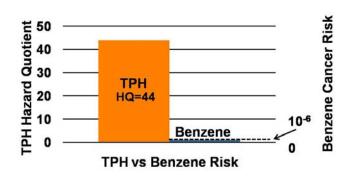
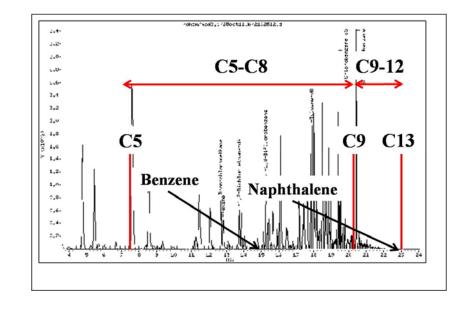
# **Petroleum Vapor Intrusion Facts, Fallacies and Implications**







Roger Brewer, PhD roger.brewer@doh.hawaii.gov Hawai'i Department of Health, HEER July 2015 (9am Hawaii Time)

## Acknowledgments

- Lots of regulators, consultants and oil company scientists over the past twenty years;
- Field study discussed funded through HDOH grant from USEPA Region IX.

#### **Third in Vapor Intrusion Webinar Series (recorded):**

- 1. Climate-Based Vapor Intrusion Risk Regions and Region-Specific Screening Levels (HDOH, February 2015);
- 2. Collection and Interpretation of Active and Passive Soil Gas Samples (M. Schmidt & H. O'Neill, March 2015);
- 3. Petroleum Vapor Intrusion Review (HDOH, July 2015);
- 4. Long-Duration Indoor Air Samples and High-Purge Subslab Soil Gas Samples (coming this fall???)

HEER Web Page: http://eha-web.doh.hawaii.gov/eha-cma/Leaders/HEER/Webinar

## **PVI Webinar Outline**

- Vapor Intrusion Basics;
- Evolution of Vapor Intrusion Science;
- Petroleum Vapor Intrusion FACTS;
- Petroleum Vapor Intrusion Semi-FACTS;
- Petroleum Vapor Intrusion Fallacies;
- Implications.

### Hawai'i DOH PVI References

Vapor Intrusion Action Levels: *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* http://hawaii.gov/health/environmental/hazard/

VI Field Investigations: *Technical Guidance Manual*: Hawai'i Department of Health, http://www.hawaiidoh.org/

Field Investigation of the Chemistry and Toxicity of TPH in Petroleum Vapors, Implications for Potential Vapor Intrusion Hazards (see also Brewer et al 2013): Hawai'i Department of Health http://www.hawaiidoh.org/

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#### **Recent Additional PVI References**

*Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* (June 2015): US Environmental Protection Agency, EPA 510-R-15-001.

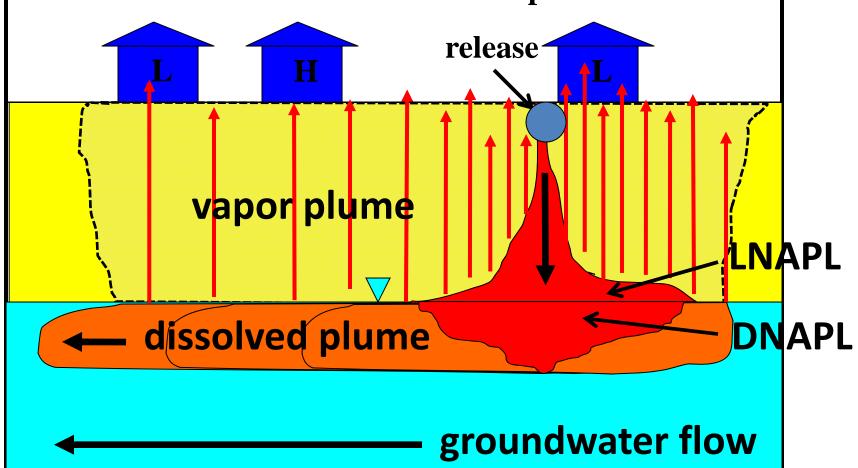
Petroleum Vapor Intrusion: Fundamentals of Screening, Investigation, and Management (October 2014): \*Interstate Technology Regulatory Council (ITRC).

\*Public-private coalition of regulators, consultants and industry representatives.

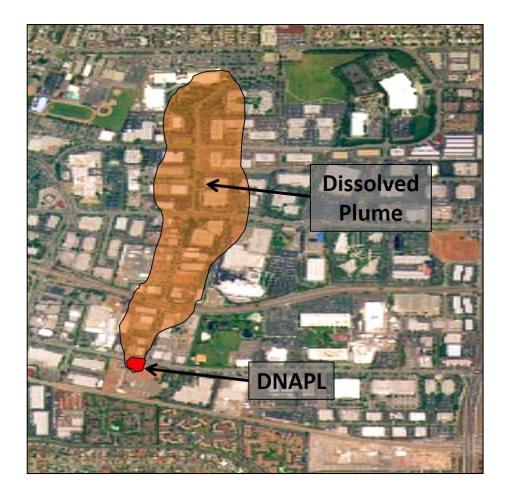
# **Vapor Intrusion Basics**

• Wind, exhaust fans, heating, etc., *under-pressurize* building (A/C can *over-pressurize* lower floors);

• Potential intrusion of subsurface vapors.



#### **Evolution of VI and Chlorinated Solvents**



#### <u>Pre-1990s</u>

•VI not considered;

**Mid-1990s** 

• Possible VI risk from DNAPL;

#### Early 2000s

•VI risk from high-concentration dissolved plumes;

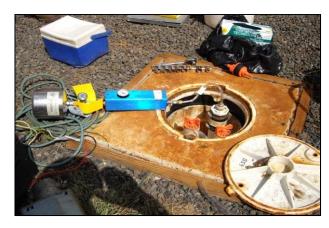
#### <u>Mid 2000s</u>

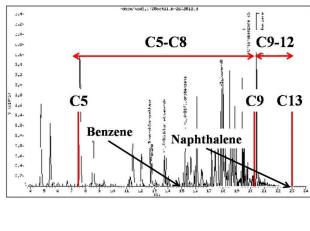
•VI risk from lower-concentration dissolved plumes;

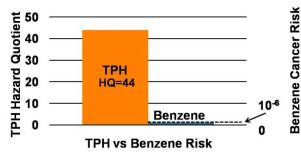
#### **Current**

- Better understanding of building leakage and ventilation, attenuation factors, spatial and temporal heterogeneity, more representative samples, etc.;
- •High-risk VI problems rare.

#### **Evolution of VI and Petroleum**







#### <u>Pre-1990s</u>

•VI not considered;

#### <u>Mid-1990s</u>

- Possible VI risk from shallow (<15ft) LNAPL (lower risk than solvents);
- •Risk-based evaluation of TPH carbon ranges (mostly for soil);

#### **Early 2000s**

- Natural degradation limits on vapor transport widely recognized;
- Solvent models "don't work";
- Minimal risk from dissolved plumes;

#### <u>Current</u>

- •Additional supporting data for reduced VI risk compared to solvents;
- Field studies of petroleum vapor plume chemistry;
- •Updated guidance.

## **PVI Webinar Outline**

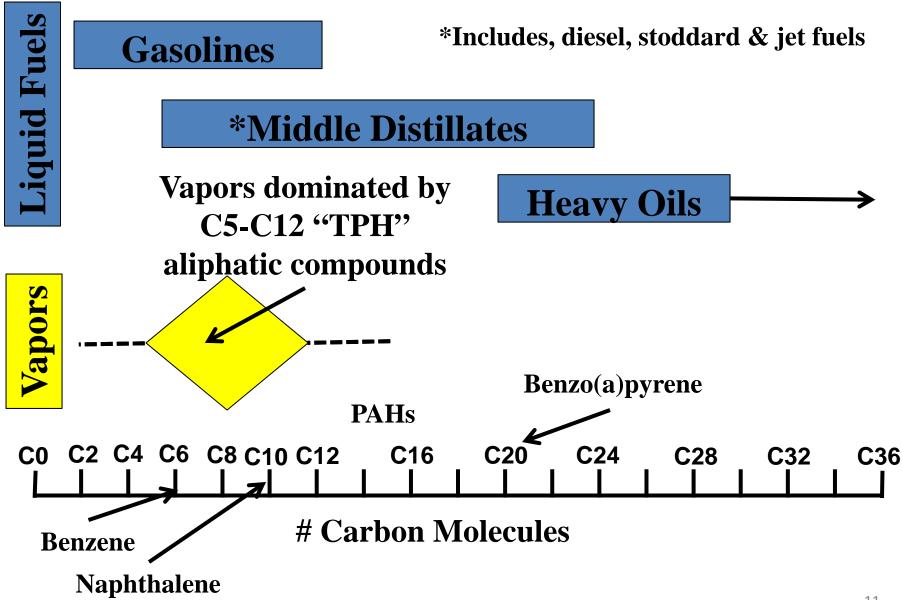
- Vapor Intrusion Basics;
- Evolution of Vapor Intrusion Science;
- Petroleum Vapor Intrusion FACTS;
- Petroleum Vapor Intrusion Semi-FACTS;
- Petroleum Vapor Intrusion Fallacies;
- Implications.

#### **Petroleum Vapor Intrusion \*FACTS**

- Both *chlorinated solvents and petroleum* can pose vapor intrusion risks under some circumstances;
- Total number of *petroleum-release sites* far outweighs number of solvent-release sites;
- Petroleum fuel vapors are dominated by *aliphatic* compounds (vs BTEXN);
- Natural *biodegradation* of petroleum vapors significantly reduces potential vapor intrusion risks;
- Models used for solvents significantly *over predict* vapor concentrations away from source area;
- *Field data* required to more accurately assess vapor intrusion risks (e.g., soil gas +/- indoor air).

\*Strong agreement between HDOH, USEPA & ITRC guidances

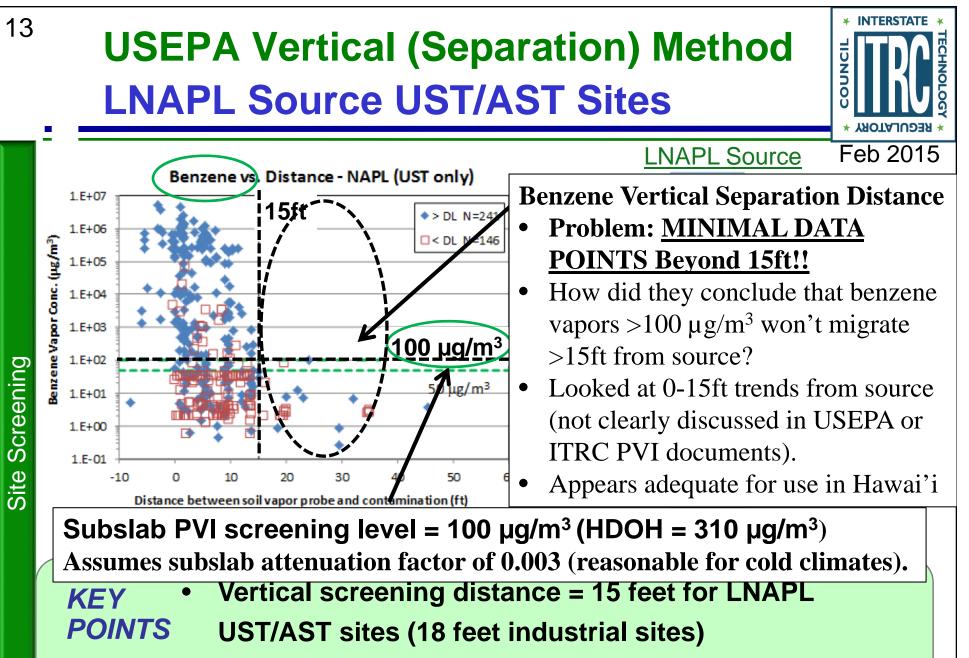
# **Chemistry of Liquid Fuels vs Soil Vapors**



### **Petroleum Vapor Intrusion \*SEMI-FACTS**

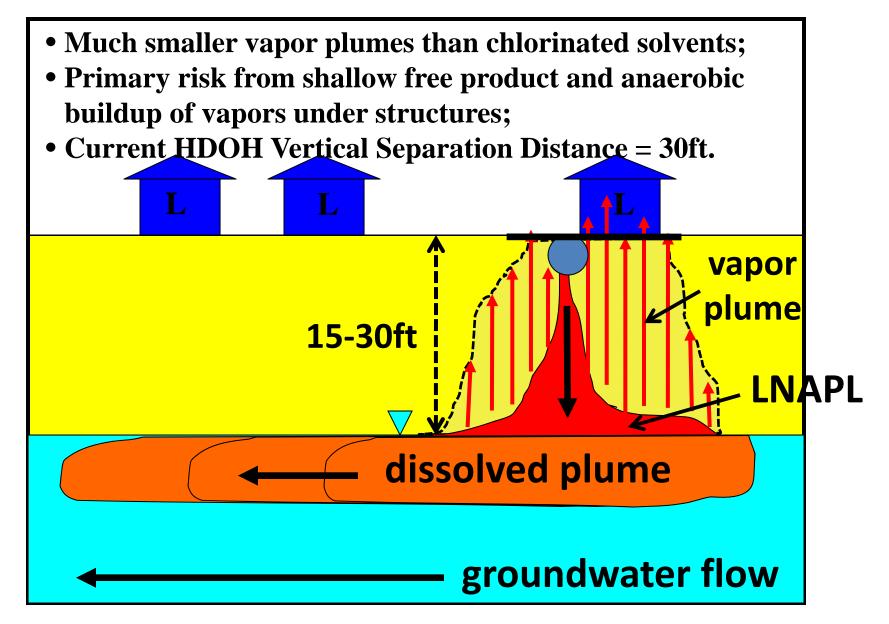
- *Free product* in vadose-zone soil or on groundwater required to pose significant PVI risks;
- Small *de minimis volumes* of contaminated soil (e.g., 10 cyds?) or small areas of free product on groundwater (e.g., <100ft<sup>2</sup>?) do not pose significant, *long-term* PVI risks, regardless of concentrations (not discussed in USEPA or ITRC PVI documents);
- Vapors unlikely to exceed potential PVI levels of concern greater than *15-30ft* from the source ("Vertical Separation Distance");
- "Lateral Separation Distance" default = 100ft.

\*General agreement between HDOH, USEPA & ITRC guidances



• Benzene requires the greatest distance to attenuate

# **Additional PVI Considerations**



#### **Petroleum Vapor Intrusion \*FALLACIES**

- 1. Diesel fuel is not volatile and does not pose a PVI risk (Hint: If you can smell it then it's volatile);
- 2. Risk-based indoor air and soil gas action (screening) levels cannot be developed for the non-BTEXN, Total Petroleum Hydrocarbons (TPH) component of vapors;
- 3. Benzene or other individual aromatics always drive PVI risks over TPH;
- 4. TPH compounds in vapors will not migrate >2-3ft from source above potential levels of concern for PVI (vs 15ft for benzene).

\*Common past misconceptions still sometimes mentioned in PVI workshops

#### **Fallacy #1: Diesel Fuel is Not Volatile**

**1. Diesel fuel is not volatile and does not pose a PVI risk (Hint: If you can smell it then it's volatile).** 



- Diesel included as a potential PVI concern in USEPA 2015 PVI guidance;
- Implied to not be sufficiently volatile for potential PVI concerns in 2014 ITRC guidance.

## HDOH Field Study: Chemistry and Toxicity of Petroleum Vapors

- Soil vapor samples collected at five sites on O'ahu;
- Focus on jet fuels and diesel (supplement to USEPA PVI database for gasoline sites);
- Reviewed other published data (including PVI database);
- Results discussed in Appendix C of 2014 ITRC PVI guidance.

Field Investigation of the Chemistry and Toxicity of TPH in Petroleum Vapors, Implications for Potential Vapor Intrusion Hazards (December 2012): Hawai'i Department of Health, HEER, http://www.hawaiidoh.org/

Brewer et al, 2013, *Risk-Based Evaluation of Total Petroleum Hydrocarbons in Vapor Intrusion Studies*: International Journal of Environmental Research and Public Health, Volume 10, pp 2441-2467. http://www.mdpi.com/1660-4601/10/6/2441/

### **Soil Vapor Sample Collection**

#### Summa Canisters (C5-C12)

Sorbent Tubes (C12-C18)





- Most samples collected 5 to 15+ft from source;
- Each Sample:
  - TPH (total), TPH carbon ranges, BTEXN;
  - Calculated weighted TPH toxicity factor;
  - TPH to Benzene ratio (assess risk driver).

## **TPH Dominates BTEXN in Vapors**

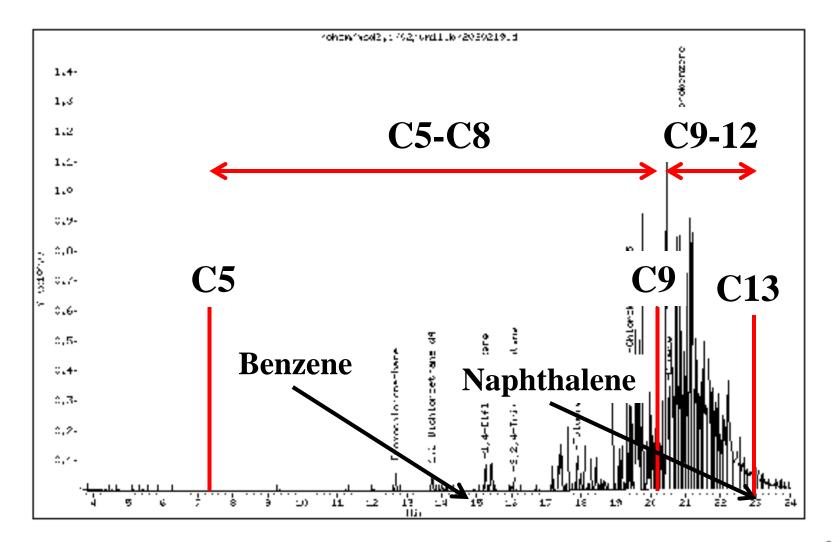
	Average Soil Gas Composition		
Site/Fuel Type	<sup>1</sup> TPH	<sup>2,3</sup> BTEXN	<b>TPH:Benzene</b>
<sup>1</sup> USEPA PVI Database (mostly gasoline)	>95% (estimate)	<5% (estimate)	300:1 (median)
Site A: (mostly AVGAS)	99.6%	0.4%	1,500:1
Site D: (mostly JP-4)	98.3%	1.7%	9,000:1
Site E: (mostly diesel)	99.9%	0.1%	19,000:1

1. Total Petroleum Hydrocarbons, excluding BTEXN.

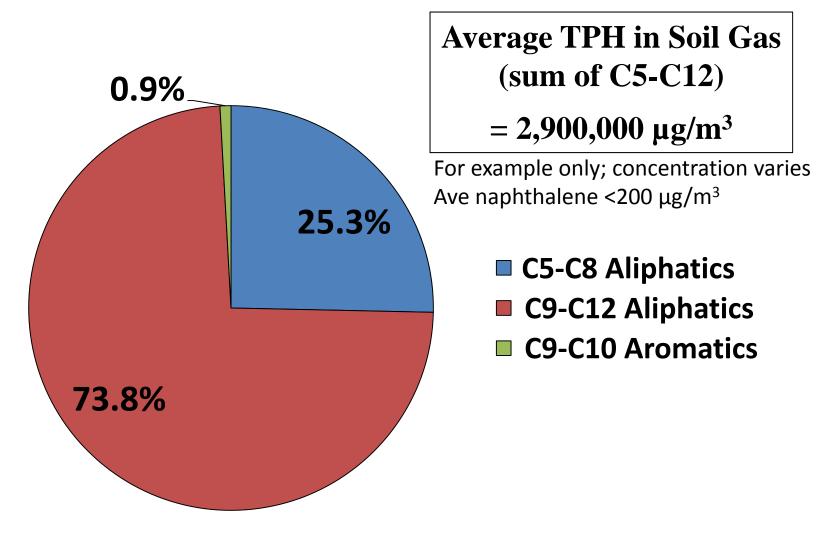
2. Toluene, ethylbenzene, xylenes and naphthalene data not consistently included; TPH:Benzene ratio highly variable between samples (5:1 to >450,000:1).

**3.Total BTEXN normally dominated by xylenes.** 

## Gas Chromatograph of Diesel Soil Vapors (Study Site E)

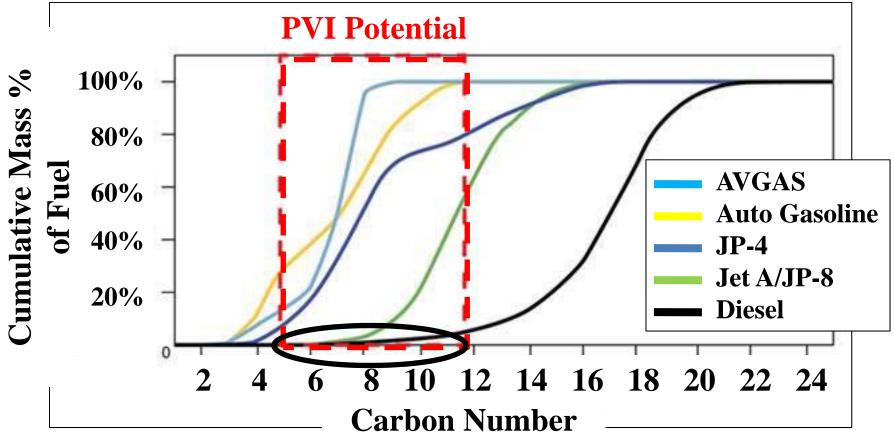


#### Study Site E TPH Carbon Range Makeup (diesel)



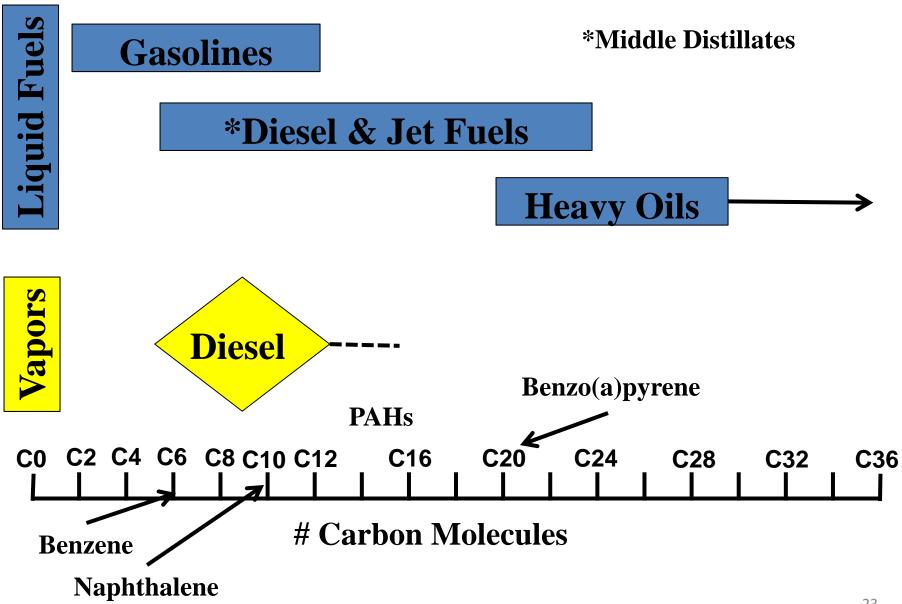
Based on TO-15 Summa Data

#### Small but Important Component of Diesel Fuel (after ITRC 2014)



- C5-C12 component of diesel generates vapor plume;
- TPH vapors high enough concentrations to pose PVI risks;
- Important to ask lab to report TPH in air or soil vapors as sum of C5-C12+ for <u>all</u> fuel types (not "TPHg" or "TPHd<sup>??</sup>).

## **Chemistry of Liquid Fuels vs Vapors**



## **Diesel is Volatile**

- Significant vapors from diesel and other middle distillates;
- Dominated by C9-C12 TPH aliphatics;
- Lower TPH concentrations compared to gasoline;
- Potential PVI risks from shallow (<15ft) free product;
- Naphthalene was typically ND or very low and not a risk driver at study sites.

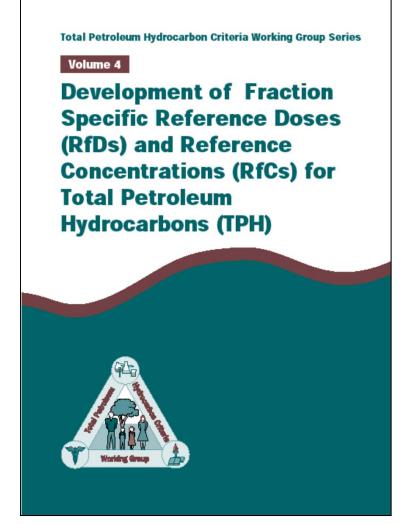
#### **PID Factoid (low readings at site):**

- PIDs respond primarily to aromatics;
- Poor response to aliphatic-only vapor plumes.

#### **Fallacy #2: No TPH Action Levels for PVI**

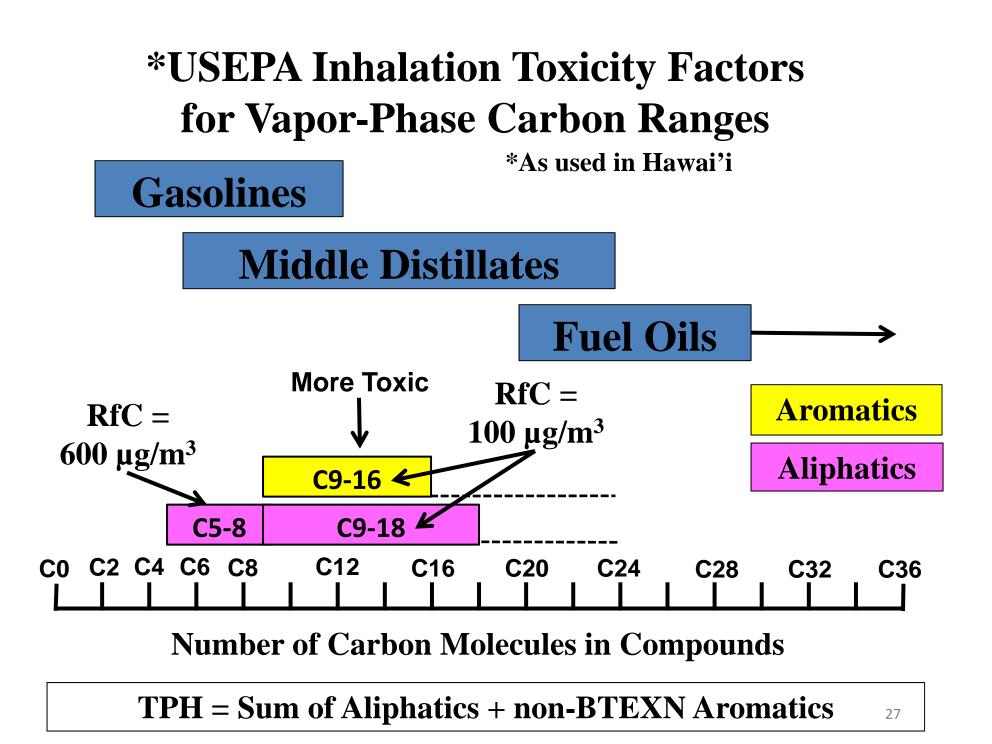
2. Risk-based indoor air and soil gas action (screening) levels cannot be developed for the non-BTEXN, Total Petroleum Hydrocarbons (TPH) component of vapors.

## **Toxicity of Total Petroleum Hydrocarbons TPH Working Group (mid/late 1990s)**



#### **Published TPH Toxicity Factors**

- Massachusetts DEP (1997+)
- USDHHS (1999)
- Washington DOE (2006)
- California EPA (DTSC 2009)
- USEPA (2009)
  - Several states publish riskbased screening levels for TPH (mostly for soil);
  - Only California and Hawai'i have TPH indoor air and soil gas screening levels for PVI?



## **TPH Carbon Range Action Levels**

Carbon Range	<sup>1</sup> Inhalation RfC (μg/m <sup>3</sup> )	<sup>2</sup> Indoor Air (µg/m <sup>3</sup> )	<sup>3</sup> Subslab Soil Gas (µg/m <sup>3</sup> )
C5-C8 Aliphatics	600	630	630,000
C9-C18 Aliphatics	100	100	100,000
C9-C16 Aromatics	100	100	100,000

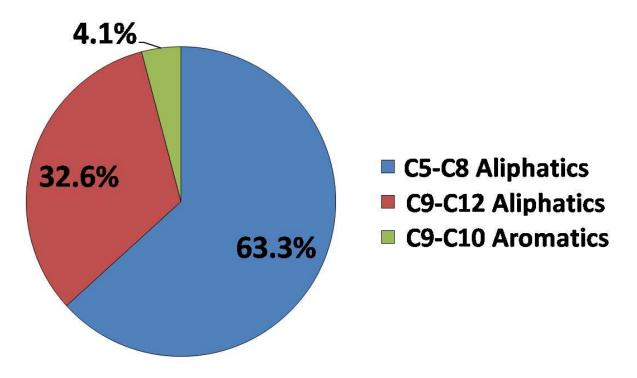
1. After USEPA 2009; variably aromatic RfCs presented.

2. Residential exposure (see also USEPA Regional Screening Levels).

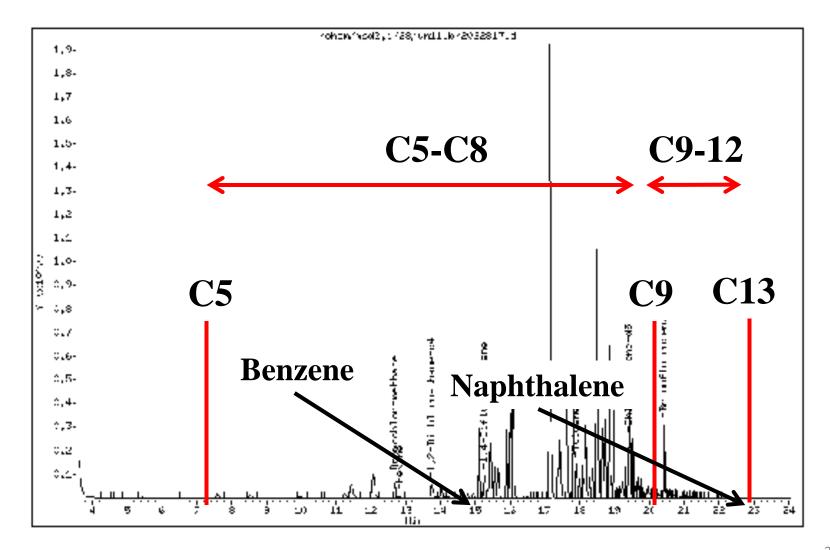
3. Assumes 1/1,000 vapor attenuation factor.

## Weighted Indoor Air & Soil Gas TPH Action Levels

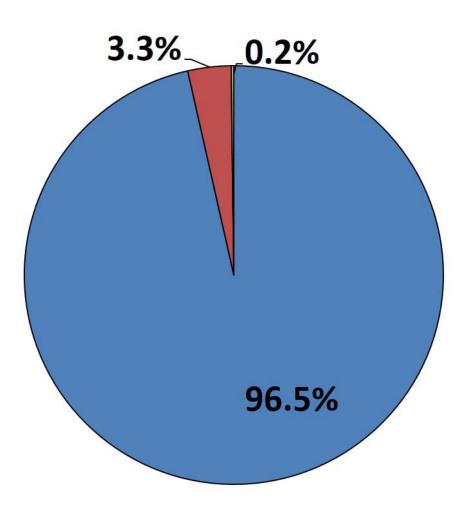
- Calculate site-specific, weighted Inhalation Reference Concentration based on TPH carbon range makeup (see Brewer et al, 2013);
- Reduces need for site carbon range data (\$\$\$)
- Use default carbon range makeup for generic screening levels.



## Gas Chromatograph of AVGAS Soil Vapors (Study Site A)



#### Weighted TPH Action Levels for AVGAS Soil Vapors (Site A)



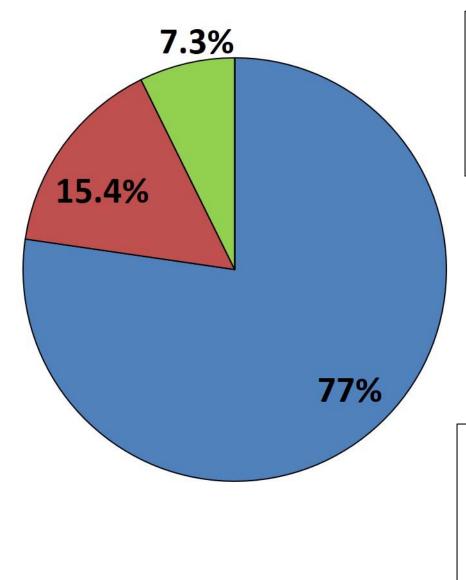
Weighted RfC= 510  $\mu$ g/m<sup>3</sup> Indoor Air<sub>res</sub> = 530  $\mu$ g/m<sup>3</sup> Soil Gas<sub>res</sub> = 530,000  $\mu$ g/m<sup>3</sup> Ave TPH:Benzene = 1,500:1

Residential action levels; subslab soil gas

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

Based on TO-15 Summa Data

#### \*Weighted TPH Action Levels for Gasoline Soil Vapors (average of USEPA PVI Database)



Weighted RfC= 275  $\mu$ g/m<sup>3</sup> Indoor Air<sub>res</sub> = 290  $\mu$ g/m<sup>3</sup> Soil Gas<sub>res</sub> = 290,000  $\mu$ g/m<sup>3</sup> Med TPH:Benzene = 300:1

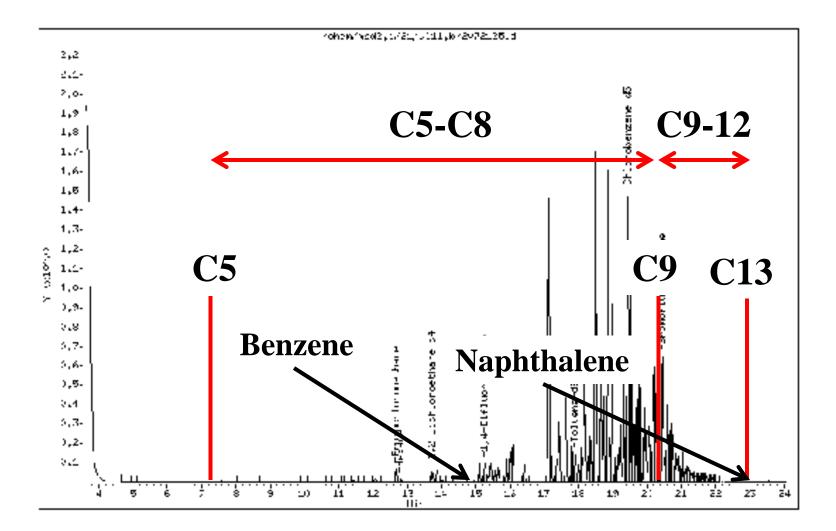
Residential action levels; subslab soil gas

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

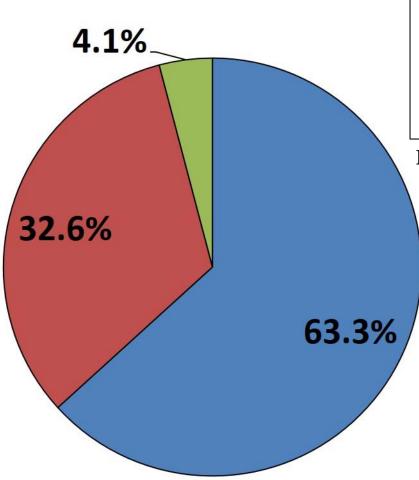
• \*Average of 35 samples from 10 of 48 USEPA PVI database sites;

 Mix of diesel or kerosene vapors at some sites (high C9-C12 aliphatics)?
 32

### Gas Chromatograph of JP-4 Soil Vapors (Study Site D)



#### Weighted TPH Action Levels for JP-4 Soil Vapors (Site D)



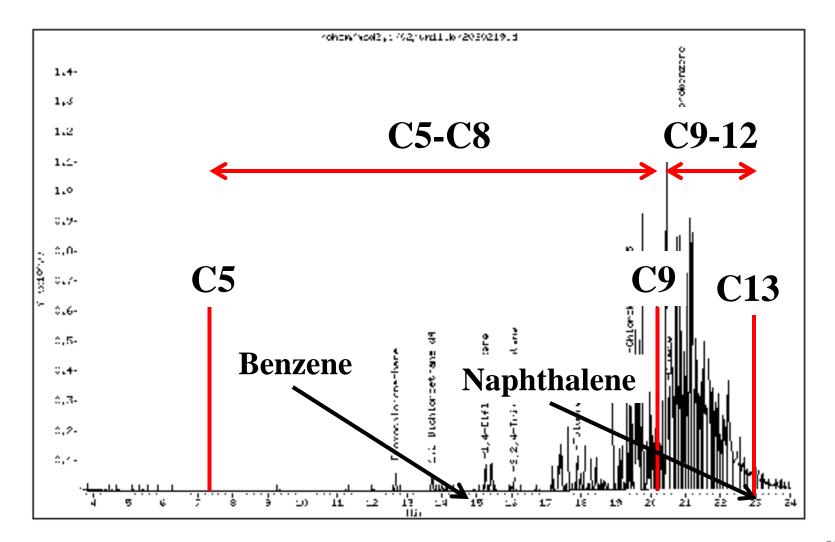
Weighted RfC= 211  $\mu$ g/m<sup>3</sup> Indoor Air<sub>res</sub> = 220  $\mu$ g/m<sup>3</sup> Soil Gas<sub>res</sub> = 220,000  $\mu$ g/m<sup>3</sup> Ave TPH:Benzene = 9,100:1

Residential action levels; subslab soil gas

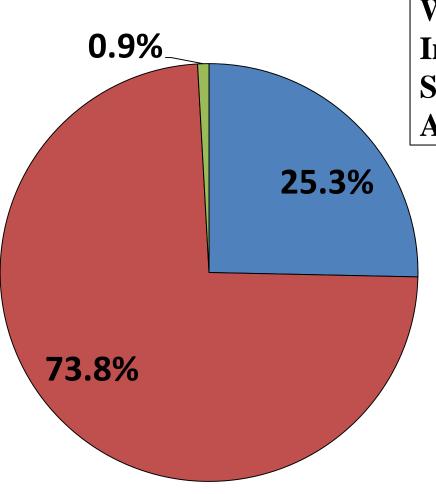
C5-C8 Aliphatics
C9-C12 Aliphatics
C9-C10 Aromatics

Based on TO-15 Summa<sup>34</sup>Data

## Gas Chromatograph of Diesel Soil Vapors (Study Site E)



#### Weighted TPH Action Levels for Diesel Soil Vapors (Site E)

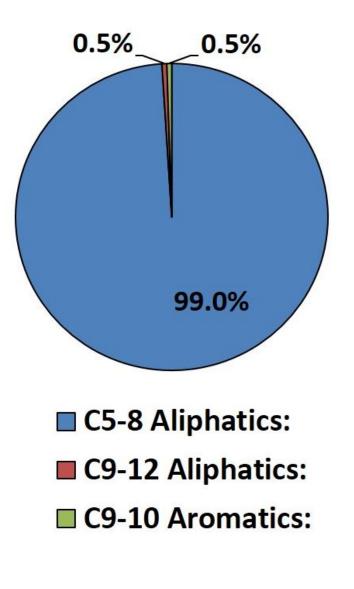


Weighted RfC= 127  $\mu$ g/m<sup>3</sup> Indoor Air<sub>res</sub> = 130  $\mu$ g/m<sup>3</sup> Soil Gas<sub>res</sub> = 130,000  $\mu$ g/m<sup>3</sup> Ave TPH:Benzene = 54,500:1

- **C5-C8** Aliphatics
- C9-C12 Aliphatics
- C9-C10 Aromatics

Based on TO-15 Summa Data

#### **Default HDOH TPH Action Levels – Gasoline Vapors** (based on published data, including Biovapor 2010, etc.)



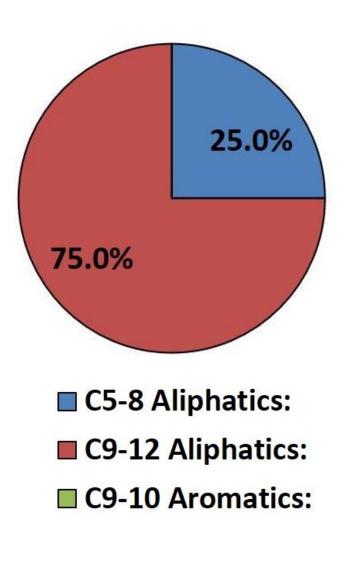
\*Weighted RfC= 571 ug/m<sup>3</sup> Indoor Air<sub>res</sub> = 600 ug/m<sup>3</sup> Soil Gas<sub>res</sub> = 600,000 ug/m<sup>3</sup>

**Residential action levels noted; subslab soil gas** 

- Vapors dominated by lower-toxicity, C5-C8 aliphatics;
- Minor heavier aliphatics and aromatics.

Gasoline Odor Recognition Threshold: 0.2 to 1.0 ppmv (750 to 4,000 ug/m<sup>3</sup>)

#### **Default TPH Action Levels – Diesel Vapors** (based on 2012 HDOH field study and published data)

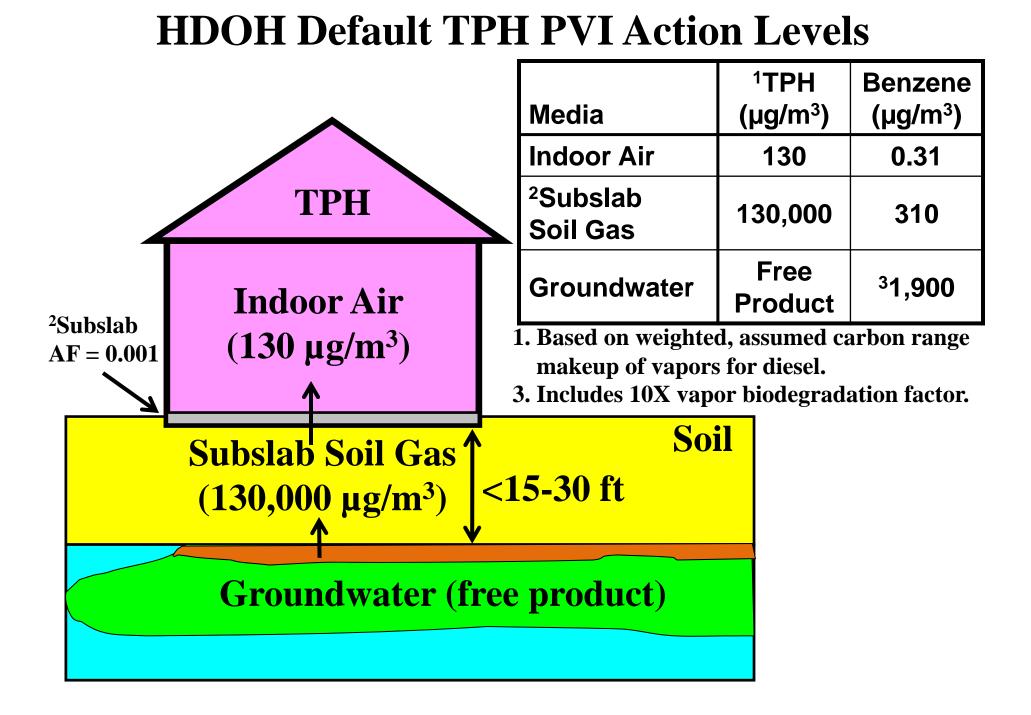


\*Weighted RfC= 126 ug/m<sup>3</sup> Indoor Air<sub>res</sub> = 130 ug/m<sup>3</sup> Soil Gas<sub>res</sub> = 130,000 ug/m<sup>3</sup>

Residential action levels noted; subslab soil gas

- Dominated by higher-toxicity C9-C12 aliphatics;
- Used as default in HDOH vapor intrusion guidance;
- Apparent mix of gasoline and diesel vapors common at many petroleum sites.

**Diesel Odor Recognition Threshold:** 0.5 to 1.0 ppmv (3,500 to 7,000 ug/m<sup>3</sup>) 38



## Fallacy #3: Just Check the Benzene...

**3. Benzene or other individual aromatics always drive PVI risks over TPH.** 



- No specific discussion of PVI risk drivers in either the USEPA or the ITRC guidance documents;
- Focus on benzene examples in documents and training workshops does not imply that that TPH (or other VOCs) can be ignored.

## **Determining the PVI "Risk Driver"**

- Risk Driver = No significant risk from other chemicals when risk posed by this chemical is addressed;
- Example:
  - Soil contaminated with high concentrations of lead and very low concentrations of dioxins;
  - Cleanup to meet lead action levels also addresses dioxin contamination;
  - Cleanup to meet dioxin action levels only does not fully address lead contamination;
  - Lead is the "risk driver";
- Could TPH in vapors still pose a PVI risk when benzene action level is met (i.e., can TPH "drive risk" over benzene)?
- At some ratio of TPH to Benzene TPH will begin to be the main risk driver.

## **TPH:Benzene "Critical Threshold Ratio"** (generic or site-specific)

### Critical Threshold Ratio = <u>TPH Action Level</u> Benzene Action Level

#### **Default HDOH TPH:Benzene CTR**

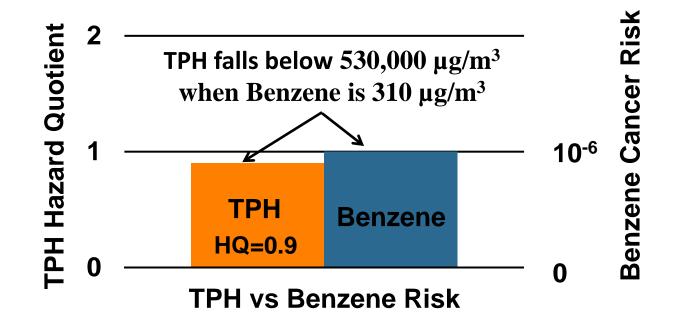
	<sup>1</sup> TPH Action Level	<sup>2</sup> Benzene Action Level	<b>TPH:Benzene</b>
Media	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	<b>Critical Ratio</b>
Indoor Air	130	0.31	420.1
Subslab Soil Gas	130,000	310	420:1

- 1. HDOH default; based on noncancer HQ = 1 (collect TPH carbon range data to develop site-specific TPH action levels);
- 2. Based on 10<sup>-6</sup> excess cancer risk.

Begin considering TPH as potential PVI risk driver when site-specific TPH:Benzene ratio >420:1

### Site A PVI Risk Driver (AVGAS)

#### Critical TPH:Benzene Ratio = 1,710:1 Average Measured TPH:Benzene Ratio = 1,513:1

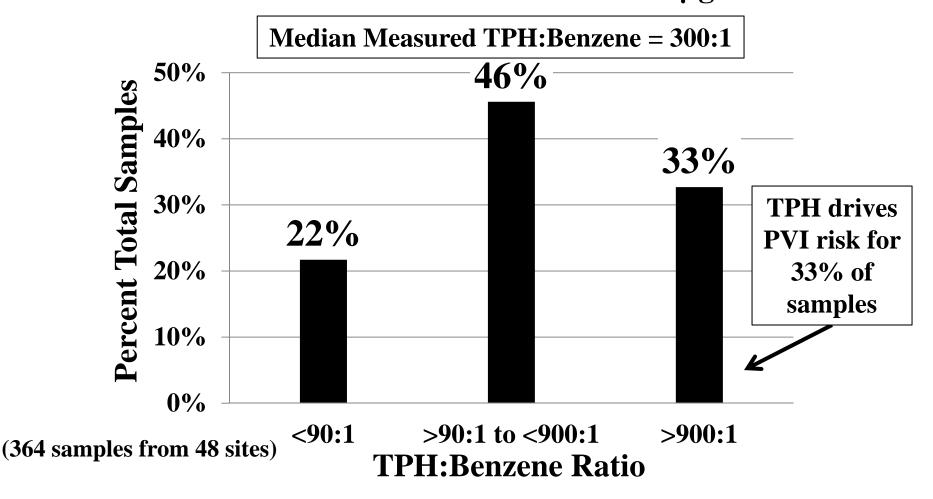


Based on TO-15 Summa Data

Benzene adequate to evaluate vapor intrusion hazards provided that a target 10<sup>-6</sup> cancer risk is used. (TPH noncancer HQ<1 when benzene risk = 10<sup>-6</sup>)

43

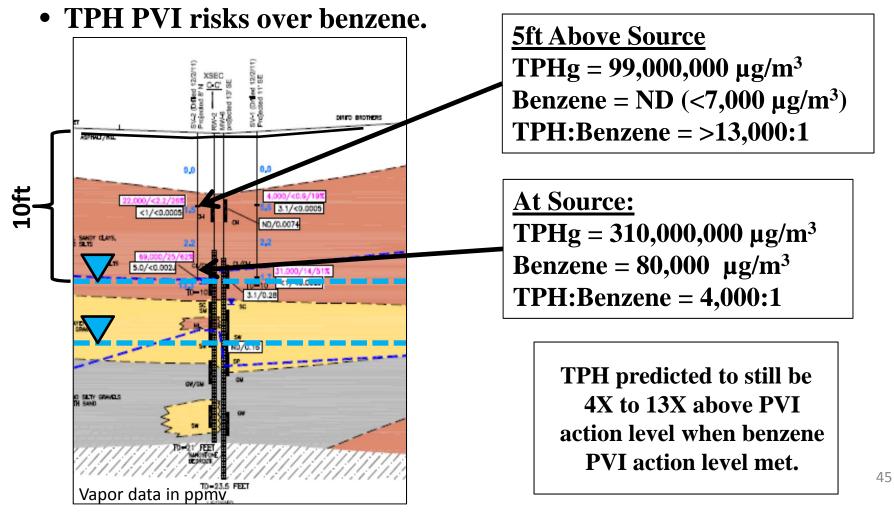
# USEPA PVI Database Risk Drivers (gasoline sites) TPH:Benzene Critical Threshold Ratio = $\frac{290 \ \mu g/m^3}{0.31 \ \mu g/m^3} = 900:1$



TPH noncancer HQ>1 possible for 79% of samples even when benzene risk = 10<sup>-5</sup>;
Suggests important to use 10<sup>-6</sup> benzene cancer risk for PVI screening and remediation.

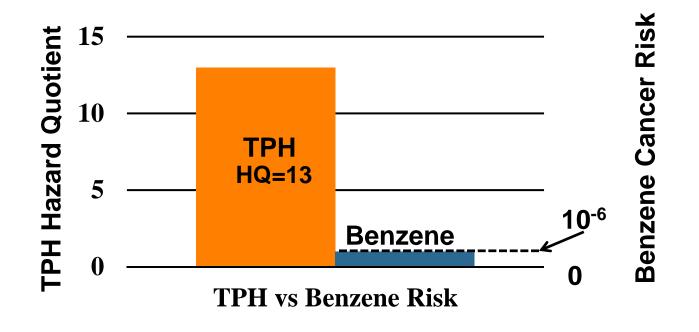
### **Example Gasoline Site in California (Part 1)**

- Groundwater-only source (low-benzene gasoline);
- Carbon range makeup: 80% C5-C8, 20% C9-C12
- TPH RfC =  $308 \ \mu g/m^3$  (indoor air screening level =  $320 \ \mu g/m^3$ );
- Critical TPH:Benzene Ratio =  $1,000:1 (320 \ \mu g/m^3/0.31 \ \mu g/m^3);$



### Site D PVI Risk Driver (JP-4)

Critical TPH:Benzene Ratio = 710:1 Average Measured TPH:Benzene Ratio = 9,100:1

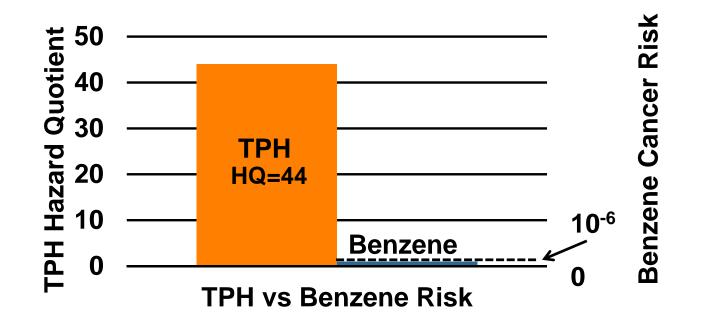


Based on TO-15 Summa Data

#### TPH *always* drives potential vapor intrusion hazards. (TPH noncancer HQ>1 even when benzene risk = 10<sup>-6</sup>)

### Site E PVI Risk Driver (Diesel)

#### Critical TPH:Benzene Ratio = 410:1 Average Measured TPH:Benzene Ratio = 54,000:1



Based on TO-15 Summa Data

#### TPH *always* drives potential vapor intrusion hazards. (TPH noncancer HQ>1 even when benzene risk = 10<sup>-6</sup>)

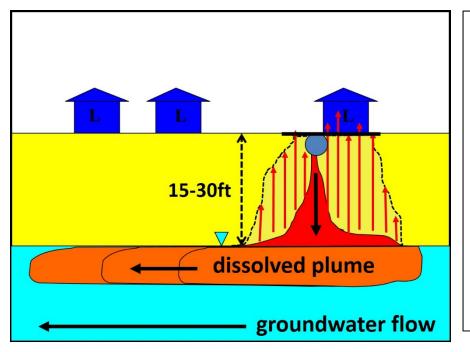
## **TPH vs Benzene as Vapor Intrusion Risk**

	Vapor Intrusion Risk Driver	
	TPH	*Benzene
Site/Fuel Type	<b>Drives Risk</b>	<b>Drives Risk</b>
USEPA PVI Database	х	V
(mostly gasoline)	^	^
Site A	x	х
(mostly AVGAS)		^
Site D	Х	
(mostly JP-4)	<b>^</b>	
Site E	х	
(mostly diesel)	^	

\*Assuming a target, 10<sup>-6</sup> cancer risk is used for benzene.

**Fallacy #4: TPH Vapors Quickly Gone** 

4. TPH in vapors will not migrate >2-3ft from source above potential levels of concern for PVI (vs 15ft for benzene).



Hypothesis:

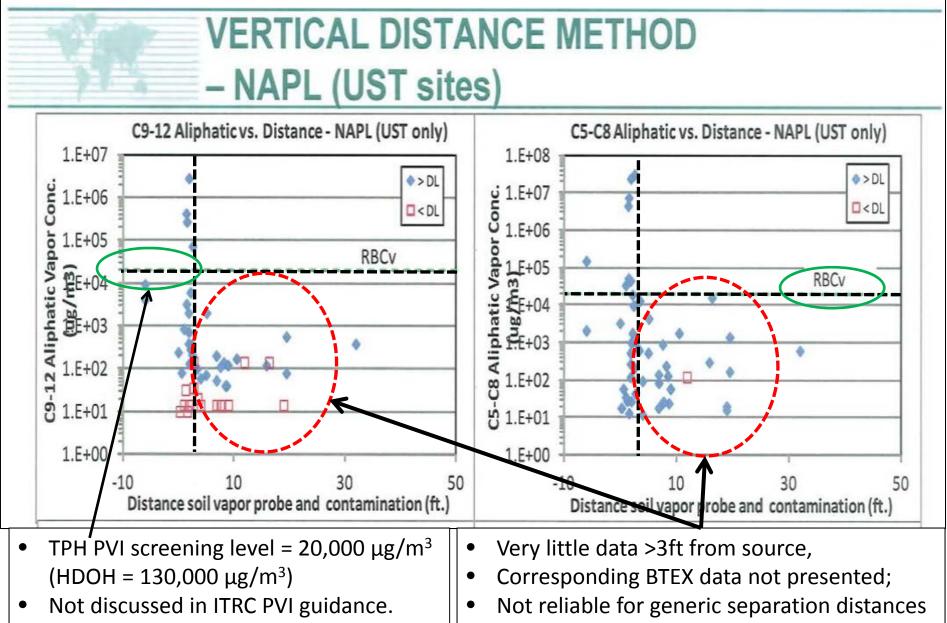
- Aliphatics more quickly removed from vapor plume by degradation;
- Aromatics (e.g., benzene) ultimately drive risk away from source;
- Easily testable in the field.

## **TPH Vertical Separation Distance**

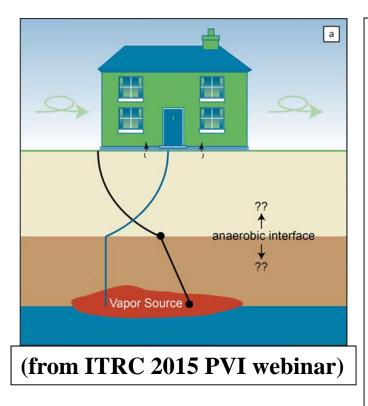
- Assumes *TPH subslab PVI screening level* = 20,000 μg/m<sup>3</sup> (Not included in ITRC or USEPA PVI documents)
- 2-3ft vertical separation distance proposed in early drafts of ITRC PVI guidance and referenced publications;
  - Based on very *limited field data*;
  - Models that assume a *higher*, *relative degradation rate for aliphatic* vs aromatic compounds in vapor plumes;
  - Predicts *relative enrichment* of vapors in BTEX away from source (i.e., TPH:Benzene ratio *decreases* as aliphatics are more rapidly removed);
  - 2-3ft vertical separation distance not supported buy field data;
  - BTEX enriched vapor plumes *not observed* in field data (*opposite* suggested in Brewer et al 2013 but also limited data).

### **Field Data vs TPH Vertical Separation Distance**

(Hers & Truesdale 2012; Lahvis & Hers 2013)



## Model-Based Separation Distances (e.g., Biovapor) (refer ITRC PVI webinar training)

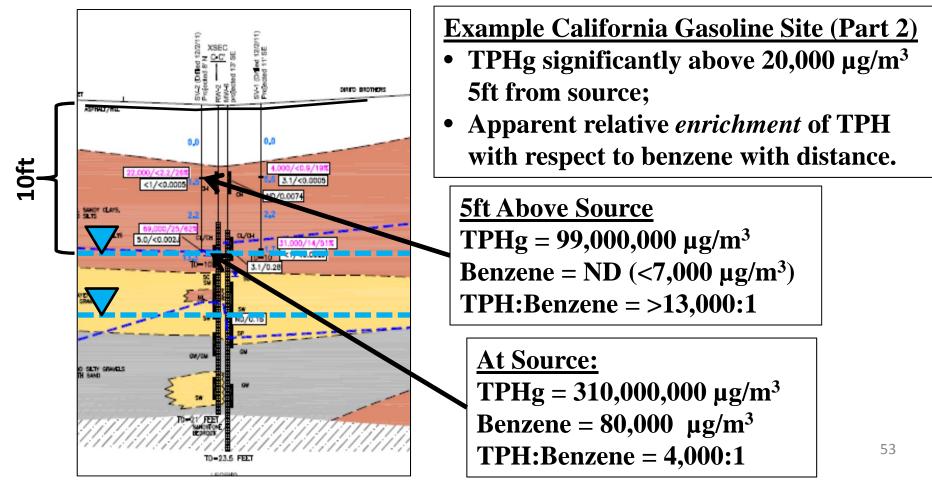


### **Vapor Intrusion Models**

- Models are great learning tool;
- Use to assist development of remedial actions and long-term management plans;
- "Models tell you exactly what you tell them to tell you."
- Significant variability within and between sites;
- Model results can be highly inaccurate;
- <u>Always</u> confirm F&T PVI models with field data.

### **TPH Soil Vapor Field Data**

- HODH field study: TPH significantly >130,000 µg/m<sup>3</sup> five- to tenplus feet from source (free product present);
- Similar observations at other sites in Hawai'i and from mainland;
- Default TPH vertical separation distance of 2-3ft isn't protective;
- 15-30ft separation distance appears adequate for most sites.



### Where's the Benzene?

- Preferential biodegradation of aromatics relative to aliphatics (inconsistent with laboratory studies)
- Preferential removal of aromatics from vapors due to partitioning into soil moisture (higher solubility);
- Original release of low-benzene gasoline;
- Most likely latter based on lack of consistent trend of relative *aliphatic:aromatic enrichment* in vapors away from source areas (limited data reviewed).

## **Benzene Vertical Separation Distance Applies to TPH for Screening Purposes**

ITRC PVI Guidance: Appendix F (F.12): "Based on reviews of the PVI database, maximum vertical screening distances derived for other individual, indicator compounds (e.g., benzene) are also considered to be adequate for noncompound-specific TPH fractions."

## **PVI Summary and Implications**

- *Natural degradation* significantly reduces vapor intrusion risks from petroleum in comparison to chlorinated solvents;
- *Shallow (<15ft) petroleum free product* in soil or on groundwater can pose potential PVI risks;
- Vapor plumes from *jet fuels and diesel* are lower concentration than for gasoline, but can still pose potential PVI concerns;
- Petroleum vapors are dominated by TPH aliphatics;
- Risk-based *indoor air and soil gas action (screening) levels* can be developed for TPH (site-specific or generic);
- *Benzene usually drives PVI* risk for older releases of gasoline (high benzene);
- *TPH usually drives PVI risk* for middle distillates and newer lowbenzene gasoline releases;
- Small pockets of residual contamination do not pose a long-term, PVI risk regardless of concentration (limited mass);
- PVI concerns can typically be addressed by *removal of gross* contamination.

## **Questions (use Zoom comment box)?**

**PVI Remediation: Former Gasoline Tank Farm (Honolulu)** 



Treatment of Grossly Contaminated Soil



Passive subslab venting.



Liquid Boot membrane.



**Final Lowe's Store**