Latest Developments in Total Petroleum Hydrocarbon (TPH) Risk-Based Strategies

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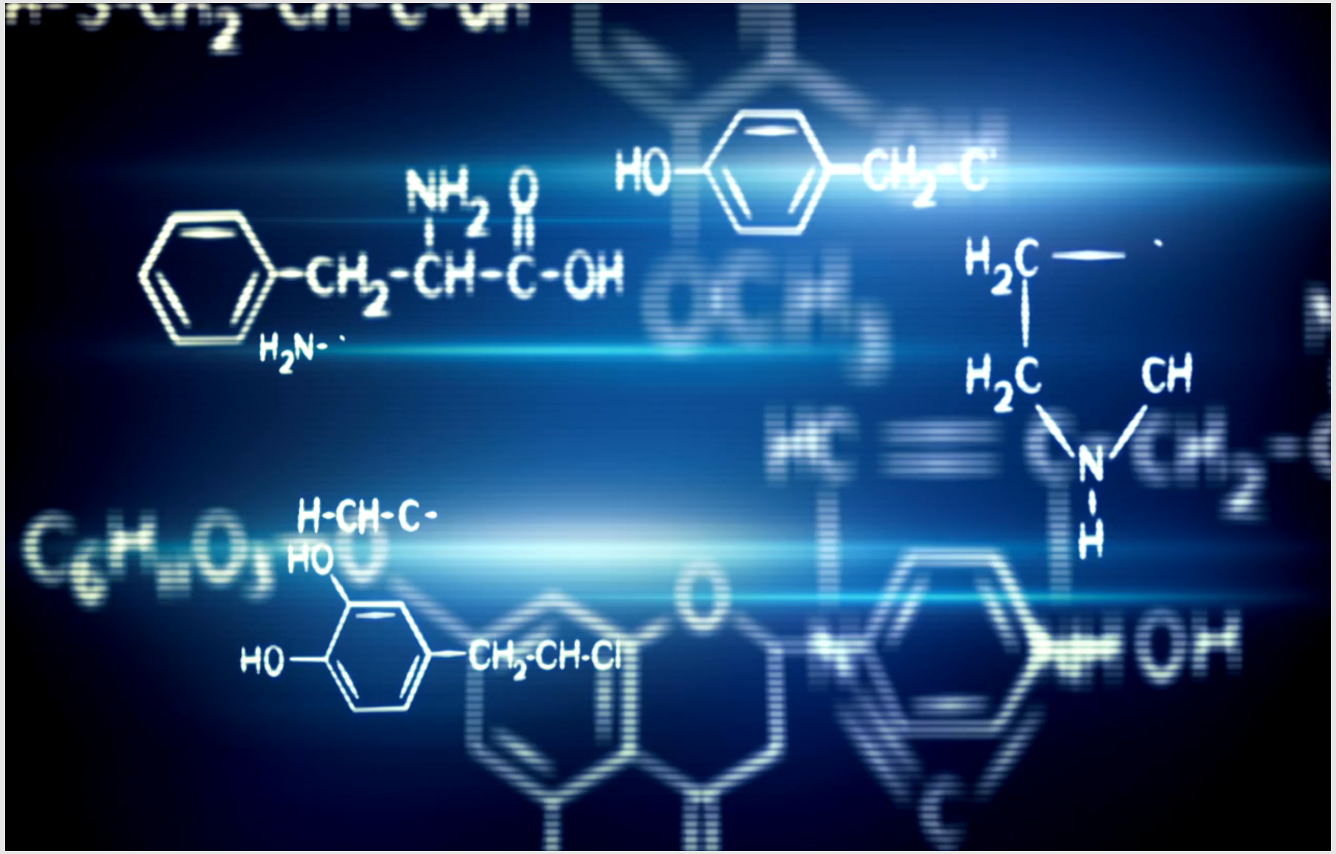
TPH Risk-Based Strategies - Overview

Understanding Biodegradation is the KEY

- Is **biodegradation** occurring at my site?



Adding Biodegradation Lines of Evidence (LOE) into Risk Assessment Process:

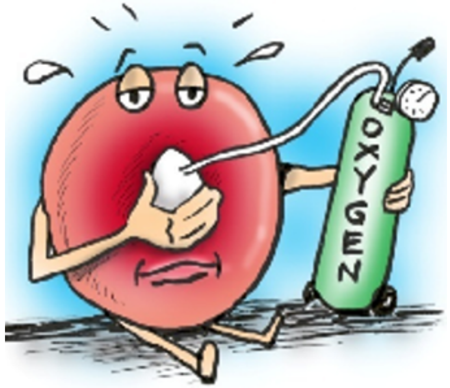
- Data Analysis
- Toxicity assessment
- Exposure / Conceptual Site Model (CSM)
- Characterizing risk

Biodegradation LOE leads to understanding:

- Nature & extent of TPH exposure risks
- Nature & extent of **biodegradation**/presence of polar metabolites
- Realistic Risk Management options on road to site closure

Biodegradation 101

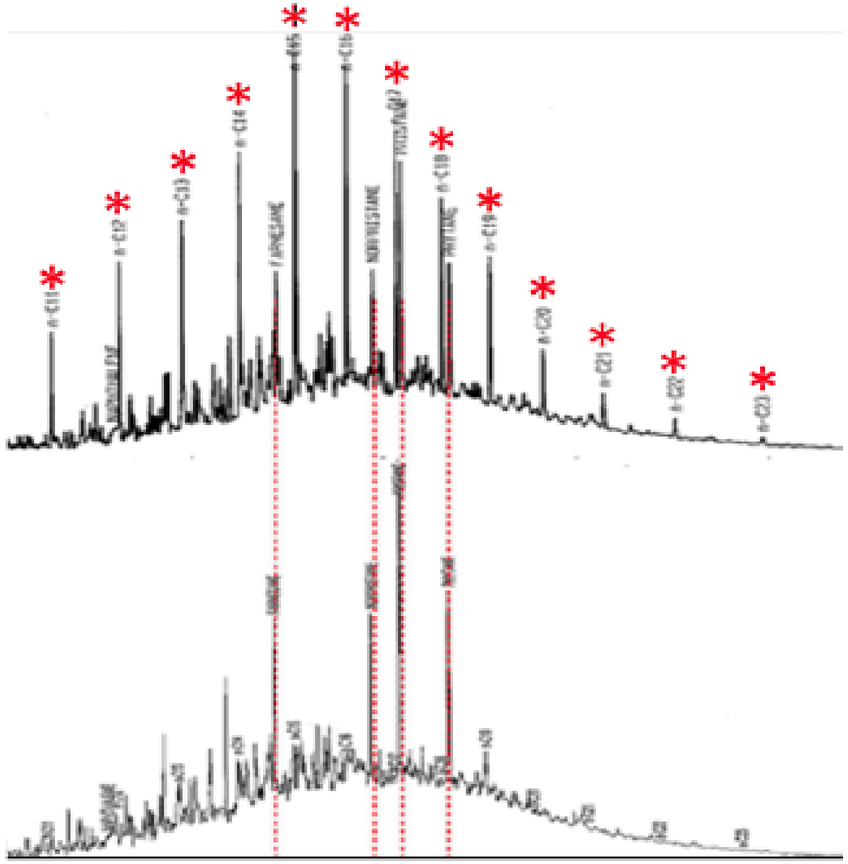
Hydrocarbons (HCs) are <u>susceptible to biodegradation</u>, but some degrade faster than others



Characteristics

- Stepwise process leads to new metabolites that can be further degraded
- Rapid under aerobic conditions*
- Slower under anaerobic conditions and more prone to buildup c metabolites
- Non-aqueous phase liquid (NAPL) takes longer to degrade than vapor or dissolved phases

*laboratory conditions suggested may not reflect actual field conditions



Highly Branched Alkanes Remain After Biodegradation

ITRC TPHRisk-1: Figure A5-3

TPH Fate – Production of Petroleum (Polar) Metabolites

Hexane Polar Metabolites

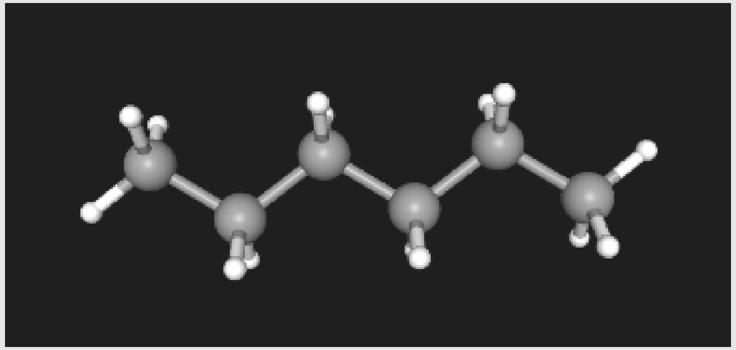
- **2-Hexanone**
- **Hexanoic acid**

Chemical	Formula	BP (°C)	Koc (L/kg)	Solubility (µg/L)
n-Hexane	C_6H_{14}	69	131.5	9.5E+03
2-Hexanone	$C_6H_{12}O_1$	128	14.98	7.7E+06
Hexanoic Acid	$C_6H_{12}O_2$	205	40.63	5.8E+06

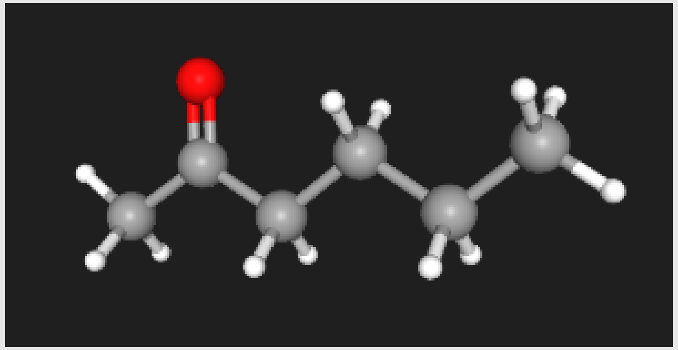
Source: USEPA EPI Suite™

- Oxygen = polar
- More soluble / mobile than hexane

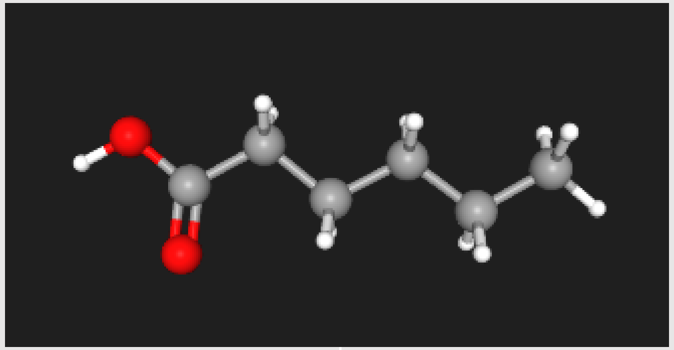
n-Hexane



2-Hexanone



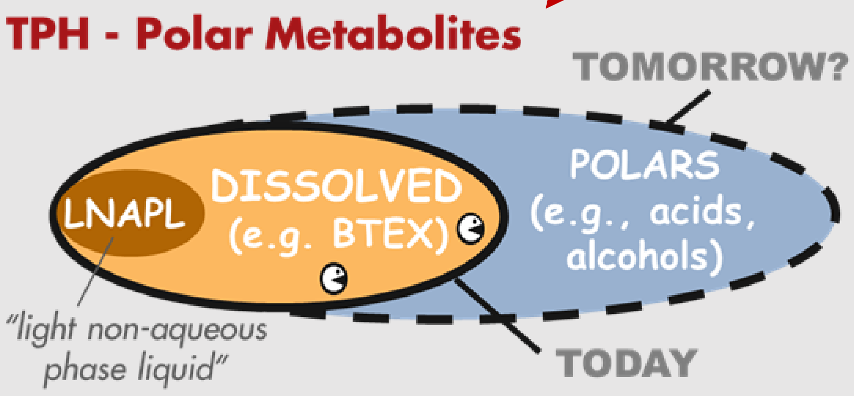
Hexanoic acid



TPH Fate – Detection of Petroleum Metabolites

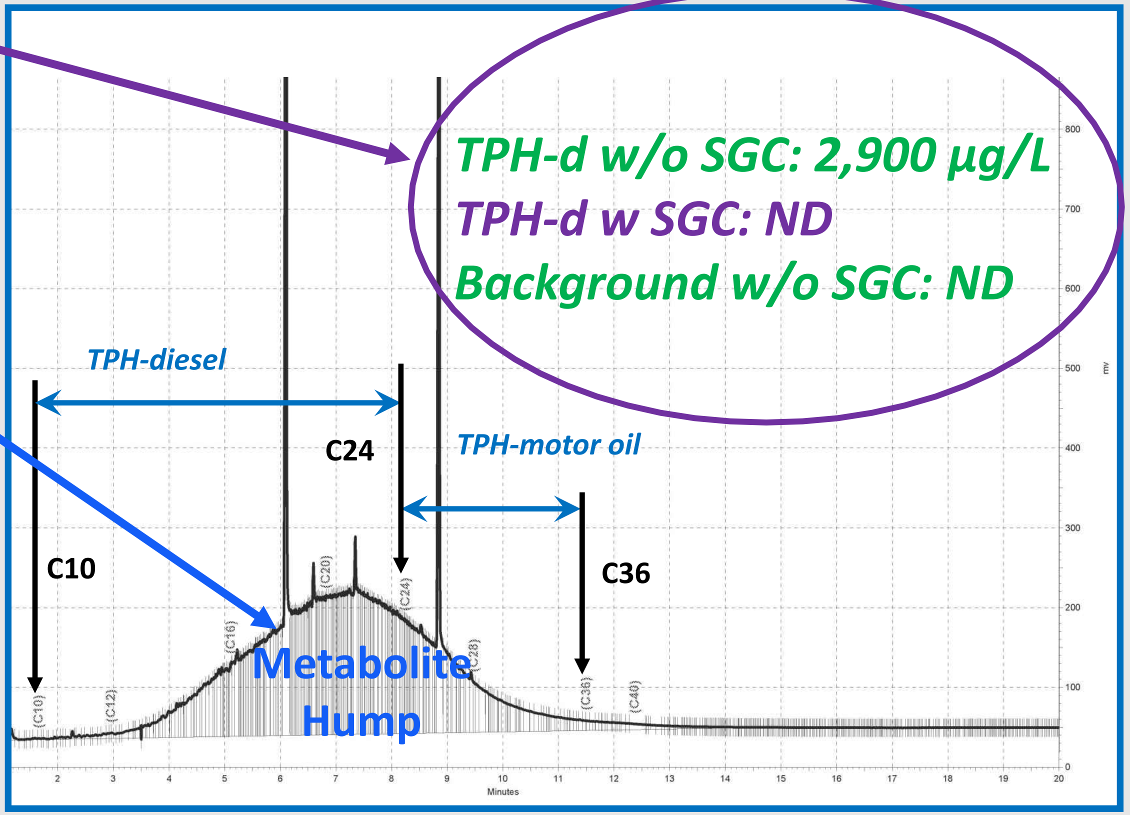
Identify metabolites using:

- Analysis w/ & w/out SGC
- Chromatogram pattern
- Conceptual site model (e.g., more mobile/soluble)



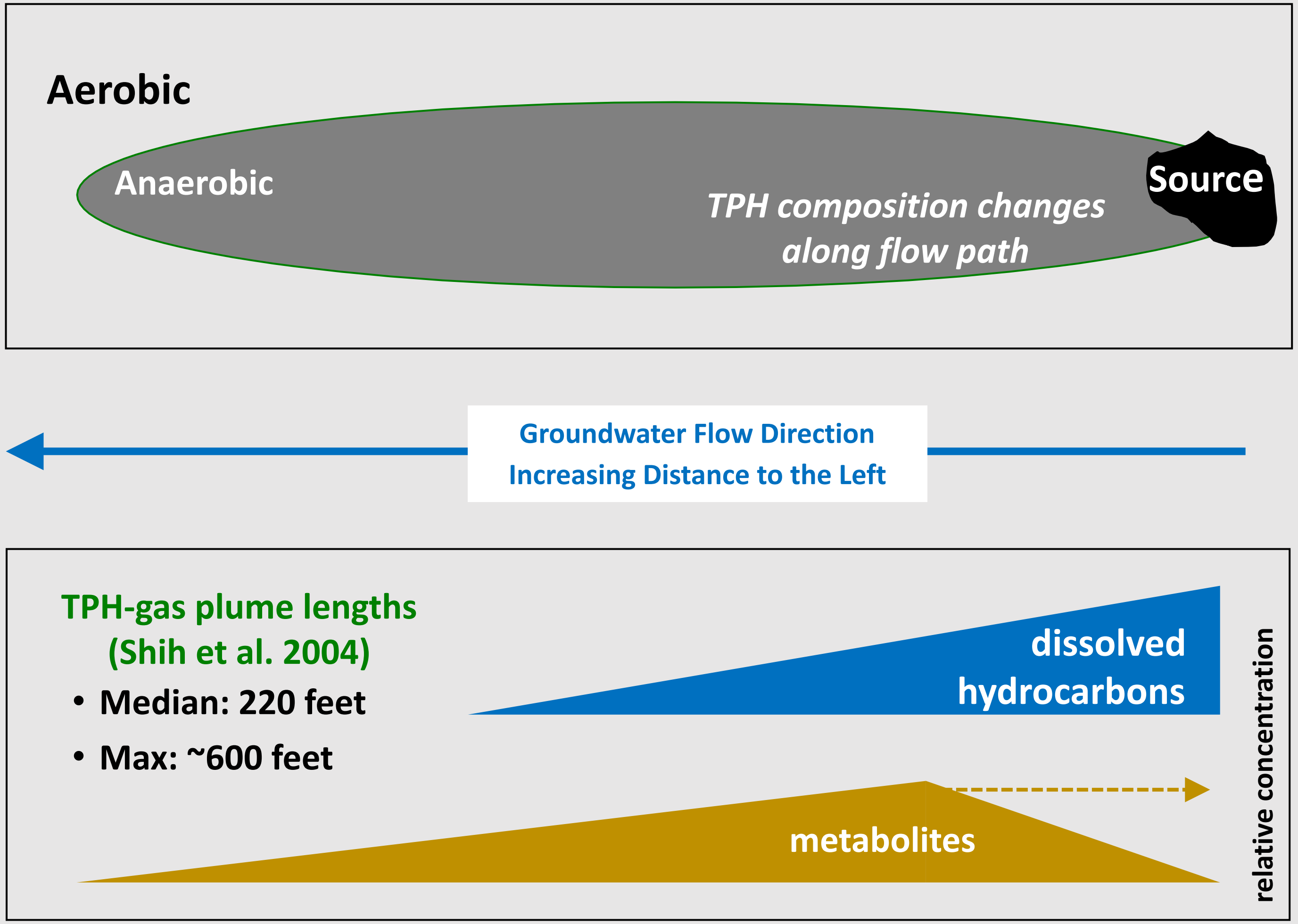
(*Zemo et al.* 2016)

Metabolites detected as TPH when silica gel cleanup (SGC) not used



ITRC TPHRisk-1: Figure A5-5
(data from CA site)

TPH Fate in Groundwater



Information on relative HC/ metabolite concentrations

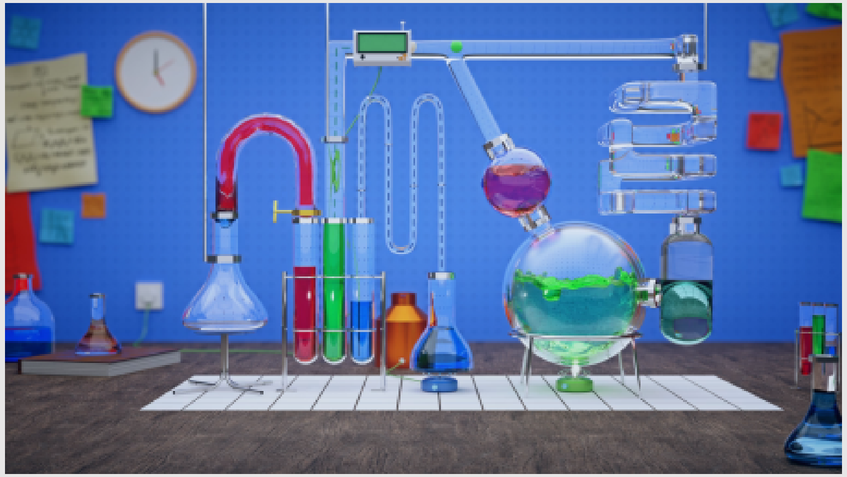
(*Zemo et al. 2016*)

Natural attenuation of fuels & chlorinated solvents in the subsurface

(*Wiedemeier et al. 1999*)

Data Analysis: Selecting Appropriate TPH Lab Methods

TPH is Defined by the Analytical Method

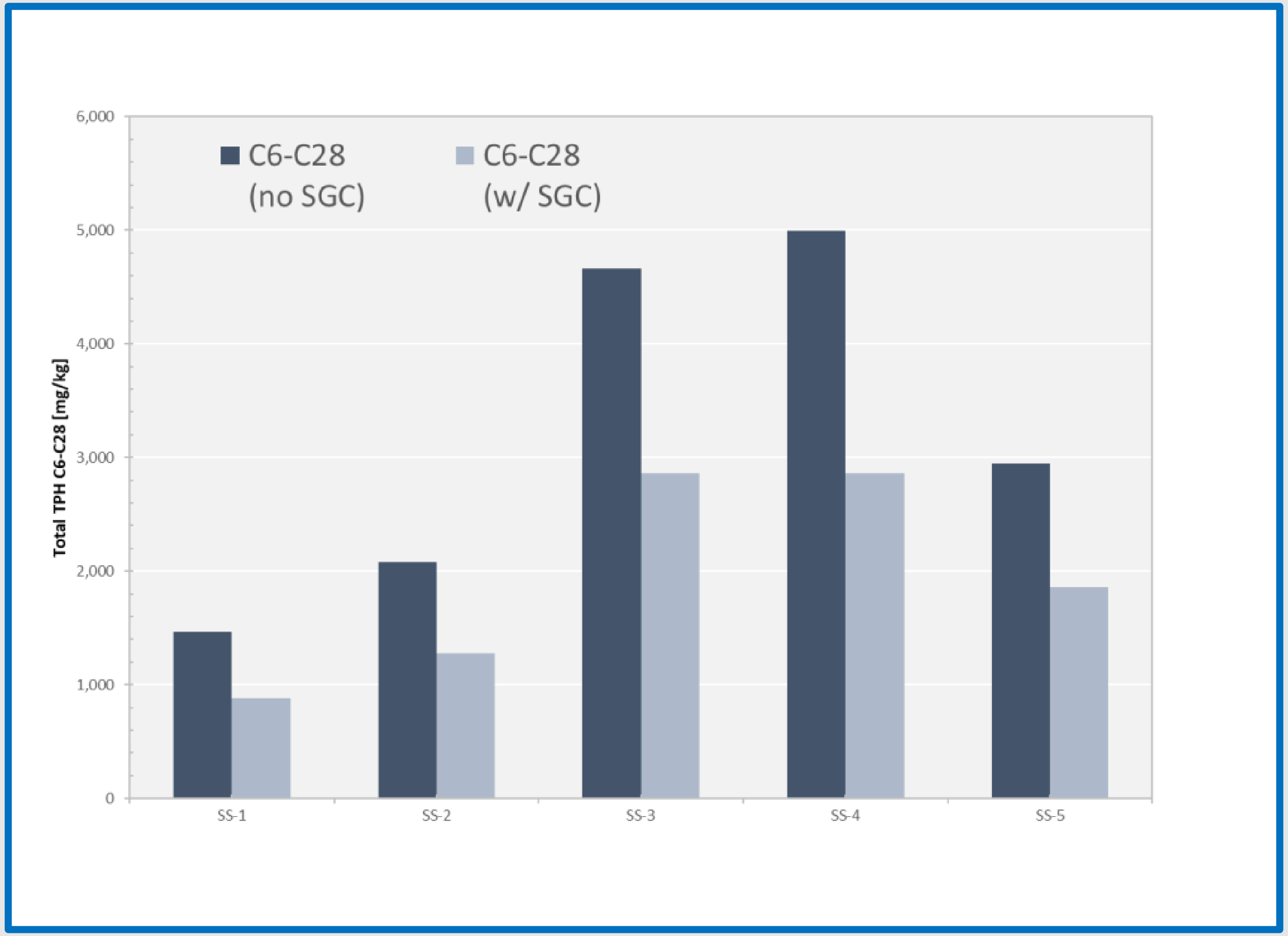


- **BULK ANALYSIS:** Extent of total extractable organics
  - **Use:** *preliminary site assessment*
  - **Data:** C6-C12 GRO, >C12-C28 DRO, >C28-C35 ORO
  - **Methods:** 8015 and 8260, TX1005, KS LRH/MRH/HRH
- **FRACTIONATED ANALYSIS:** Refinement of TPH into aliphatics and aromatics
  - **Use:** *human health/ecological risk assessment, F&T*
  - **Data:** aliphatics & aromatics separated, analyzed as shorter fraction ranges (4 aliphatic ranges & 3 aromatic ranges for C6-C12)
  - **Methods:** TX1006, MADEP VPH/EPH, WA Dep Ecology
- **SILICA GEL CLEANUP:** Fate of TPH
  - **Use:** *Biodegradation LOE*
  - **Methods:** EPA Method 3630C with 8015, 8260; EPA Method 3630C **with TX1005 (optional)**

TPH Fate – Petroleum Metabolite Case Study

Biodegradation is occurring

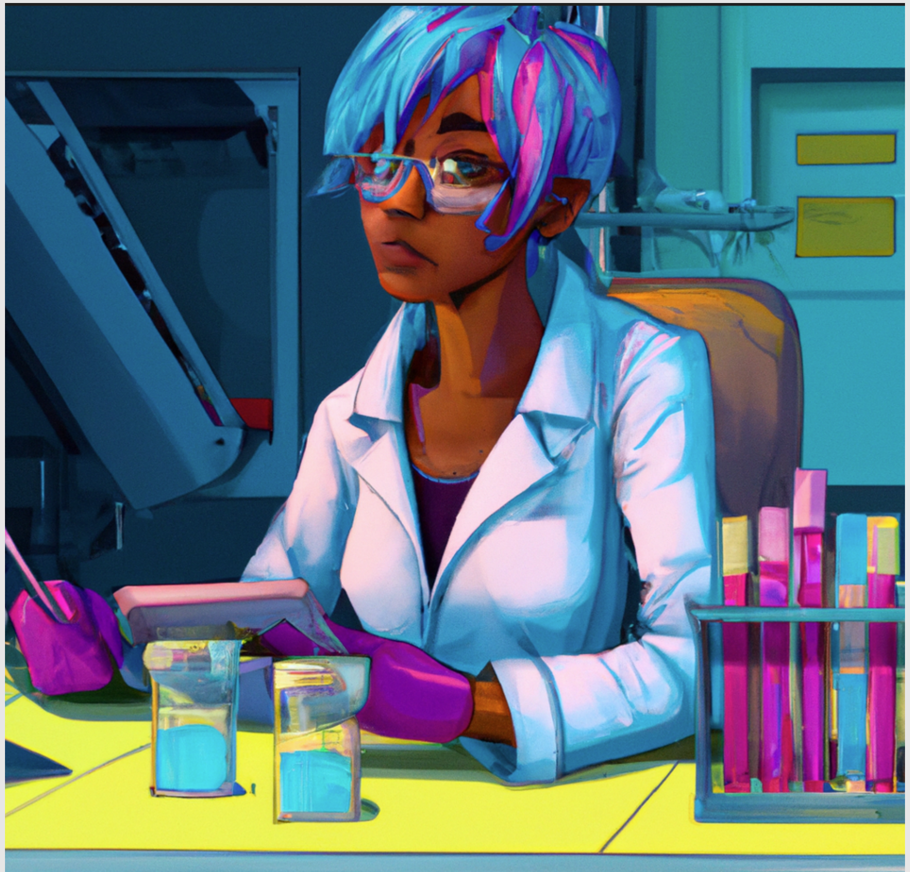
- based on split soil sample (bulk TPH analytical) results @ weathered diesel release site



ITRC TPHRisk-1: Figure A5-5 (data from CA site)

TPH Fractionation

- **Fractionation relies on the use of silica gel to separate the sample into aliphatic & aromatic classes***
- **Fractions are injected into a GC for carbon range separation**
- **Pros/Cons of TPH Fractionation**
  - More expensive than bulk TPH
  - Raises reporting limits
  - Non-hydrocarbons/metabolites removed from analysis
  - Toxicity values assigned to fractions (e.g., USEPA RSL Table)



* Class separation in the volatile range does not rely on silica gel

Fractionated Analysis vs. USEPA Toxicity Values

<table>
<tr><th></th><th colspan="32">Aliphatic</th><th colspan="32">Aromatic</th></tr>
<tr><td>Carbon Chain Length</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td><td>13</td><td>14</td><td>15</td><td>16</td><td>17</td><td>18</td><td>19</td><td>20</td><td>21</td><td>22</td><td>23</td><td>24</td><td>25</td><td>26</td><td>27</td><td>28</td><td>29</td><td>30</td><td>31</td><td>32</td><td>33</td><td>34</td><td>35</td><td>36</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td><td>13</td><td>14</td><td>15</td><td>16</td><td>17</td><td>18</td><td>19</td><td>20</td><td>21</td><td>22</td><td>23</td><td>24</td><td>25</td><td>26</td><td>27</td><td>28</td><td>29</td><td>30</td><td>31</td><td>32</td><td>33</td><td>34</td><td>35</td><td>36</td></tr>
<tr><td>USEPA Toxicity Category</td><td colspan="4">Aliphatic Low</td><td colspan="10">Aliphatic Medium</td><td colspan="18">Aliphatic High</td><td colspan="4">Aromatic Low*</td><td colspan="8">Aromatic Medium</td><td colspan="16">Aromatic High</td><td></td><td></td><td></td><td></td></tr>
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*EPA removed in November 2022 RSL Table

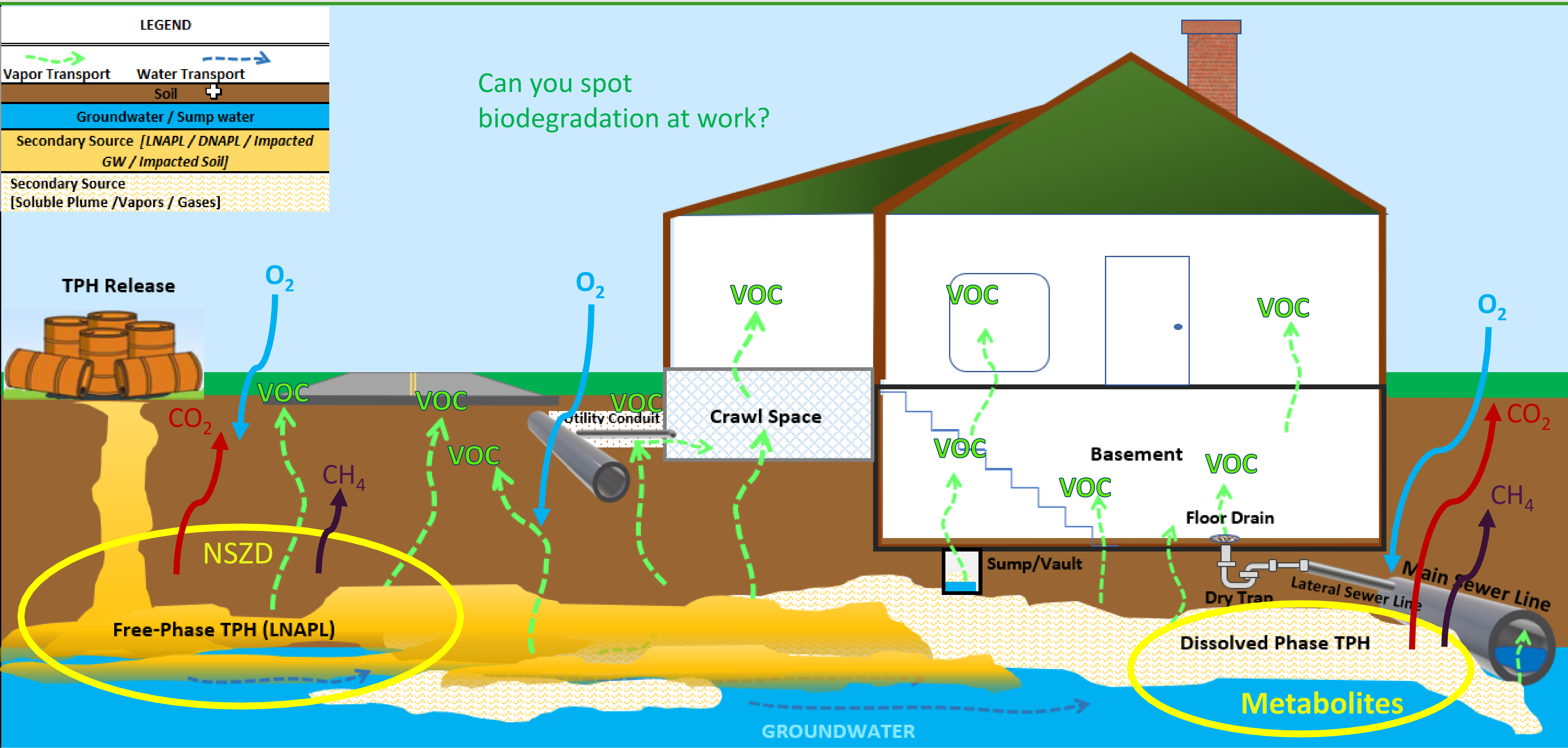
Toxicity and Chemical-specific Information													Contaminant
SFO (mg/kg-day)$^{-1}$	key	IUR (ug/m^3)$^{-1}$	key	RfD$_o$ (mg/kg-day)	key	RfC$_i$ (mg/m^3)	key	vol	mutagen	GIABS	ABS$_d$	C$_{sat}$ (mg/kg)	Analyte
				3.0E+00	P			V		1		3.4E-01	Total Petroleum Hydrocarbons (Aliphatic High)
				5.0E-03	P	4.0E-01	P	V		1		5.2E+01	Total Petroleum Hydrocarbons (Aliphatic Low)
				1.0E-02	X	1.0E-01	P	V		1		6.9E+00	Total Petroleum Hydrocarbons (Aliphatic Medium)
				3.0E-04	P	2.0E-06	P		M	1	0.13		Total Petroleum Hydrocarbons (Aromatic High)
				1.0E-02	P	6.0E-02	P	V		1		2.3E+02	Total Petroleum Hydrocarbons (Aromatic Medium)

Toxicity of Metabolites

- **Challenge assessing metabolite risks**
  - Limited toxicity information for individual metabolites and mixtures

- **Petroleum metabolites less "toxic" than undegraded hydrocarbons, in general**
- **Options for evaluating metabolite toxicity**
  - Exclude metabolites from evaluation
  - Use metabolite toxicity from Rogers et al. (2002) study
  - Adopt toxicity ranking model from Zemo et al. (2013, 2016)
  - Assume bulk hydrocarbon toxicity as surrogate for metabolites (HIDOH, 2017) and (SFB-RWQCB, 2016)

TPH Exposure / Conceptual Site Model (CSM)



Fixed Gas vs Pet HC Vertical Profile

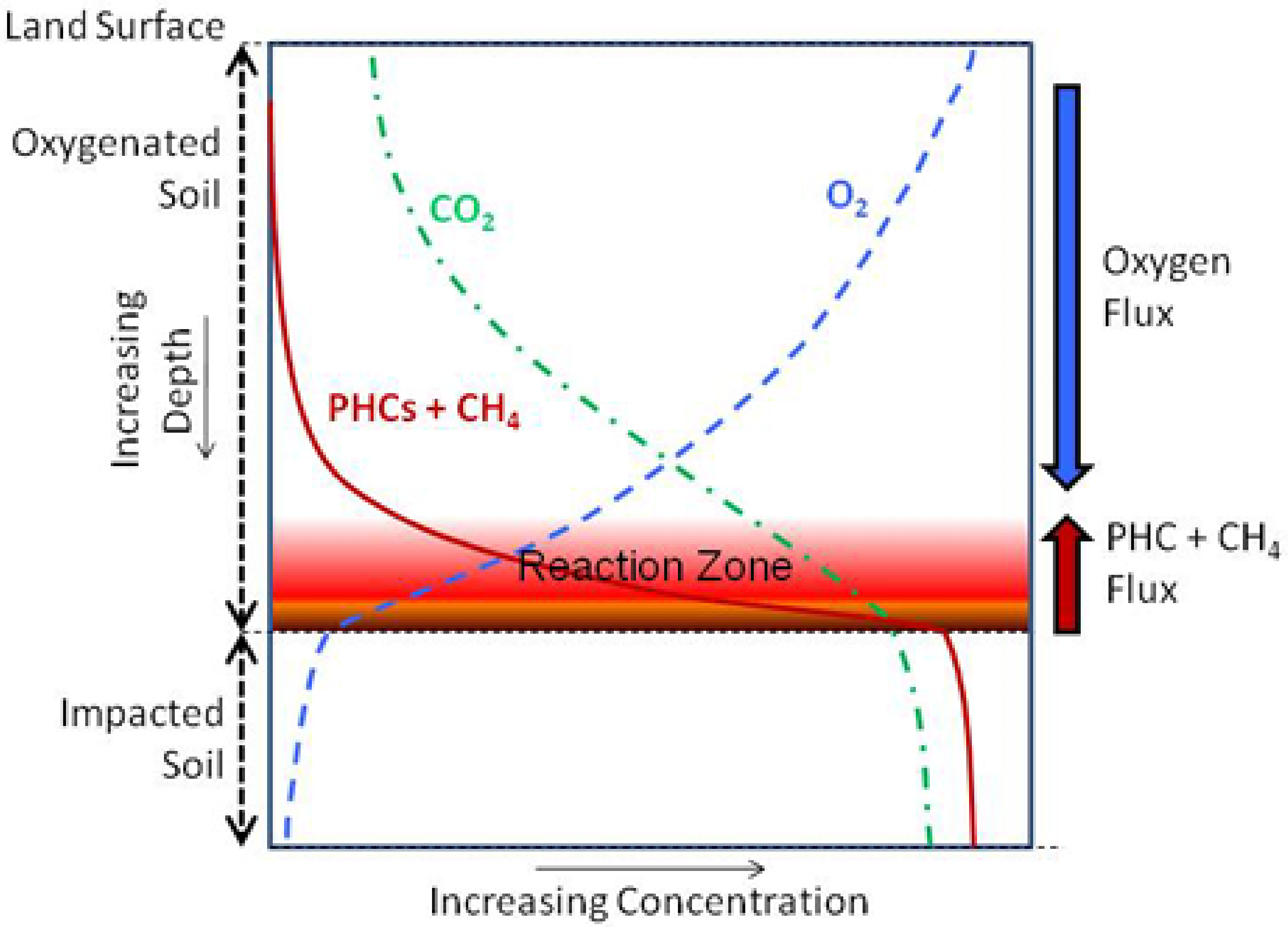
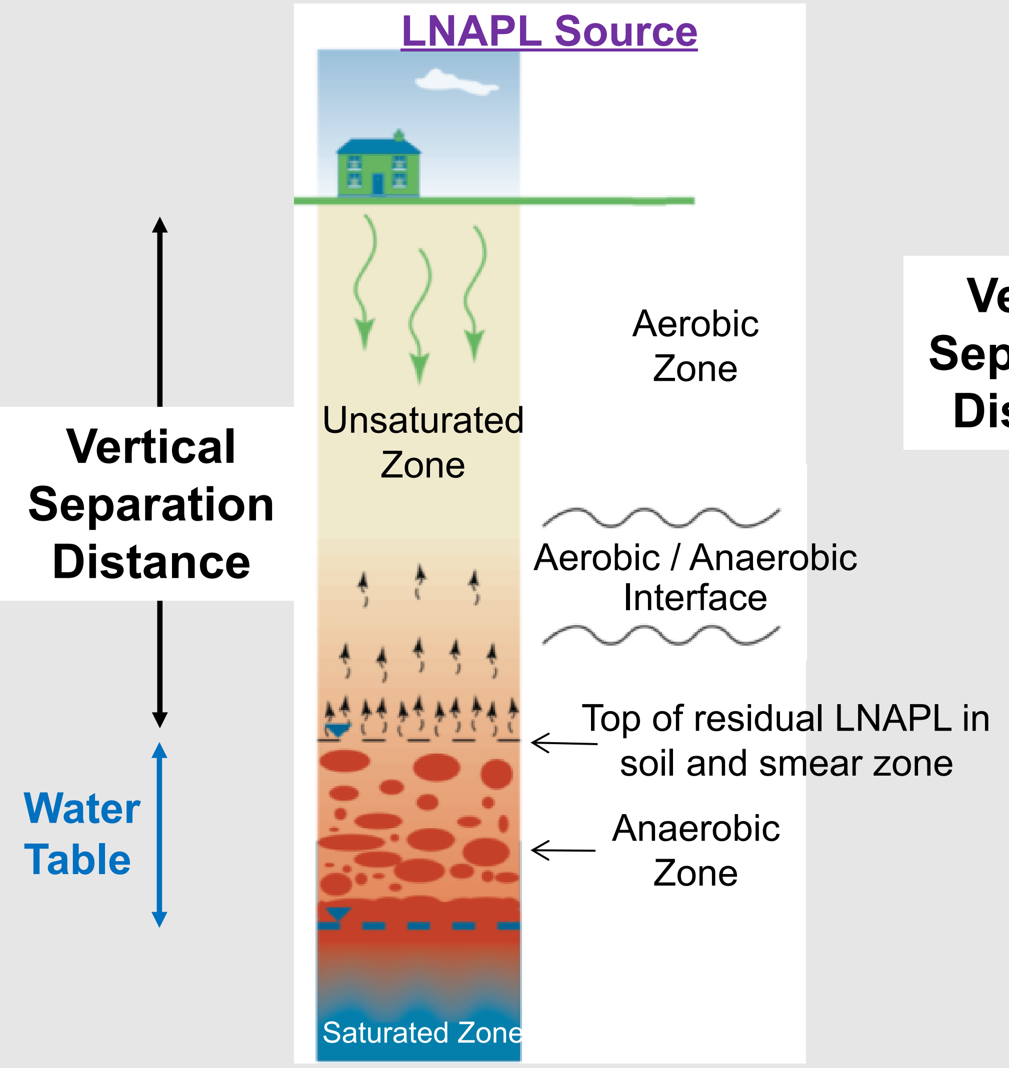


Figure 1. Typical vertical concentration profile in the unsaturated zone for PHCs, carbon dioxide, and oxygen **(USEPA, 2015)**

PVI Vertical Screening Distances

- 18 feet – LNAPL sources (petroleum industrial sites) (ITRC)
- 15 feet – LNAPL sources (petroleum UST/AST sites) (EPA & ITRC)
- 6 feet – dissolved-phase sources (EPA)
- 5 feet – dissolved-phase sources (ITRC)



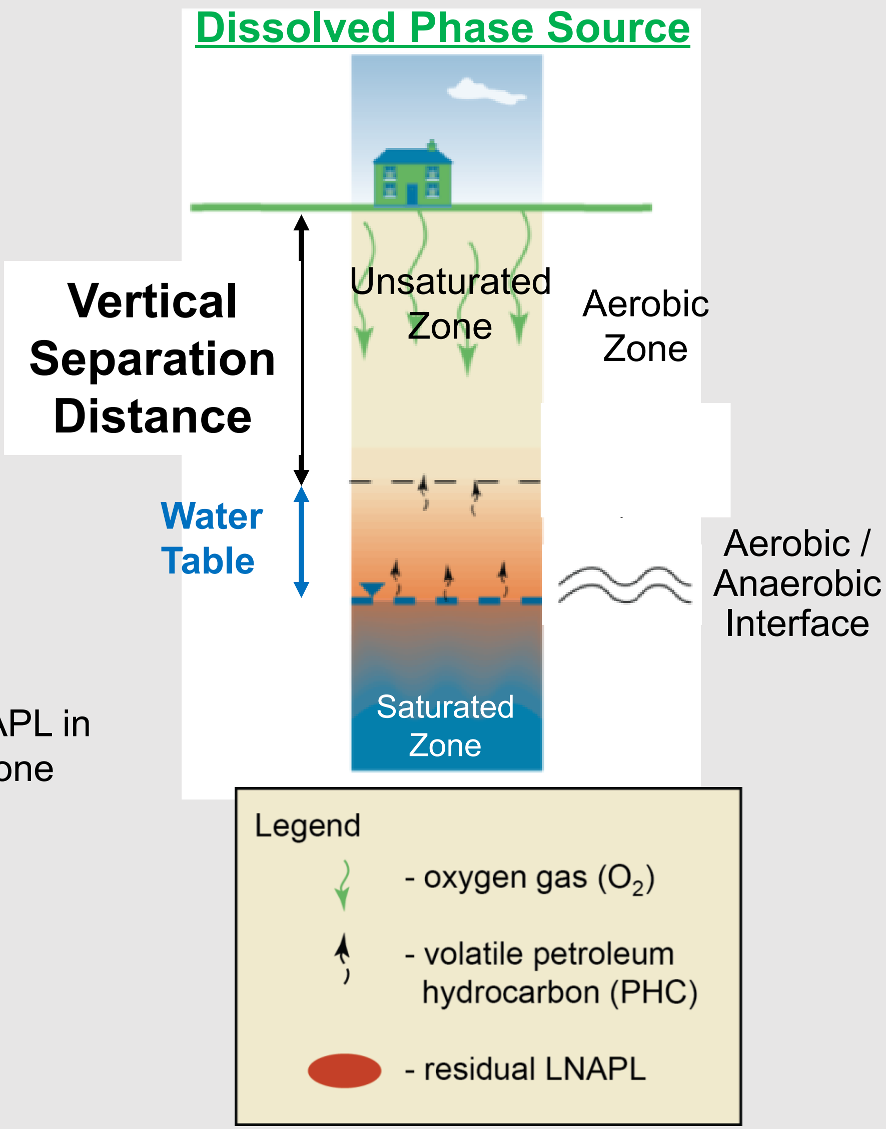
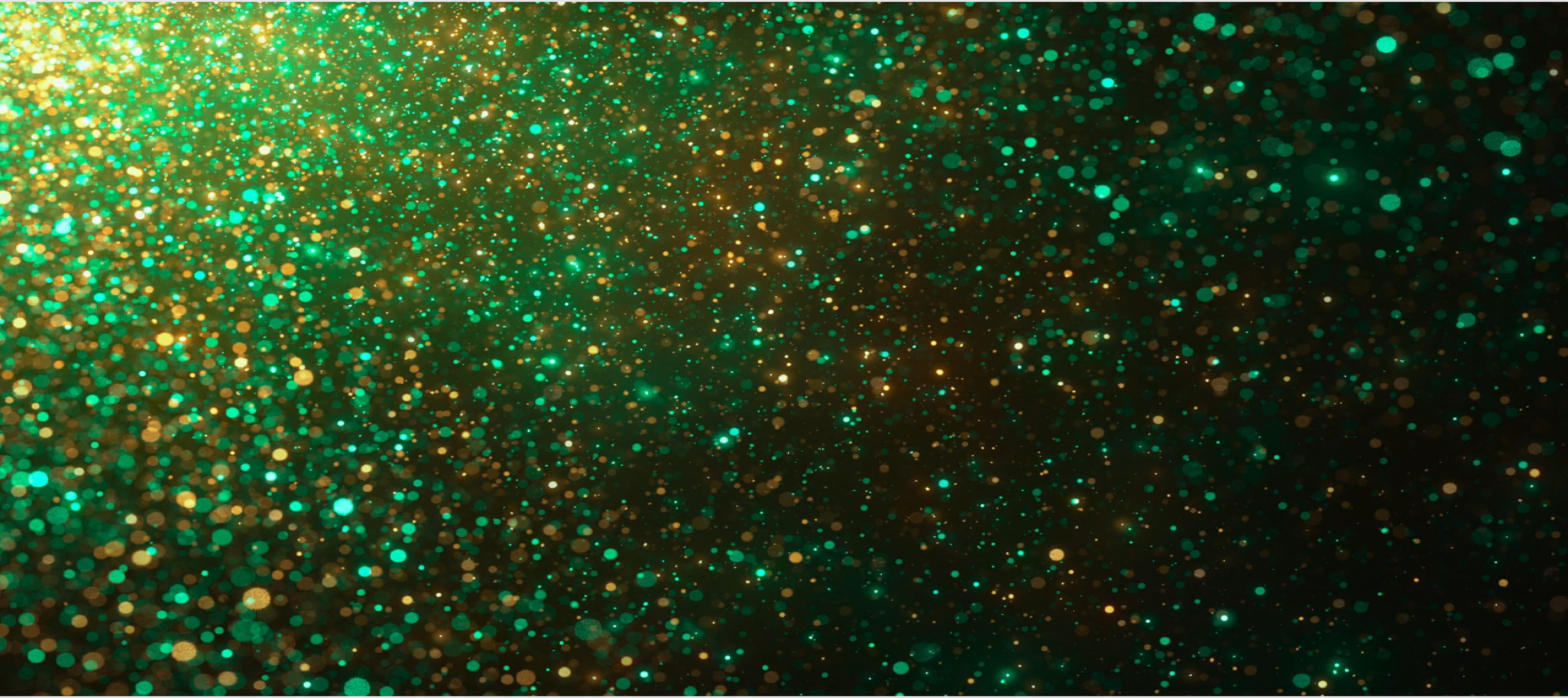


Figure 3-1, ITRC PVI-1, 2014

Summary: Assessing Human Health Risk from TPH

- TPH is a complex mixture
- Unique fate and transport properties of TPH (biodegradation and metabolite production) affect how risk should be assessed
- Varying types of TPH data lend themselves to a tiered assessment approach (bulk vs fractionated)
- Understanding TPH analytical data, CSM, and regulatory framework is critical in Realistic Risk Management options on road to site closure

Thank You!



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