

**There are three methods to
gain knowledge:**

**The first, reflection, is the
noblest;**

**The second, imitation, is the
easiest;**

**And the third, experience, is
the bitterest.**

Confucius

Evaluation of Petroleum Contaminated Soil and Groundwater in Hawai'i



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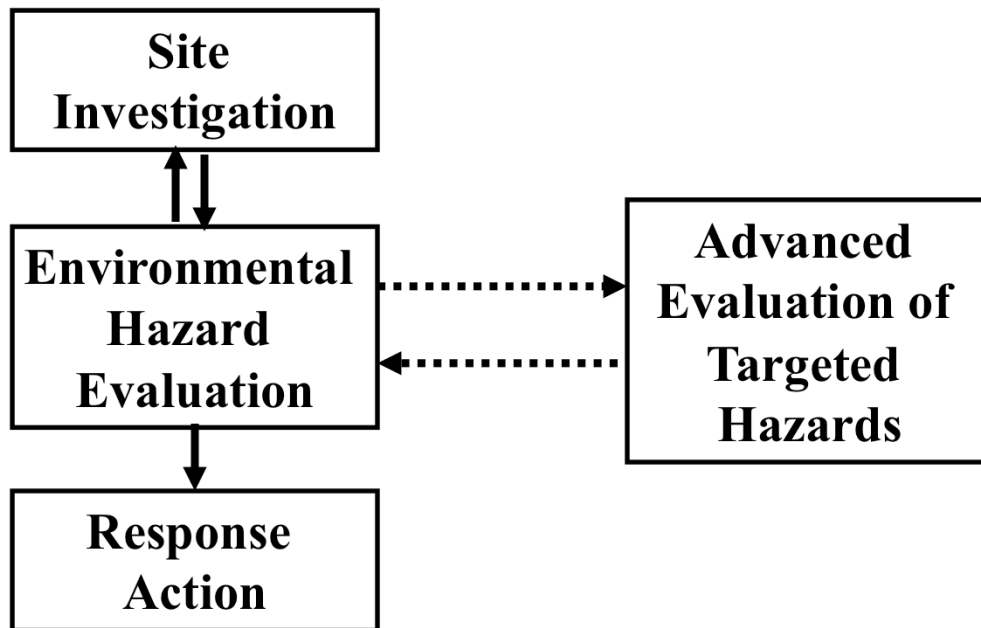
References:

Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater, Pacific Basin Edition (Summer 2008, last updated March 2009):
<http://hawaii.gov/health/environmental/hazard/pacificbasin.html>

- Similar guidance available from CalEPA and Hawai'i DOH;
- Pacific Basin edition more closely follows USEPA guidance

Technical Guidance Manual: Hawai'i Department of Health, <http://www.hawaiidoh.org/>

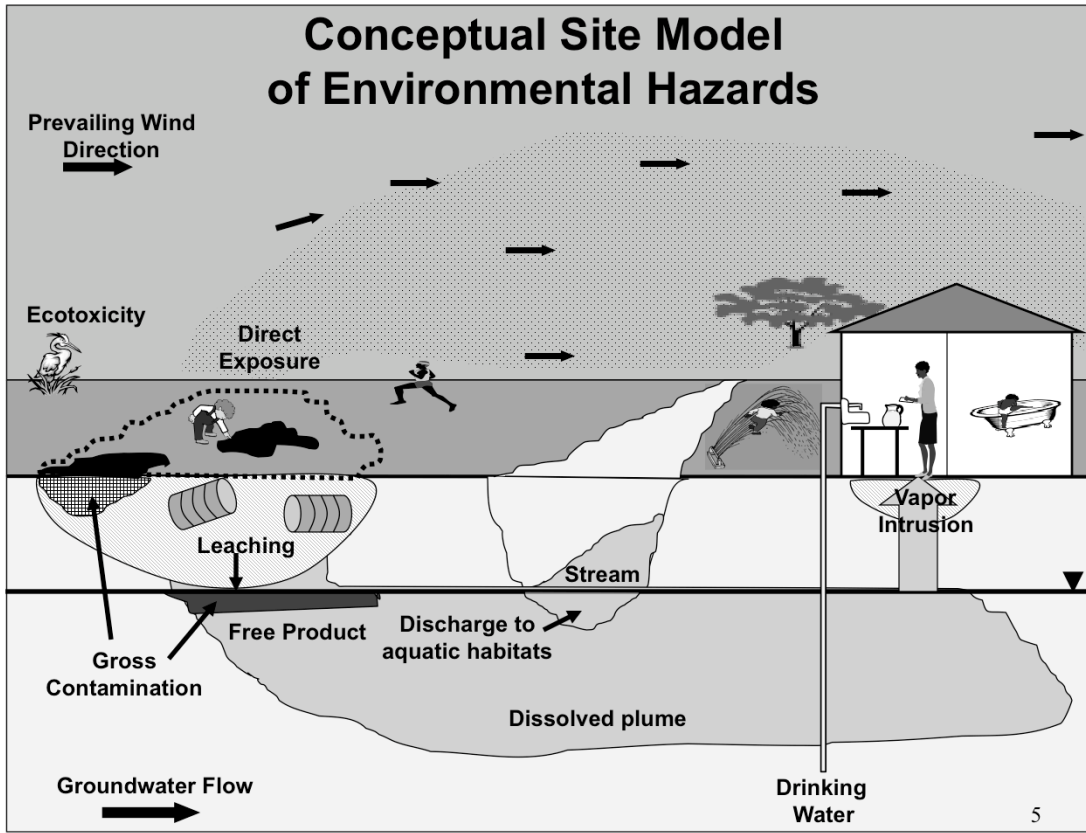
Environmental Hazard Evaluation

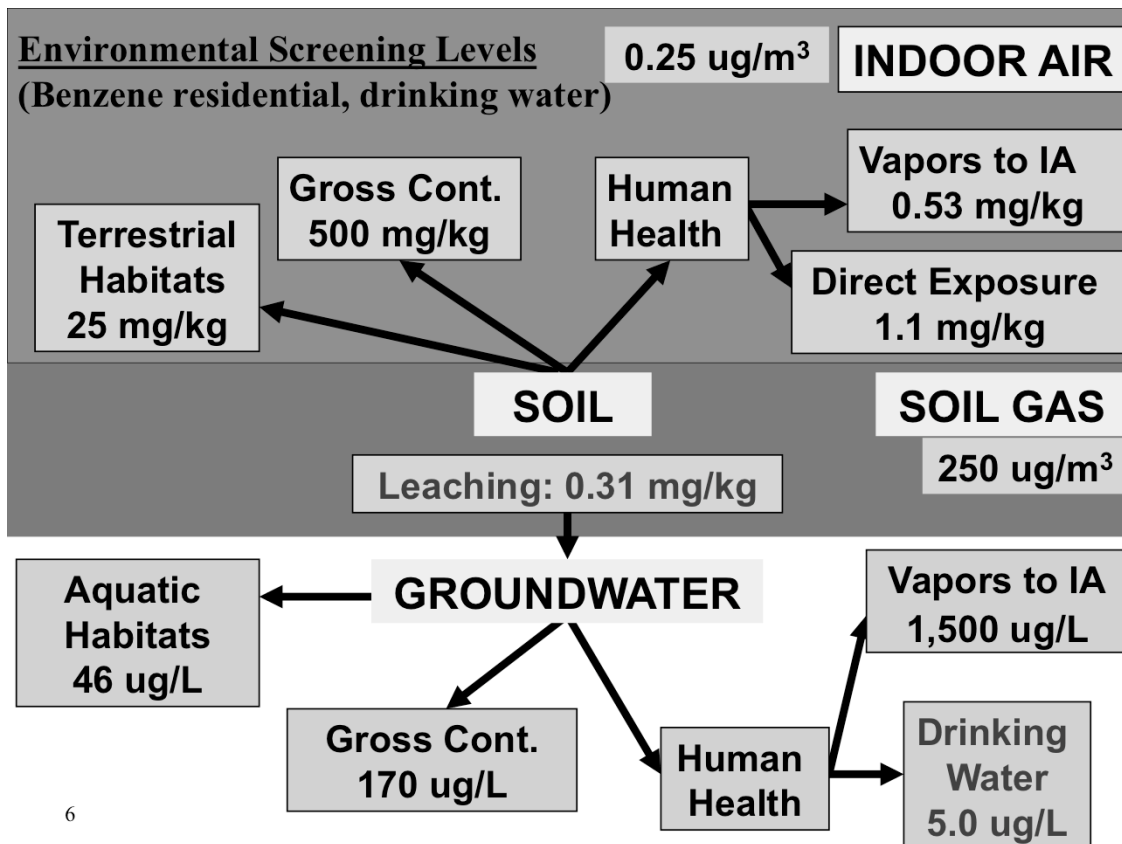


4

Use the EHE to pose questions about the site and help design the investigation as well as any remedial action.

Conceptual Site Model of Environmental Hazards





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Benzene Soil Action Levels (assume unrestricted/residential land use, exposed soils, over drinking water)

Final soil Tier 1 EAL = 0.31 mg/kg (based on leaching hazards)

Leaching drives soil contamination concerns for benzene in this scenario (i.e., action level for leaching lower than all other soil action levels).

Final groundwater Tier 1 EAL = 5 ug/l (based on drinking water toxicity hazards)

Drinking water toxicity concerns drive groundwater contamination concerns (i.e., action level for drinking water toxicity lower than all other gw action levels).

Environmental Screening Levels (ESLs)

- **ESLs for 150 common contaminants**
- **Soil, Groundwater, Surface Water; Soil Gas, Indoor Air**
- **No significant environmental hazards if concentration of contaminant is less than the ESL**
- **Volume 1: Tier 1 Final ESLs**
- **Volume 2: Detailed Screening levels**

Use of ESLs

- **Screen out “low-risk” sites**
- **Use to complete investigations & delineate areas of potentially significant contamination**
- **Quickly identify potential environmental hazards**
- **Focus on advanced evaluation of tentatively identified hazards as needed**

ESL Surfer

- **Electronic lookup tables;**
- **Rapidly screen data and identify potential environmental hazards;**
- **Printable report summaries**

Other Tools:

- **Tier 2 direct exposure screening levels**
- **Batch Test Leaching Model**
- **Vapor intrusion model**

ESL Surfer (Pacific Basin Edition)

Tier I Environmental Screening Levels Surfer



Worksheet is write protected. Disable protection under "Tools" if you have trouble selecting options. (password = ESL)

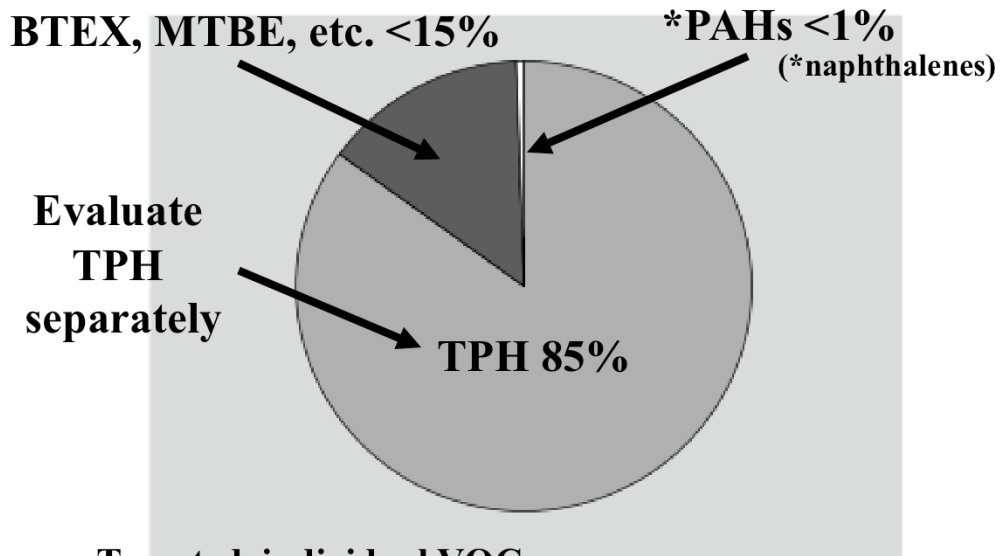
Pacific Basin Edition
(Guam EPA Summer 2008,
updated March 2009)

Steps 1 and 2:

Click in cell and use pull-down boxes to make selection.

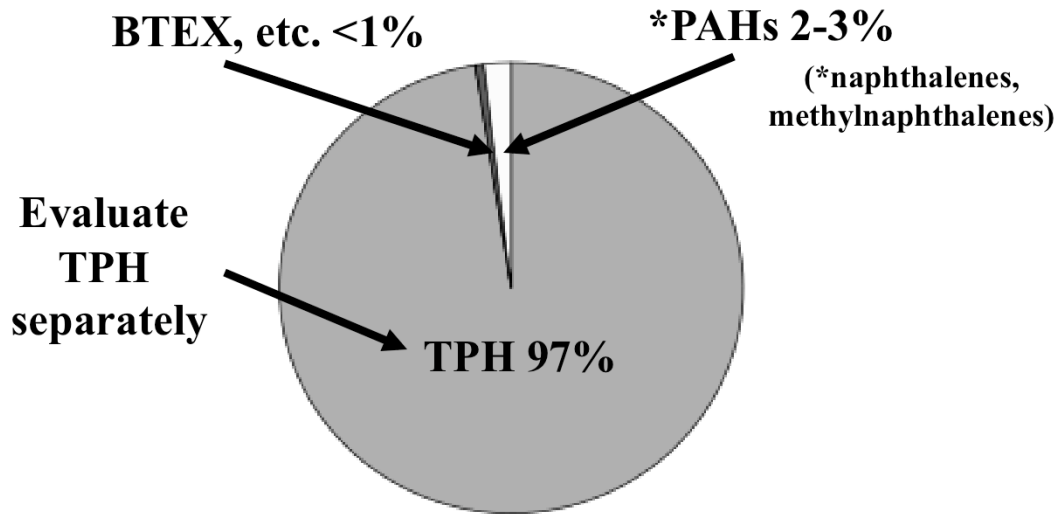
<p>STEP 1: Select ¹Site Scenario:</p> <p>²Land Use: <input type="text" value="Unrestricted"/></p> <p>³Groundwater Utility: <input type="text" value="Drinking Water Resource"/></p> <p>⁴Depth of Impacted Soil: <input type="text" value="Shallow"/></p>	<p>Final Tier I ESLs</p> <p>Soil (mg/kg): 3.1E-01 X</p> <p>Groundwater (ug/L): 5.0E+00 X</p> <p>Soil Gas (ug/m³): 2.5E+02 X</p>
<p>STEP 2: ⁵Select Contaminant</p> <p><input type="text" value="BENZENE"/></p>	<p>EALs exceeded. Refer to Detailed EALs (next tab) to identify specific environmental hazards that may be posed by contamination.</p>
<p>STEP 3 (optional): Enter site data. (Potential environmental hazards highlighted in Red on Detailed ESL worksheet.)</p> <p>Soil (mg/kg): <input type="text" value="5"/></p> <p>Groundwater (ug/L): <input type="text" value="150"/></p> <p>Soil Gas (ug/m³): <input type="text" value="500"/></p>	<p>Notes:</p> <p>Volatile chemical. Collect soil gas data for site-specific evaluation of vapor intrusion hazards if Tier I screening levels for this hazard exceeded (see Advanced EHE Options tab of Surfer).</p>

Petroleum Contaminants of Potential Concern (gasolines)



- Targeted, individual VOCs.
- Non-targeted VOCs are added together and evaluated separately as “Total Petroleum Hydrocarbons” (TPH) ¹¹

Petroleum Contaminants of Potential Concern (middle distillates)



- Targeted, individual VOCs.
- Non-targeted VOCs are added together and evaluated separately as “Total Petroleum Hydrocarbons” (TPH) ¹²

Based on typical diesel fuel

Petroleum Carbon Ranges

-Toxicity Factors & Fate & Transport Constants-

Carbon Range	Koc (cm³/g)	Henry's Constant (H')	Reference Dose (mg/kg-d)	Inhalation RfC (ug/m³)
Aliphatics				
C5 to C8	2,265	54	0.04	200
C9 to C12	150,000	65	0.1	200
C9 to C18	680,000	69	0.2	200
C19 to C36	immobile	-	2.0	-
Aromatics				
C9 to C10	1,800	0.33	0.03	50
C11 to C22	5,000	0.03	0.03	50

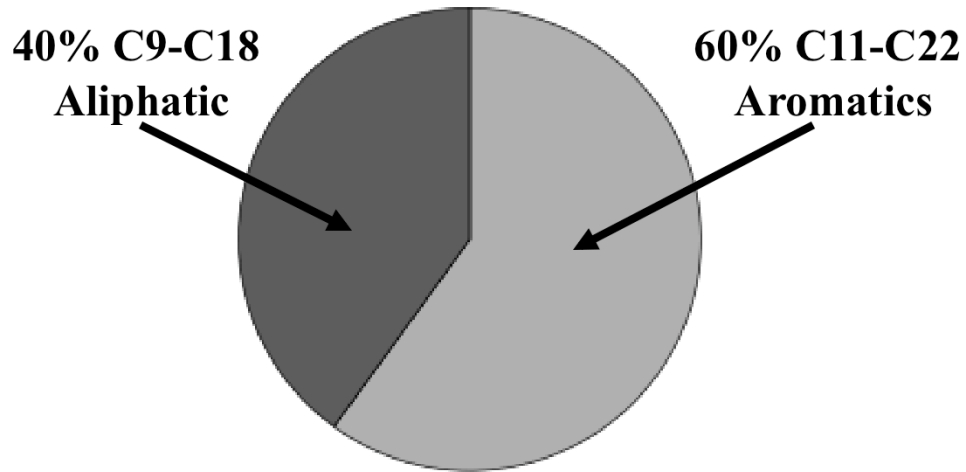
Assumed Carbon Range Composition of Gasolines



**100% C11-C22
Aromatics**

**TPHg action levels based on toxicity factors and
constants for C11-C22 Aromatics**

Assumed Composition of Petroleum Fuels -Middle Distillates (e.g., diesel)-



TPHmd action levels based on weighted toxicity factors and constants for C9-C18 Aliphatics & C11-C22 Aromatics¹⁵

Total Petroleum Hydrocarbons (TPH)

-Toxicity Factors & Fate & Transport Constants-

TPH Category	Koc (cm³/g)	Henry's Constant (H')	Reference Dose (mg/kg-d)	Inhalation RfC (ug/m³)
TPHg	5,000	65	0.03	50
TPHmd	5,000	69	0.06	110
TPHrf	-	-	0.06	210

*Gasolines, Middle Distillates (diesel, etc.) and Residual Fuels

TPH Soil Action Levels


*Target Hazard	TPHg	TPHmd
Direct Exposure	600 mg/kg	**500 mg/kg
Vapor Intrusion	(use soil gas)	(use soil gas)
Leaching	100 mg/kg	100 mg/kg
Gross Contamination	100 mg/kg	500 mg/kg

***Residential land use; groundwater is a source of drinking water. Target HQ = 0.5.**

****Ceiling level for presence of free product (C_{sat})**

Vapor intrusion, leaching and gross contamination hazards typically drive need for cleanup

Gross Contamination Hazards

- 
- **Odors & nuisance**
 - **Explosive vapors (not tested for in 1990s)**
 - **Potentially mobile free product**
 - **Interference with future development**
 - **General resource degradation**

TPH Groundwater Screening Levels

Target Hazard	TPHg	TPHmd	TPHrf
DW Toxicity	100 ug/L	100 ug/L	100 ug/L
DW Taste & Odors	100 ug/L	100 ug/L	100 ug/L
Vapor Intrusion	(use soil gas)	(use soil gas)	(methane hazard)
*Aquatic impacts	500 ug/L	640 ug/L	640 ug/L

*Potential discharges to aquatic habitats

Drinking Water Gross Contamination ("Secondary MCLs")



Should be able to taste or smell TPH in drinking water at or prior to significant toxicity hazards. 20

Drinking water standards or action levels for noncarcinogenic, petroleum-related contaminants usually based on taste & odor concerns (e.g., TPH, xylenes, toluene, plus phenols, etc.).

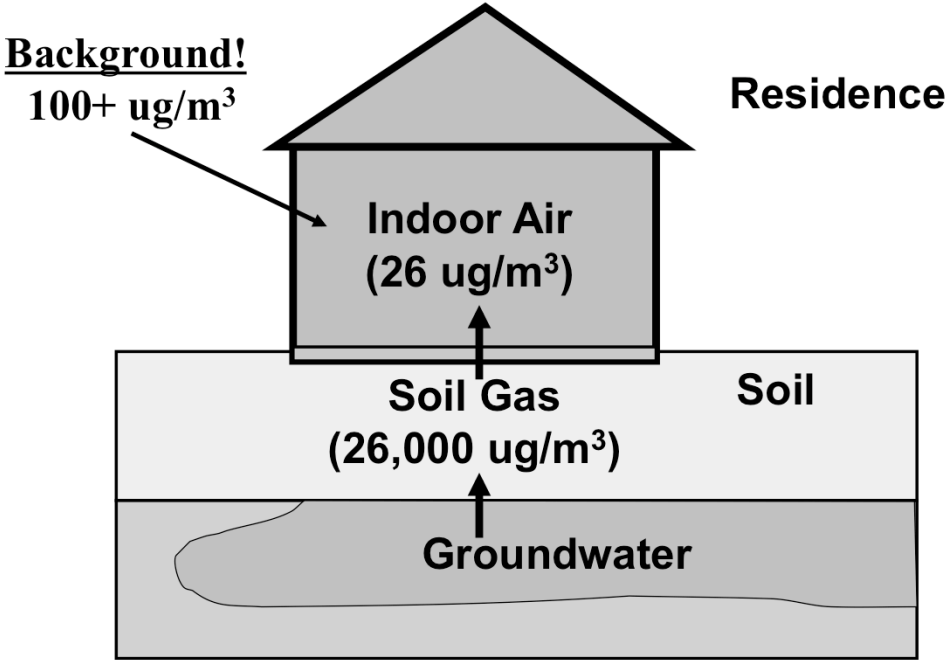
***TPH Indoor Air & Soil Gas Screening Levels**

Target Hazard	TPHg	TPHmd
Indoor Air	26 ug/m³	57 ug/m³
Soil Gas	26,000 ug/m³	57,000 ug/m³

***For evaluation of vapor intrusion into buildings
(residential, assumes 1:1,000 dilution). Target HQ = 0.5.**

**Vapor intrusion hazards often identified
at heavily contaminated sites
(including methane production).**

Vapor Intrusion Hazards (example TPHg action levels)



Example Soil Gas Data (percent total volatile contaminants)

Site	TPH	B	TEX	Naph
Honolulu Harbor (heavy/gas/diesel)	*99.97%	0.01%	0.01%	0.00%
Pearl Harbor (gas/diesel)	*99.41%	0.04%	0.00%	0.55%
Aloha Station (gasoline)	*99.71%	*0.27%	0.032	0.00%
GASCO (MGP)	*21.20%	*78.80%	0.00%	0.00%

***Drives vapor intrusion risk at site. Methane may also pose potential explosion hazards.**

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Aloha Gas Station: TPH HQ >200; Benzene ECR 7×10^{-5} .
 GASCO: TPH HQ >36; Benzene ECR 1×10^{-2} .

Example Sites

- **ConocoPhillips/Lowes**
 - **Environmental Hazard Evaluation**
- **IDPP-Honolulu**
 - **LNAPL saturation and mobility**

Alternative Carbon Range Approach

- **Allowed on site-specific basis**
- **Rarely used (no current Hawai'i guidance)**
- **Recent US Air Force guidance (Hickam Air Force Base, Hawai'i)**

Environmental Hazard Maps ConocoPhillips Site, Honolulu



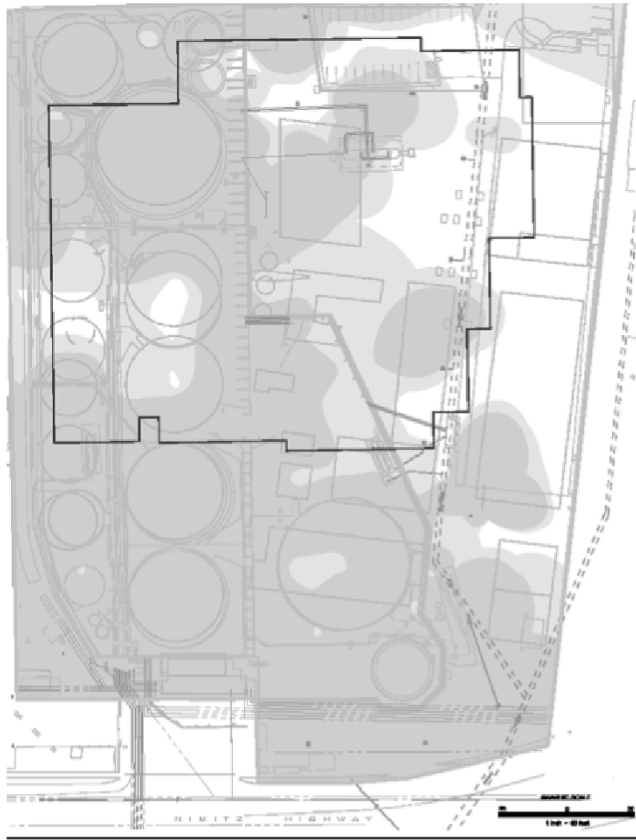
**March 2008 Environmental Hazard Evaluation
(Environmental Science International, Hawai'i)**

Soil Direct Exposure Hazards



ESI, Honolulu²⁷

Combined map of all contaminants that pose potential soil direct exposure hazards (TPH, lead, etc.)>



Soil Gross Contamination Hazards

ESI, Honolulu²⁸

Combination of all contaminants that pose potential soil gross contamination hazards (mostly TPH).

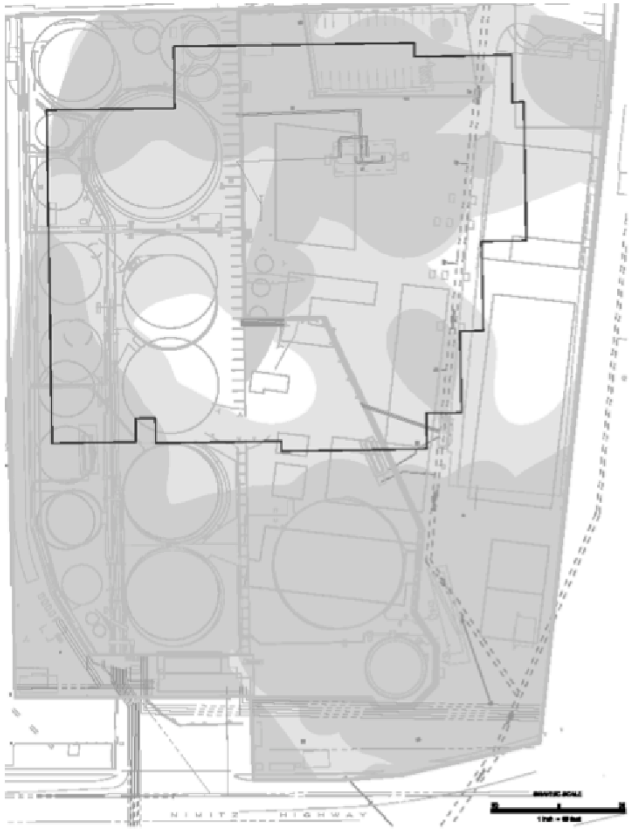


Vapor Intrusion Hazards (soil gas data)

ESI, Honolulu²⁹

Combination of all contaminants that pose potential vapor intrusion hazards based on soil gas data (mostly TPH, +/- benzene, methane also present).

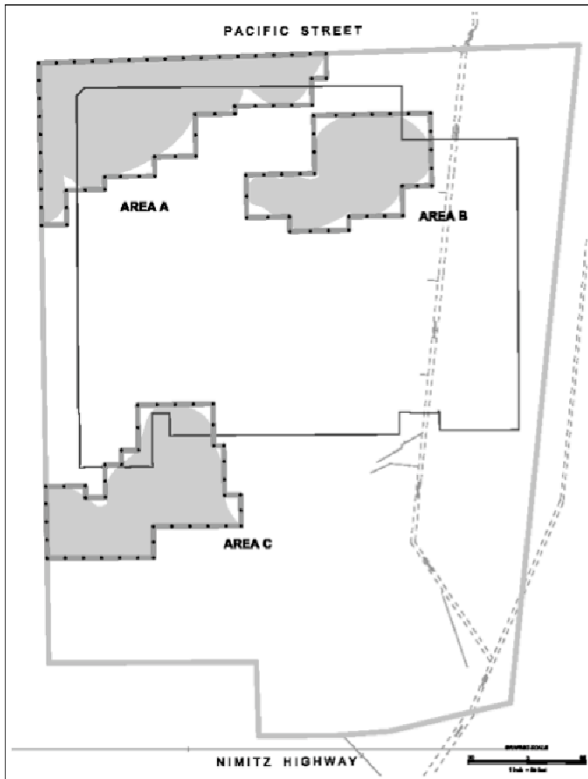
Always collect soil gas data to confirm tentatively flagged vapor intrusion hazards based on soil or groundwater data.



Groundwater Discharge to Surface Water Hazards

ESI, Honolulu³⁰

Combination of all contaminants that pose potential groundwater aquatic toxicity hazards (potential discharges of groundwater to aquatic habitats; TPH, BTEX, methylnaphthalene, etc.).



(Final excavations significantly expanded)

Target Soil Treatment Areas

Objective
Remove primary
vapor source mass



ESI, Honolulu ³¹

Final remedial actions based on environmental hazard maps.

Setting Risk-Based Cleanup Goals for Total Petroleum Hydrocarbons:

*Cumulative Risk Assessment of multiple chemicals/exposures
under Washington State's Cleanup Regulation (MTCA)*

*Hun Seak Park: hpar461@ecy.wa.gov
Toxics Cleanup Program: <http://www.ecy.wa.gov>*

**Washington State Department of Ecology,
Olympia, WA**

June 16, 2009



Topics

- Problem Statement on TPH/ Cleanup Level Establishment/Risk Goals/ Exposure Pathways
- Fractionation of TPH: Equivalent Carbons
- Toxicological interactions for multiple chemicals (TPH fractions)
- Chemical-chemical interactions and the nature of the medium: Transport
- Spreadsheet tool to estimate cumulative risk from TPH contamination - Setting Cleanup Levels (CULs)

Petroleum Contamination

- Fuels drive remediation - over 70% of hazardous waste sites are petroleum related.
- Petroleum hydrocarbons are complex mixtures with 100's to 10,000's of constituents: complexities on toxicological interactions.
- Constituents exhibit large range of behavior in environmental media: chemical-chemical interaction and the nature of the medium.
- Risk for petroleum left on site need to quantify for:
 - ✓ Protection of human health and environment
 - ✓ Scientifically defensible & consistent process
 - ✓ Practical and cost-effective

Overview for Setting Cleanup Levels

1. Evaluate beneficial uses of land, groundwater, & surface water.
2. Design conceptual site model.
3. Determine applicability of cleanup goals.
4. Select indicator hazardous substances (or COC).
5. Identify CULs: Surfacewater -> Groundwater -> Soil
6. Adjust CULs: PQLs, backgrounds, cumulative risks/ exposures, applicable state and federal laws, etc...
7. Identify points of compliance.
8. Demonstrate the compliance of CULs.

Risk Goals to Establish Cleanup Levels Under MTCA

Method A:

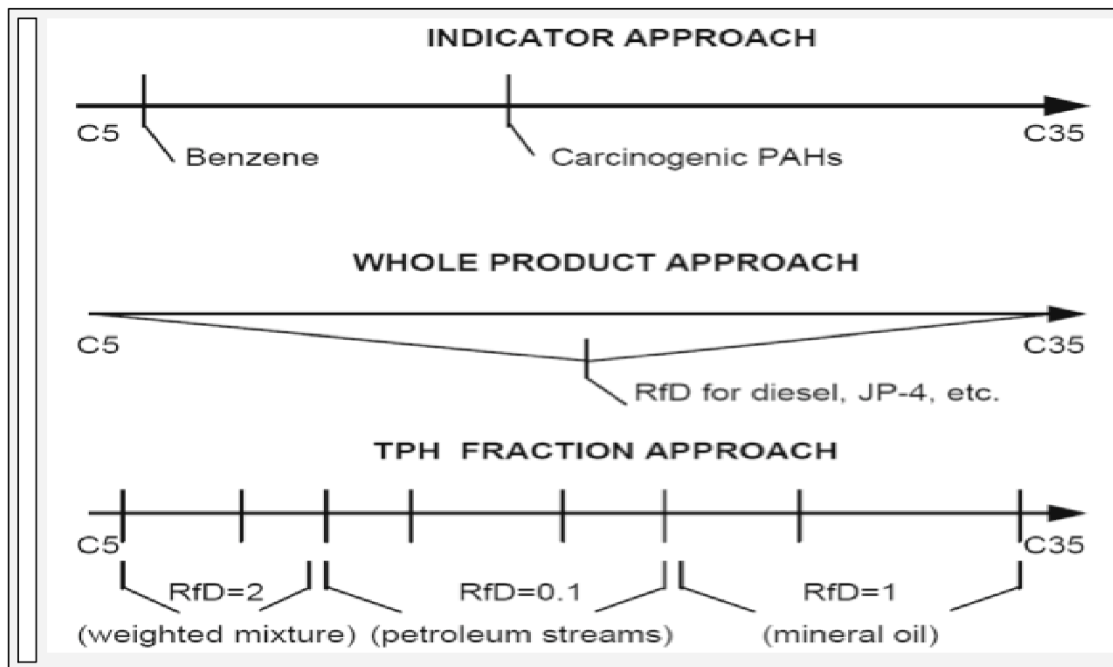
- Designed for "simple sites"
- Look-up table values in rule for groundwater & soils

Methods B & C:

- Methodology (site-specific risk-based equations) & policy defined by rule
- Exposure parameters/Target risks are defined by rule

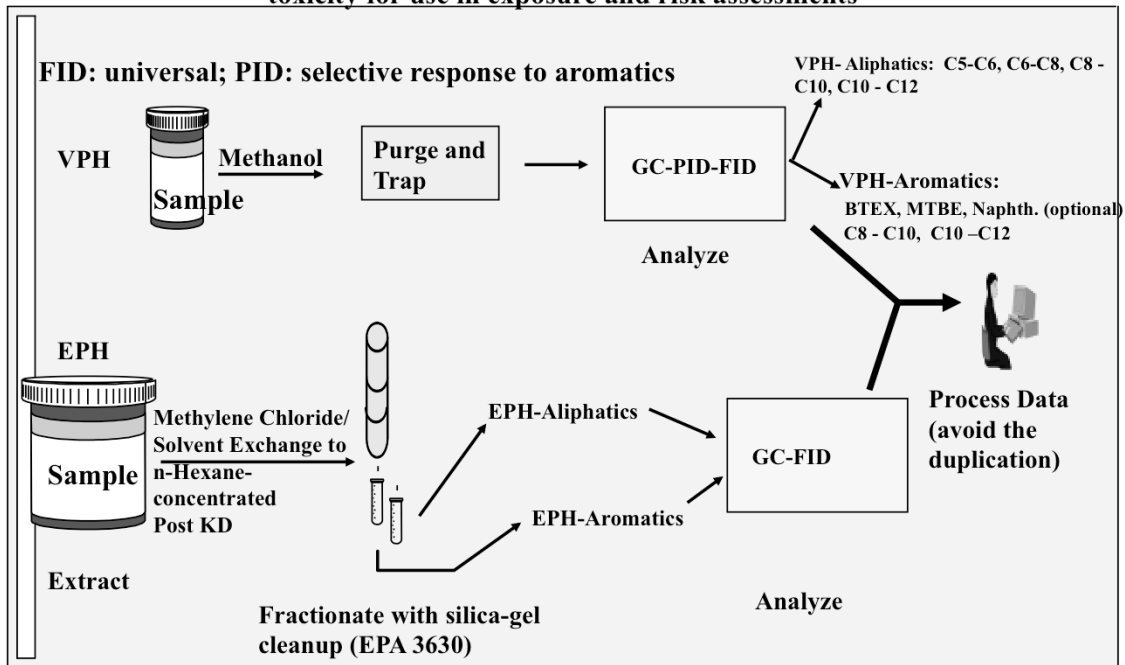
Target Risk Level @ Exposure Point			
	HI	Cancer risk for individual chemical	Total Cumulative Cancer risk
Method B	1	1×10^{-6}	1×10^{-5}
Method C	1	1×10^{-5}	1×10^{-5}

Various TPH Risk Assessment Methods



VPH & EPH Analysis for TPH

Defining a number of fractions with specific fate and transport properties and toxicity for use in exposure and risk assessments



Exposure Pathways to be evaluated for TPH Cleanup Goals

For Groundwater CUL:

- **Human health protection - potable (ingestion) or not**
- **Discharge to surface water beneficial uses**
- **Other pathway- "site-specific"**

For Soil CUL:

- **Human health protection: concurrent exposure due ingestion & dermal exposure**
- **Leaching- protection of Groundwater quality - need to convert from soil conc to ground water conc via transport modeling/tests - Physical/chemical properties**
- **Terrestrial ecological evaluation**
- **Other pathways if necessary- "site-specific"**

Cumulative Toxicity Assessment for TPH (Ingestion pathway)

- Adverse effects or cancer risks resulting from exposure to two or more hazardous substances with similar types of toxic responses (e.g., TPH) are assumed to be additive unless scientific evidence is available to demonstrate otherwise. - Policy choice.
- TPH CUL is a function of the weight composition of the product and represents a weighted average toxicity of all of the components in a given product. - Policy choice.

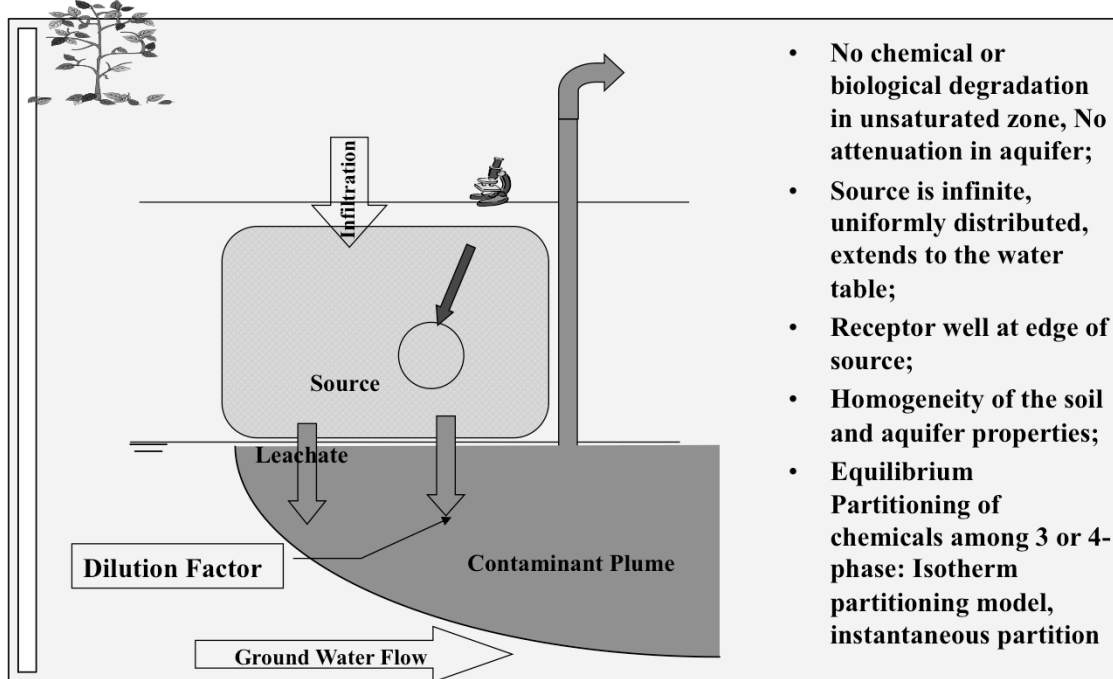
Base formula to set up "TPH CUL" is...

$$CUL_{TPH} = \frac{1}{\sum_{i=1}^n \left(\frac{W_i \cdot Fraction_i}{CUL_i} \right)}$$

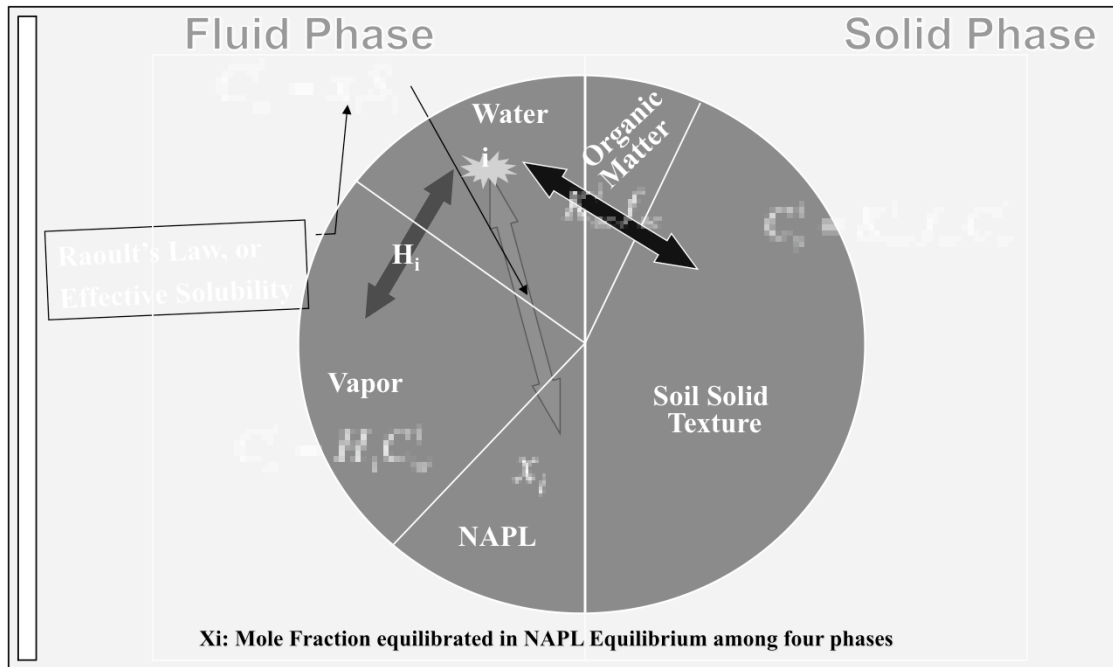
Methods: Leaching Pathway Evaluation

- Major mechanisms; Persistence, Partitioning, Mobility;
“Old method: 100 x Groundwater CULs”
- New evaluation methods:
 - **Default method:** 4-phase Partitioning-equilibrium model: favorable presence in certain media
= f(sorption, volatilization, vapor saturation & solubility limit, mass/volume conservation, dilution/attenuation factor): chemical & site-specific info needed
 - Leaching tests
 - Empirical demonstration
 - Alternative fate & transport models/tests

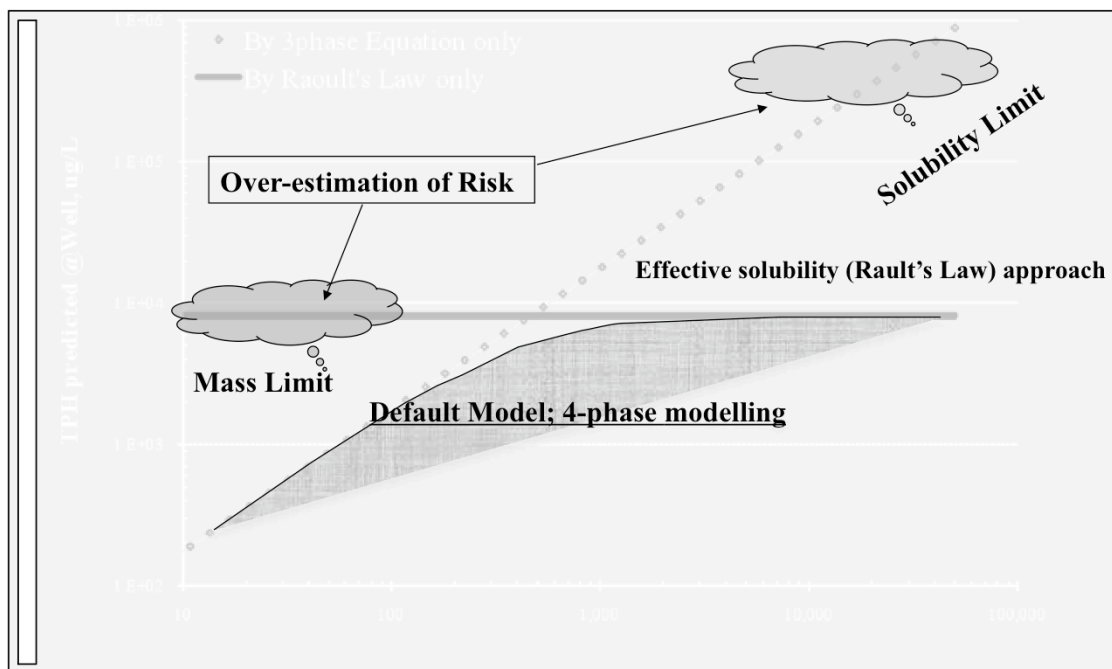
Assumptions/Conceptual Model of Soil-to-Groundwater Pathway



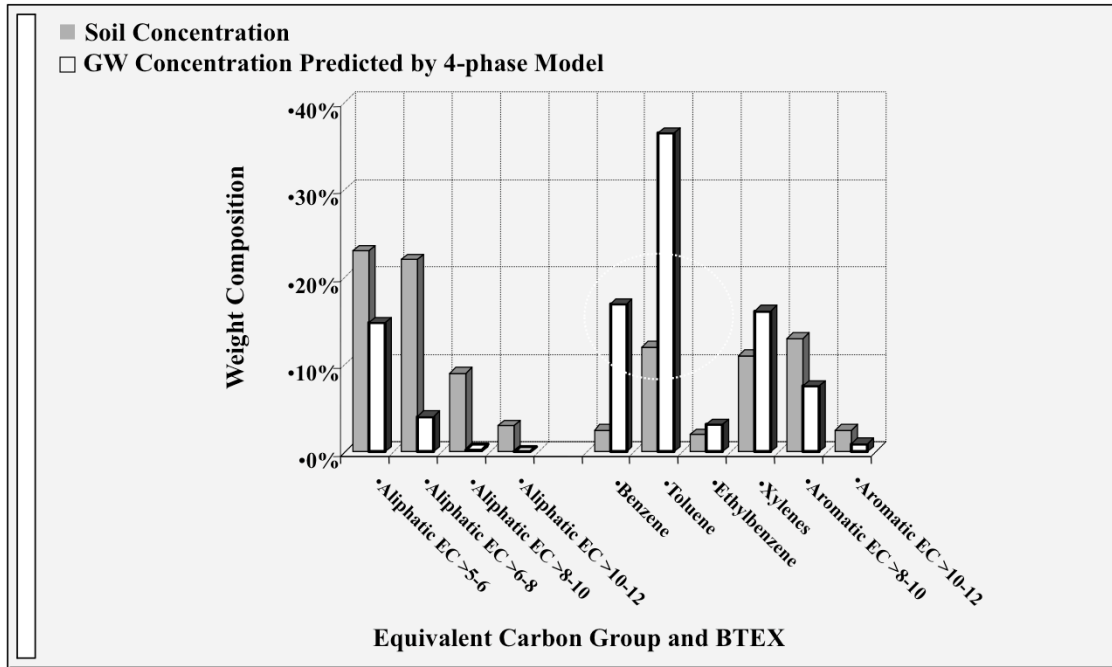
**Phase Equilibrium and Partitioning
where Non Aqueous Phase Liquid (NAPL) exists**



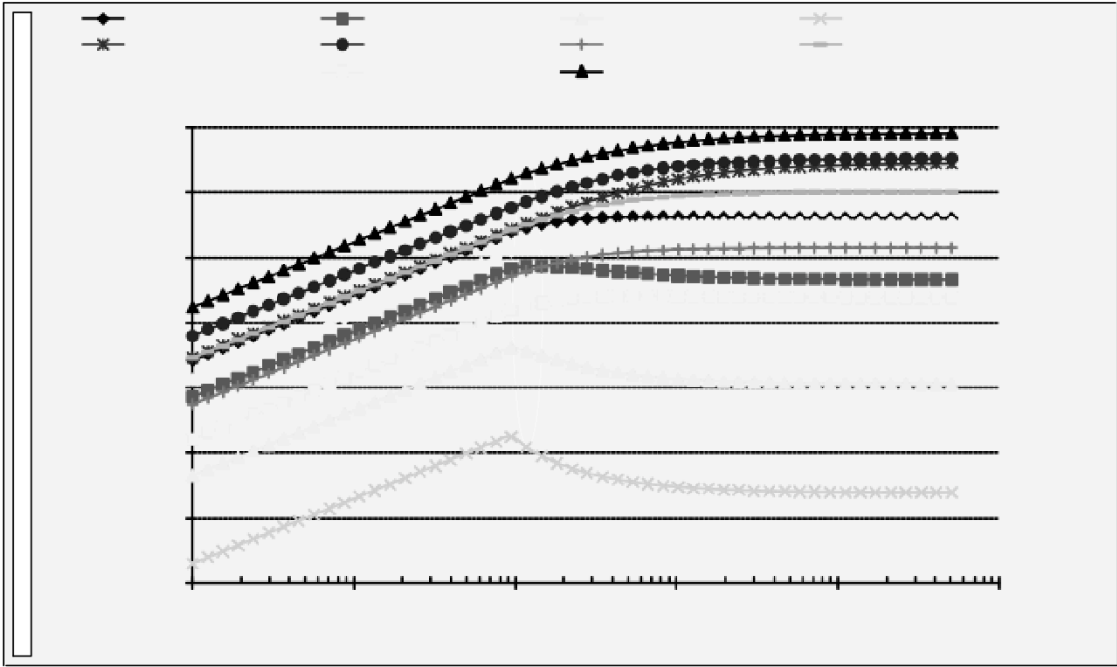
Default Model: Predicting concentration of Groundwater from soil TPH with a model (@ Fresh Gasoline)

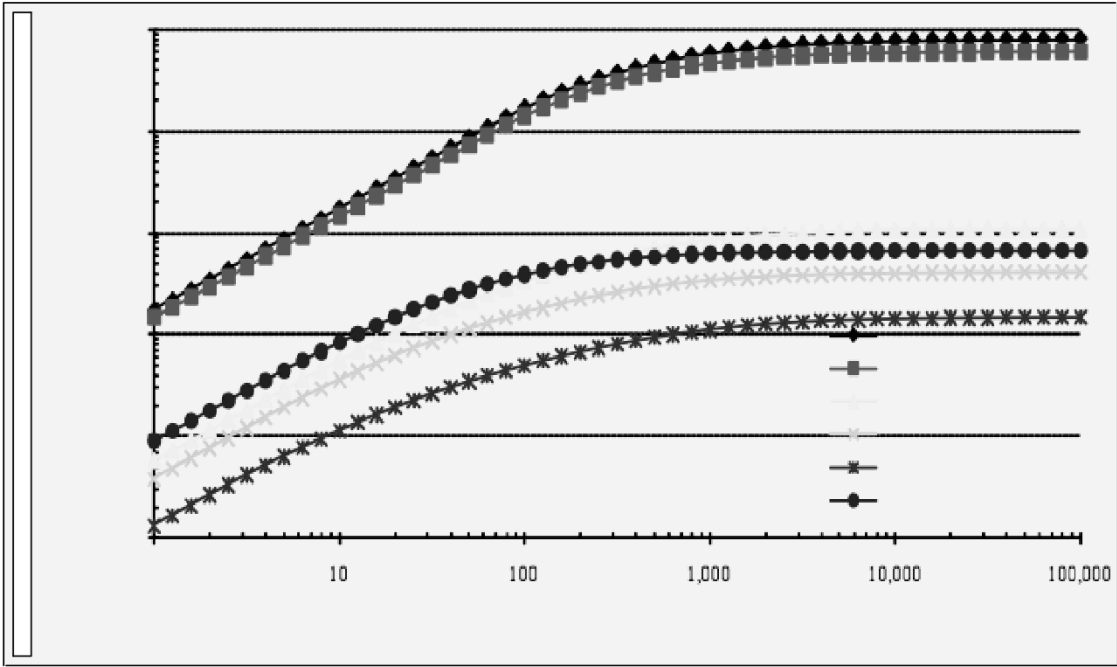


Relative Mass Distribution of Equivalent Carbon group in different media with fresh gasoline contaminated soil at TPH of 100 mg/kg



*Groundwater Concentrations as a function of
Soil Concentrations (@Fresh Gasoline)*





Spreadsheets- MTCATPH 11.1

Input Worksheet

⇒

1. Enter Site Information

Date: 08/19/05
 Site Name: ABC site
 Sample Name: spg_12

Preview Main END
Print Input & Output

2. Enter Soil Concentration Measured

Chemical of Concern or Equivalent Carbon	Measured Soil Conc dry basis mg/kg	Composition Ratio %
Petroleum EC Fraction		
AL_EC >5-6	35	4.22%
AL_EC >6-8	20	2.45%
AL_EC >9-10	40	4.82%
AL_EC >10-12	57	6.87%
AL_EC >12-16	125	15.06%
AL_EC >16-21	300	36.94%

Notes for Data Entry **Set Default**

Clear All Soil Concentration Data Entry Cells
 Restore All Soil Concentration Data cleared

REMARK:
 Enter site-specific information here.....

3. Enter Site-Specific Hydrogeological Data

Total soil porosity: 0.43 Unitless
 Volumetric water content: 0.3 Unitless
 Volumetric air content: 0.13 Unitless
 Soil bulk density measured: 1.5 kg/L
 Fraction Organic Carbon: 0.001 Unitless
 Dilution Factor: 20 Unitless

4. Target TPH Ground Water Concentration (if adjusted)
 If you adjusted the target TPH ground water concentration, enter 500 ug/L

Output Worksheet

⇒

A2 Soil Cleanup Levels: Calculation and Summary of Results. Refer to WAC 173-340-720, 740, 745, 747, 750

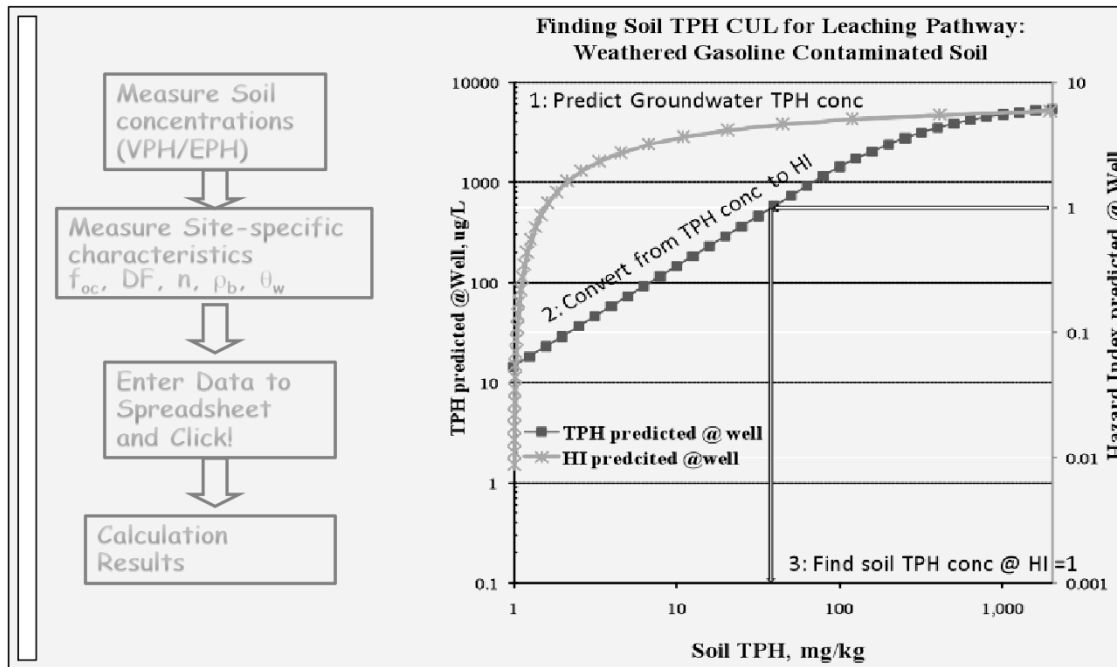
Site Information

Date: _____
 Site Name: _____
 Sample Name: _____
 Measured Soil TPH Concentration, mg/kg: _____

1. Summary of Calculation Results

Exposure Pathway	Method/Goal	Protective Soil TPH Conc, mg/kg	With Measured Soil Conc		Does Measured Soil Conc Pass or Fail?
			RISK @	HI @	
Protection of Soil Direct Contact: Human Health	Method B				
Protection of Method B	Method C				
Protection of Method B	Potable GW: Human Health Protection				
Ground Water Quality	Target TPH GW Conc. @ 500 ug/L		NA	NA	

How the Spreadsheet Model is used for Soil-to-Groundwater Pathway Evaluation



Typical TPH Soil and Groundwater CULs

A. Groundwater: Human Health Protection (ingestion); µg/L

Product type	Gasoline	Diesel	Heavy Oil	Mineral Oil
	100 ~ 800	400 ~ 650	300 ~ 600	450 ~ 500

B. Soil: Unrestricted Land Use; mg/kg

Product type/ pathway	Gasoline	Diesel	Heavy Oil	Mineral Oil
Ingestion	1,300 ~ 2,800	2,000 ~ 3,400	~ 7,000	5,000 ~ 7,800
Leaching ¹	~ 100	widely varied	No limit	No limit
Critical pathway	Leaching	Leaching/ Ingestion/ RSL ²	Ingestion/RSL	Ingestion/RSL

Note:

1. For the protection of potable groundwater (drinking water).

2. RSL (Residual Saturation Limit): Ceiling level that prevents the migration and presence of free product in groundwater.

Summary

- Petroleum Hydrocarbons are complex mixtures of thousands of compounds: Fractions defined by order of magnitude differences in behavior in the environment.
- The toxicity, fate and transport of petroleum hydrocarbons in the environment depends on the individual components of the mixture and their relative proportions in the mixture.
- Identity/fate/toxicity and transport of degradation products of petroleum are still unknown or neglected.
- Policy choice is very important: A choice of Additive & weighted average, transport model
- Washington State's TPH approach is not perfect, but scientifically valid; legally defensible risk-based, and cost-effective approach.

References

Hun Seak Park and C. San Juan, *Soil and Sediment Contamination*, 9(6): 611-632 (2000), A Method for Assessing Leaching Potential for Petroleum Hydrocarbons Release Sites: Multi-phase and Multi-substance Equilibrium Partitioning, 2000.

Washington State Department of Ecology, Model Toxics Control Act, Publication No 94-06, 2007.

<http://www.ecy.wa.gov/biblio/9406.html>

Washington State Department of Ecology, Tools for Calculating Soil and Ground Water Cleanup Levels under the Model Toxics Control Act (MTCA) Cleanup Regulation.

<http://www.ecy.wa.gov/programs/tcp/tools/toolmain.html>

- [Workbook Tools \(MS EXCEL-formatted\)](#)
- [User's Guide](#)

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