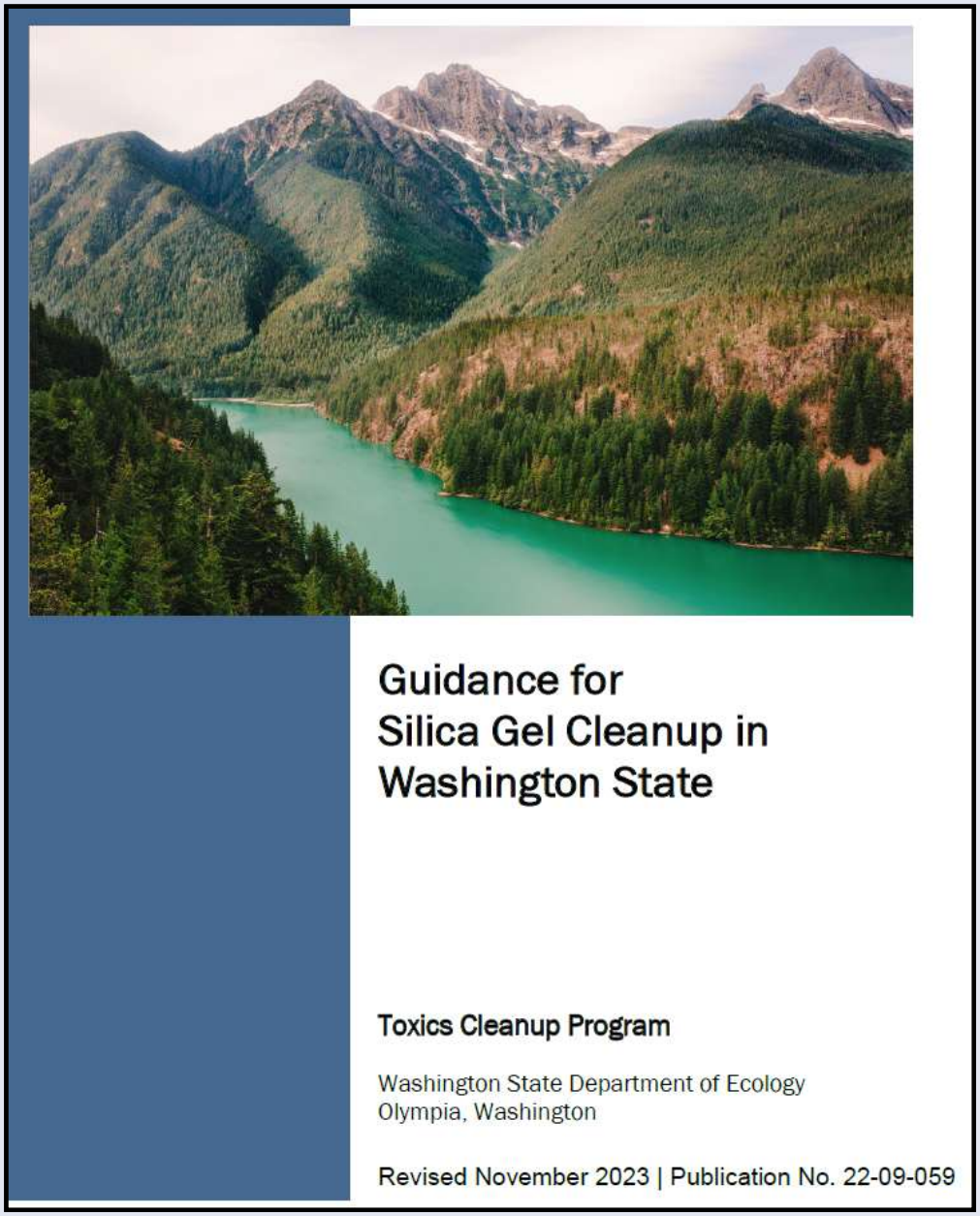
# Silica Gel Guidance Update

*Use of Silica Gel at Petroleum Cleanup Sites*




https://apps.ecology.wa.gov/publications/SummaryPages/2209059.html

# NWTPH Analysis

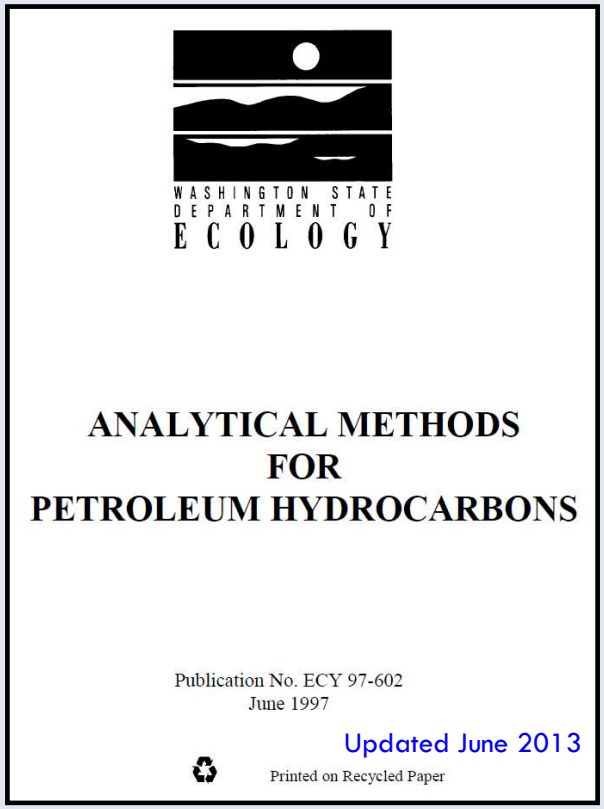


## NWTPH-Dx Analytical Method

- Quantitative analysis of semivolatile petroleum products including diesel fuels through heavy oils

## NWTPH-Gx Analytical Method

- Quantitative analysis of volatile petroleum products including gasolines, mineral spirits, solvents, and naptha



# NWTPH Analysis

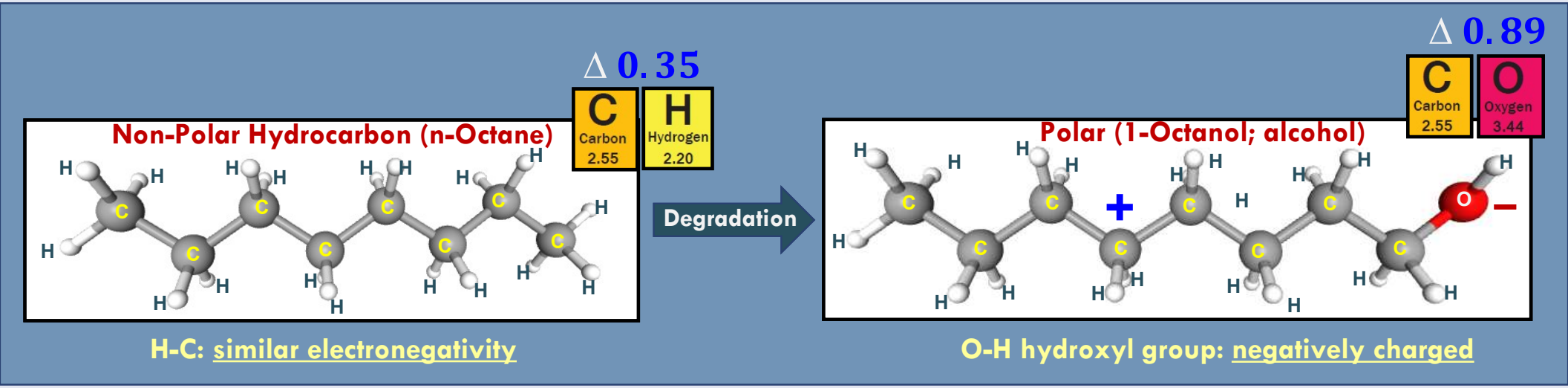


## NWTPH Methods (Dx and Gx)

- **Whole product analyses**
- **Not specific to hydrocarbons** – Measures all organics extracted from the sample and quantified within specified retention times that matches product standards.
- **Results may include both**
  - Non-polar hydrocarbons and
  - Polar non-hydrocarbons
- **Used to determine compliance with Method A TPH levels**

**Table 720-1**
**Method A Cleanup Levels for Ground Water.[a]**

| Hazardous Substance | CAS Number | Cleanup Level |
|---|---|---|
| Total Petroleum Hydrocarbons[x] | | |
| [Note: Must also test for and meet cleanup levels for other petroleum components--see footnotes!] | | |
| Gasoline Range Organics | | |
| Benzene present in ground water | | 800 ug/liter |
| No detectable benzene in ground water | | 1,000 ug/liter |
| Diesel Range Organics | | 500 ug/liter |
| Heavy Oils | | 500 ug/liter |
| Mineral Oil | | 500 ug/liter |



# TPH Analysis



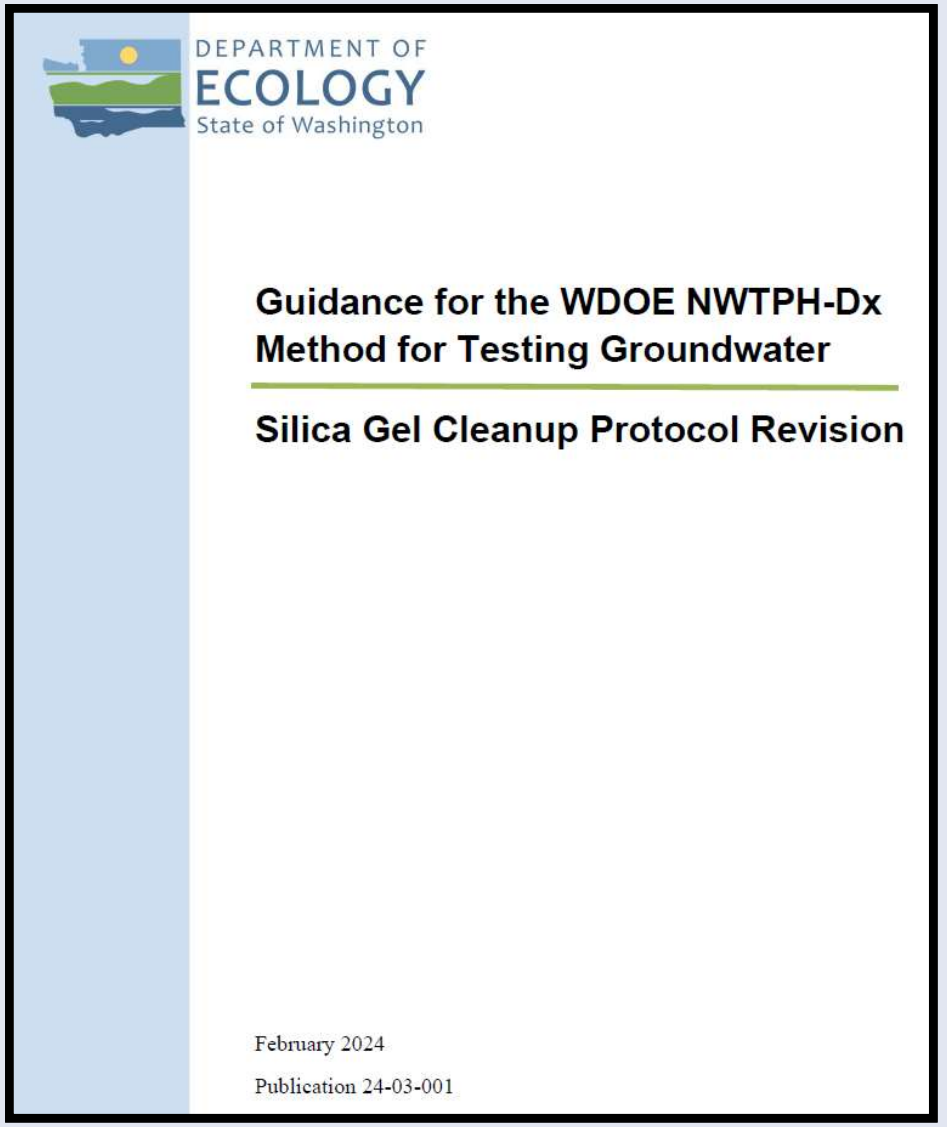
## Silica Gel Cleanup Protocol Update

- Based on published silica gel column approaches (not "shake") and EPA Method 3630
- Eliminates sulfuric acid step
- Extraction solvent: use methylene chloride
- See "Results and Discussion" Section for the Revised SGC Protocol

**Existing SGC Protocol**
- 10 ml sample extract
- Add 1ml sulfuric acid
- Add 400mg silica gel free-flowing
- Repeat sulfuric acid step

**Revised Option #1**
- 3ml silica column with 500mg silica gel
- Clean silica column with 5ml methylene chloride
- Add 1ml sample extract
- Add 1ml methylene chloride

**Revised Option #2**
- 5 ¾" Pasteur pipette glass wool plug at bottom; fill with 3cm of silica gel
- Clean silica column with 5ml methylene chloride
- Add 1ml sample extract
- Add 1ml methylene chloride



# Sources of Polar Compounds



- Biodegraded petroleum (i.e., from weathering)

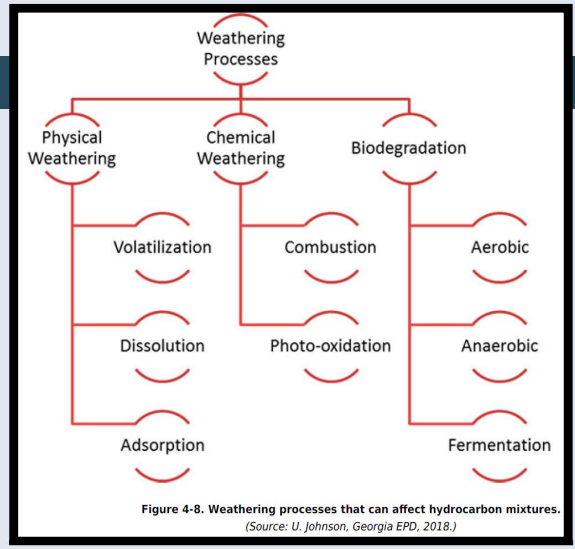
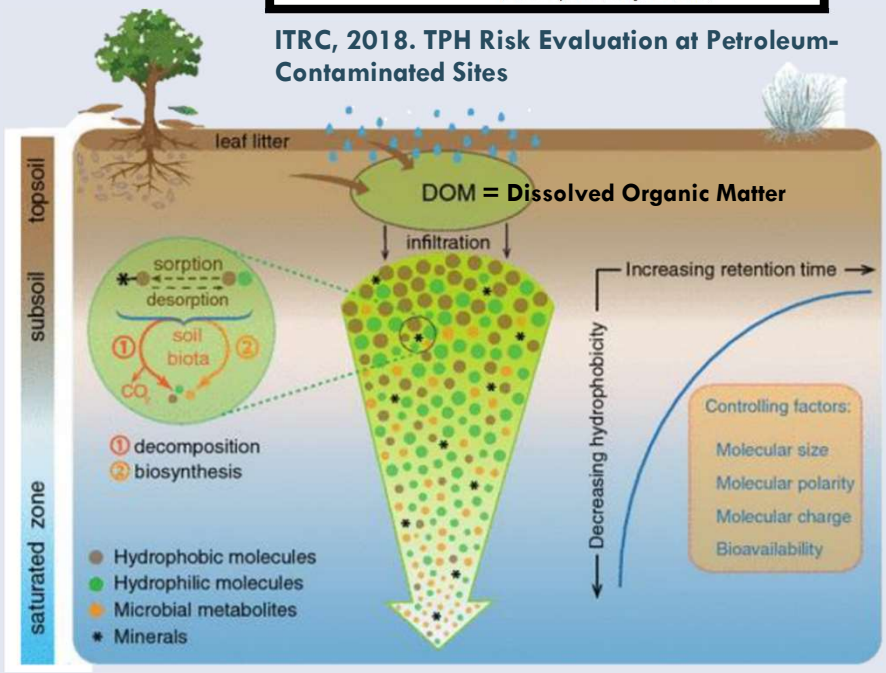



Figure 4-8. Weathering processes that can affect hydrocarbon mixtures. (Source: U. Johnson, Georgia EPD, 2018.)

ITRC, 2018. TPH Risk Evaluation at Petroleum-Contaminated Sites

- Naturally occurring organics (i.e., biogenic interference)

- Crude oils with compounds that contain nitrogen, sulfur, or oxygen




Chapelle, 2024. Dissolved Organic Carbon in Groundwater Systems. January 2024

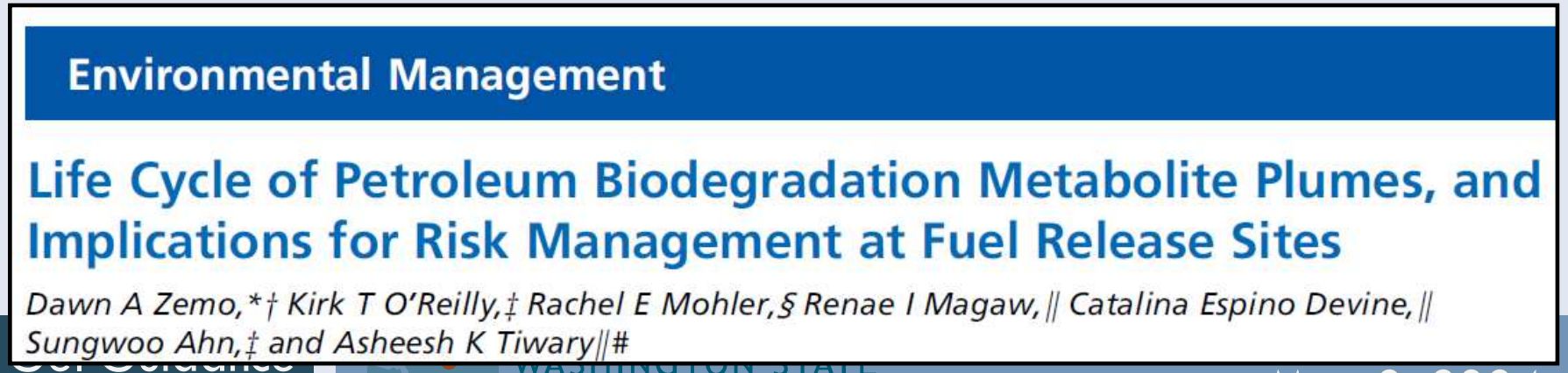
# Petroleum Groundwater Study

Integr Environ Assess Manag 2017:714–727



**5-Yr Chevron Funded Study (2011-2015)** – *Nature and Toxicity of Petroleum Biodegradation Metabolites in Groundwater at Fuel Release Sites*

- **Goal:** To inform the makeup and toxicity of polar metabolites at various biodegradation stages
- **83 Groundwater Samples** collected from biodegrading petroleum release sites
  - 16 Fuel Terminals – highly biodegraded diesel and gasoline releases
  - 5 Service Stations – less biodegraded, mostly gasoline releases
- **Sampled:** Source Area, Depleted Smear Zone, and Downgradient Areas



Environmental Management

Life Cycle of Petroleum Biodegradation Metabolite Plumes, and Implications for Risk Management at Fuel Release Sites

*Dawn A Zemo,*† Kirk T O'Reilly,‡ Rachel E Mohler,§ Renae I Magaw,‖ Catalina Espino Devine,‖ Sungwoo Ahn,‡ and Asheesh K Tiwary‖#*

# Biochemistry of Petroleum Biodegradation



Identified **5 families and 22 structural classes of polars** expected from aerobic and anerobic biodegradation of refined petroleum fuels (e.g., diesel, gas).

| Polar Family | Specific Structural Class |
|---|---|
| Alcohols (and diols) | (n- and alkyl) alcohols |
| | (alkyl) cyclic alcohols |
| | (alkyl) polycyclic alcohols |
| | (alkyl) aromatic alcohols |
| | (alkyl) polyaromatic alcohols |
| | |
| Acids/esters (and diacids/succinates) | (n-and alkyl) acids/esters |
| | (alkyl) cyclic acids/esters |
| | (alkyl) polycyclic acids/esters |
| | (alkyl) aromatic acids/esters |
| | (alkyl) polyaromatic acids/esters |

| Polar Family | Specific Structural Class |
|---|---|
| Ketones (and diones) | (n- and alkyl) ketones |
| | (alkyl) cyclic ketones |
| | (alkyl) polycyclic ketones |
| | (alkyl) aromatic ketones |
| | (alkyl) polyaromatic ketones |
| | |
| Aldehydes | (n-and alkyl) aldehydes |
| | (alkyl) cyclic aldehydes |
| | (alkyl) polycyclic aldehydes |
| | (alkyl) aromatic aldehydes |
| | (alkyl) polyaromatic aldehydes |
| | |
| Phenols | phenol |
| | alkylphenols |

# Petroleum Groundwater Study



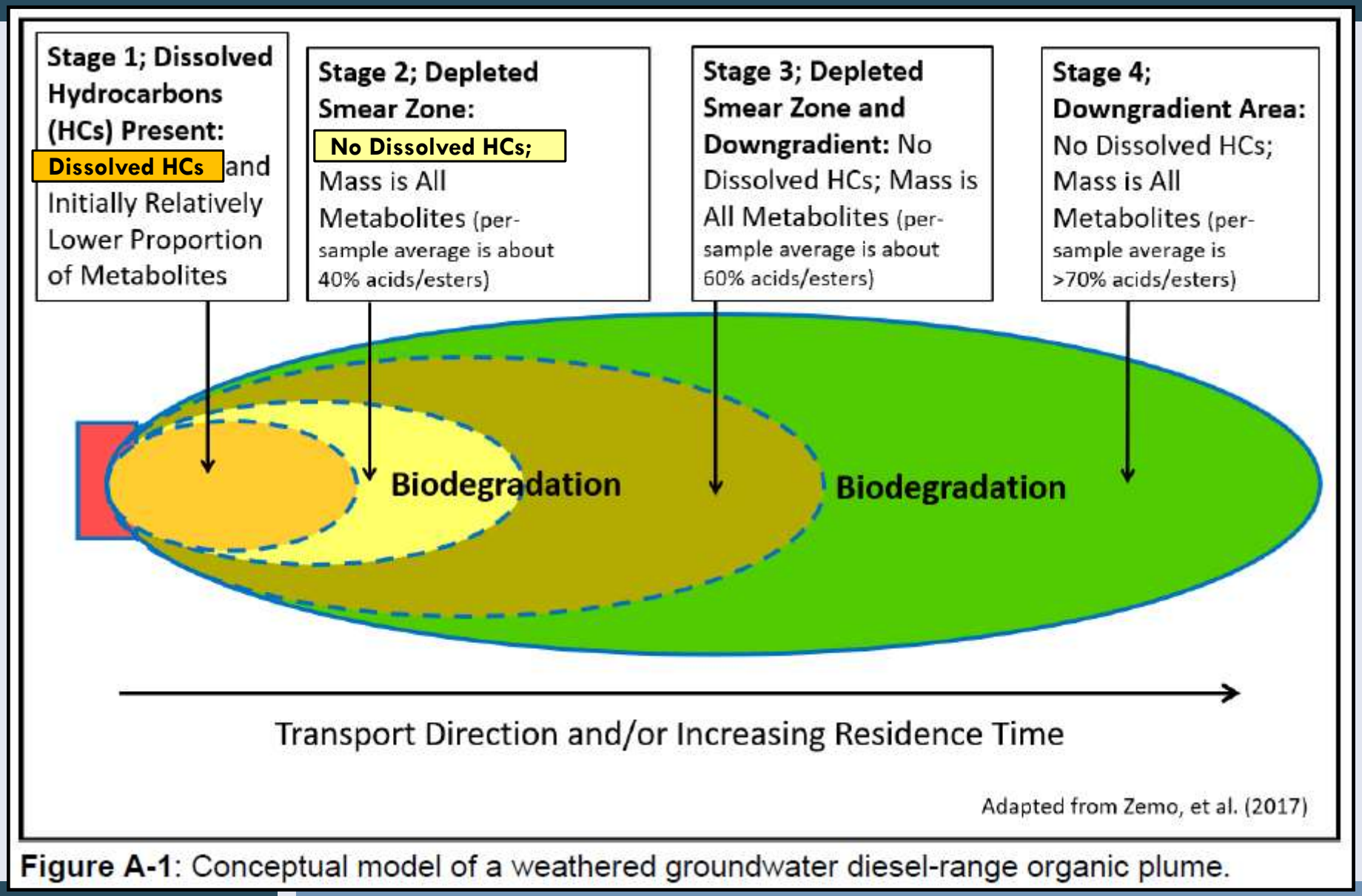



**Figure A-1**: Conceptual model of a weathered groundwater diesel-range organic plume.

# Petroleum Groundwater Study

Integr Environ Assess Manag 2017:714–727



## 5-Yr Chevron Funded Study (2011-2015) – Continued

- **Analyzed** all samples for
  - **Diesel Range Organics** with and without Silica Gel
  - **Targeted list of 76 potential polar metabolites** (primarily based on toxicity, chemical structure, and availability of analytical standards)
  - **Qualitative** Nontargeted GC-MS library search using GCxGC Time of Flight Spectrometry – *can identify significantly more compounds than GC*

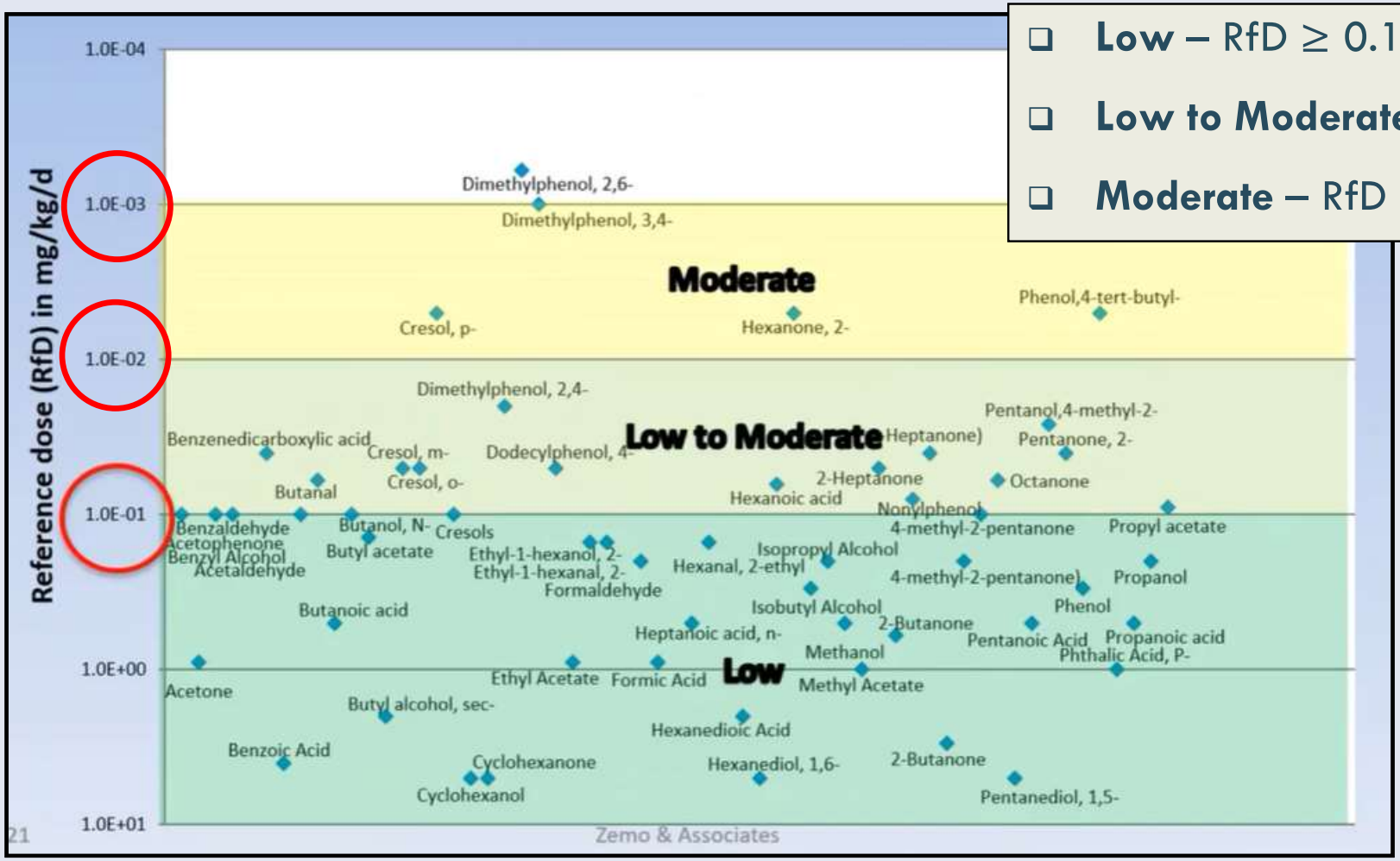
**Targeted Polar Compounds for Quantitative Analysis**

| Alcohols | Ketones | Acids | Aldehydes | Phenols |
|---|---|---|---|---|
| cyclopentanol | 5,6-dimethoxy-1-indanone | cyclohexaneacetic acid* | **benzaldehyde** | 4-tert-amylphenol* |
| 1-decanol* | 2-dodecanone* | cyclohexanecarboxylic acid [100] | decanal* | **4-tert-butylphenol*** |
| 2,4-dimethyl-3-pentanol | 9-fluorenone* | dodecanoic acid | dodecanal* | 4-cumylphenol* |
| 1-dodecanol | **2-hexanone** | 2-hydoxy-1-naphthoic acid | heptanal* | **2,4-dimethylphenol*** |
| 1-heptanol* | 2-methyl-1-indanone | 1-hydroxy-2-naphthoic acid [50] | hexanal | **2,6-dimethylphenol** |
| 1-hexanol* | 3-methylacetophenone | 4-MCacetic acid | **nonanal*** | **3,4-dimethylphenol** |
| 2-methyl-1-pentanol | 4-methylacetophenone | 4-methyl hexanoic acid* | octanal* | **2-methylphenol** |
| 2-methyl-2-hexanol | 2-nonanone* | **pentanoic acid** [250] | 3,5,5-trimethylhexanal* | **4-methylphenol (p-cresol)** |
| 1-nonanol* | 2-pentadecanone | phenylacetic acid [50] | undecanal* | 4-octylphenol |
| 1-octanol* | 2,6,8-trimethyl-4-nonanone | undecanoic acid [100] | 2-ethylbutyraldehyde | 4-pentylphenol* |
| 2-phenylethanol (benzene ethanol) | 2-undecanone* | methylbenzoate (ester)* | | 2-phenylphenol |
| 1-tetradecanol [50] | **acetophenone** | **hexanoic acid [50]** | | 2,3,5-trimethylphenol* |
| 2,4,4-trimethyl-1-pentanol* [50] | **anthraquinone** | **phthalic acid [240]** | | 4-sec-butylphenol |
| 1-undecanol* | **benzophenone** | | | 2,3-dimethylphenol |
| 1-naphthol | **2-heptanone** | | | 2-isopropylphenol |
| 1-tetradecanol [50] | 1-indanone | | | 4-tert-octyl-phenol |
| | **4-methyl-2-pentanone (MIBK)** | | | 2-n-propylphenol |
| | **2-octanone** | | | 2-isopropyl-5-methylphenol (thymol) |
| | **2-pentanone** | | | 2,3,6-trimethylphenol |

# Toxicity of Polar Metabolites



## RfD-Based Toxicity Ranking for all 22 Structural Classes




- **Low** – RfD ≥ 0.1
- **Low to Moderate** – RfD < 0.1 to 0.01
- **Moderate** – RfD < 0.01 to 0.001

# Toxicity of Polar Metabolites



## Per-Sample Avg% for Structural Classes per Biodegradation Stage

**Table A-3: Summary of Structural Classes and Toxicity for "Biodegradation Stages" 1-4[1]**

| Polar Family | Specific Structural Class | Expected Chronic Oral Toxicity for Humans[3] | Biodegradation Stages[2] | | | |
|---|---|---|---|---|---|---|
| | | | Stage 1 | Stage 2 | Stage 3 | Stage 4 |
| | | | Per-Sample Average (%)[4] | | | |
| Alcohols (and diols) | n- and Alkyl alcohols | Low | 20 | 11 | 9 | 8 |
| | Cycloalkyl alcohols | Low | 13 | 10 | 6 | 4 |
| | Bicyclic alkyl alcohols | Low | 1 | 3 | 3 | 3 |
| | Aromatic alcohols | Low | 2 | 2 | 1 | 1 |
| | Polycyclic aromatic alcohols | Low to moderate | 0 | 0 | 0 | 0 |
| | | ***Totals*** | *36* | *26* | *19* | *16* |
| Acids (and esters) | n-and Alkyl acids/esters | Low | 15 | 30 | 52 | 63 |
| | Cycloalkyl acids/esters | Low | 2 | 5 | 4 | 4 |
| | Bicyclic alkyl acids/esters | Low | 0 | 2 | 1 | 0 |
| | Aromatic acids/esters | Low | 4 | 5 | 7 | 8 |
| | Polycyclic aromatic acids/esters | Low to moderate | 0 | 0 | 0 | 0 |
| | | ***Totals*** | *21* | *42* | *64* | *75* |
| Ketones | n-and Alkyl ketones | Low to moderate | 10 | 8 | 5 | 3 |
| | Cycloalkyl ketones | Low | 15 | 7 | 3 | 1 |
| | Bicyclic alkyl ketones | Low | 3 | 6 | 2 | 1 |
| | Aromatic ketones | Low to moderate | 4 | 4 | 2 | 1 |
| | Polycyclic aromatic ketones | Low to moderate | 0 | 0 | 0 | 0 |
| | | ***Totals*** | *32* | *25* | *12* | *6* |
| Aldehydes | n-and Alkyl aldehydes | Low to moderate | 4 | 6 | 2 | 1 |
| | Cycloalkyl aldehydes | Low to moderate | 1 | 0 | 0 | 0 |
| | Bicyclic alkyl aldehydes | Low to moderate | 0 | 0 | 0 | 0 |
| | Aromatic aldehydes | Low to moderate | 2 | 1 | 0 | 0 |
| | Polycyclic aromatic aldehydes | Low to moderate | 0 | 0 | 0 | 0 |
| | | ***Totals*** | *7* | *7* | *2* | *1* |
| Phenols | non-C14 Alkyl phenols | Moderate | 2 | 0 | 0 | 0 |
| | C14 Alkyl phenols[5] | Low | 1 | 1 | 0 | 1 |
| | Phenol | Low | 0 | 0 | 1 | 1 |
| | | ***Totals*** | *3* | *1* | *1* | *2* |
| | | | | | | |
| | | ***Total Avg Tox L/L-M/M[6]*** | 78/20/2 | 81/19/0 | 90/10/0 | 95/5/0 |

# Toxicity of Polar Metabolites



## Calculation of Polar Metabolite Cleanup Levels

- Developed two cleanup levels.
  - *For sites or plumes <u>with detects of hydrocarbons</u> (anywhere on-site)* – use **500 ug/L** (based on toxicity data from **Stages 1 and 2**)
  - *For sites or plumes where <u>hydrocarbons are no longer detected</u>* – use **700 ug/L** (based on toxicity data from **Stages 2 and 3**)

$$\text{Stage 1 RfD weighted avg} = \frac{1}{\left(\frac{78\%}{0.1} + \frac{20\%}{0.01} + \frac{2\%}{0.001}\right)} = 0.021 \text{ mg/kg-day}$$

weight factor

low → mod

$$\text{Stage 2 RfD weighted avg} = \frac{1}{\left(\frac{81\%}{0.1} + \frac{19\%}{0.01} + \frac{0\%}{0.001}\right)} = 0.037 \text{ mg/kg-day}$$

$$\text{Stage 3 RfD weighted avg} = \frac{1}{\left(\frac{90\%}{0.1} + \frac{10\%}{0.01} + \frac{0\%}{0.001}\right)} = 0.053 \text{ mg/kg-day}$$

**[Equation 720-1]**

$$\text{Ground water cleanup level (ug/l)} = \frac{\text{RfD} \times \text{ABW} \times \text{UCF} \times \text{HQ} \times \text{AT}}{\text{DWIR} \times \text{INH} \times \text{DWF} \times \text{ED}}$$