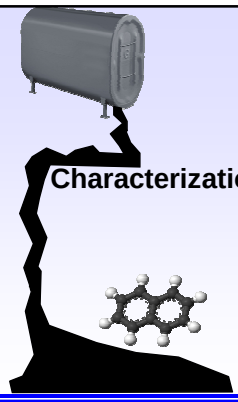

Characterization of #2 Fuel Oil Spills

John Fitzgerald, MassDEP
October 2013

MassDEP

Today's Agenda

- Nature and Scope of Problem
- Conceptual Site Model
- NAPL
- Soil
- Groundwater
- Indoor Air

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Nature and Scope of Problem

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Fate and Transport Characteristics of Home Heating Oil Releases Based Upon a Review of Empirical Data from Actual Releases

Jonathan Kitchen & Joseph Salvetti

27th Annual International Conference on Soils, Sediments, Water and Energy

October, 2011

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Sites that were Evaluated

100 residential oil spills, 1993 – 2011

53% of sites had known/est. spill quantities

98% of sites reported soil impacts

65% of sites reported groundwater impacts

32% of sites reported concentrations of hydrocarbons in GW above standards

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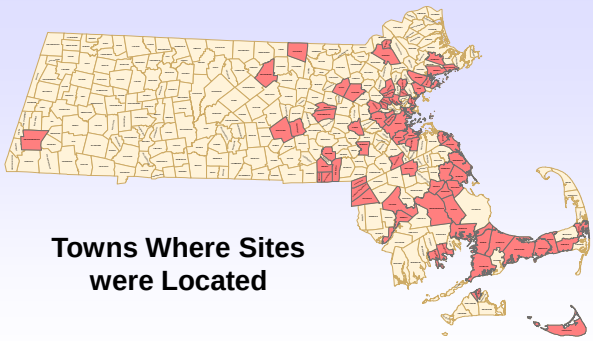

Towns Where Sites were Located

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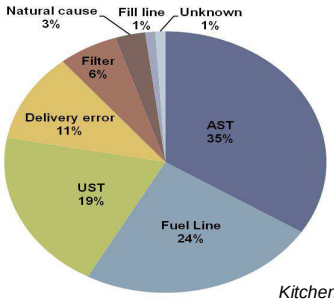
Cause of Residential Fuel Oil Spills



Kitchen/Salvetti, 2011

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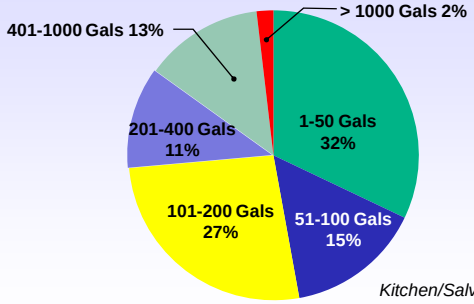
Quantity of Oil Spilled



Kitchen/Salvetti, 2011

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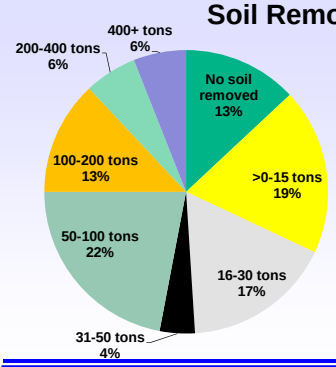
Soil Removal



98% of sites had soil impacts

87% of sites had some soil removal

Average Removal in GW-1 Area was 160 tons

Average Removal in non-GW-1 Area was 90 tons

Kitchen/Salvetti, 2011

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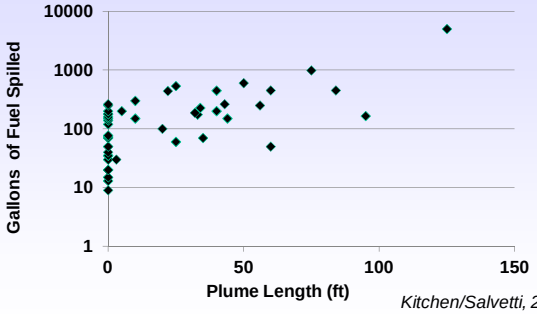
Groundwater Plume



Kitchen/Salvetti, 2011

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NAPL

Visible NAPL was observed at 30 out of the 100 sites.

Out of those 30 sites, 60% reported groundwater contaminant levels greater than one or more groundwater standard.

Kitchen/Salvetti, 2011

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Indoor Air

Only 10 sites reported an indoor air impact detected.

Only 3 sites required (or elected) additional remedial action, the remaining 7 attenuated to background conditions with time and ventilation.

Kitchen/Salvetti, 2011

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Soil Closure/Remediation Drivers

GW-1 areas:

- **2-methylnapthalene (72% of time)**
- **C_9-C_{18} Aliphatic HC (16% of time)**
- **C_9-C_{10} Aromatics (8% of time)**

Non GW-1 Areas:

- ***C_9-C_{18} Aliphatic Hydrocarbons***

Kitchen/Salvetti, 2011

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GW Closure/Remediation Drivers

GW-1 areas:

- **C_{11}-C_{22} Aromatic HC (~60% of time)**
- **2-methylnapthalene (23%)**
- **C_9-C_{10} Aromatic HC (12%)**

Non GW-1 Areas:

- ***C_9-C_{18} Aliphatic Hydrocarbons***

Kitchen/Salvetti, 2011

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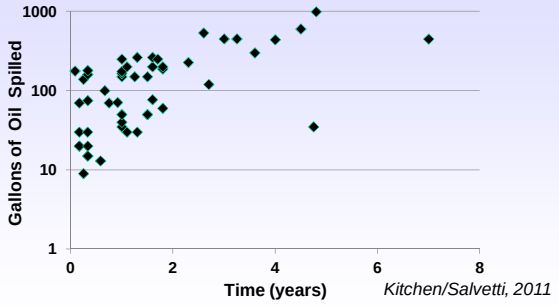
Time to Closure



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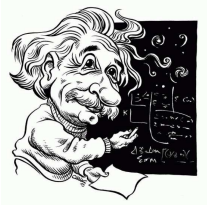
Conceptual Site Model

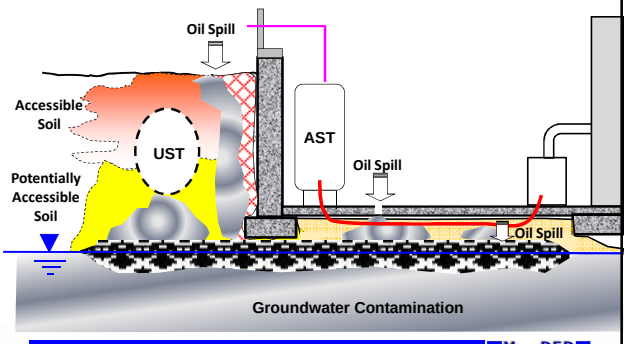


"Knowledge is Good"

Emil Faber

MassDEP

Typical Scenarios



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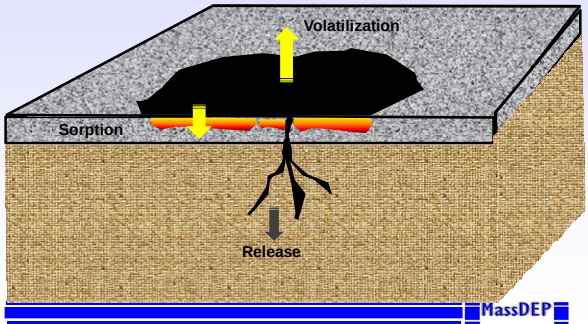
Fate



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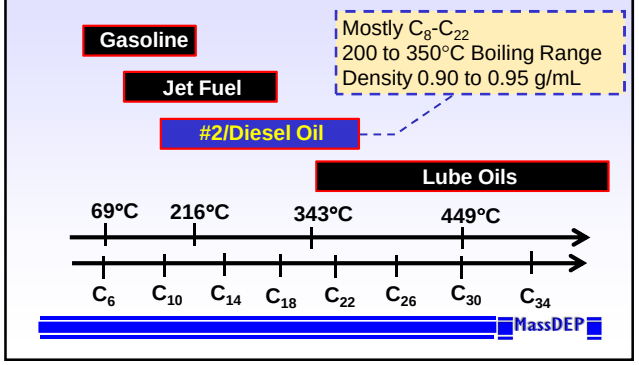
#2 Fuel Oil



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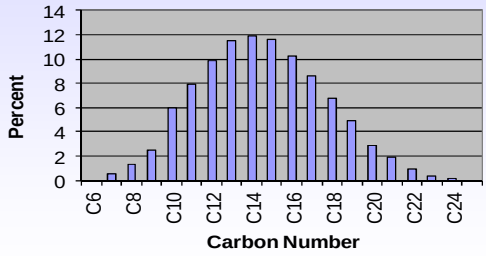
#2 Fuel Oil Hydrocarbons



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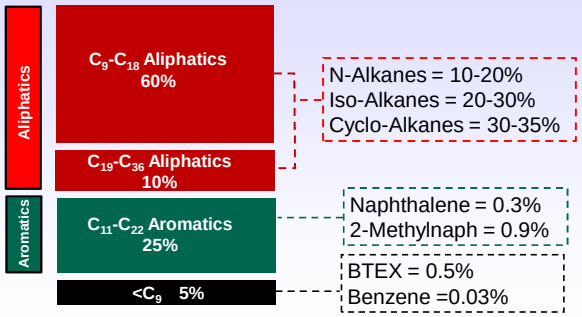
Hydrocarbon Chemistry of Fresh #2 Fuel Oil



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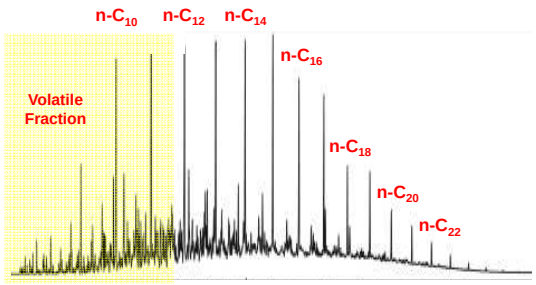
#2 Fuel Oil Chromatogram (Fresh)



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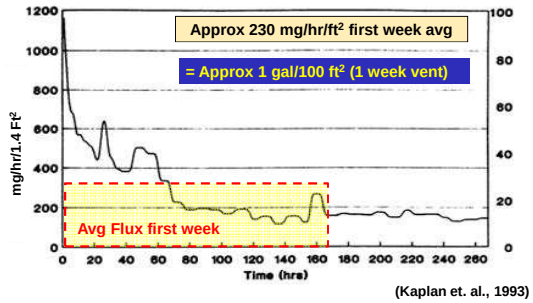
#2 Fuel Oil Evaporation Rate



(Kaplan et. al., 1993)

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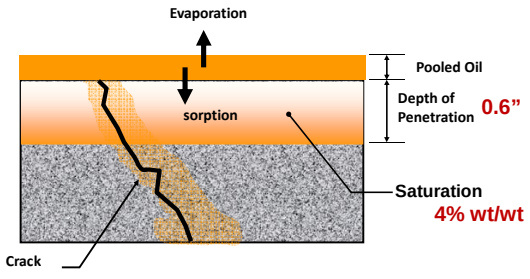
Discharge to Concrete Floors



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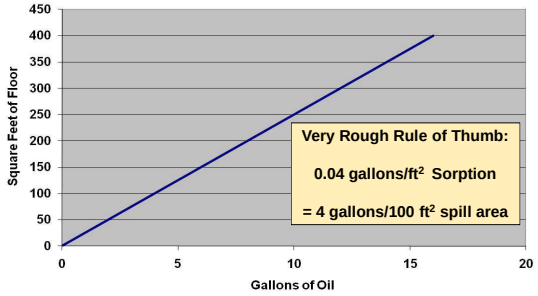
Sorption of Oil into Concrete



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Bulk Movement of Separate Phase Oil Through Environmental Media

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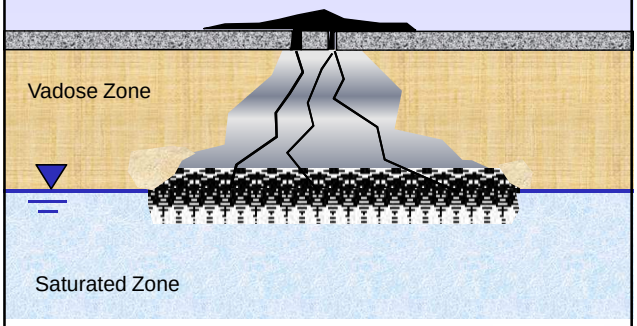
Release of Fuel Oil



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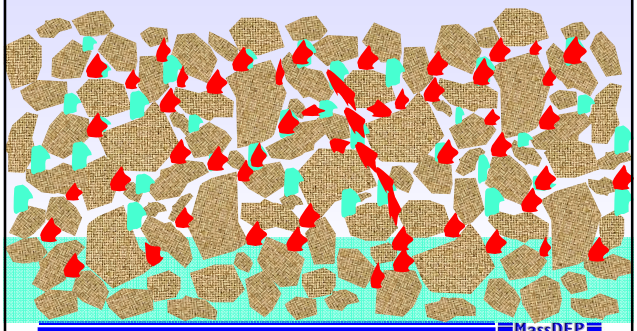
The Battleground



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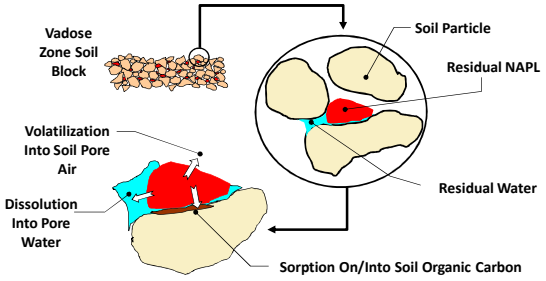
Residual NAPL in Vadose Zone



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Partitioning/Residual NAPL for #2 Fuel Oil in Soil

Soil Type	Typical Soil Properties			Concentration (mg/kg)	
	Porosity θ_T	Pore Water θ_W	Fraction OC F_{oc}	Theoretical Partitioning Saturation	Residual NAPL
Coarse Gravel	0.28	0.02	0.001	2	2000 +/-
Coarse Sand & Gravel	0.35	0.03	0.002	4	4000 +/-
Med to Coarse Sand	0.39	0.04	0.003	5	8000 +/-
Fine to Med Sand	0.41	0.043	0.005	9	13,000 +/-
Silt to Fine Sand	0.44	0.045	0.01	18	22,000 +/-

(API, 2000)

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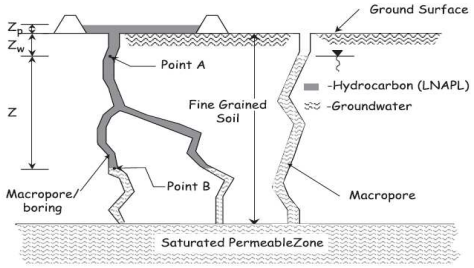
"Fingering" in the Vadose Zone



Adamski et.al, 2005

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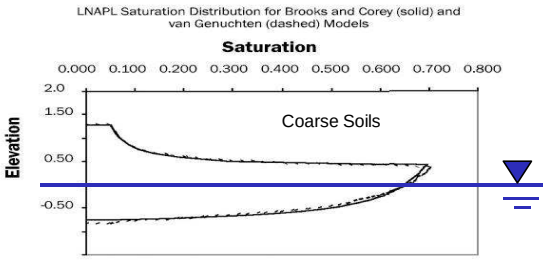
Water Table Interface



API, 2004

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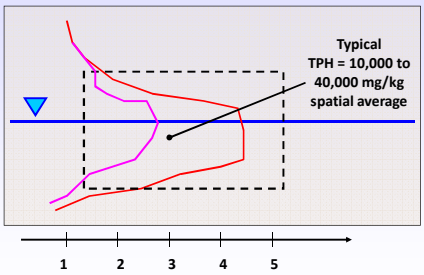
Fuel Oil in Smear Zone



Mass/Mass TPH Concentration % by Weight

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(L)NAPL

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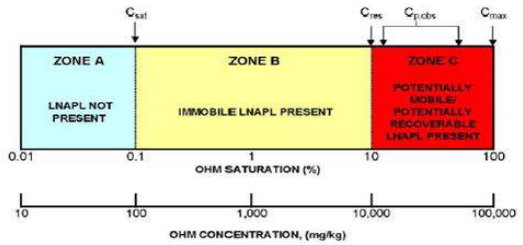
NAPL Continuum



LSPA, 2008

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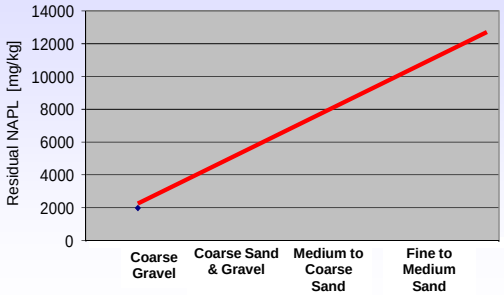
Residual Saturation for #2 Fuel Oil



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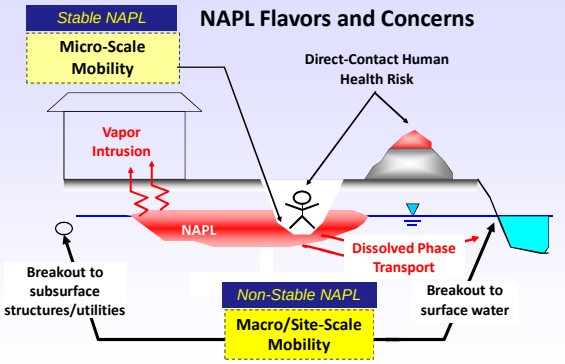
NAPL Flavors and Concerns



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Micro-Scale NAPL Mobility?

Yes if

- NAPL Visible in a monitoring well
- NAPL Visible in an excavation

Maybe if

Hydrocarbons in Soil > Residual Saturation

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Macro-Scale NAPL Mobility?

Yes if

- NAPL Discharge to Drains/Water Bodies
- NAPL Movement in Preferred Flow Path

Maybe if

Very High Hydrocarbons in Soil

Elevated NAPL thickness in Wells

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Example of Monitoring Well Criteria

British Columbia Protocol 17 (Golder Assoc.)

Soil Type	Characteristic Fraction	Percent Fines (silt/clay)	LNAPL Thickness (m) (inches) [1]
Coarse sand/gravel	> 20% Coarse sand	< 3	0.03 **(1.2 inch)**
Coarse sand/gravel	> 20% Coarse sand	3-10	0.05 **(2 inches)**
Medium sand	Medium sand	< 10	0.1 **(4 inches)**
Fine sand	Fine sand	< 10	0.2 **(7.9 inches)**
Silty sand	Sand	> 10	0.3 **(12 inches)**

[1]If present at this thickness over more than 50 m^2

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Implications

Micro-Scale NAPL Mobility:

- Concern with Vapor Intrusion Pathway
- Concern with direct human contact risks
- May require AUL

Macro-scale NAPL Mobility:

- Requires Remedial Measures

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Federal/Proposed MCP Requirements:

Recover LNAPL to the Extent Feasible

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LNAPL Transmissivity (T_n)

the quantity of LNAPL that will flow through a unit aquifer width in a unit time for a unit gradient

Function of:

- LNAPL Properties
- Degree of LNAPL Saturation
- Formation Properties

Empirically determined via LNAPL bail-down or recovery operations

MassDEP

LNAPL Transmissivity (T_n)

Hydraulic Recovery of LNAPL to the Maximum Extent Feasible?

Current thinking :

to a T_n value of 0.1 to 0.8 ft^2/day

(ITRC, 2009)

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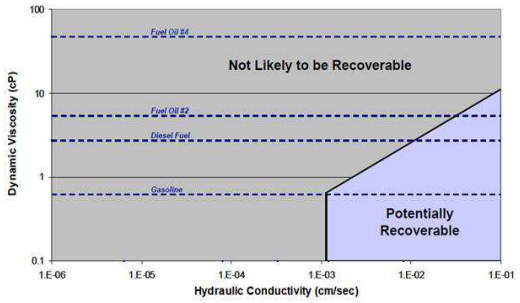
Generic Approach

API LNAPL Interactive Guide, 2004, for up to 5 inches Apparent Well Thickness



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Soil Contamination

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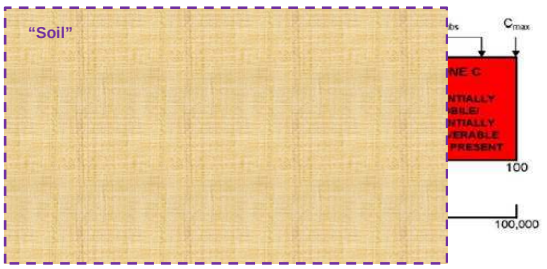
NAPL Continuum



LSPA, 2008

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Typical Chemistry of #2 Fuel Oil EPH Soil Data

MassDEP Evaluation of 378 EPH Data Reports from 23 Sites where Fuel Oil #2 was Spilled (2007)

MassDEP, 2007

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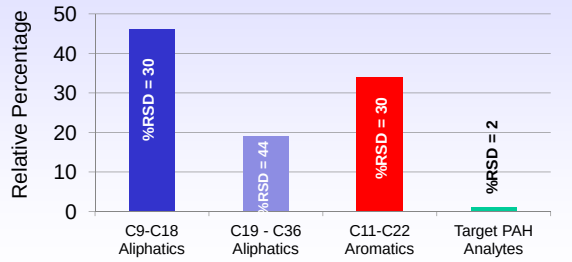
Typical Chemistry of #2 Fuel Oil EPH Soil Data

378 Samples from 23 Sites



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Soil Sampling at #2 Fuel Oil Sites

VPH/EPH Implementation Policy, 2002

EPH Target Analytes:

- Acenaphthene
- Naphthalene
- 2-Methylnaphthalene
- Phenanthrene

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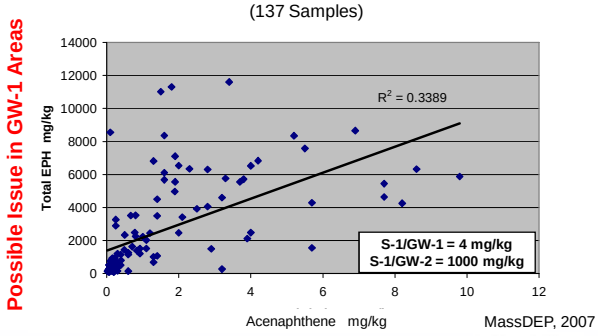
Total EPH (TPH) vs Acenaphthene

(137 Samples)



MassDEP, 2007

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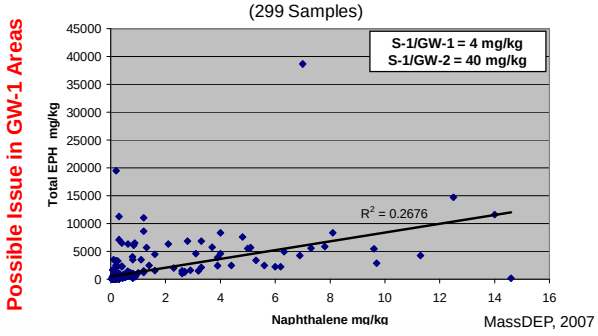
Total EPH (TPH) vs Naphthalene

(299 Samples)



MassDEP, 2007

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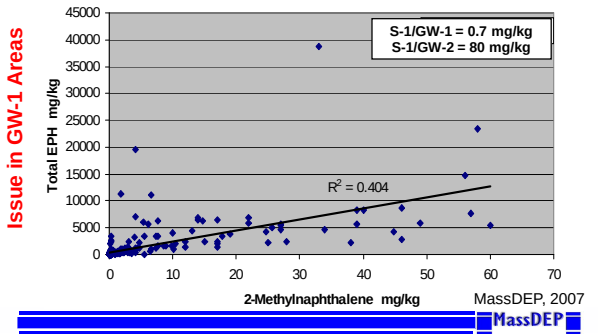
Total EPH (TPH) vs 2-Methylnaphthalene

(298 Samples)

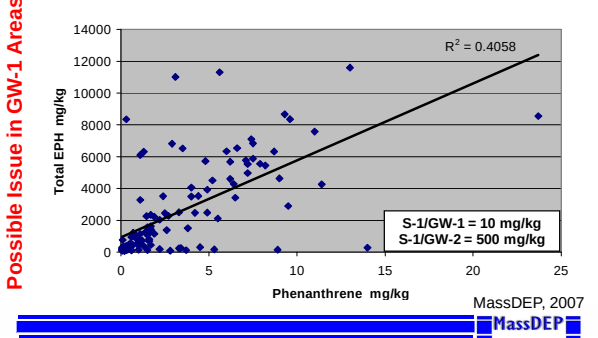


MassDEP, 2007

MassDEP

Total EPH (TPH) vs Phenanthrene

(137 Samples)



MassDEP, 2007

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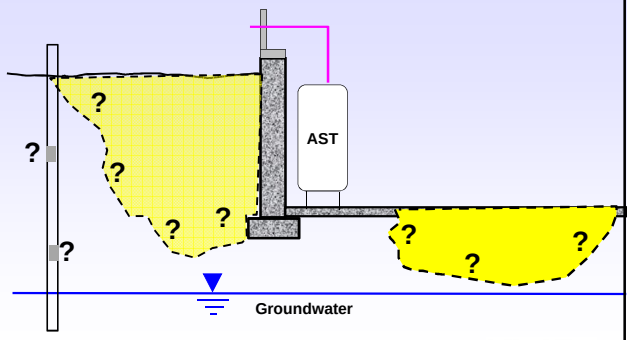
Soil Sampling Strategy



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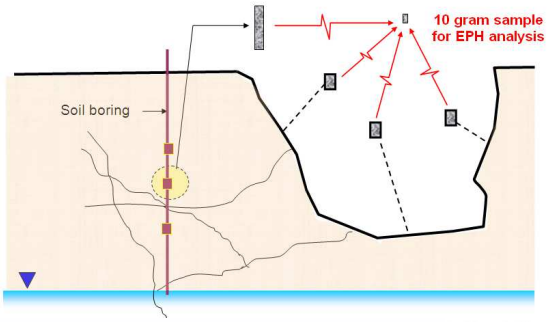
Representativeness ?



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More Data = Better Characterization

PID Headspace = Cheap & Effective

EPH Data for Confirmation

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MassDEP Jar Headspace Procedure

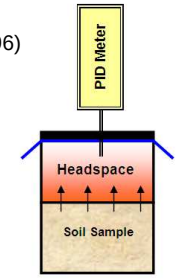
#WSC-94-400 (1994)
UST Closure Manual, DFS/DEP (1996)

Half fill 8-16 oz glass jar

Apply aluminum foil/cap

Shake twice for 15 seconds over 10 minute period

Puncture foil and obtain reading



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Jars are Old School - Plastic Bags are easier…..

Plastic "Ziploc" Type Bags have been Replacing Glass Jars for headspace testing

Is this a valid approach?

MassDEP

Preliminary Studies – MassDEP – 2012

By Intern

Evaluated Glass Jar, Plastic Baggies, Plastic Jars, Foil Lined Bags

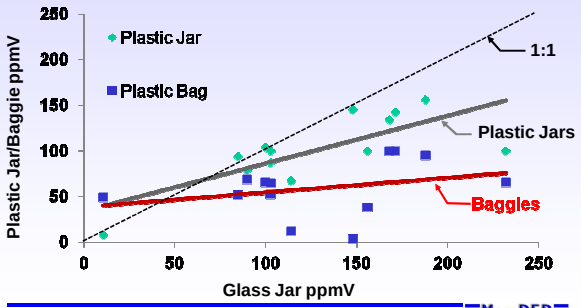
Short and Long term, Static and Dynamic Headspace Development

Water and Soil, mostly gasoline contaminants

MassDEP

Glass Jars vs Plastic Jars vs Baggies

All Data



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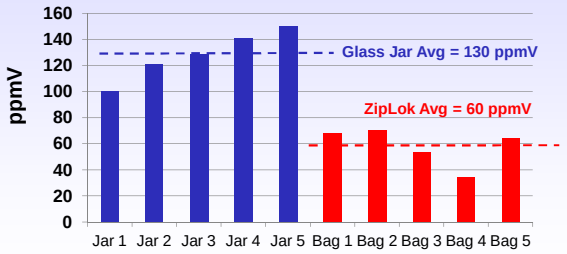
Headspace Conc Glass Jars vs Ziploc Bags

Replicate Sand Samples – 15 minute Dynamic Headspace Development



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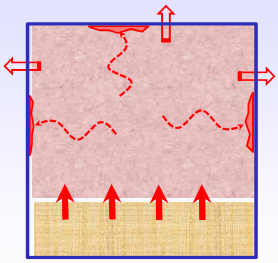
Why are Headspace Data so Poor for Baggies?



Preliminary Indications:

- Poor Dis-aggregation of wet/cohesive soils
- Sorption of Hydrocarbons on the LDPE
- Permeation Through the LDPE

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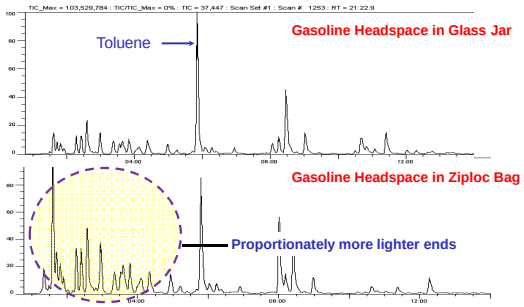
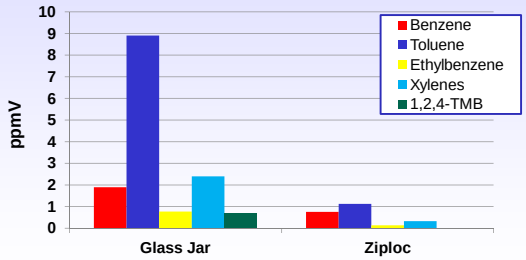
Headspace Chemistry (GC/MS)



MassDEP

Headspace Chemistry (GC/MS)



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Time to Bag the Bag!

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Interpreting (Jar) Headspace Data

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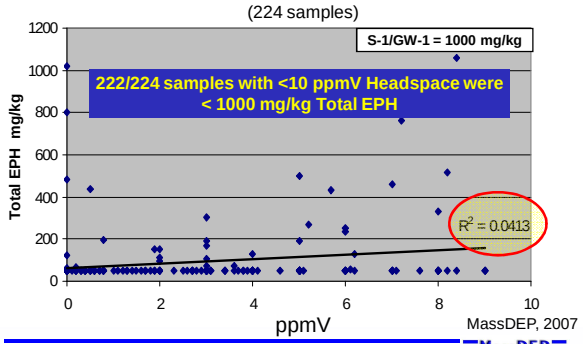
Jar Headspace vs Total EPH (i.e., TPH)



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EPH Fractions when Total EPH = 1000 mg/kg		
	Typical Soil Conc mg/kg	MCP S-1 Conc mg/kg
C9-C18 Aliphatic Hydrocarbons	500	1000
C19-C36 Aliphatic Hydrocarbons	150	3000
C11-C22 Aromatic Hydrocarbons	340	1000

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Utility of Soil Headspace Screening

For most sites where #2 Fuel oil was spilled, soils with < 10 ppmV Jar Headspace values will likely meet S-1 Cleanup Standards for EPH fractions.

May still have problems meeting S-1 standards for Naphthalene and 2-Methylnaphthalene

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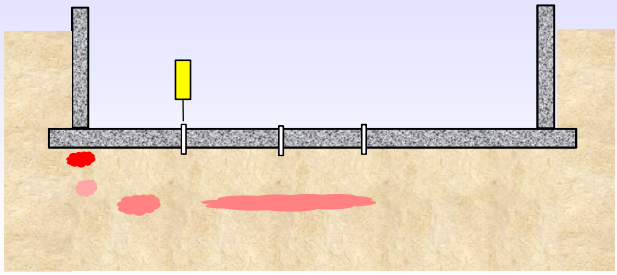
PID Screening to Evaluate sub-slab soils



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Final Word on Testing Soils for #2 Fuel Oil Contamination – 3 Letters

V P H

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Soil Sampling at #2 Fuel Oil Sites

VPH/EPH Implementation Policy, 2002

"Fresh" Contamination (≥100 ppmV Headspace)

EPH and VPH

"Weathered " Contamination (<100 ppmV Headspace)

Just EPH

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Excessive VPH Testing

From 2007 File Review Project, 141 soil samples tested for both VPH and EPH, including 110 samples where soil headspace < 100 ppmV

Of this universe of 110:

- All VPH Target Analytes << S-1/GW-1 Standards
- All C9-C12 Aliphatics < S-1/GW-1 Standard
- 97% C5-C8 Aliphatics < S-1/GW-1 Standard
- 91% C9-C10 Aromatics < S-1/GW-1 Standard (and rest exceeded C11-C22 Standard)

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Dissolution

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Solubility of #2 Fuel Oil and Key Constituents (Raoult's Law)

Constituent	Concentration [mg/L]				
	In Fresh Fuel Oil #2	Water in Contact w/ #2 Fuel	MCP GW-1	MCP GW-2	MCP GW-3
Acenaphthene	100-600	.004-0.014	0.02	NA	6
Naphthalene	350-1500	0.08-0.3	0.14	1	20
2-Methylnaphthalene	3500-9000	0.18-0.34	**0.01**	2	20
Phenanthrene	100-1500	.015-0.025	0.04	NA	10
Total Maximum Solubility of #2 Fuel Oil = 2 - 6 mg/L					

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Estimated Maximum Solubility of #2 Fuel Oil Hydrocarbon Fractions

Fraction	Concentration [mg/L]			
	Likely Upper Limit of Solubility	MCP GW-1	MCP GW-2	MCP GW-3
C_9-C_{18} Aliphatics	0.5 – 1.0	0.7	5	50
C_{19}–C_{36} Aliphatics	< 0.01	14	NA	50
C_{11}-C_{22} Aromatics	1 – 3	**0.2**	50	5

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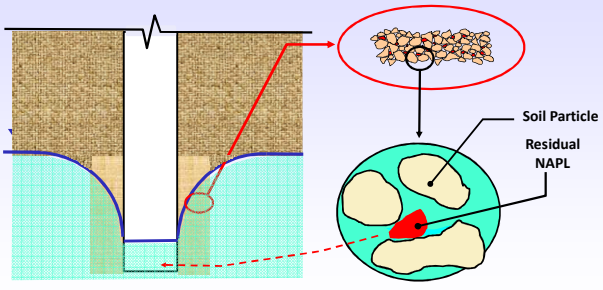
Why Do So Many Sites Exceed GW Standards?



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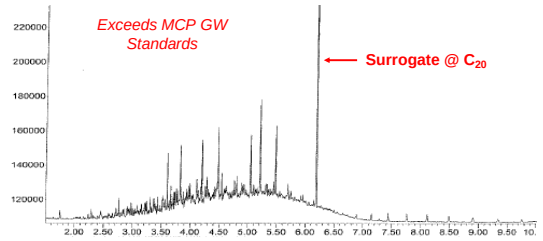
Example – Fuel Oil Spill in Peabody, MA

Groundwater EPH data from well in tank grave – sampled with bailer



Aliphatic FID Chromatogram

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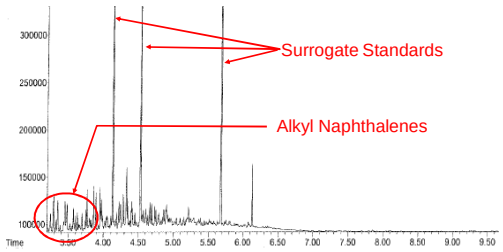
Example – Fuel Oil Spill in Peabody, MA

Groundwater EPH data from well in tank grave – sampled with bailer



Aromatic FID Chromatogram

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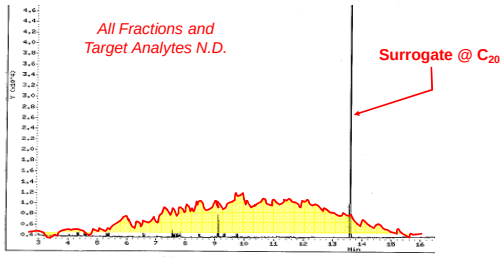
Example – Fuel Oil Spill in Peabody, MA

Re-sampled with Low Stress/Low Flow Technique



Aliphatic FID Chromatogram

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Recommendations for GW Sampling

Per VPH/EPH Implementation Policy, filtering of samples is NOT preferred. Low Stress/Low Flow Sampling is recommended, at least in source areas with likely past history of mobile NAPL

Do NOT use bailers or other high-stress/high flow techniques, at least in source areas

Request and view Chromatograms!

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Vapor Intrusions/Indoor Air

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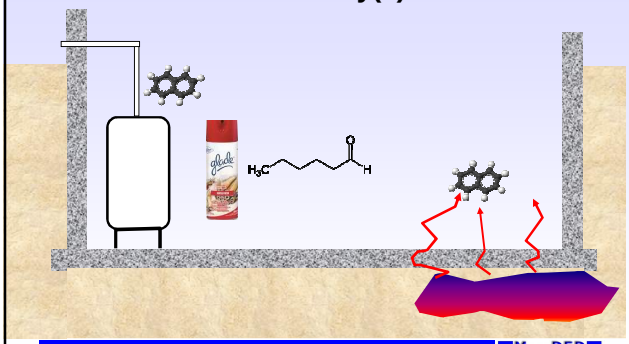
Pathway(s)



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Lines of Evidence

Indoor Air Data

Sub-Slab Soil Gas Data

Sample Chemistry – Obtain and Review Chromatograms!

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Air-Phase Petroleum Hydrocarbons (APH)

GC/MS Procedure

Total Ion Chromatogram used to Quantify Aliphatic Fractions

Extracted Ions (120 and 134 m/z) used to Quantity Aromatic Fraction

Characteristic and Quant ions used to identify and quantify Target Analytes

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Air-Phase Petroleum Hydrocarbons (APH)

Like VPH and EPH, APH test method has built-in assumptions that are designed to provide a positive (health-protective) bias. This is disclosed in the method.

APH bias is more problematic than VPH/EPH test, given "background" stuff in indoor air:

- Fuel Oil if still stored/used on-site
- Common household chemicals

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Air-Phase Petroleum Hydrocarbons (APH)

Table 7 of the Method

	Potential Non-APH Compounds
C_5-C_8 Aliphatic Hydrocarbons	**Acetone** may co-elute/interfere with isopentane. **Isopropyl alcohol, methyl ethyl ketone**, trichloroethene, **tetrachloroethene,** tetrahydrofuran, **hexanal,** 1-butanol, hexamethylsiloxane
C_9-C_{12} Aliphatic Hydrocarbons	**Terpenes (e.g., a-pinene, d-limonene**), phenol, **benzaldehyde**, **n-chain aldehydes**, 2-ethyl-1-hexanol, siloxanes, dichlorobenzenes
C_9-C_{10} Aromatic Hydrocarbons	Siloxanes, a-pinene, and d-limonene may slightly interfere if present at high concentrations (contribute to the area of ions 120/134)

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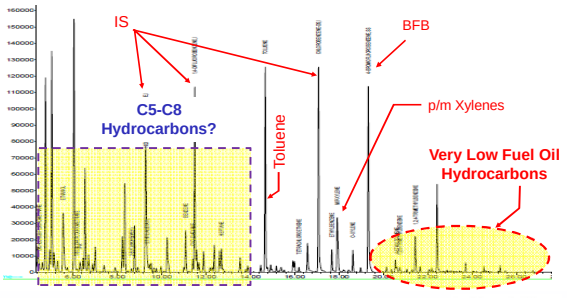
Example – Fuel Oil Spill in Westfied, MA

Basement Air – APH Total Ion Chromatogram



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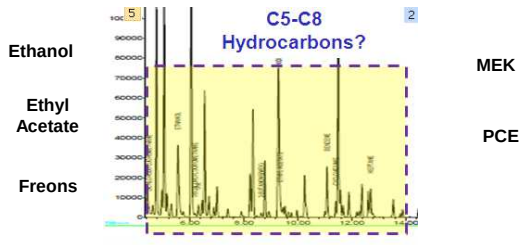
Example – Fuel Oil Spill in Westfied, MA

Basement Air – APH Total Ion Chromatogram



And Similar Chromatogram for Second Floor

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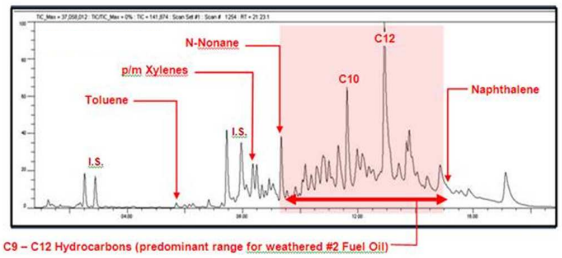
Example – Fuel Oil Spill in Westfied, MA

More Lines of Evidence – Soil Gas Chromatogram



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Example – Fuel Oil Spill in Westfied, MA

Once analytes not associated with Vapor Intrusion Pathway were subtracted from the APH data, site could be closed out.

Take Home Message – Assemble Lines of Evidence and always ask for the Total ion Chromatograms!

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Questions?

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