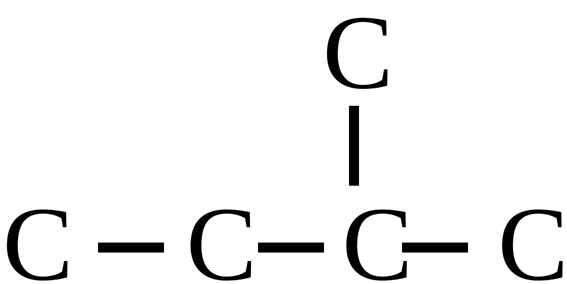

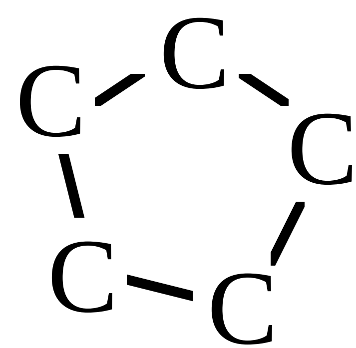

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ALKENES

C — C — C — C = C

ALKYNES

C — C ≡ C — C

A L I P H A T I C S / A L I C Y C L I C S

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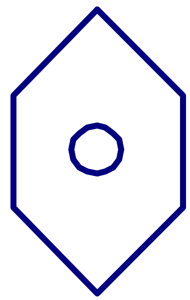
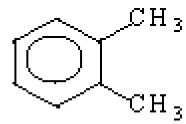
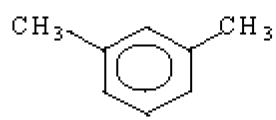


ALKYLBENZENES

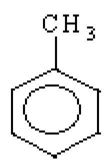


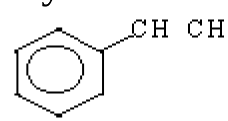
o - xylene



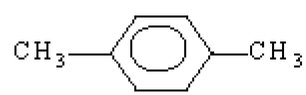
m - xylene

toluene





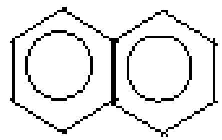
ethyl benzene



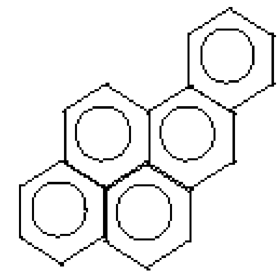
p - xylene

POLYNUCLEAR AROMATICS

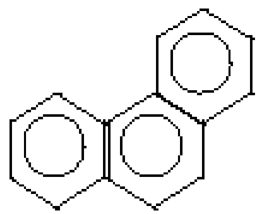
NAPHTHALENE
$C_{10}H_8$



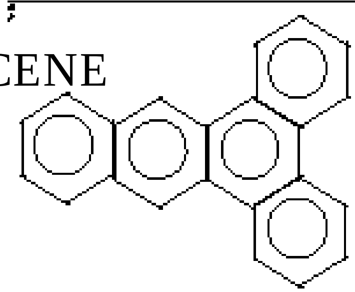
BENZO(a)PYRENE
$C_{20}H_{12}$



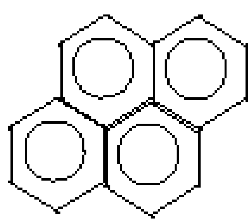
PHENANTHRENE
$C_{14}H_{10}$



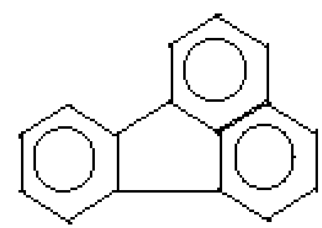
DIBENZ (a,h)ANTHRACENE
$C_{22}H_{14}$



PYRENE
$C_{16}H_{10}$



FLUORANTHENE
$C_{16}H_{10}$



PETROLEUM COMPOSITION TERMINOLOGY

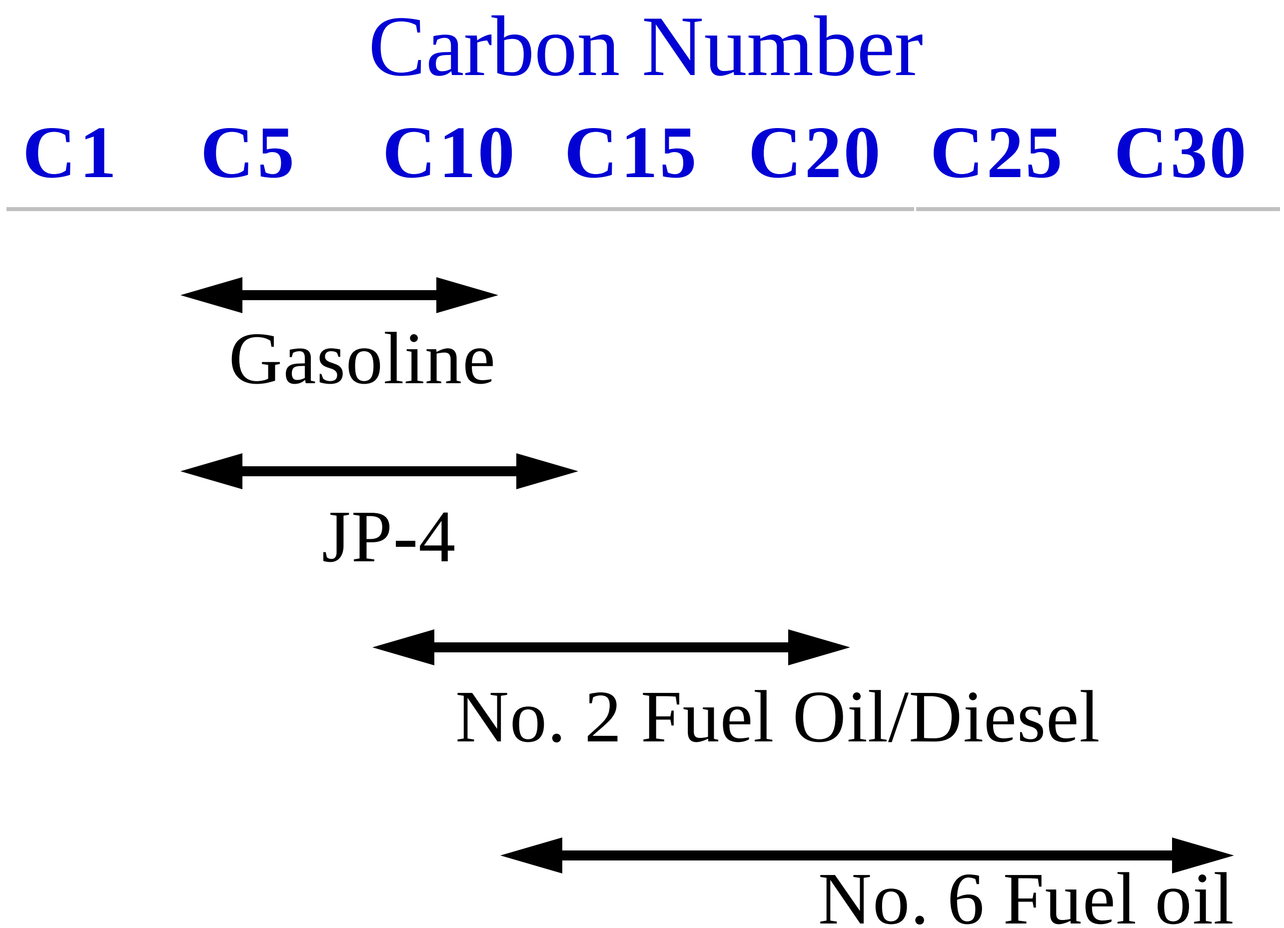
ALIPHATICS

- ALKANES (normal and iso-) (C C)
  Saturated. Syn.: Paraffins (normal, iso-)
- ALKENES(unsaturated. C=C bonds)
  Syn.: olefins
  unsaturated aliphatics
- ALKYNES (C C)

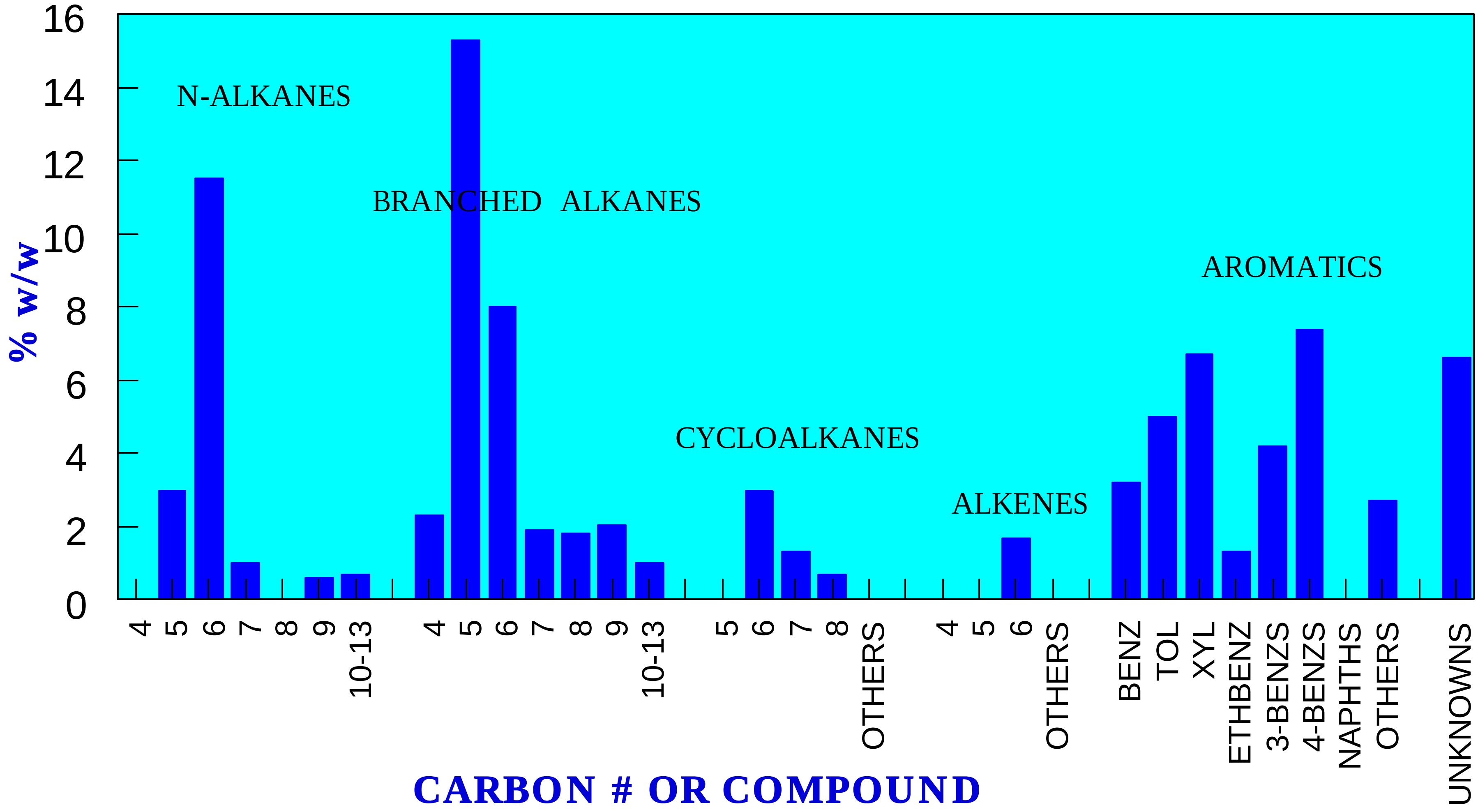
CYCLIC

- CYCLOPARAFFINS
- AROMATICS

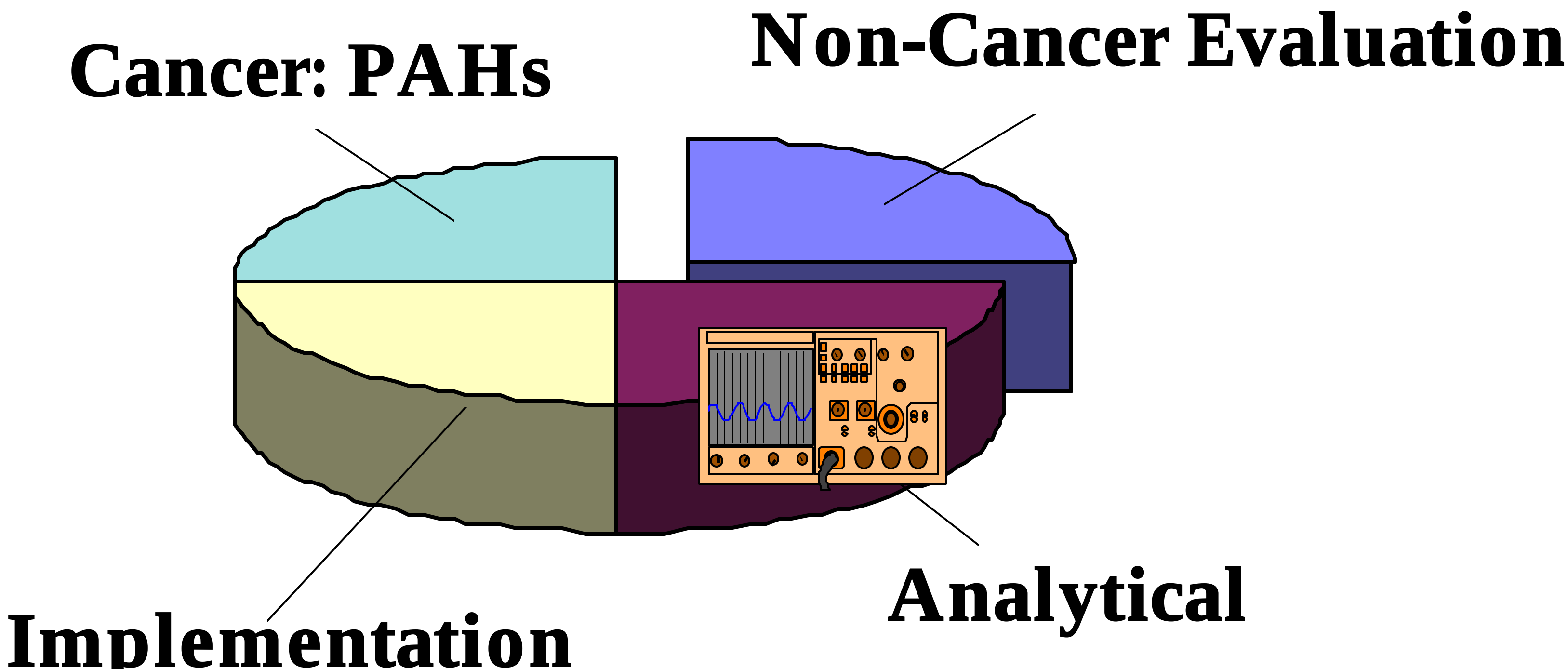
CARBON RANGES FOR FUEL PRODUCTS



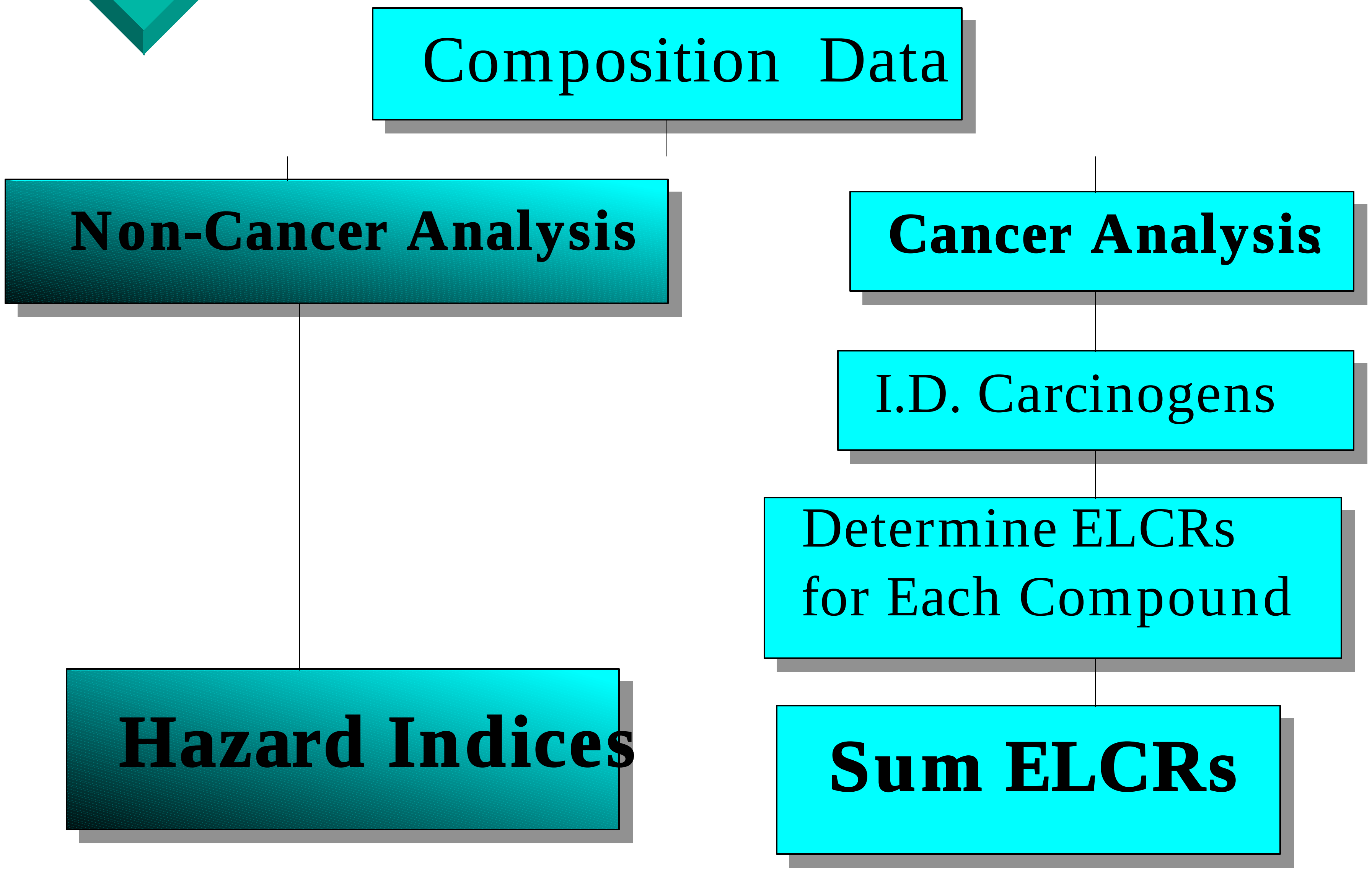
HYDROCARBON COMPOSITION OF UNLEADED FUEL



PHC SITE HEALTH RISK EVALUATION



EVALUATION SEQUENCE



TPH PARAMETER:

- Total concentration of petroleum hydrocarbons in sample
- Method-specific results - can range from limited number of compounds, to entire range of C_4 to C_{32}

HISTORICAL HEALTH RISK APPROACHES

- TPH
- INDICATOR COMPOUNDS (BTEX)
- WHOLE PRODUCT TOXICITY

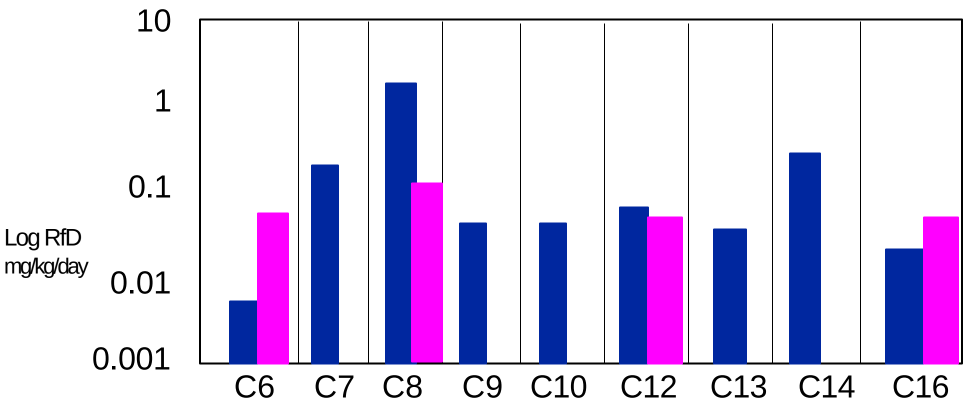
AVAILABLE TOXICITY INFORMATION

- WHOLE PRODUCT
  gasoline, JP-4, JP-5
- SPECIFIC COMPOUNDS
- STRUCTURE ACTIVITY RELATIONSHIPS

Oral Dose Response Values for Whole Petroleum Products

Whole Product	RfD (mg/kg/day)	SF $(mg/kg/day)^{-1}$	Source
Gasoline	0.2	0.0017	USEPA, 1992
JP-4	0.08	ND	USEPA, 1992
JP-5	0.02	ND	USEPA, 1992
No. 2/Diesel	ND	0.00109	Millner et al, 1992

Oral RFDs for Specific Petroleum Hydrocarbons



Compound	Toxic Effect
Benzene (C6)	Hematological
n-Hexane (C6)	Neuropathy
Toluene (C7)	Liver, Kidney
Xylene (C8)	Hyperactivity Decr. Body Wt.
Ethyl Benzene (C8)	Liver, Kidney
Cumene (C9)	Kidney
Naphthalene (C10)	Hematological, Kidney, Liver
Acenapthene (C12)	Liver
Biphenyl (C12)	Kidney/CNS
Fluorene (C13)	Hematological
Anthracene (C14)	None Obsv.
Pyrene (C16)	Kidney/Liver
Fluoranthene (C16)	Kidney/Liver

ALKANE TOXICITY

THRESHOLD	NON-THRESHOLD
NEPHROTOXICITY	INSUFFICIENT DATA
CNS EFFECTS, NARCOSIS	
SKIN/MEMBRANE IRRITATION	
PERIPHERAL NEUROPATHY	

AROMATIC HYDROCARBONS (C6 TO C8)

- THRESHOLD EFFECTS
  - NEPHROTOXICITY
  - CNS EFFECTS
  - HEPATOTOXICITY
- NON-THRESHOLD
  - BENZENE - EPA CLASS A CARCINOGEN

MAJOR ISSUES

WEATHERING

DIFFERENTIAL TOXICITY

COSTS

POSSIBLE APPROACHES

TPH

FINGERPRINT

RANGES BASED ON CARBON NUMBER

FULL COMPOSITION CHARACTERIZATION

APPROACH

1) Divide C Range into Groups

2) I.D. Tox. Values for Chemicals in Each Group

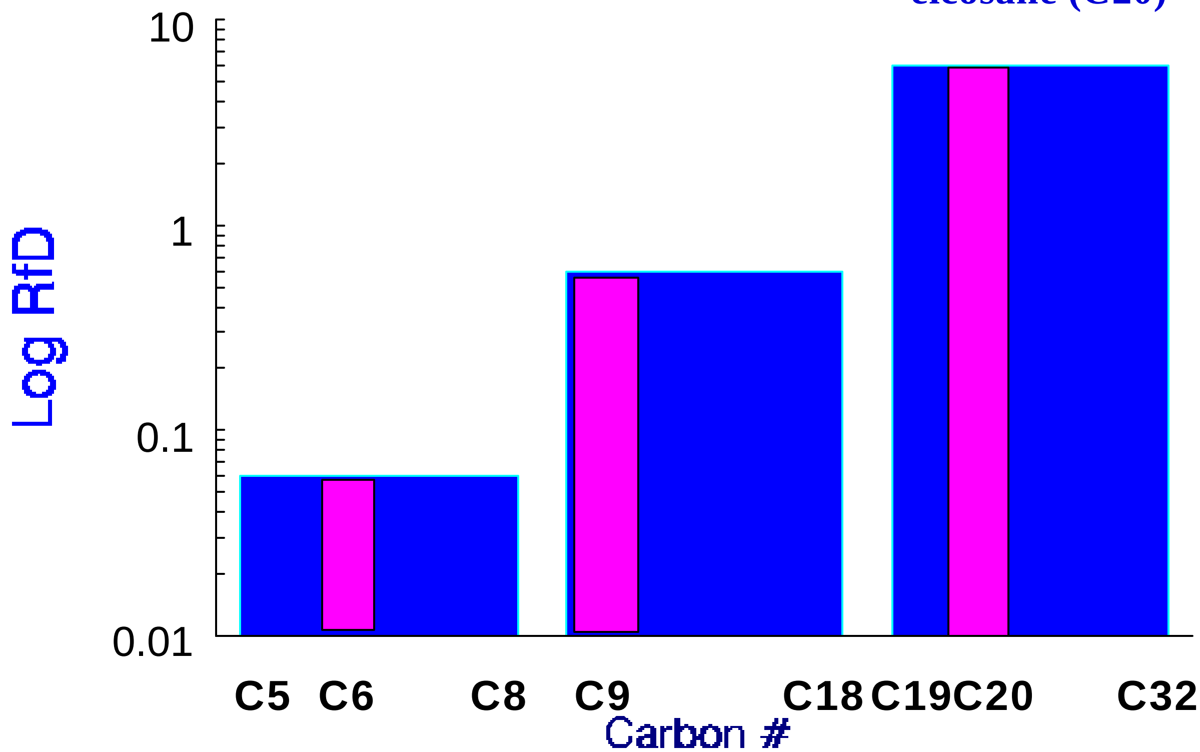
3) Assign Tox. Values to Indicator Compounds

APPROACH cont.

- Reject whole product toxicity approach in most cases becasue of weathering/identification uncertainties
- Develop analytical method which quantifies specific ranges of petroleum hydrocarbons

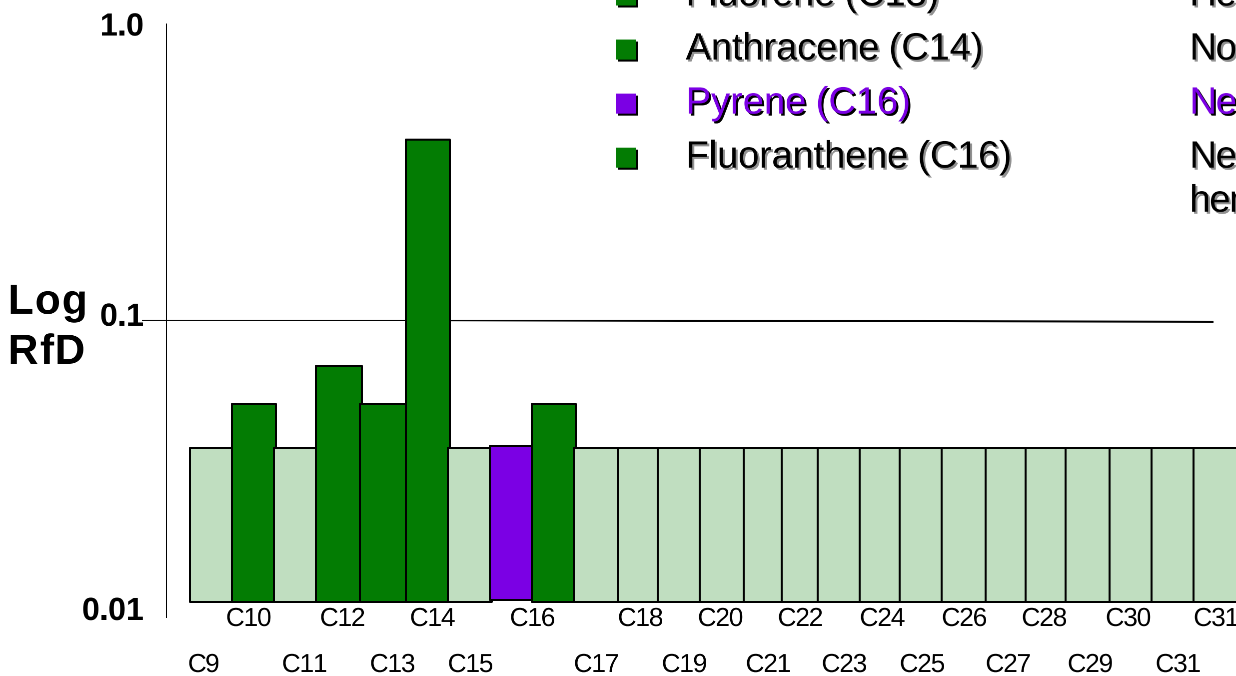
RfDs for C Number Ranges - Alkanes/Cycloalkanes

Reference Compound	Toxic Effect
n-hexane (C6)	neurotoxicity
n-nonane (C9)	neurotoxicity
eicosane (C20)	functional changes/irritation



Proposed Alternate RfD for Aromatics/Alkenes

	Reference Compound	***Toxic Effect***
■	Naphthalene (C10)	Decreased body weight
■	Acenaphthene (C12)	Hepatotoxic
■	Fluorene (C13)	Hematological
■	Anthracene (C14)	None Obsv.
■	Pyrene (C16)	Nephrotoxic
■	Fluoranthene (C16)	Nephrotoxic, hematological



Chemical Groups, Indicators and Toxicity Values

	Reference Compound	Toxic Effect	Alternate RfD
Alkanes/ Cycloalkanes			
C_5 - C_8	n-hexane	neurotoxicity	**0.06**
C_9 - C_{18}	n-nonane	neurotoxicity	**0.6**
C_{19} - C_{32}	eicosane	irritation	**6**
Aromatics/ Alkenes			
C_9 - C_{32}	pyrene	neurotoxicity	**0.03**

COMPOUND SPECIFIC APPROACH FOR:

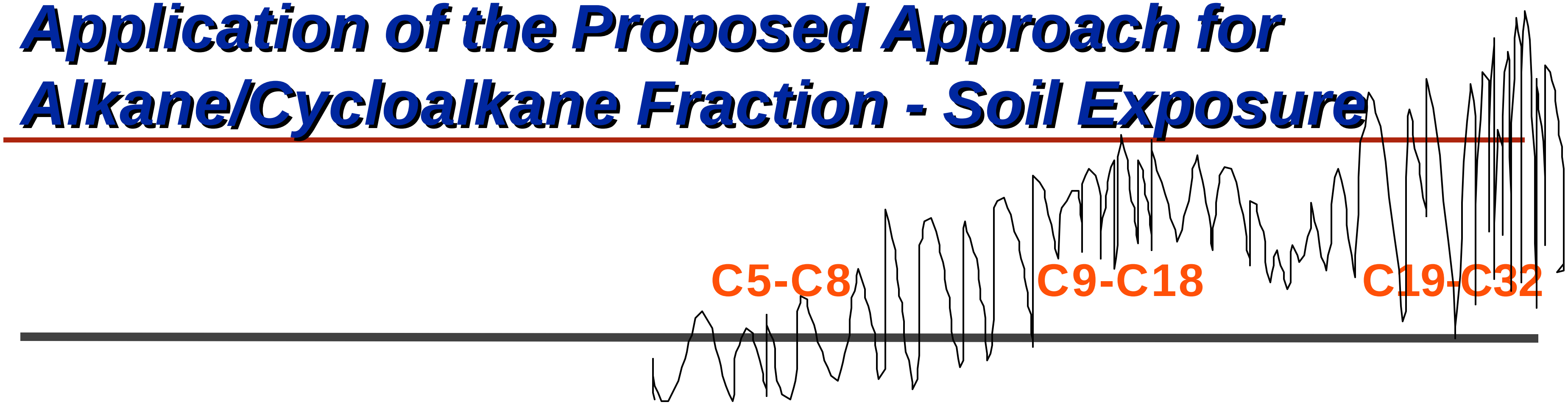
	Oral RfD (mg/kg/d	Cancer Slope Factor $(mg/kg/d)^{-1}$
Non-Cancer		
Toluene	0.2	-
Ethylbenzene	0.1	-
Xylene	2.0	-
Cancer		
Benzene	0.005	0.029
Benzo(a)pyrene	-	7.3

Compound Specific Approach for:

	Oral RFD (mg/kg/day)	Cancer Slope Factor (mg/kg/day)$^{-1}$ (MA RPF)
Noncancer		
Toluene	0.2	-
Ethylbenzene	0.1	-
Xylene	2.0	-
Cancer		
Benzene	0.005	0.029
Benzo(a)Pyrene	-	7.3
Naphthalene	NA	-
Methylnaphthalene	NA	-
Phenanthrene	NA	-
Anthracene	NA	-
Fluoranthene	NA	-
Benzo(a)Anthracene	NA	(0.1)
Chrysene	NA	(0.01)*
Benzo(b)Fluoranthene	NA	(0.1)
Benzo(k)Fluoranthene	NA	(0.01)
Indeno(1,2,3-cd)Pyrene	NA	(0.1)
Dibenzo(a,h)Anthracene	NA	(4.0)*
Benzo(g,h,i)Perylene	NA	(0.001)

** Different from USEPA RPFs*

Application of the Proposed Approach for Alkane/Cycloalkane Fraction - Soil Exposure

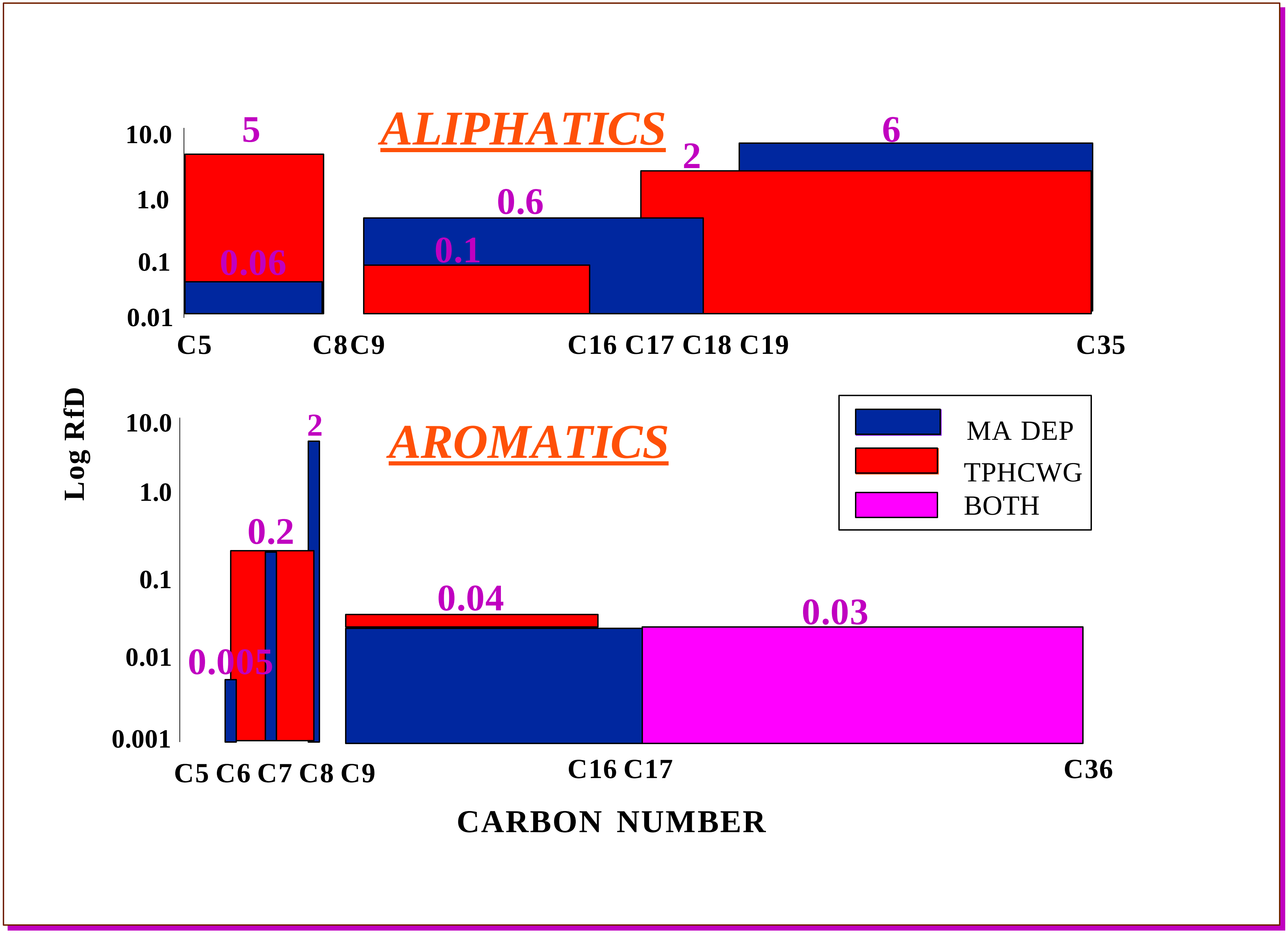


	C5-C8	C9-C18	C19-C32
Concentration of Petroleum Hydrocarbon	**20 mg/kg**	**100 mg/kg**	**200 mg/kg**
Dosage Calculation*	**2.5×10^{-4} mg/kg/day**	**1.3×10^{-3} mg/kg/day**	**2.5 x 10-3 mg/kg/day**
Proposed Alternate RfD	**0.06**	**0.6**	**6**
Hazard Index	**4.2×10^{-3}**	**2.2×10^{-3}**	**3.8×10^{-4}**
Total Hazard Index			**6.8 x 10-3**

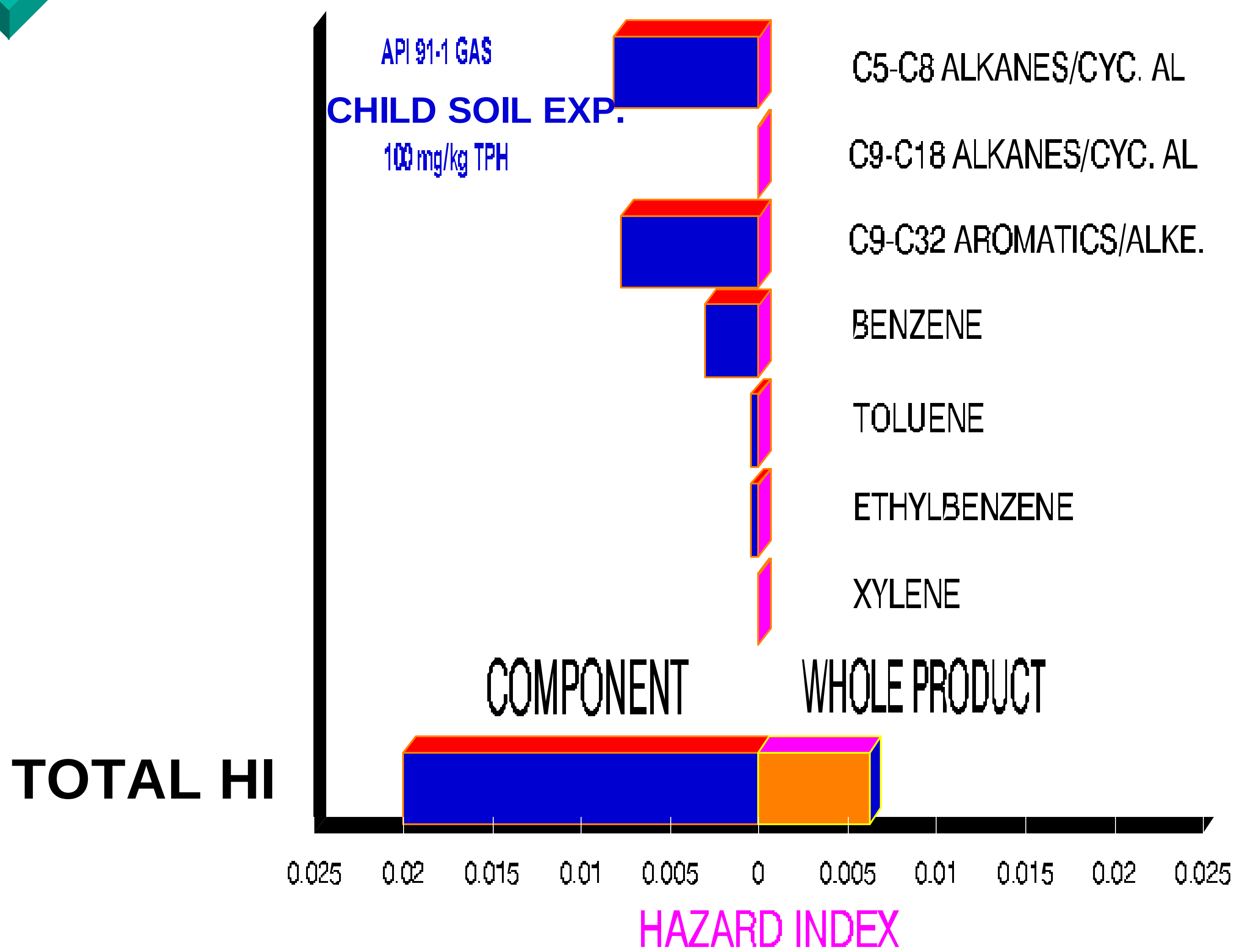
**Assume a 16 kg child consumes 200 mg soil per day, 365 days per year*

SUMMARY OF THE TPH ALTERNATIVE

- FULLER ACCOUNTING OF HYDROCARBON CONTENT: USES C # RANGES
- DOSE-RESPONSE VALUES SPECIFIC TO EACH RANGE
- ACKNOWLEDGES QUALITATIVE DIFFERENCES IN TOXICITIES OF "TPH" VALUES
- MORE COMPLETE INFORMATION FOR HUMAN HEALTH RISK ASSESSMENT


ALIPHATICS
10.0
1.0
0.1
0.01
5
0.06
0.6
0.1
2
6
C5
C8 C9
C16 C17 C18 C19
C35
Log RfD
AROMATICS
10.0
1.0
0.1
0.01
0.001
2
0.2
0.005
0.04
0.03
C5 C6 C7 C8 C9
C16 C17
C36
MA DEP
TPHCWG
BOTH
CARBON NUMBER

COMPONENT AND WHOLE PRODUCT TOXICITY PREDICTIONS (HAZARD INDEX)



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Session 2:
Analytical Methods

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Analytical Methods for Characterizing Petroleum Contaminated Soil and Water

Nicholas D. Anastas

Department of Environmental Protection

What the Audience will Learn

- The Methods that are Available for Petroleum Characterization
- Use and Theory of VPH and EPH Analysis
- Principles of QA/QC
- Reporting VPH and EPH Results
- Use of VPH and EPH Results

Analytical Mandate

- Characterize petroleum from C5 thru C36
- Ranges set by the health-based approach
- Aliphatics/cycloalkanes must be separated from Aromatics

Vocabulary

- EPH Extractable petroleum hydrocarbons
- VPH Volatile petroleum hydrocarbons
- TPH Total petroleum hydrocarbons
  - (usually the sum of VPH + EPH)
  - T-EPH: MCP defined as > C9
- FRACTIONS- Carbon number ranges of compounds from C5 through C36

Carbon Number Ranges defined by the Toxicology Data

- VPH
- ***Aliph.*** ***Aromatics***
  - **C5-C8** **C9-C10**
  - **C9-C12** **Benzene**
    Toluene
    Ethylbenzene
    Xylenes
    - **MTBE**

- **EPH**
- ***Aliph.*** ***Aromatics***
  - **C9-C18** **C11-C22**
  - **C19-C36** **PAHs**

Gas Chromatography

- Separation of complex mixtures is based on differential sorption
- Column provides a sorptive surface
- Compounds that do not adsorb well will elute first; “stickier” compounds elute later
- Eluant flows into a detector which is either general or specific

GC Detectors

- Detectors can be general (FID) or specific (PID or MS)
- Response of detector is based on characteristics of compounds in eluant
  - FID: all carbon containing compounds
  - PID: compounds with *pi* bonds
- Response of a detector to the presence of compounds results in chromatograms

Chromatograms

- Responses are a series of “peaks”
- Peak heights represent the relative concentrations of detected compounds
- Retention time is the primary characteristic of the identity of a compound using FID or PID
- Retention time is based on boiling points and molecular structure

VPH Sampling Issues-Water

- Containers: glass; no headspace
- Preservation: HCL
- Holding Times: 14 days from sampling date

Methanol Preservation for Soils

- Necessary to minimize escape of VOCs from sample vials
- Use only 200ul of the extract
- Potential Problems
  - MEOH in the field
  - weighing proper amount of soil:MEOH
  - preweigh at lab
  - syringe and fill to the line

VPH Analysis Overview

- Purge and Trap
- Photoionization Detector (PID) and Flame Ionization Detection (FID) in series

VPH Interpretation

- FID is a universal detector (detects carbon)
- PID is relatively* selective for compounds with *pi* bonds (* aliphatics also respond)
- PID is more selective when the lamp voltage is < 10.2 eV.

VPH vs. GRO

- GRO is FID only; no separation of aromatics
- Can assume worst-case conditions
- Cannot be used in the Massachusetts health-based approach without modifications

VPH vs. 8015M

- Same problems as with GRO
- Used to analyze for non-halogenated VOCs in the gasoline range
- Standardized using a gasoline standard

Potential Concerns with VPH

- Double counting
- Methanol Preservation
- Inherent Assumptions
  - RT is correct for individual cmpds.

EPH Sampling Issues

Matrix	Container	Preserv.	Holding Times
Aqueous	1 liter amber glass	5ml 1:1 HCL; 4 ^{o}	Extract within 14 d Run extract w/40d
Soil/Sediment	4oz.wide mouth jar	4 ^{o} C	Extract w/ 14d Run extract within 40 d

Extractable Petroleum Methods

- Extraction of compounds from media of interest using different solvents
- Fractionation of the mixture of complex hydrocarbons into aliphatic/cyclics and aromatic/unsaturated compounds
- Separation of the fractionated mixtures into carbon number ranges by FID

Fractionation of EPH Components

- Sample loaded onto column (post-KD)
- First solvent is hexane (removes non-polar aliphatics and alicyclics)
- Second solvent is methylene chloride (removes aromatics; including PAHs)

Fractionation Considerations

- **Silica Gel Cartridges**
  - limited capacity
  - moisture
  - bleeding of plasticizers
- **Columns**
  - labor intensive
  - higher capacity
- **HPLC**
  - Very high theoretical plates (more separation/fractionation power)
  - Expensive and not generally available

Fractionation Check Solution

- FCS is necessary to ensure that there is no breakthrough of one fraction into another
  - aromatics into the aliphatic
  - aliphatics into the aromatic
- Whole Product or Compound Specific

EPH Interpretation

- Two separate runs for each sample
- Evaluate FCS
- Proper assignment of RT windows
- Integration of individual peaks and UCM
- Identification of targeted analytes including PAHS
- Use of GCMS to confirm PAHs

EPH vs. 8270

- GC *vs*. GCMS methods
- EPH does not generate unequivocal identification of compounds, *e.g*, PAHS
- 8270 not developed to separate petroleum hydrocarbons into fractions

EPH vs. 8100M

- Method 8100 was designed to detect PAHs
- Is a GC-FID Method
- If run as written, will not detect aliphatics
  - does not divide mixture into ranges
- Method can be modified; 8100M (no silica clean-up) to detect aliphatics

California and Wisconsin Methods

- GC-FID Analysis
- No fractionation into aliphatics and aromatics
- Carbon number range up to 20-24

Infra-red Analysis (418.1)

- Generally a screening method
- Detects compounds with a C-H stretch at 2930 cm-1
- Lose low and high end compounds
- Will not detect aromatics
- Should be used in the new **Health-Based** approach with caution

QA/QC

- **Quality Assurance:** An integrated system of management activities to ensure that a process is of the quality expected
- **Quality Control:** An overall system of technical activities to monitor the attributes and performance of a process compared to defined standards.

Components of QA/QC

- Establishing Detection Limits
- Blanks
- Calibration
- Surrogates
- Spikes
- Duplicates

Reasons to Have QA/QC

- Precision
- Accuracy
- Representativeness

Precision

- How close the results are to each other
- Precision is measured by using duplicates
- Field and Lab duplicates
- Relative Percent Difference

Accuracy

- Measures how close a result is to a true or known value
- Monitored in analytical method using spiked samples

Detection Limits

Types of Detection Limits: Instrument (IDL), Method (MDL) and Practical (PQL)

- **IDL**: The lowest amount of material that can be determined to be different from the baseline under optimal conditions
- **MDL**: Minimum amount of material that can be measured and reported with 99% confidence that the analyte concentration is greater than zero under **method** conditions
- **PQL:** Considers other method peculiarities. Has a "comfort factor" of 3 -10x MDL built in.

Blanks

- Used to monitor for contamination
  - System or Instrument Blanks
  - Field Blanks
  - Trip Blanks
  - Matrix Blanks

Calibration

- Must generate a reference point for compound retention times and for calibration
- Regression lines are generated for calculating the concentration in samples
- Internal *vs* External Calibration

Surrogates

- Compounds that are added at known concentrations to monitor accuracy
- Monitor conditions of the analysis

Spikes and Spike Duplicates

- Used to monitor for:
  - precision
  - accuracy
  - matrix effects

QA Principles

Parameter	Measurement Endpoint
Precision	Duplicates
Accuracy	Spike Recoveries
Representativeness	Sanple Conditions
Completeness/Comparability	DQO

VPH Calibration

- 3-Level Initial Calibration
- Daily Continuing Calibration
- Surrogate is 2,5-dibromotoluene
- Aliphatic:
  - C5-C8 (pentane to nonane)
  - C9-C12 (nonane to 2,5-DBT)
- Aromatic:
  - C9-C10 (nonane to 2,5 DBT)

VPH QC

- Individual or Collective RFs
- RPD
  - 3 Level: 20%
  - Daily: 25%
- Surrogate Recovery: 80- 120%
  - Currently being evaluated

VPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Endnding Marker Compound
C5-C8 Aliphatics (FID)	Pentane	Just before Nonane
C9-C12 Aliphatics (FID)	Nonane	Naphthalene
C9-C10 Aromatics (PID)	1,2,4-trimethylbenzene	Naphthalene

EPH Calibration

- 5 level calibration
- Daily continuing calibration
- Surrogates: OTP (ortho terphenyl) and OCD (octachlorodecane)
- Aliphatic: C9 - C18; C19 - C36
- Aromatic: C11 - C22, including individual PAHs

EPH QC

- Individual or Collective RFs
- RPD :
  - – 5 level 20%
  - – Daily 25%
- Surrogate Recovery 60-140%

EPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C9-C18 Aliphatics	Nonane	Just before Nonadecane
C19-C36 Aliphatics	nonadecane	Hexatriacontane
C11-C22 Aromatics	Just after Naphthalene	Benzo[g,h,i]perylene

Certified Laboratories

- Certification is only one aspect of a complete QA/QC Plan
- Certification does not necessarily mean that your data are acceptable
- Certification is useful for:
  - identifying existence of facility and equipment
  - demonstrating that a lab can meet certain QA requirements
  - demonstrating that a lab can pass PE

Certification for Soils

- There is currently no certification program for the analysis of soils
- A robust QA/QC program is therefore critical to ensure data quality

Current Certification for Soil Analysis

- DEP does not currently certify labs for soil analysis
- The MCP does not require that a certified lab be used

Summary

- Now have the knowledge of what types of data are necessary for input into the Health-based approach for characterizing petroleum contaminated media
- Are familiar with the available VPH and EPH methodlogies used to generate those data
- Are aware of some of the concerns with other availble methods for pteroleum analysis

MA DEP/LSPA Spring Training Seminar
Understanding and Using the New VPH/EPH Approach

Session 3:
Screening

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Screening for Petroleum Hydrocarbons

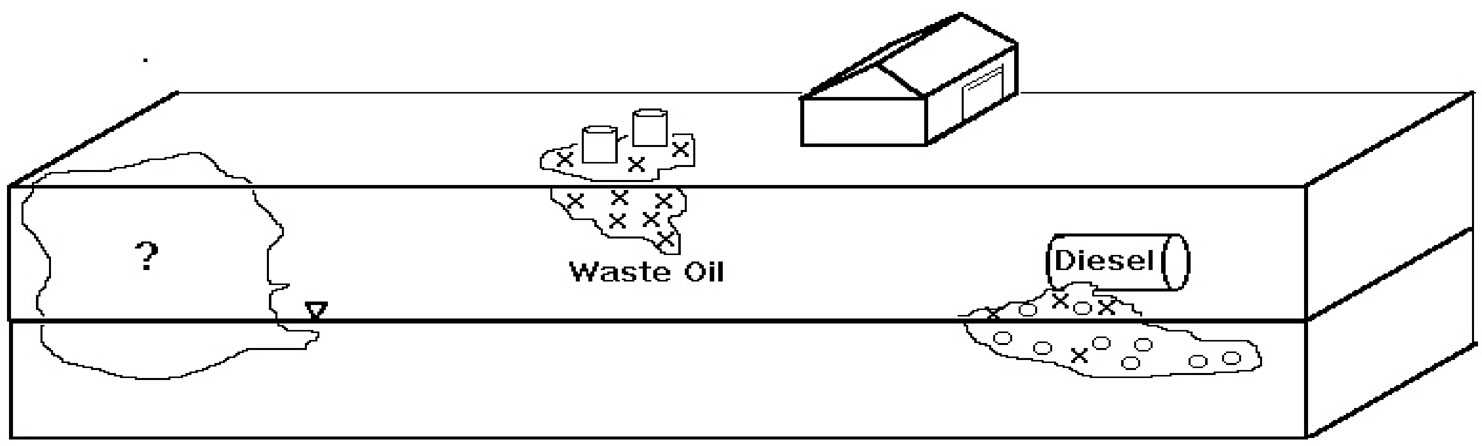
- Better, cheaper and/or faster site characterization;

- General Performance Standards:

  Comparing to VPH and EPH data;
  Applying information collected

Applications: Site Assessment

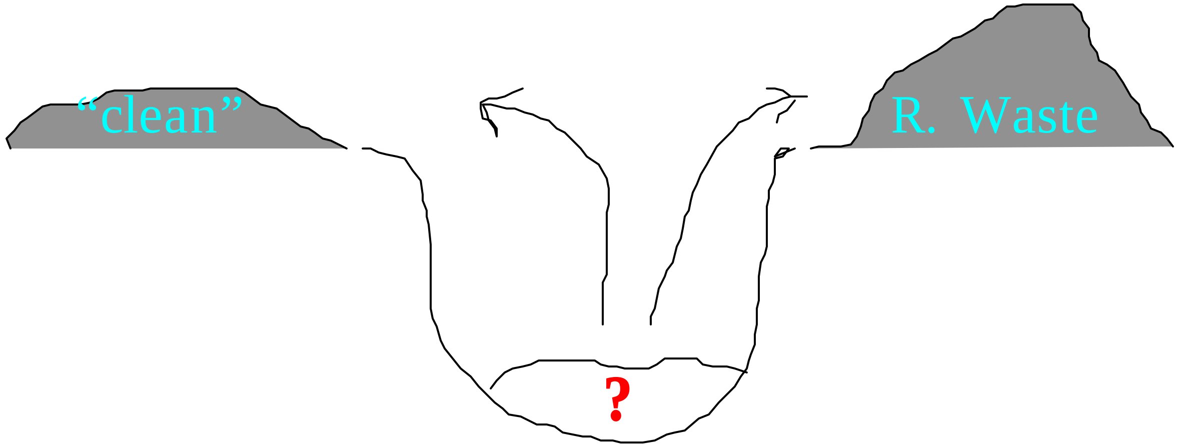
- Identification of: hot-spots; discrete areas of contamination; locations for follow-up sampling
- Periodic monitoring



Applications: Soil Management

Use to:

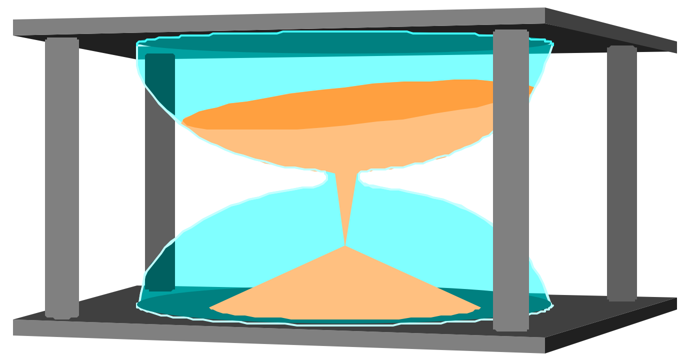
- segregate contaminated soil
- provide greater certainty at closure



Economic/Logistical Benefits

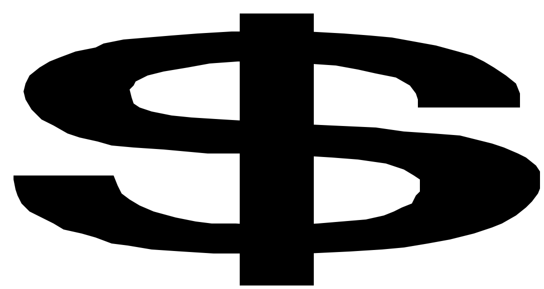
Save Time

- minimize field time
- speed up restoration measures



Save Money

- lower labor and equipment needs
- targeted assessment and remediation
- collect more data



Regulatory Framework

310 CMR 40.0017, Environmental Sample Collection and Analysis

- Data must be ***scientifically valid and defensible***;
- Documentation of:

    sampling procedures;

    analytical method(s);

    performance of the method(s).

Scientifically Valid and Defensible

- Use appropriate sampling protocols:
  - for the medium(a) sampled;
  - for the analyte(s) measured.

- Use appropriate analytical methods and instruments

40.0017(2): Analytical Methods

- published methods;
- ***unpublished methods;***
- ***modifications of published methods.***

Data Quality Requirements

- Depends on "use" of the data

  preliminary indicator data vs.

  stand-alone data suitable to assess risk

- Supporting Documentation

  - comparability to other data
  - calibration, detection limits, precision and accuracy, etc..

Recommended Screening Procedures

Petroleum Product	VPH	EPH
Gasoline	X	
Fresh Diesel/#2 Fuel Oil	X	X
Weathered Diesel/#2 Fuel Oil		X
#3-#6 Fuel Oils		X
Waste (Crankcase) Oil	X	X
Jet Fuel/Kerosene	X	X
Mineral/Dielectric Oils		X
Unknown Oils/Sources	X	X

Typical Composition of Petroleum Products

Product	Carbon Range	Percent Aliphatic	Percent Aromatic
Gasoline	C_4 - C_{12}	35% - 80%	***10% - 40%***[a]
#2/Diesel	C_8 - C_{21}	60% - 70%	30% - 40%
#3-#6 Fuel Oil	C_8 - C_{30+}	20% - 50%	30% - 40+%
Waste (Crankcase) Oil	C_{15} - C_{50+}	50% - 90%	10% - 30%
Jet Fuel/Kerosene	C_9 - C_{16}	60% - 80%	5% - 20%
Dielectric Oils	C_{12} - C_{22} (?)	80+%	?

[a] includes BTEX compounds

VPH Screening

Jar Headspace

- For soil and groundwater samples
- Relies on partitioning between phases
- Total VOCs vs. Individual Compounds
- PID vs. FID

VPH Screening

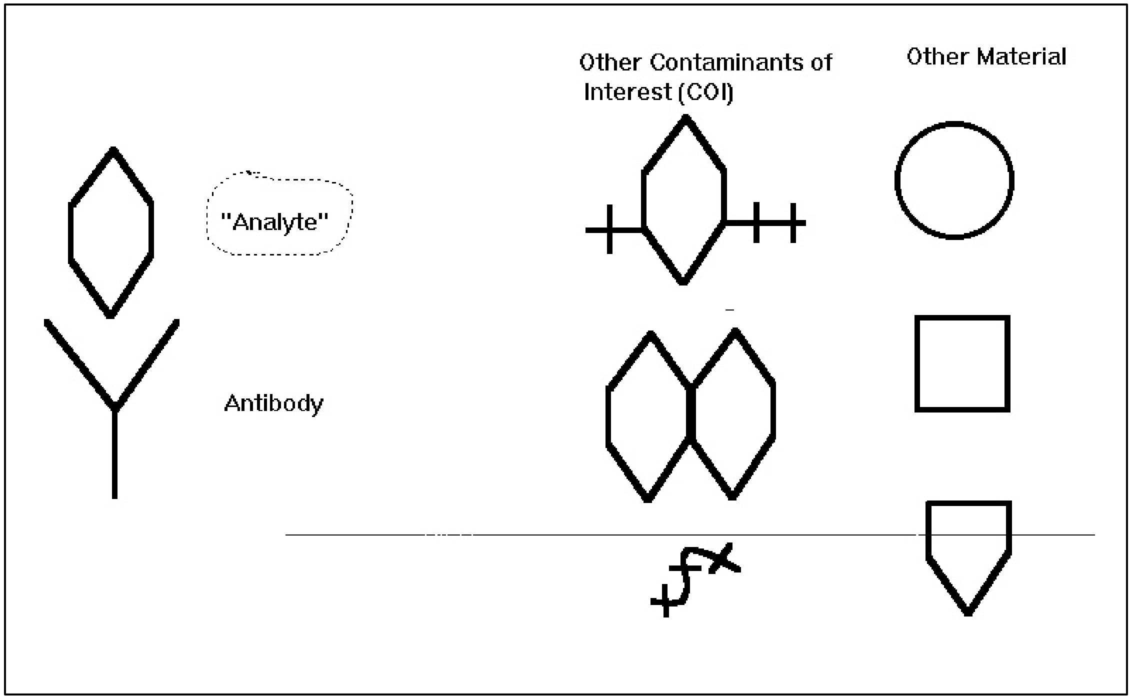
- Fiber optic based technologies:

- in-well monitoring;
- direct measurements;
- selective detection;
- calibration requirements;
- confirmatory lab analysis

EPH Screening

Immunoassays

- rely on a field extraction
- sensitive to aromatics, not aliphatics
- calibration requirements
- comparison to non-screening data



EPH Screening

Emulsion-based kits

- rely on a field extraction
- less discriminating between aromatic and aliphatic groups
- calibration requirements
- compare to non-screening data

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Session 4:
Methods 1, 2 and 3

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Methods 1, 2 and 3

Derivation of MCP Numerical Standards

- Groundwater:

  GW-1, GW-2 and GW-3

- Soil:

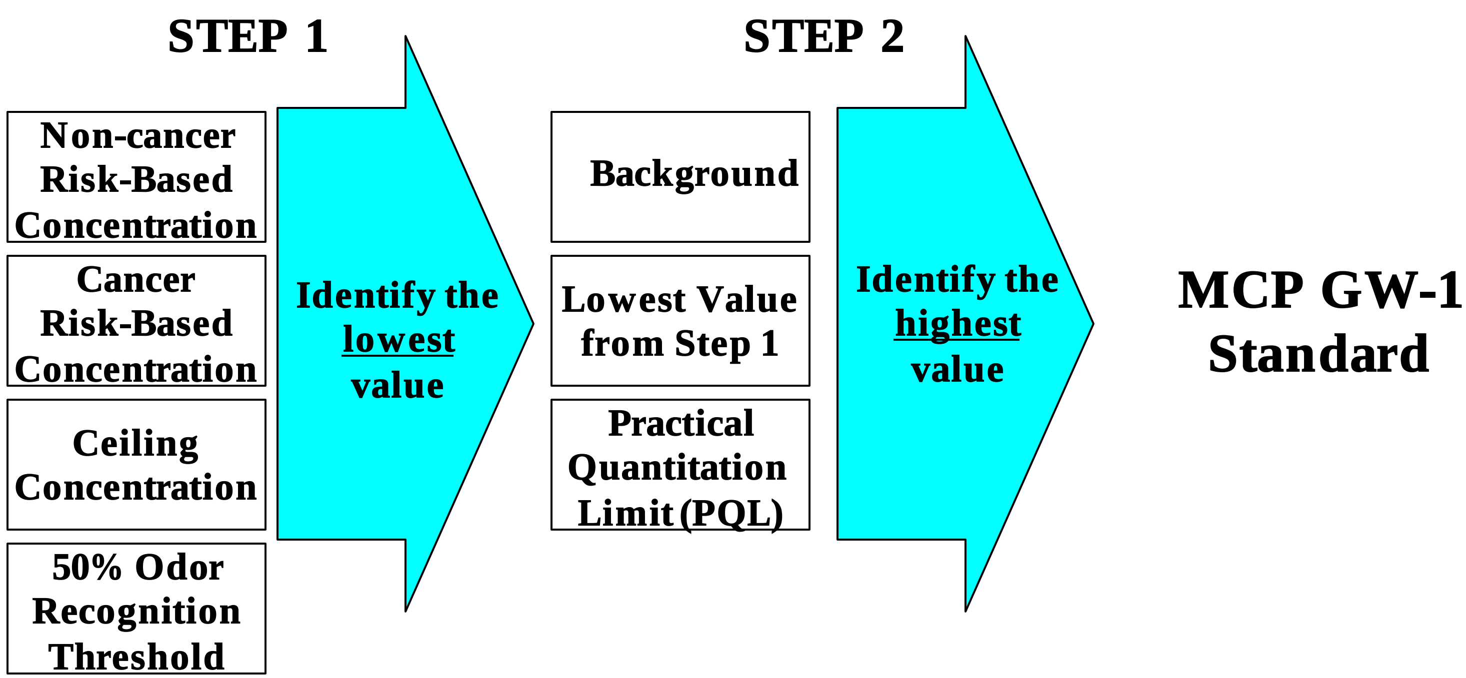
  S-1, S-2 and S-3; direct contact and leaching-based

- Upper Concentration Limits (UCLs)

- Reportable Concentrations (RCs)

Groundwater GW-1

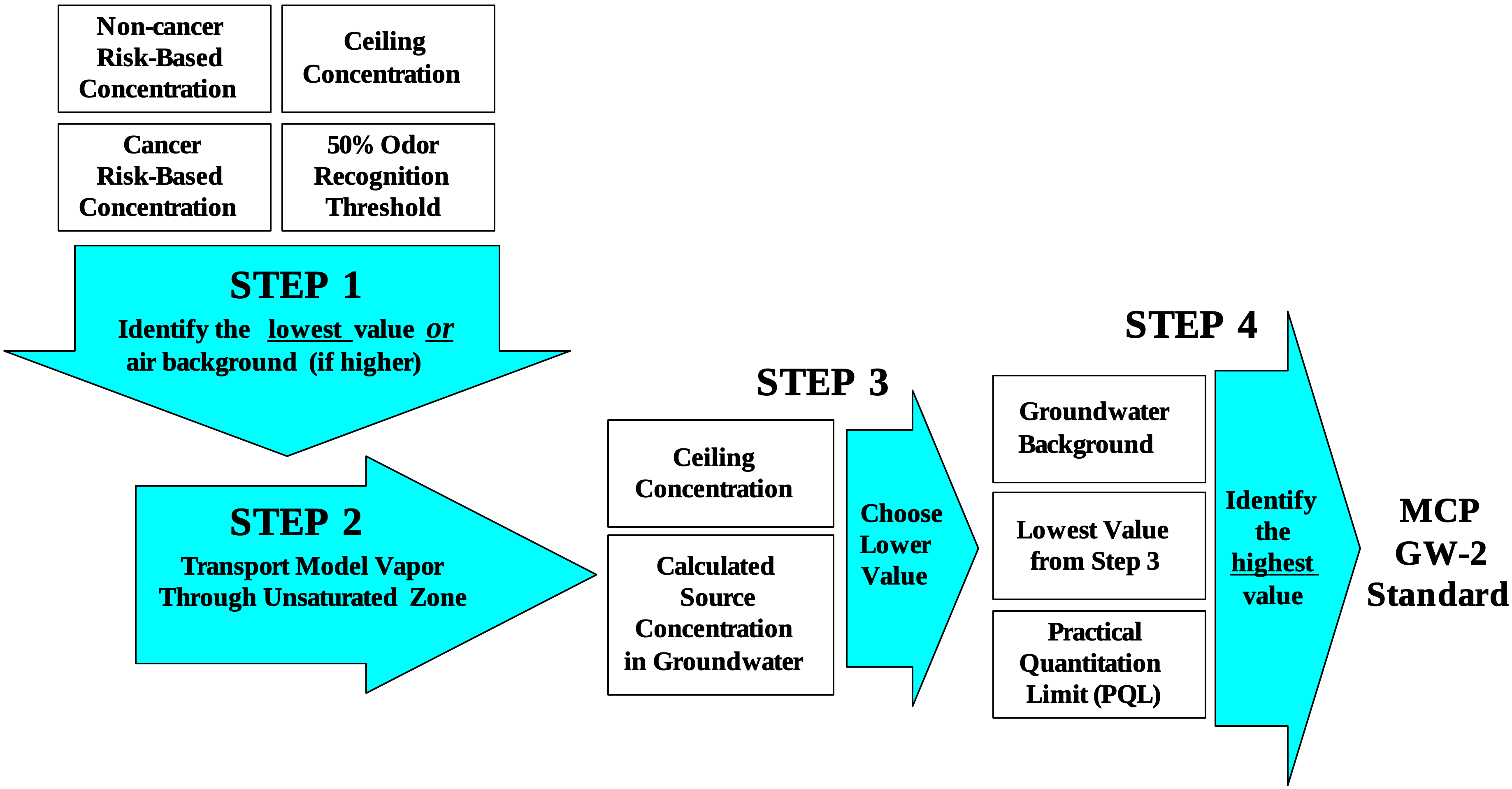
➤Adopt an existing MMCL or Drinking Water Guideline, or if there is none:



Basis of New GW-1 Standards

Fraction	ug/L	Basis
TPH (Generic)	200	Lowest EPH fractional standard
C5 - C8 Aliphatic	400	Threshold Effects
C9 - C12 Aliphatic	4,000	Threshold Effects
C9 - C18 Aliphatic	4,000	Threshold Effects
C19 - C36 Aliphatic	5,000	Ceiling Concentration
C9 - C10 Aromatic	200	Threshold Effects
C11 - C22 Aromatic	200	Threshold Effects

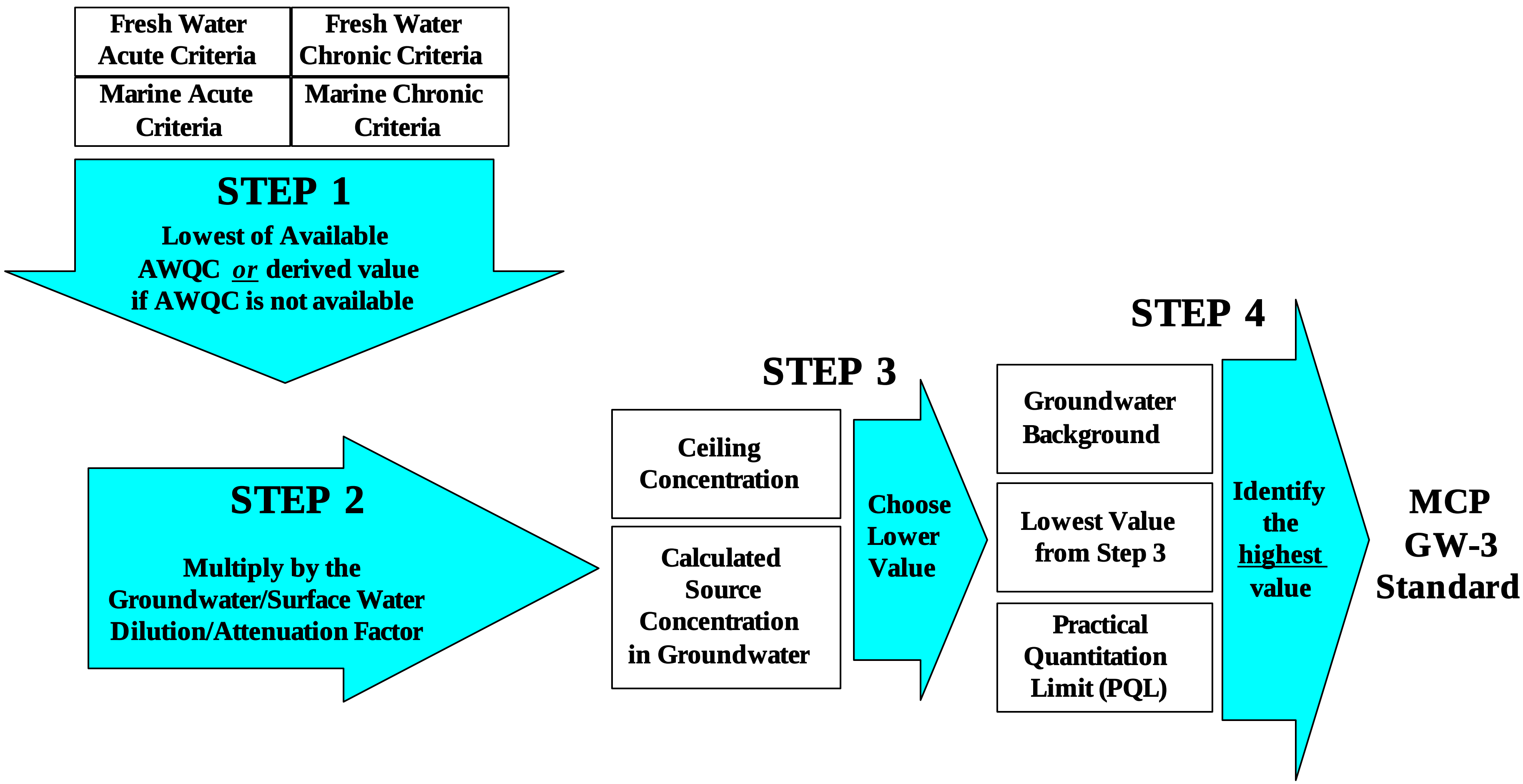
Groundwater GW-2



Basis of New GW-2 Standards

Fraction	ug/L	Basis
TPH (Generic)	1,000	Lowest EPH fractional standard
C5 - C8 Aliphatic	1,000	Risk Management
C9 - C12 Aliphatic	1,000	Risk Management
C9 - C18 Aliphatic	1,000	Risk Management
C19 - C36 Aliphatic	N/A	Considered non-volatile
C9 - C10 Aromatic	5,000	Risk Management
C11 - C22 Aromatic	50,000	Ceiling

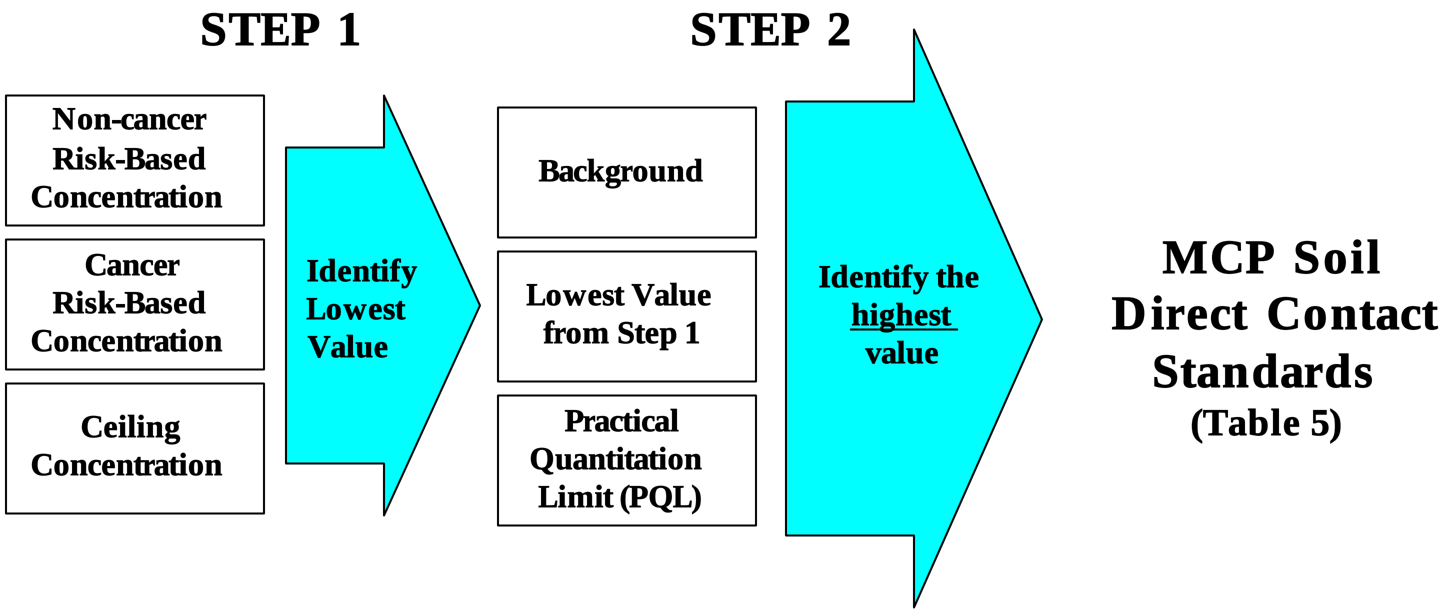
Groundwater GW-3



Basis of New GW-3 Standards

Fraction	ug/L	Basis
TPH (Generic)	20,000	Lowest EPH fractional standard
C5 - C8 Aliphatic	40,000	Aquatic Toxicity - Hexane
C9 - C12 Aliphatic	20,000	Aquatic Toxicity - Decane
C9 - C18 Aliphatic	20,000	Aquatic Toxicity - Decane
C19 - C36 Aliphatic	50,000	Ceiling
C9 - C10 Aromatic	4,000	Aquatic Toxicity - Ethylbenzene
C11 - C22 Aromatic	30,000	PAHs AWQC

Soil Standards - Direct Contact



Basis of New S-1 Direct Contact Standards

Fraction	mg/kg	Basis
TPH (Generic)	800	Lowest EPH fractional standard
C5 - C8 Aliphatic	100	Ceiling
C9 - C12 Aliphatic	1,000	Ceiling
C9 - C18 Aliphatic	1,000	Ceiling
C19 - C36 Aliphatic	2,500	Ceiling
C9 - C10 Aromatic	100	Ceiling
C11 - C22 Aromatic	800	Noncancer Effects

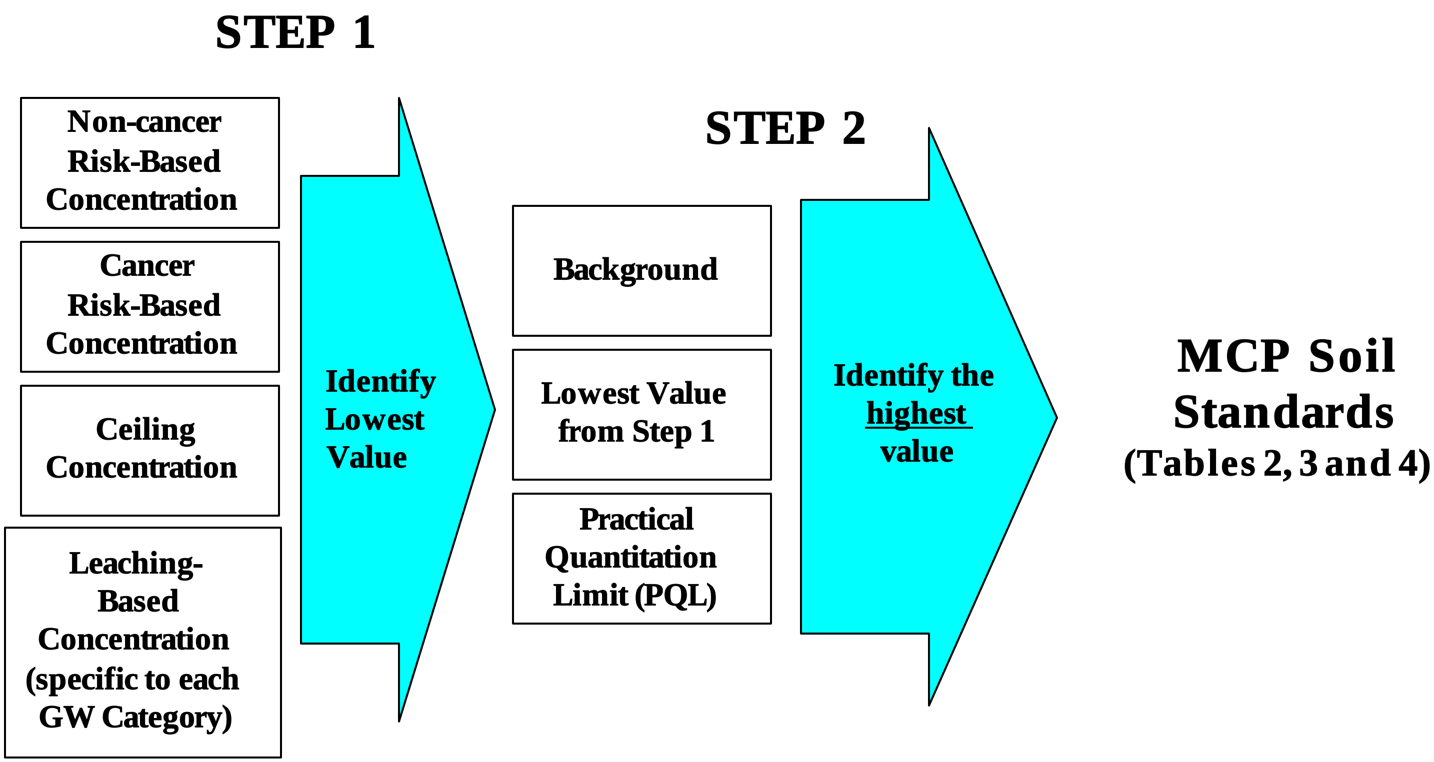
Basis of New S-2 Direct Contact Standards

Fraction	mg/kg	Basis
TPH (Generic)	2,000	Lowest EPH fractional standard
C5 - C8 Aliphatic	500	Ceiling
C9 - C12 Aliphatic	2,500	Ceiling
C9 - C18 Aliphatic	2,500	Ceiling
C19 - C36 Aliphatic	5,000	Ceiling
C9 - C10 Aromatic	500	Ceiling
C11 - C22 Aromatic	2,000	Noncancer Effects

Basis of New S-3 Direct Contact Standards

Fraction	mg/kg	Basis
TPH (Generic)	5,000	Lowest EPH fractional standard
C5 - C8 Aliphatic	500	Ceiling
C9 - C12 Aliphatic	5,000	Ceiling
C9 - C18 Aliphatic	5,000	Ceiling
C19 - C36 Aliphatic	5,000	Ceiling
C9 - C10 Aromatic	500	Ceiling
C11 - C22 Aromatic	5,000	Ceiling

Soil Standards - Considering Leaching to Groundwater

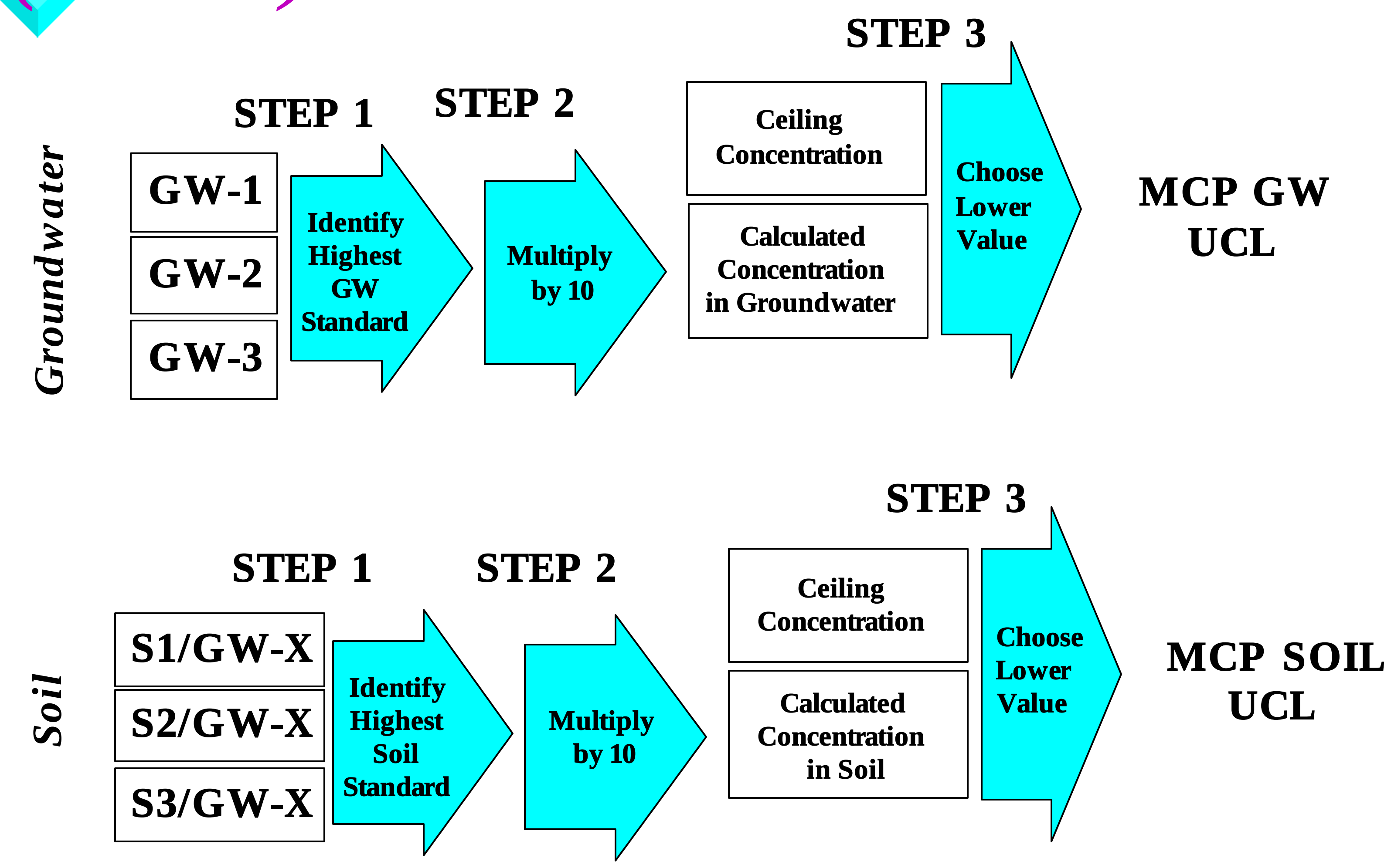


S-1, S-2 and S-3 Standards Based on Leaching Consideration

Tables 2, 3 and 4

S-1/GW-1	**C9 - C10 Aromatic (100 mg/kg)** **C11 - C22 Aromatic (200 mg/kg)**
S-2/GW-1	**C9 - C10 Aromatic (100 mg/kg)** **C11 - C22 Aromatic (200 mg/kg)**
S-3/GW-1	**C9 - C10 Aromatic (100 mg/kg)** **C11 - C22 Aromatic (200 mg/kg)**

Upper Concentration Limits (UCLs)



Basis of New Soil UCLs

Fraction	mg/kg	Basis
TPH (Generic)	10,000	Ceiling
C5 - C8 Aliphatic	5,000	10 x highest Method 1 standard
C9 - C12 Aliphatic	20,000	Risk Management
C9 - C18 Aliphatic	20,000	Risk Management
C19 - C36 Aliphatic	20,000	Risk Management
C9 - C10 Aromatic	5,000	10 x highest Method 1 standard
C11 - C22 Aromatic	10,000	Ceiling

Basis of New Groundwater UCLs

Fraction	ug/L	Basis
TPH (Generic)	100,000	Ceiling
C5 - C8 Aliphatic	100,000	Ceiling
C9 - C12 Aliphatic	100,000	Ceiling
C9 - C18 Aliphatic	100,000	Ceiling
C19 - C36 Aliphatic	100,000	Ceiling
C9 - C10 Aromatic	100,000	Risk Management
C11 - C22 Aromatic	100,000	Ceiling

Reportable Concentrations (RCs)

RCGW-1	The lowest of the following Method 1 standards: **GW-1, GW-2 and GW-3**
RCGW-2	The lowest of the following Method 1 standards: **GW-2 and GW-3**
RCS-1	The lowest of the following Method 1 standards: **S-1/GW-1, S-1/GW-2, S-1/GW-3, S-2/GW-1 and S-3/GW-1**
RCS-2	The lowest of the following Method 1 standards: **S-2/GW-2, S-2/GW-3, S-3/GW-2 and S-3/GW-3**

New Groundwater RCs

Fraction	RCGW-1 mg/L	RCGW-2 mg/L
TPH (Generic)	0.2	1
C5 - C8 Aliphatic	0.4	1
C9 - C12 Aliphatic	1	1
C9 - C18 Aliphatic	1	1
C19 - C36 Aliphatic	5	50
C9 - C10 Aromatic	0.2	4
C11 - C22 Aromatic	0.2	30

New Soil RCs

Fraction	RCS-1 mg/kg	RCS-2 mg/kg
TPH (Generic)	200	2,000
C5 - C8 Aliphatic	100	500
C9 - C12 Aliphatic	1,000	2,500
C9 - C18 Aliphatic	1,000	2,500
C19 - C36 Aliphatic	2,500	5,000
C9 - C10 Aromatic	100	500
C11 - C22 Aromatic	200	2,000

Method 1

Selection of Method: 310 CMR 40.0942

Considerations:

- Existing Method 1 Standard for all Contaminants of Concern

- Contamination present in a medium other than soil or groundwater

- Bioaccumulating chemicals present in the top two feet of soil

Method 1
Contaminants of Concern

- **Section 2.4 of *Guidance Document***

- **VPH/EPH Considerations**

Chemicals which would be included in the VPH/EPH fraction ranges would _*not*_ be considered distinct Contaminants of Concern unless there is already a Method 1 standard for that chemical. (e.g., Trimethylbenzenes would be included in the C9-C10 Aromatics and would not be a separate CoC)

Method 1
Other Environmental Media

Ambient or Indoor Air, surface water, sediments...

✷ VPH/EPH Considerations

- Odors detected in indoor or ambient air is indicative of the presence of OHM in "another environmental medium". The health risk posed by exposures which would thus occur must be evaluated.

- Odors detected in a boring or test pit would not, by themselves, invalidate the use of Method 1.

Method 1

Exposure Point Concentrations, Hot Spots and Risk Characterization

✶ VPH/EPH Considerations

Each VPH/EPH fraction is treated as if it were a single entity or a unique chemical. The general rules which apply to Method 1 Risk Characterizations also apply when VPH/EPH fractions are the Contaminants of Concern.

Method 2

Purpose of a Method 2 Risk Characterization

- Create a standard when there is no Method 1 standard for a chemical
- Modify existing Method 1 standards for fate and transport considerations

Method 2

Limitations on Use of Method 2

Considerations:

- Contamination present in a medium other than soil or groundwater
- Bioaccumulating chemicals present in the top two feet of soil

Method 2

Modifying Existing GW Standards

- GW-1: No modifications allowed
  (310 CMR 40.0982(1))

- GW-2: Modification of VPH/EPH standards limited to a demonstration of "No Impact"

- GW-3: Modifications based upon fate & transport considerations and/or
  "No Impact" demonstration.

Method 2
Modifying Existing Soil Standards

- Soil modifications limited to adjustment of the leaching component of the Method 1 standards

VPH/EPH Consideration:

Only a small number of the new VPH/EPH fractional standards are based upon the leaching component.

Method 2
Exposure Point Concentrations, Hot Spots and Risk Characterization

✴ VPH/EPH Considerations

Each VPH/EPH fraction is treated as if it were a single entity or a unique chemical. The general rules which apply to Method 2 Risk Characterizations also apply when VPH/EPH fractions are the Contaminants of Concern.

Method 3
Contaminants of Concern

- TPH, VOCs and PAHs
- VPH/EPH, VOCs and PAHs
- Trimethylbenzenes and other OHM which would be picked up under TPH or VPH/EPH would *not* be a CoC

(See Session 5 for more detail about using old TPH data.)

Method 3
Toxicity Values

Fraction	Oral RfD mg/kg/day	Inhalation RfC ug/m^3
C5 - C8 Aliphatic	0.06	200
C9 - C12 Aliphatic	0.6	2000
C9 - C18 Aliphatic	0.6	2000
C19 - C36 Aliphatic	6	N/A
C9 - C10 Aromatic	0.03	60
C11 - C22 Aromatic	0.03	71

Method 3
Exposure Point Concentrations, Hot Spots and Risk Characterization

VPH/EPH Considerations

Each VPH/EPH fraction is treated as if it were a single entity or a unique chemical. The general rules which apply to Method 3 Risk Characterizations also apply when VPH/EPH fractions are the Contaminants of Concern.

Method 3

Risk Characterization

- **Health**
  Cumulative Noncancer Risk Limit...HI=1
  Excess Lifetime Cancer Risk Limit...1 in 100,000

- **Safety**
  e.g. explosive levels of gasoline

- **Public Welfare**
  Odor Issues, UCLs

- **Environment**
  UCLs, DEP developing Stage I Screening Levels

Response Action Outcomes (RAOs)

Not Related to VPH/EPH, but...

- Risk isn't everything.
  Elimination of continuing sources (40.1003(5)) and background (40.1020) required

- New A-4/B-3 RAO Categories
  Situations under which soil concentrations may exceed Upper Concentration Limits.

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Session 5: Implementation Issues

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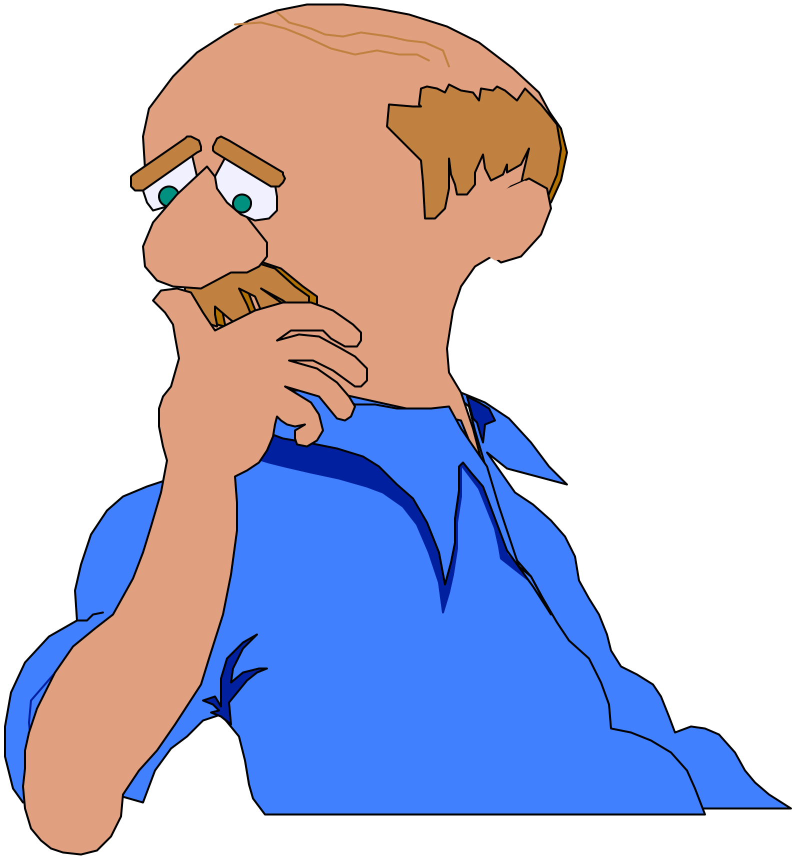
Implementation and Application

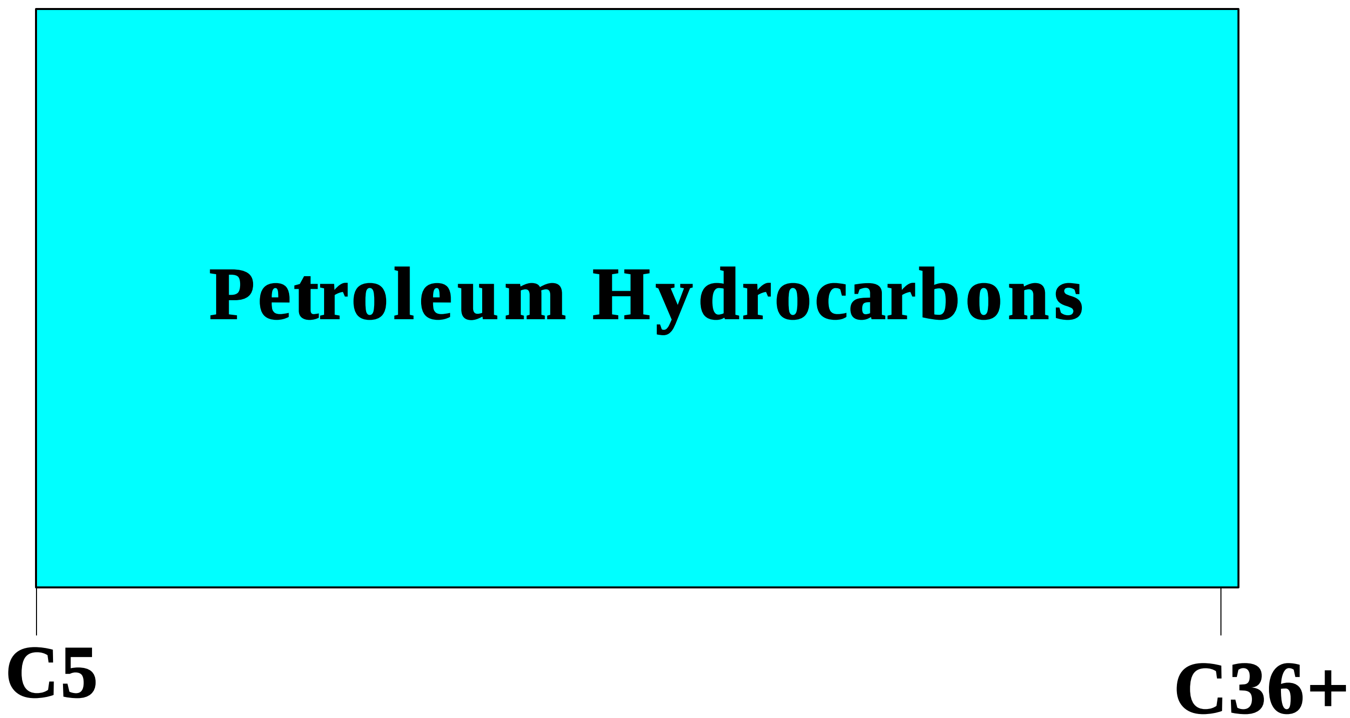
VPH / EPH Approach

Terminology and Ground Rules

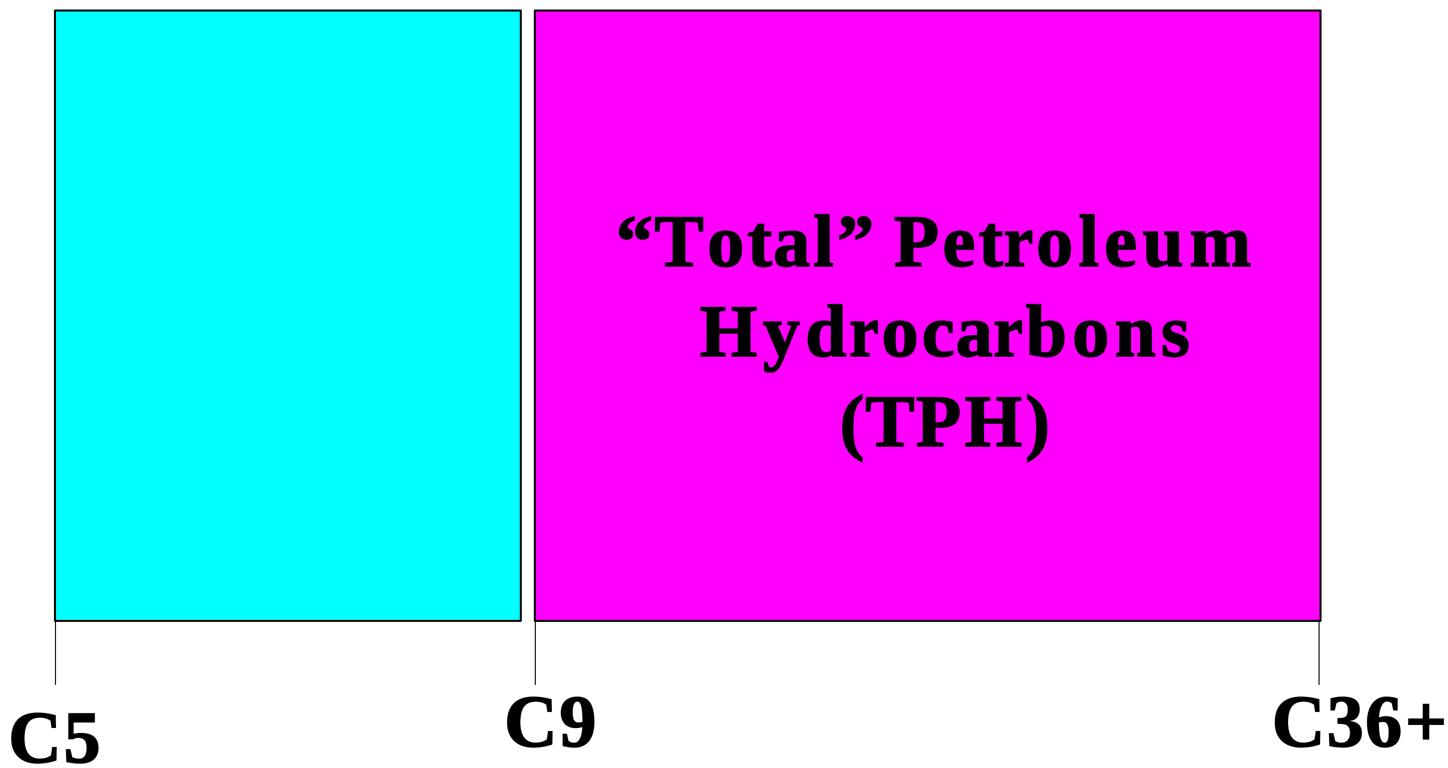
- VPH....EPH....TPH...
- Aliphatic...Alkane...
  Alkene... Al Gore....
- Fractions... Ranges...
  Gasoline Ranges...
  Electric Ranges.......



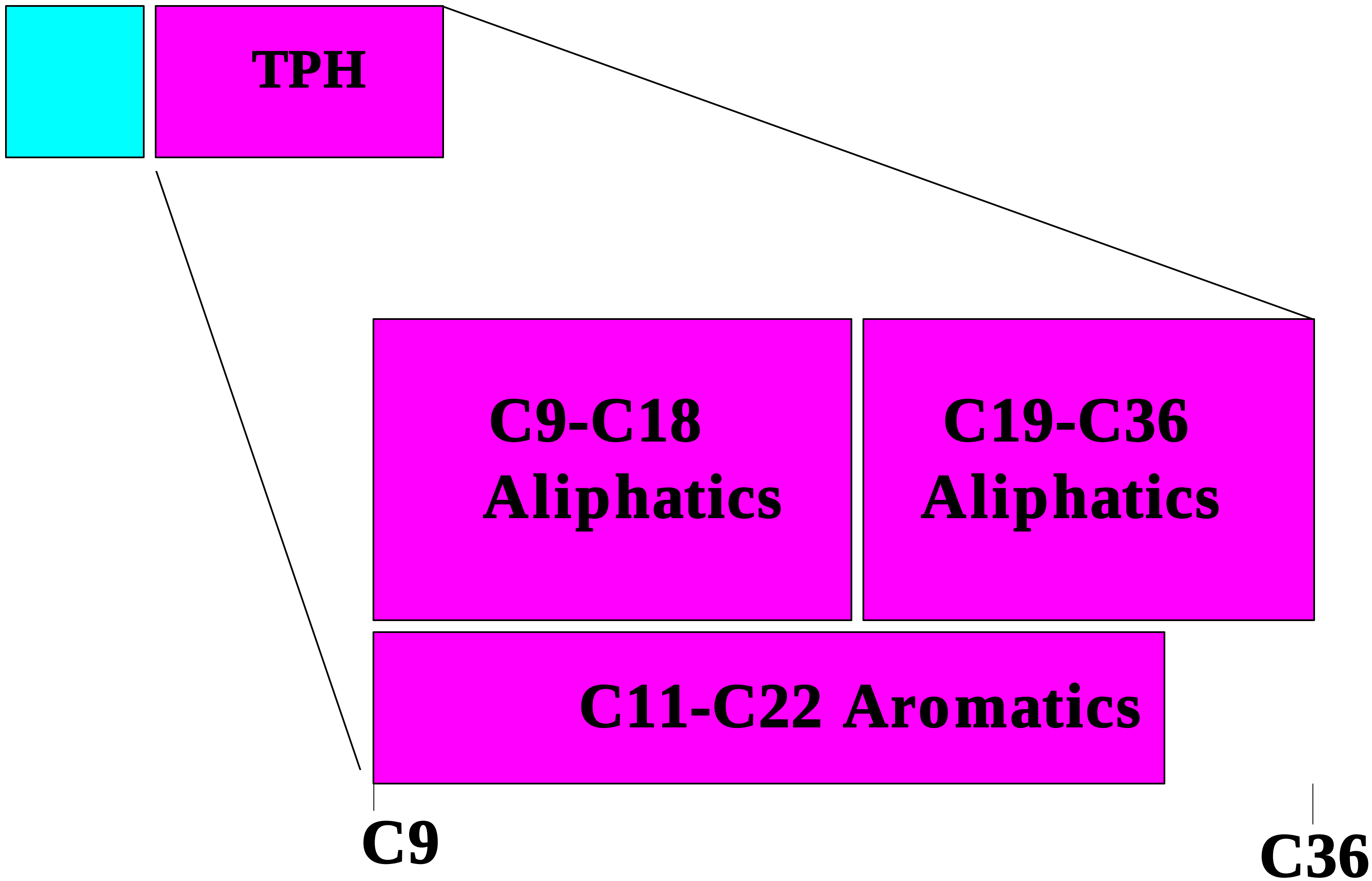
Universe of Hydrocarbons



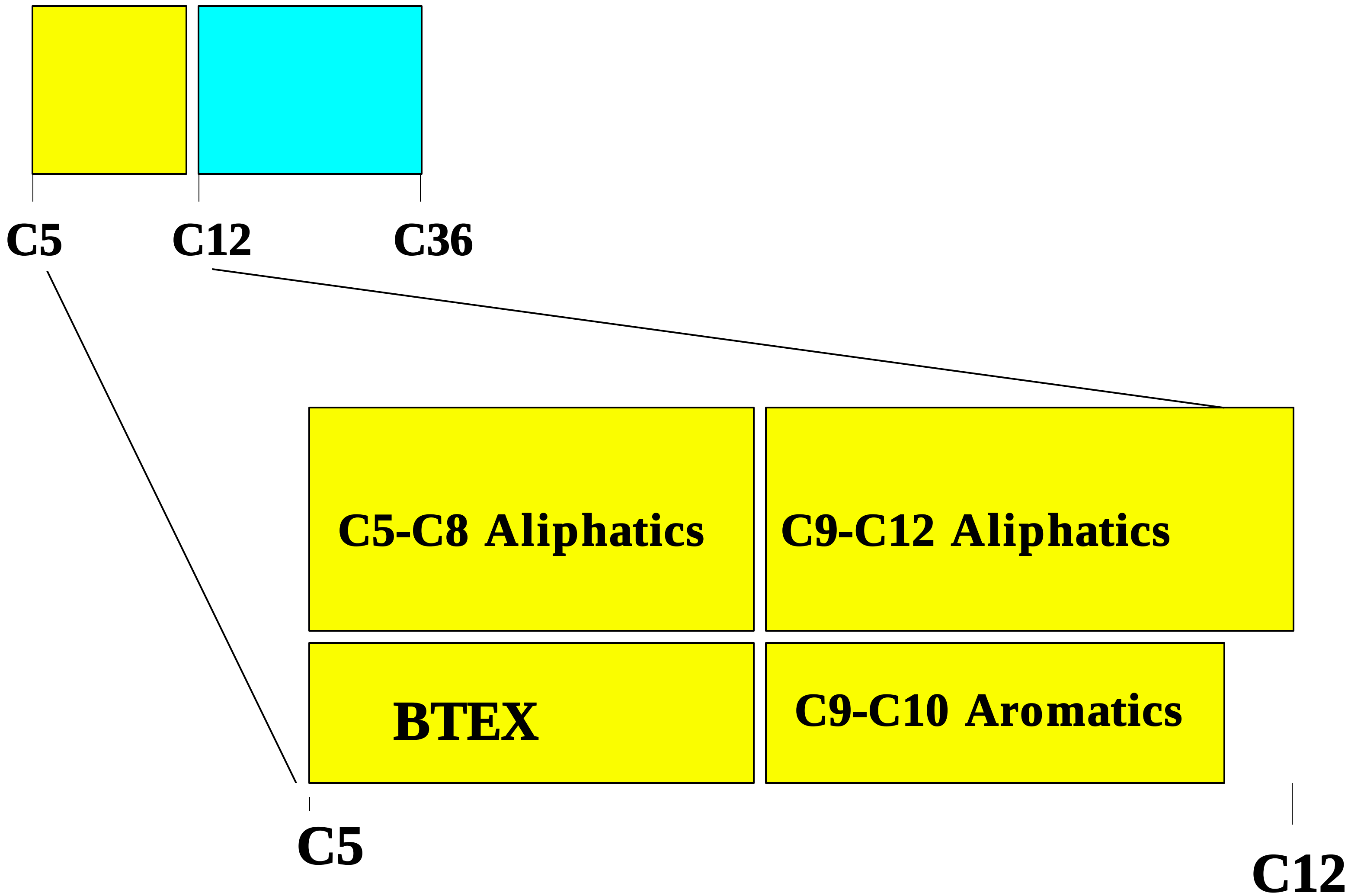
TPH



TPH and EPH

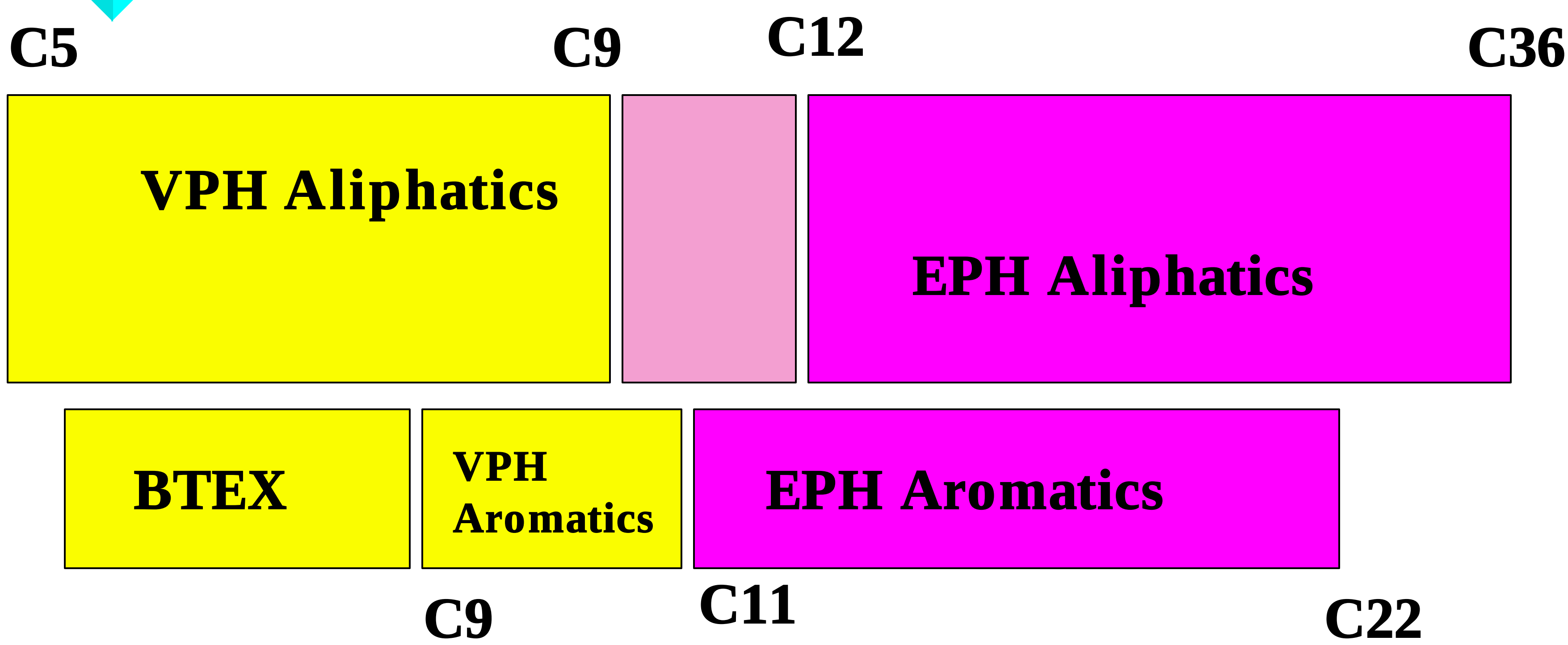

TPH
C9-C18 Aliphatics
C19-C36 Aliphatics
C11-C22 Aromatics
C9
C36

VPH



C5
C12
C36
C5-C8 Aliphatics
C9-C12 Aliphatics
BTEX
C9-C10 Aromatics
C5
C12

VPH and EPH



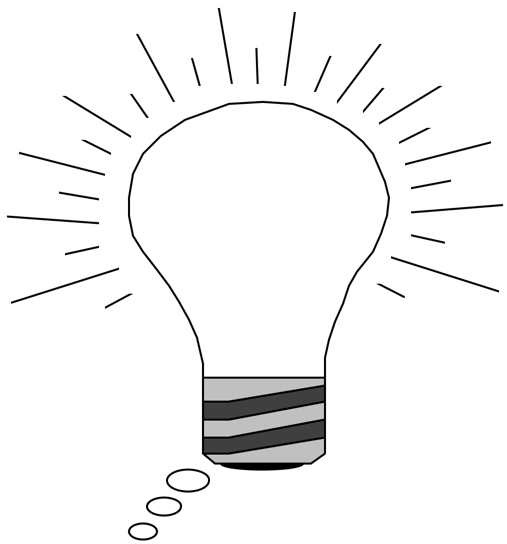
Gasoline

Diesel / #2 Fuel Oil

Standards

- There are no “VPH” or “EPH” cleanup Standards

- VPH and EPH are analytical test methods, and groupings of hydrocarbon fractions



Fractions

- Using VPH Method, you can determine :
  - C5-C8 Aliphatic Hydrocarbons
  - C9-C12 Aliphatic Hydrocarbons
  - C9-C10 Aromatic Hydrocarbons
- Using EPH Method, you can determine:
  - C9-C18 Aliphatic Hydrocarbons
  - C19-C36 Aliphatic Hydrocarbons
  - C11-C22 Aromatic Hydrocarbons

Fractions and Target Analytes

- By definition, collective hydrocarbon fractions ***exclude*** "Target Analytes"
- "Target Analytes" are petroleum constituents for which there are Method 1 Standards :
  - BTEX
  - MtBE
  - PAHs

Method 1

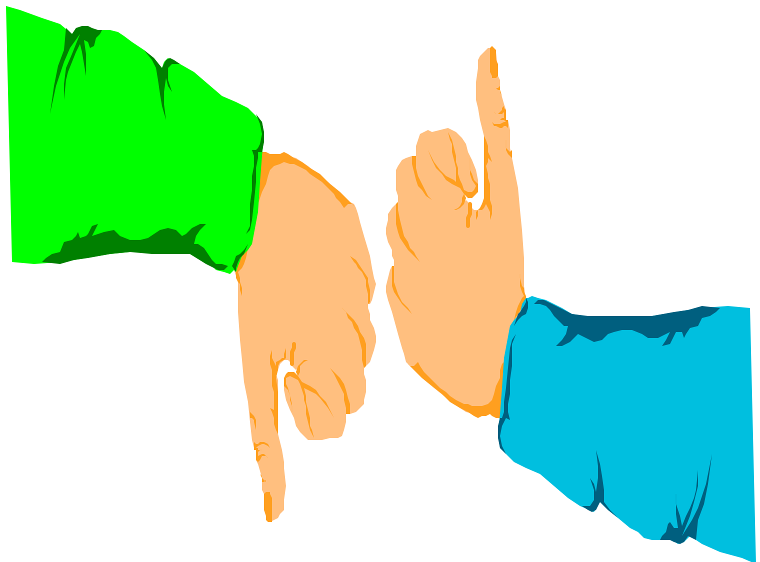
- Using Method 1 is a TWO step process:
  - Step 1: identify and evaluate Target Analytes of interest (e.g., BTEX, PAHs)
  - Step 2: identify and evaluate hydrocarbon fractions of interest, to address the rest of the hydrocarbon mixture

Application Issues

- When to test for VPH? EPH? Both?
- When to test for Target Analytes?
- When to test soil? Groundwater? Both?
- How to use TPH/Screening data?

Disclaimer!

- ***Guidance and "Rules of Thumbs" are based upon currently available information and are designed to be protective at most sites of concern***
- ***There may be unusual release or site conditions where the provided guidance may not be appropriate***



VPH? EPH? Both?

Petroleum Product	VPH	EPH
Gasoline	✓	
Fresh Diesel/#2 Fuel	✓	✓
Weathered Diesel/#2 Fuel		✓
#3-#6 Fuel Oil		✓
Mineral/Dielectric Oils		✓

VPH? EPH? Both?

Petroleum Product	VPH	EPH
Jet Fuel JP-4	✓	✓
Jet Fuel Jet A		✓
Waste Crankcase Oil	✓	✓
Unknown Oils/Source	✓	✓

EPH? VPH? Both?

- Caveats:

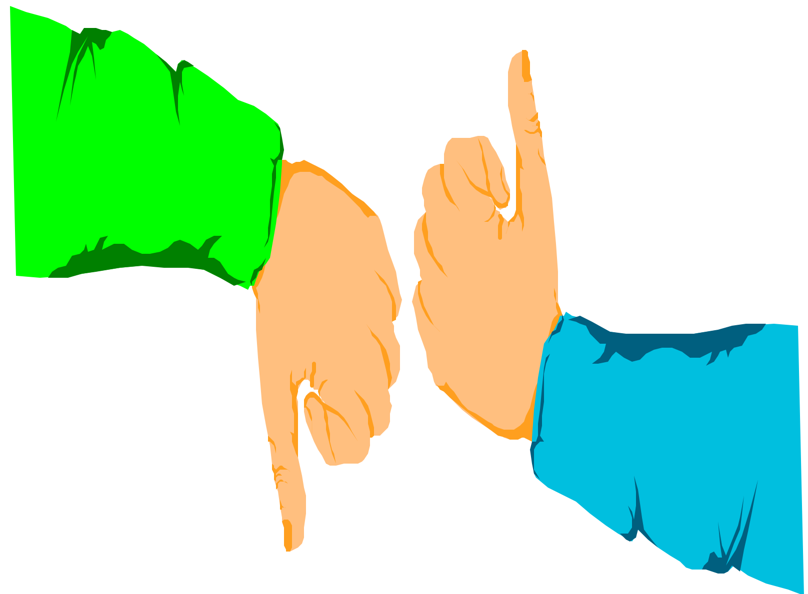
  – VPH testing recommended for drinking water wells impacted by *any* petroleum product

  – May eliminate VPH testing for fuels based upon VOC screening

  – "Fresh" soil/water samples defined as > 100 ppmv total organic vapor headspace

Target Analytes

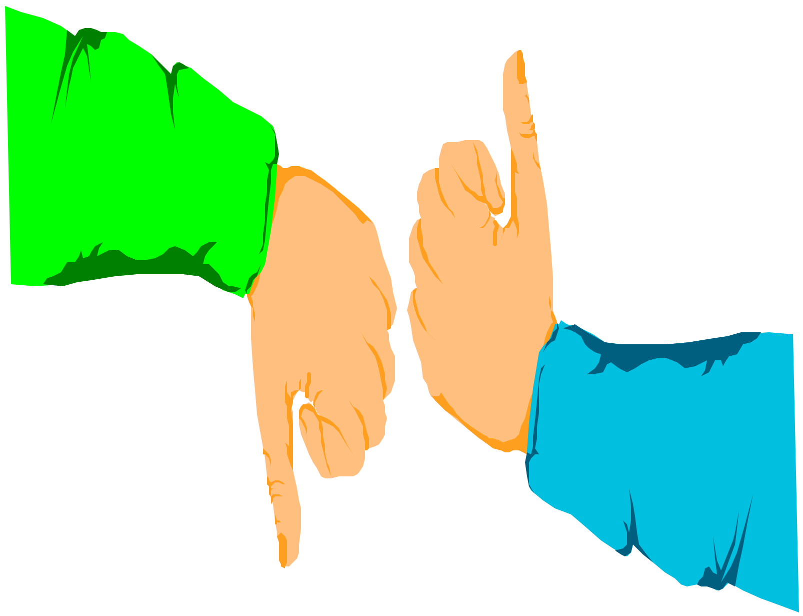
- Gasoline Releases
  - Determine BTEX and MtBE in soil and groundwater; lead and EDB where indicated



- #2 Fuel Oil Releases
  - Determine BTEX in groundwater if shallow gw or sensitive (GW-1) areas

Target Analytes

- #2 Fuel Oil Releases
  - Test for PAHs in soil if TPH > 500 ug/g
  - Test for PAHs in groundwater if near drinking water supplies

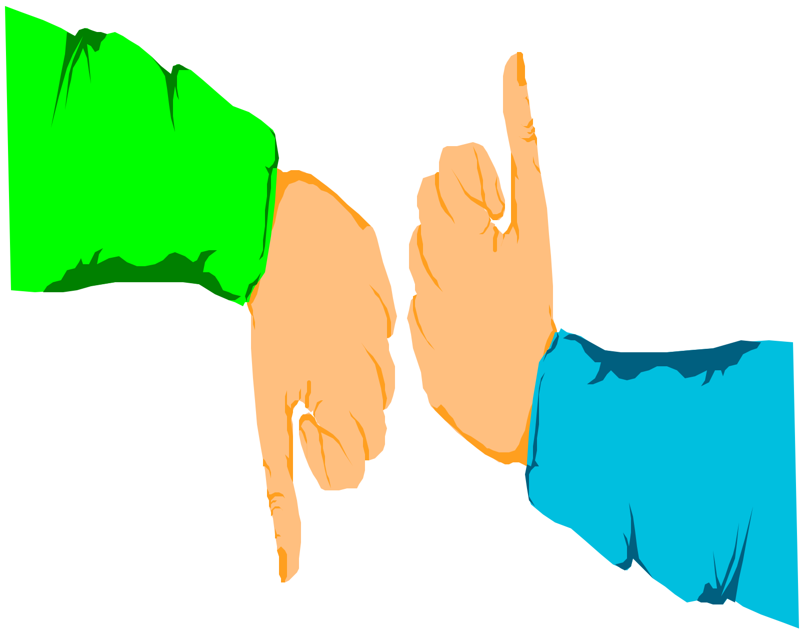


- Waste (Crankcase) Oil
  - Test for PAHs in soil and groundwater

PAHs

PAHs of Interest for #2 Fuel Oil:

- acenaphthene
- naphthalene
- 2-methylnaphthalene
- phenanthrene



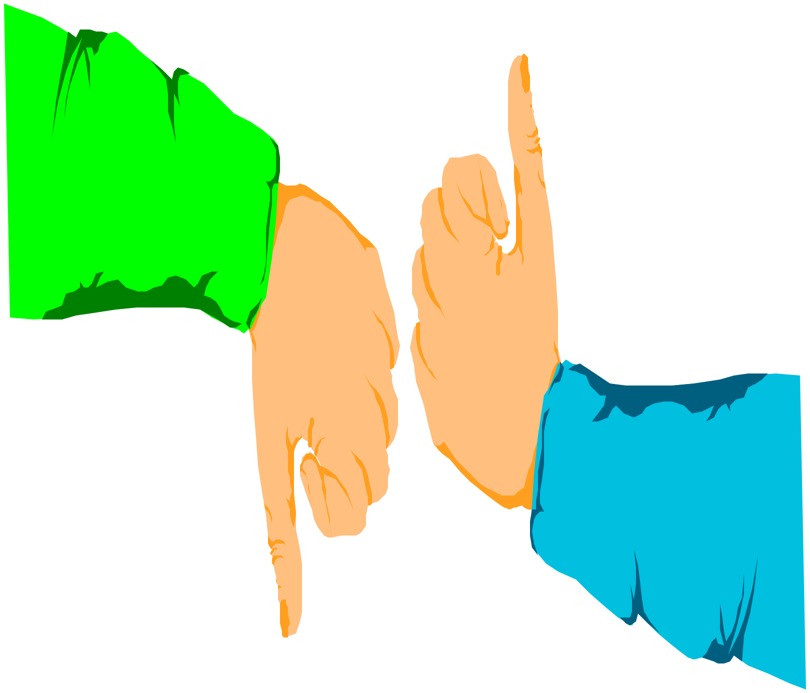
Soil? Groundwater? Both?

Site-Specific decision, based upon:

- volume/mechanism of release
- depth to groundwater
- extent of site investigation/knowledge
- sensitivity of receptors:
  - direct contact - soil
  - ingestion/inhalation - gw

Soil? Groundwater? Both?

- Rules of Thumb:
  - Gasoline Releases:
    - Characterize groundwater in most cases
  - #2 Fuel Oil Releases
    - Evaluate groundwater if shallow or if in sensitive (GW-1) area
  - Near drinking water supplies
    - Evaluate gw in most cases



To Filter, or not to Filter.....

- Not a simple or universal answer

- Performance standard:
  - Determine concentrations of contaminants moving through an aquifer, and/or impacting a receptor

- Filtering EPH gw samples may be appropriate in some cases, if conducted in this context

Using Old/New "TPH" Data

- Future TPH data may be used *directly* to characterize C9 and heavier hydrocarbons (e.g., fuel oil), by using the TPH Method 1 standards

- Old TPH data and new TPH / screening data may be used *indirectly*, by "converting" the TPH value into EPH fractional concentrations

Converting TPH data

- Making *informed* judgments on the chemistry of the TPH value(s), relative to percentage of aliphatics/aromatics, based upon:
  - chemistry/weathering of spilled product
  - available VPH/EPH data
  - default compositional assumptions

Recommended TPH Compositional Assumptions - Soil

Petro Product	C11-C22 Aromatics	C9-C18 Aliphatics	C19-C36 Aliphatics
Diesel/#2 & Crankcase	60%	40%	0%
#3-#6 Fuel Oil & JP-4	70%	30%	0%
Kerosene & Jet-A	30%	70%	0%
MODF	20%	40%	40%
Unknown Oil	100%	0%	0%

Recommended Compositional Assumptions - Water

- TPH data:
  - All non-targeted (PAH) compounds should be considered C11-C22 Aromatics
- Gasoline Range Organic data:
  - all non-BTEX/MtBE hydrocarbons should be considered C9-C10 Aromatics

Caveats and Fine Print

- LSP must use professional judgment in using and applying TPH/screening data in the VPH/EPH approach!

- Key factors to consider:
  - knowledge of released petro product
  - reliability, validity, and bias of TPH/screening techniques
  - sensitivity of pollutant receptors

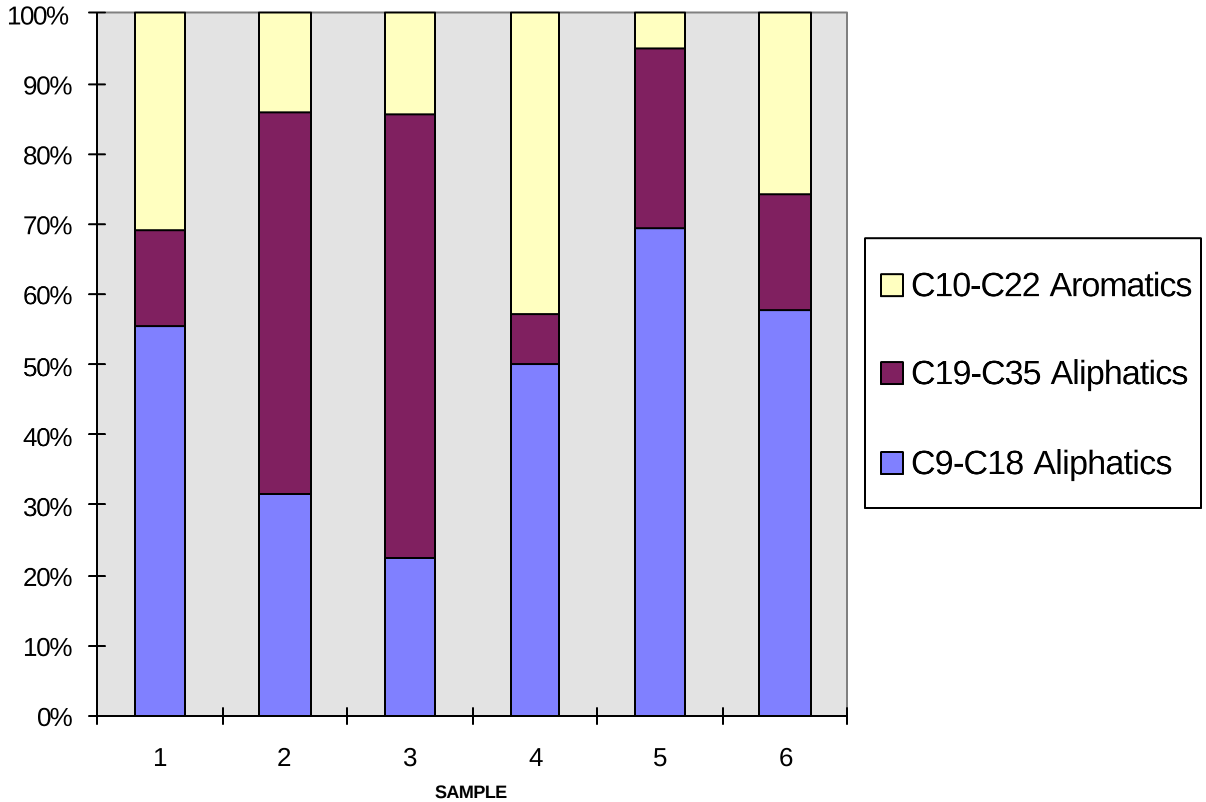
Compositional Variability

- One VPH/EPH sample usually not adequate to define hydrocarbon chemistry and relative aliphatic/aromatic percentages at a site

- Sample chemistry can vary significantly across a site

Compositional Variability

Fuel Oil Spill at a Residential Property



Soil Samples

Compositional Variability

- Considerations:
  - source vs migration areas
  - fate/transport conditions and parameters
  - presence of micro-environments

Characterization Options - The Easy Way

- Step 1: Get VPH and/or EPH fractional data
- Step 2: Calculate Exposure Point Concentration (EPC)

Characterization Options - The Harder Way

- Obtain VPH/EPH data from *key areas* and *critical exposure pathways*
- Supplement with screening/TPH data
- Consider chemistry of petroleum products, fate/transport factors, VPH/EPH data, and default conservative compositional assumptions
- Determine fractional composition/EPC for risk assessment/Method 1 Standards

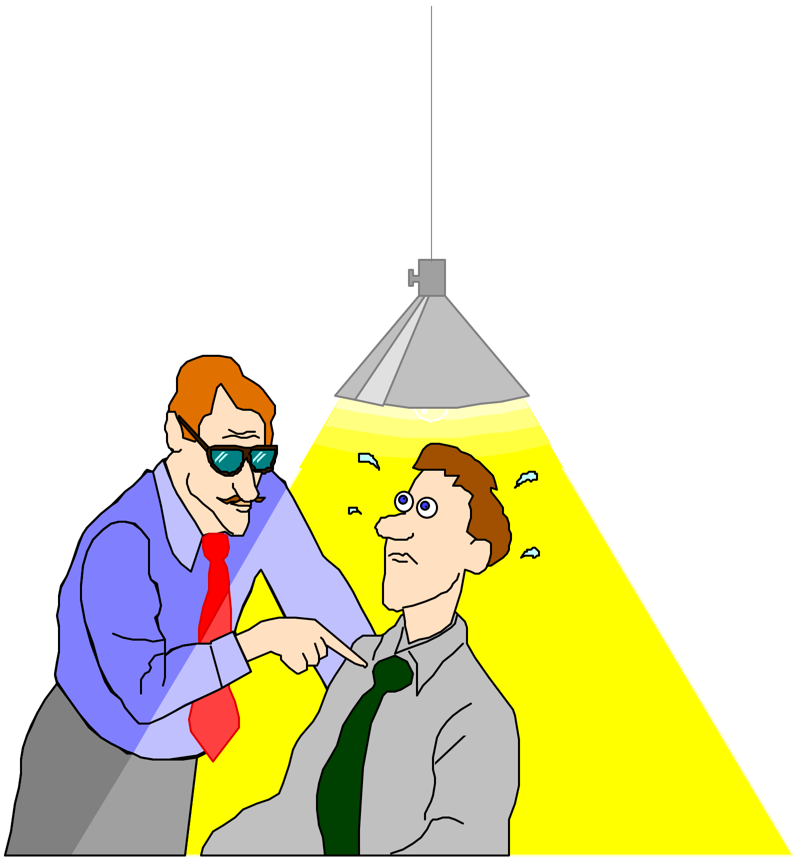
Ground Rules

- If using MCP Method 1 Fractional Standards, must have at least *some* actual VPH/EPH fractional data - not just assumed values

- In Method 3 assessment, more flexibility to "make a case" that fractional concentrations have been adequately established,without having actual VPH/EPH data

Regulatory Stuff

- Phasing in Approach
- MCP requirements
- Old / Closed sites
- What to do ***NOW***



Phasing in the new Approach

- **Effective date of MCP changes: Fall 1997**

What happens on Effective Date?

- New Reportable Concentrations in effect
- New Method 1 Cleanup Stds in effect
- New UCLs in effect

***** No Grandfathering Provisions *****

Regulatory Requirements/Context

- MCP will not "mandate" testing for VPH / EPH fractions

- Like any other standard, LSPs must decide when it is necessary to address / demonstrate compliance with these standards

- Alternative approaches acceptable via Method 3 Risk Characterizations

RAPs

- After effective date of MCP changes, there will be an expectation that LSPs will address VPH/EPH concerns at **ALL** new and open sites, per Response Action Performance Standard of 40.0191

- Prior to effective date of MCP changes, there is an expectation that LSPs will address VPH/EPH concerns *only* at those FEW sites with *direct and compelling exposure concerns*

Reopening Old Cases

- Direct and Compelling Exposures:
  - Drinking water wells impacted by gasoline releases
  - Persistent indoor air impacts from gasoline releases

Applying a New Standard?

- No.
- Risk standards in effect since 1988
- VPH/EPH not a new standard, but a new tool to evaluate and characterize risks, and document compliance with existing risk management standards

What can/should/must be done NOW?

- Use existing MCP standards and traditional approaches UNLESS direct and compelling exposure concerns

- Electively use proposed Method 1 Standards and UCLs as part of a Method 2 characterization per 40.0982(7)

- If site will not be closed out by effective date, consider use of VPH/EPH now

VPH/EPH Owners Manual

- Guidance Document will be finalized and issued prior to effective date of MCP changes

- Questions? Contact John Fitzgerald at:

(617) 932-7702, or

John.Fitzgerald@state.ma.us

For a Closer Look.....

VPH/EPH Bibliography

Spring 1997

<u>DEP Publications</u>:

- ***Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter***, August, 1994

  Summary: Original report presenting the toxicological basis of the proposed new VPH/EPH approach

- ***Method for the Determination of Volatile Petroleum Hydrocarbons (VPH),*** Public Comment Draft 1.0, August, 1995

- ***Method for the Determination of Extractable Petroleum Hydrocarbons (EPH),*** Public Comment Draft 1.0, August 1995

  Summary: Detailed Analytical Methods

- ***Issues Paper: Implementation of VPH/EPH Approach***, Public Comment Draft, May, 1996

  Summary: Detailed discussion and recommendations on how to develop MCP Method 1 cleanup standards, and otherwise incorporate new VPH/EPH approach into MCP regulatory process

- ***Revisions to the Massachusetts Contingency Plan, 310 CMR 40.0000 - Public Comment Draft***, January 17, 1997

  Summary: Proposed VPH/EPH fractional standards; discussion of risk management issues; spreadsheets of standard calculations.

All DEP publications available on the World Wide Web at http://www.state.ma.us/dep/deppubs.htm

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Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Publications

- ***A Risk-Based Approach for the Management of Total Petroleum Hydrocarbons in Soil - A Technical Overview of the Petroleum Hydrocarbon Risk Assessment Approach of the TPH Criteria Working Group*, March, 1997**

    Summary: Overview of TPHCWG framework and approach

- ***Selection of Representative TPH Fractions Based on Fate and Transport Considerations***, Volume III in a Series, Final Draft, 2/27/97

    Summary: Extensive data on physical properties of hydrocarbon compounds, discussion on fate/transport, recommendations on physical/chemical properties for aliphatic and aromatic fractions

- ***Development of Fraction Specific Reference Doses (RfDs) and Reference Concentration (RfCs) for Total Petroleum Hydrocarbons (TPH),*** Volume IV In a Series, 1996

    Summary: Extensive data on toxicological properties of hydrocarbon compounds, mixtures, and products; recommended toxicological parameters for aliphatic and aromatic fractions. NOTE: The information and recommendations contained in this report have not been peer-reviewed, and are currently being evaluated by MADEP.

TPHCWG Publications available on World Wide Web at http://voyager.wpafb.af.mil

- *click on* "publications" -

State of Wisconsin Publications

- ***Studies of Sampling, Storage and Analysis of Soils Contaminated with Gasoline & Diesel***

Summary: Extensive data, information, and recommendations on soil sampling, storage, and preservation.

Wisconsin Publications available on World Wide Web at http:www.dnr.state.wi.us/eq/errhw/

- *document to look for:* SCSSREP.ZIP -