Regulatory Challenges Posed by Petroleum Metabolites in Groundwater

The 11th International Conference on Remediation of Chlorinated and Recalcitrant Compounds by Battelle
April 12, 2018 – Palm Springs, California

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Overview

Regulatory Context

#1 – Awareness of Metabolites

#2 – Multiple Lines of Evidence Approach for TPH Data Evaluation

#3 – Assessing Risk and Setting Screening Levels

Conclusions

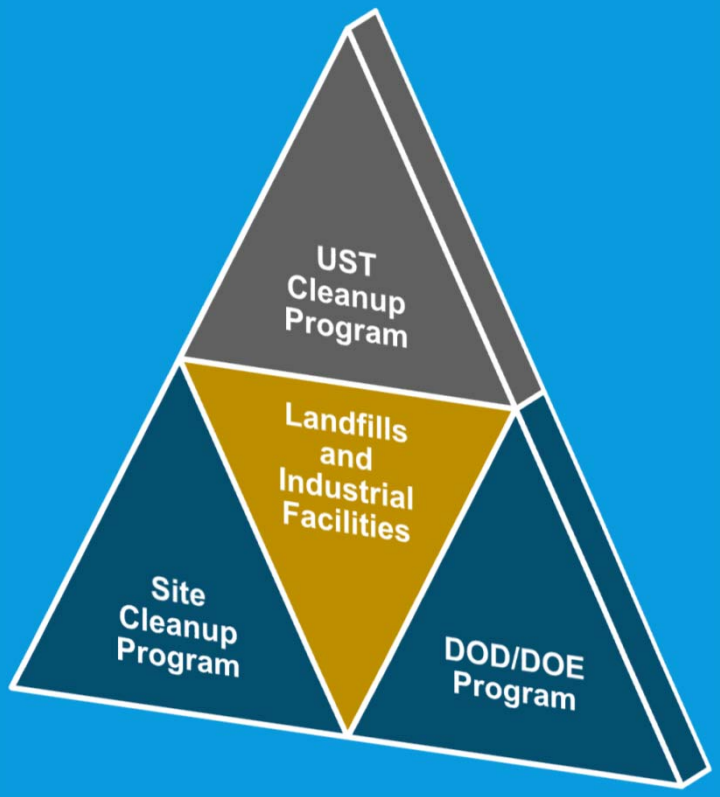
Regulatory Context

CalEPA
California Environmental Protection Agency

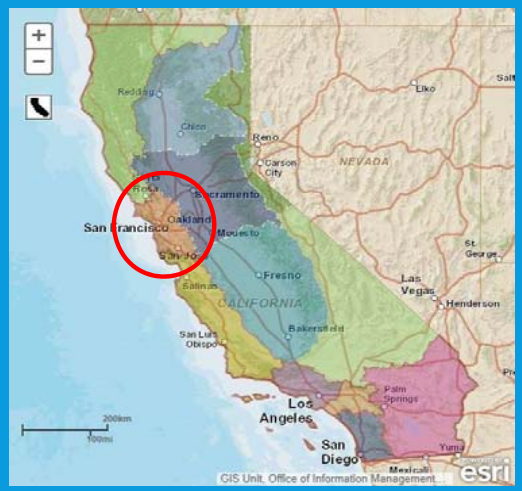
- Air Resources Board
- Cal Recycle
- Department of Pesticide Regulation
- Dept. of Toxic Substances Control
- Office of Environmental Health Hazard Assessment
- **Water Boards**
  State Board
  9 Regional Boards

81 Certified Unified Program Agencies (CUPAs) that apply regulatory standards by 5 different state agencies

Water Boards Programs for Site Cleanup and Landfill/Industrial Facilities



San Francisco Bay Regional Water Board (Region 2)
Technical Divisions



Evaluation of Petroleum at Cleanup Sites in California

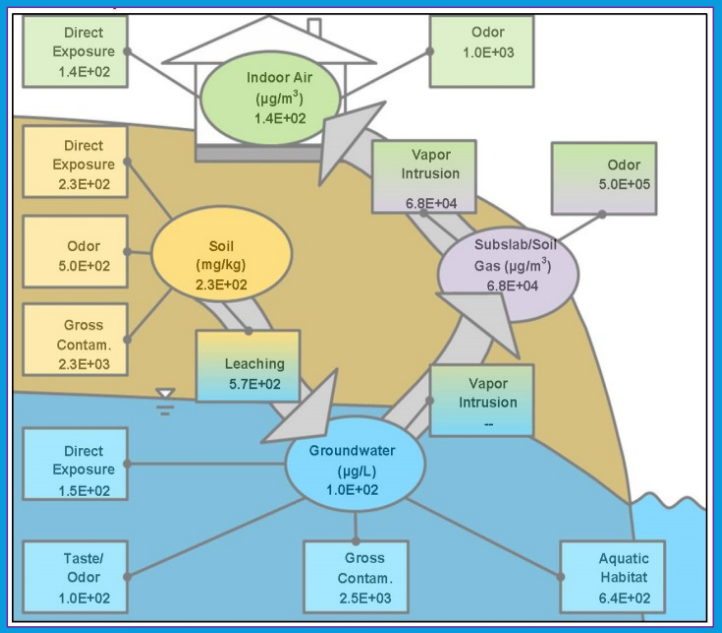
In California, regulatory oversight of petroleum-only cleanup sites typically falls to the Regional Water Boards and select local agencies

- State Water Board Low Threat UST Case Closure Policy (2012)
- San Francisco Bay Regional Water Board Environmental Screening Levels (**ESLs**) and appropriate narrative criteria
- Risk-based evaluations of Total Petroleum Hydrocarbons (TPH) usually default to the risk-based ESLs

Petroleum Screening Levels in the ESLs

Since 2000, the Environmental Screening Levels address these concerns:

- Ecological Risk
- Human Health Risk
- Gross Contamination (separate-phase liquid)
- Nuisance
- Leaching to Groundwater



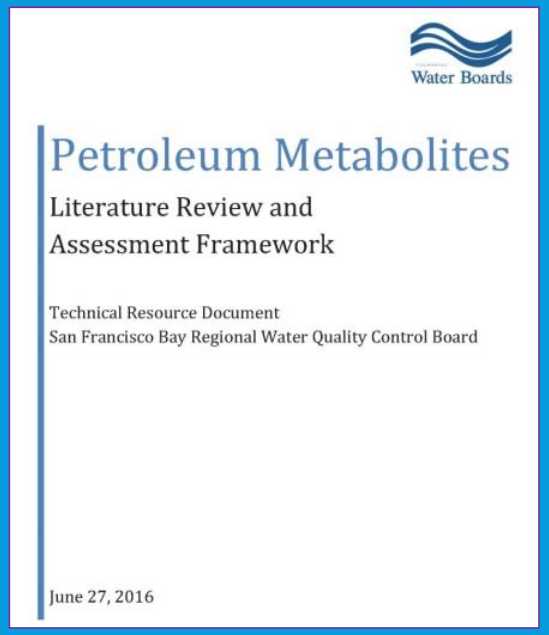
ESLs for TPH-diesel (diesel-range organics)

Petroleum Metabolites Technical Resource Document

Many requests for additional explanation regarding silica gel cleanup (SGC) after 2013 ESL Update

The current version of the tech memo (2016) addresses:

- Appropriate use of silica gel cleanup
- Treatment of the ***bulk hydrocarbons as having similar toxicity as the bulk petroleum metabolites***
- Larger releases and complex sites
- Examples involving petroleum mixtures such as diesel, Bunker fuels and crude oils.



https://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/esl.html

Challenge #1 – Awareness of Metabolites

Metabolites are intermediate breakdown products produced by living organisms to activate chemicals for further processing and distribution within the organism

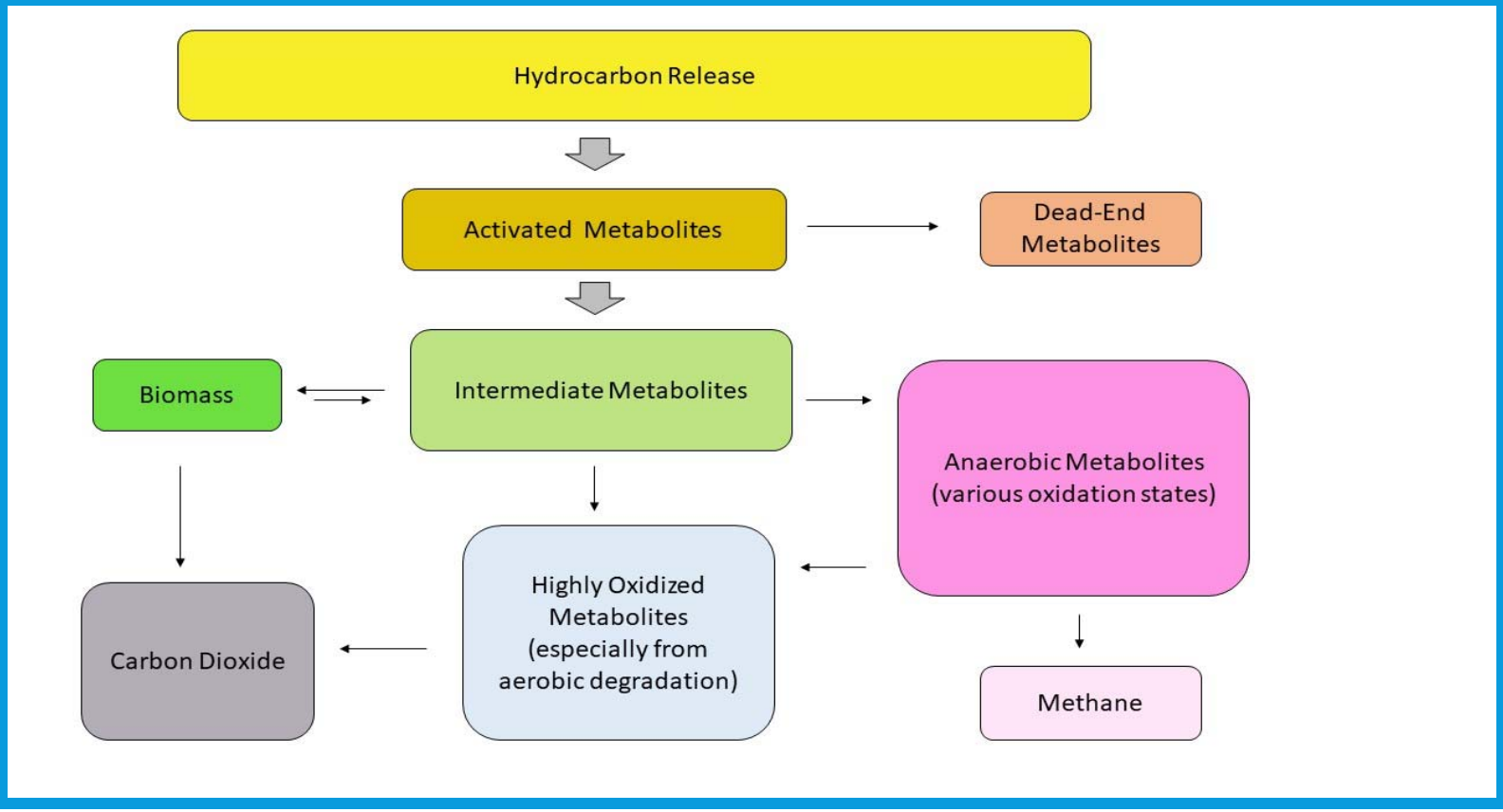
Even when biodegradation is not obvious, petroleum metabolites are generated:

- through partial oxidation of hydrocarbons in reservoirs
- after refining: during biofouling of refinery equipment
- after release to the environment mostly through microbial action (biodegradation)

Some partial breakdown products can also be the result of photo-oxidation

Petroleum metabolites are polar and preferentially partition into water

Reminder: Hydrocarbons Do Not Go Directly to CO2 During Biodegradation



ITRC TPH Risk Assessment Team

Clues for Significant Levels of Metabolites

1. Large concentrations of TPH-diesel (without silica gel cleanup or SGC) in groundwater samples: 1,000's to 100,000 µg/L
2. TPH-diesel concentrations after SGC are low to non-detect
3. Plumes persist for many decades

Additional Lines of Evidence:

- Background natural organics typically are less than 300 µg/L
- Fresh diesel solubility 3,000 to 5,000 µg/L (Shiu et al. 1990, ATSDR 1995)
- Potential sample collection issues (e.g., sheen, entrained contaminated sediment)

Challenge #2
Multiple Lines of Evidence Approach for TPH Data Evaluation

Total Petroleum Hydrocarbons (TPH) is a bulk analytical method, defined by the method

According to forthcoming ITRC TPH Risk Assessment guidance, results of TPH analysis does not capture

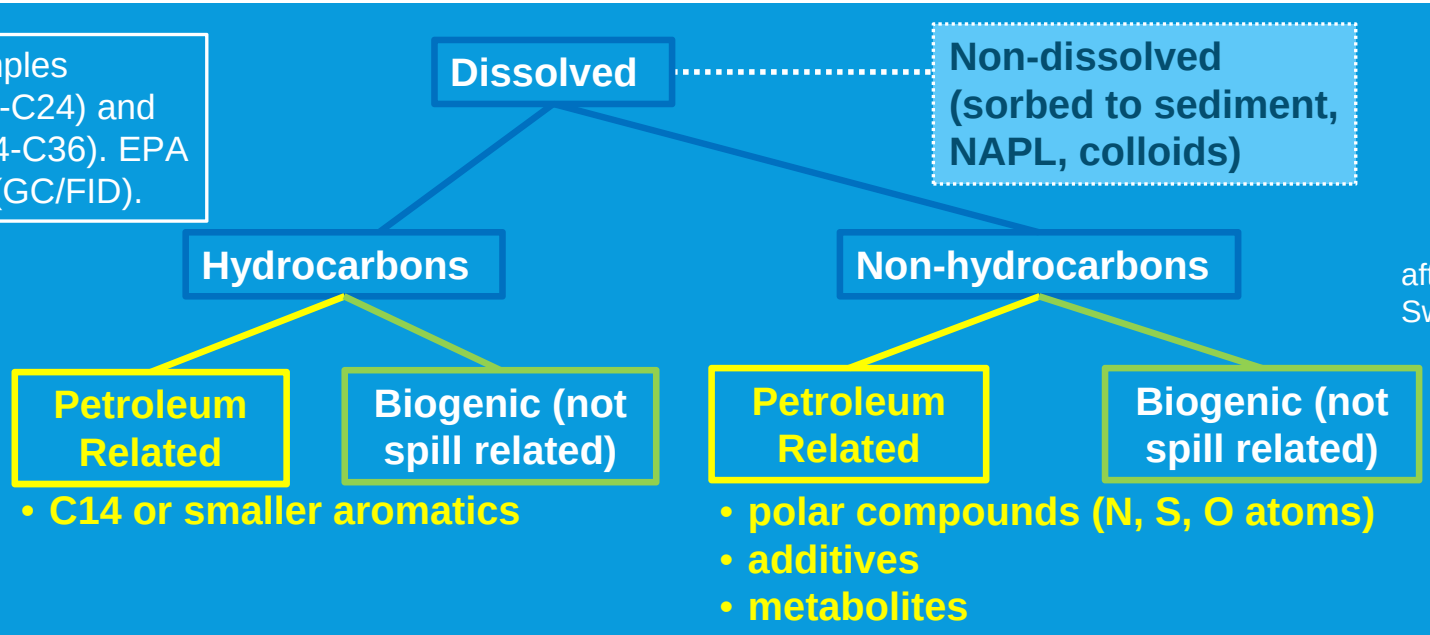
- the total mass of the release
- just petroleum compounds
- just the hydrocarbons

Bulk TPH analysis is a tool that can be used to evaluate the full effects of a release

Similar to indoor air, data interpretation requires a multiple lines of evidence approach

What Does the Extractable TPH Analysis Measure?

Water Samples
TPH-diesel (C10-C24) and TPH-motor oil (C24-C36). EPA Method 8015B (GC/FID).



after Lundegard and Sweeney (2004)

Our use for the TPH analysis:

Measure petroleum-related constituents beyond just the indicator compounds

Use of Silica Gel Cleanup (SGC)

What is silica gel – Absorbent (like salt)

What is silica gel cleanup (EPA Method 3630)

- Extract cleanup method to remove non-target polar compounds. Originally intended for cleaning up extracts of pesticides, derivatized phenols, PCBs, and PAHs.
- Absorbs polar compounds, allowing nonpolar compounds (e.g., hydrocarbons to pass through)
- Using SGC with extractable TPH analysis measures hydrocarbons only

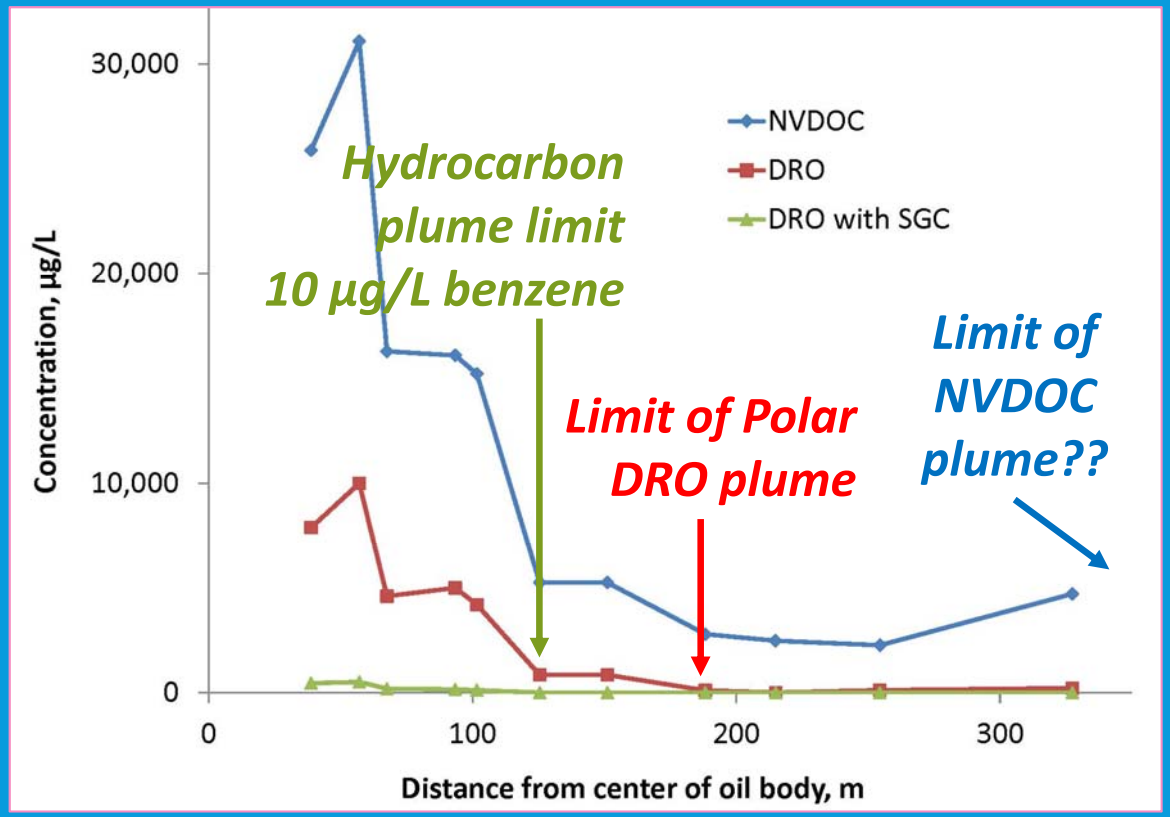
Also perform TPH analysis without SGC to measure the metabolites

Analytical Challenges for Metabolites

1. **Do not extract well in hexane or methylene chloride** (TPH Criteria Working Group 1998)
2. **Do not readily pass through the GC column** (TPH Criteria Working Group 1998)
3. **Are present outside the TPH-diesel range** (C10-C24) Bekins et al. 2016
4. **Analytical standards are not available**
5. **Analytical methods (extraction and detection) still under development**

We need better analytical methods
Preferably whole water methods

TPH-Diesel (DRO) is a Poor Method for Metabolites

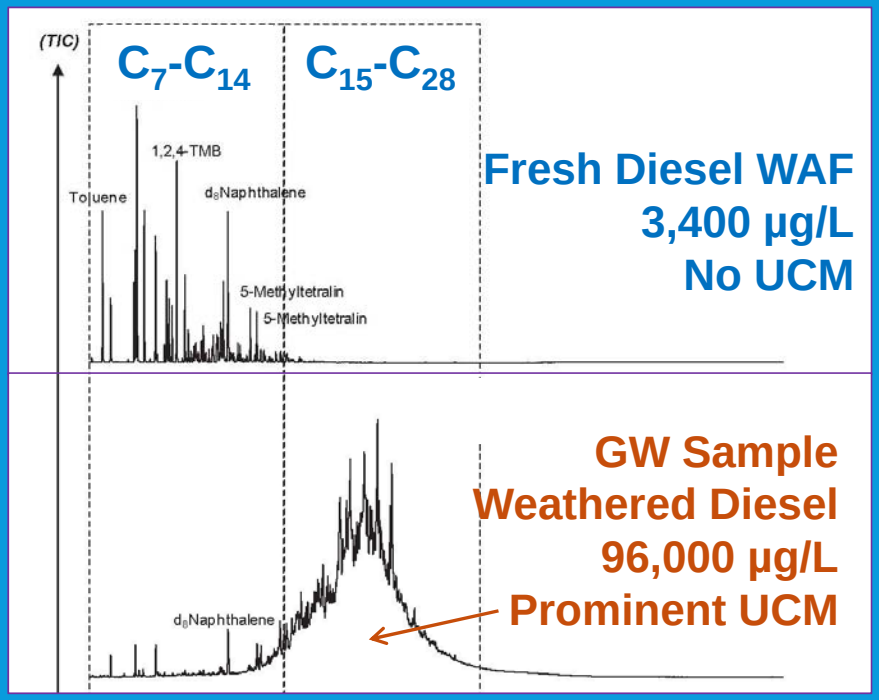


- **NVDOC = 3x DRO (TPH-Diesel)**
- **DRO may be non-detect even though metabolites are present**

USGS Crude Oil Research Site
Bemidji, MN
August 2016 data
courtesy Barbara Bekins and Isabelle Cozzarelli, USGS

NVDOC = nonvolatile dissolved organic compounds
DRO = diesel-range organics (TPH-diesel)

Chromatograms as Evidence for Metabolites



GC/MS Total Ion Chromatograms for Dissolved Organics Extracted with Methylene Chloride. Lang (2011)

- **Review the TPH Chromatograms!**
  Obtain scaled chromatograms for samples, standards, and blanks
- **High TPH-diesel typically correlates with large hump or unresolved complex mixture (UCM)**
- **Single peaks not resembling the WAF typically indicate non-petroleum-related compounds**

WAF = water-accommodated or water-soluble fraction

Considering Background Natural Organics

Soil
Contamination
Residual NAPL

Plume

GW Flow Direction

- *Similar hydrogeologic and vegetative setting!*
- *Typically less than 300 µg/L*

⊗ Groundwater (GW) Sample Location
Extractable TPH (no SGC)

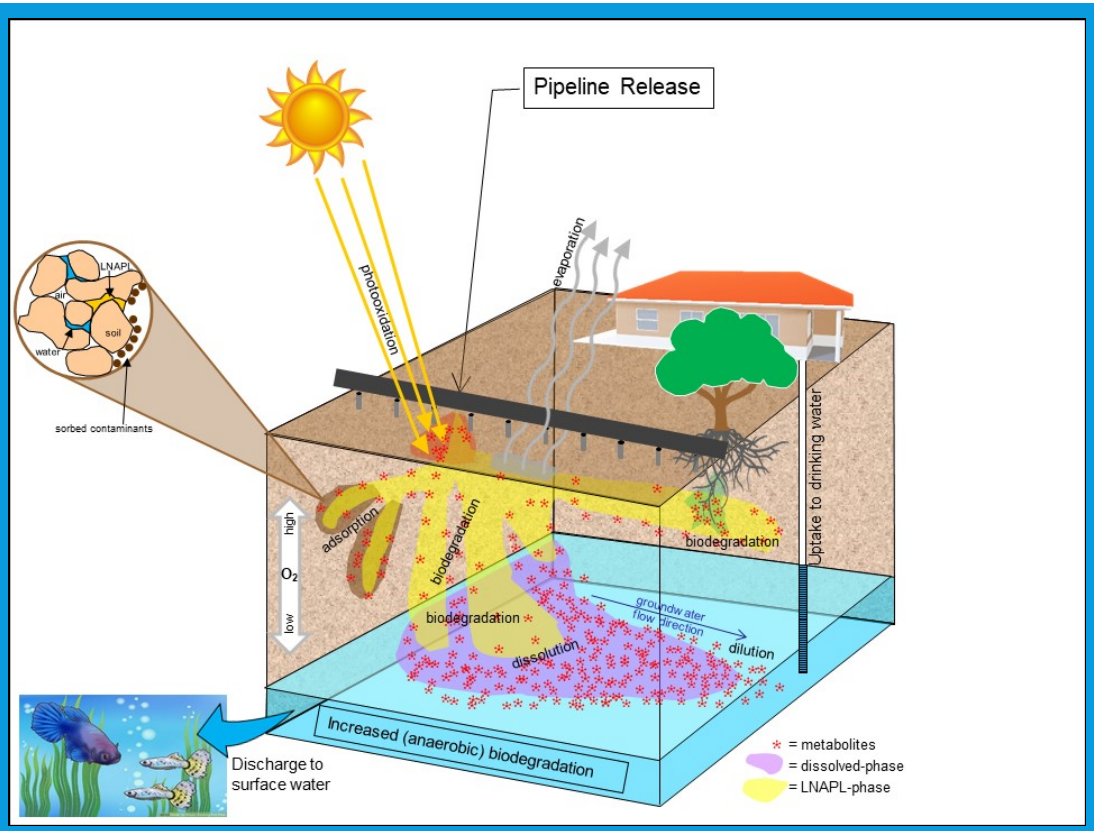
⊗ Potential Background GW Sample Location
Extractable TPH (no SGC)

Metabolites/Weathering Conceptual Model

Photo-oxidation

Adsorption

Discharge to surface water



Evaporation

Biodegradation

Dilution

ITRC TPH Risk Assessment Team

Challenge #3 – Assessing Risk and Setting Screening Levels

1. **Quality of analytical data** – detection and quantitation issues
2. **Limited toxicity information for individual metabolites**
3. **Limited toxicity information for metabolite mixtures**

We have the same problems for hydrocarbons

Human Health Risk – Available Information

- **Toxic effects of many chemicals are caused by metabolites. This is also true for hydrocarbons (e.g., hexane and naphthalene; IRIS)**
- **Rare dose-response study of a mixture of crude oil metabolites (naphthenic acids) by Rogers et al. 2002**

  Oral Reference dose (RfD) is comparable to naphthalene:
  (6.0E-02 mg/kg-day) vs. (2.0E-02 mg/kg-day)

- **Toxicity ranking model by Zemo et al. (2013, 2016)**

Options: Metabolite Health-Based Toxicity Values

1. Do nothing until better information and methods become available – ignore the metabolites
2. Use the RfD from the Rogers et al. (2002) study
3. Adopt the toxicity ranking model from Zemo et al. (2013, 2016)
4. Treat the bulk metabolites and bulk hydrocarbons as having similar toxicity

Setting Human Health Risk Screening Levels

- **Current Direct Contact Water ESLs for TPH-Diesel**
  - USEPA Regional Screening Level (RSL) tapwater algorithm
  - RfD for medium aromatics (2009 EPA PPRTV) and constants from RSLs
- **Since 2013, compare TPH-Diesel w/o SGC to Tapwater ESL**
  Toxicity of bulk metabolites can reasonably be expected to be very similar to the toxicity of bulk hydrocarbons
- **2018 ESLs – Evaluating a separate tapwater ESL for metabolites, considering their low volatility**

Aquatic Ecological Risk – More Information Overall
Literature and Site-Specific Toxicity Testing

Literature (marine oil spill focus)

Lab experiments found toxicity of weathered oils mixtures at: **1,000 to 2,000 µg/L**

Regional Water Board Bay Margin Sites – Early Testing (1990s)

Aquatic toxicity testing of hydrocarbon/metabolite mixtures in groundwater and soil elutriates: **600 to 170,000 µg/L**. Staff concluded site-specific evaluations necessary.

Updating Site-Specific Evaluation Approach

Whole Effluent Toxicity (WET) Testing of Groundwater

At one site, groundwater samples impacted by only metabolites found toxicity **between about 500 to 800 µg/L** (see earlier Chakrabarti et al. presentation)

Setting Aquatic Habitat Screening Levels

- Sources for surface water aquatic values include promulgated values, EPA Ecotox Database, other screening levels, and site-specific testing
- **Since inception of the ESLs (2000), saltwater aquatic habitat TPH-Diesel ESL is 640 µg/L** – based fresh Jet A WAF tested with the mysid shrimp
- **2018 ESLs** – Based on our literature search and recent testing, **no plans to change**.

Conclusions

1. **Bulk TPH Analyses (EPA Method 8015) measure bulk hydrocarbons and some metabolites**
2. **Don't Use Silica Gel Cleanup for Routine Bulk TPH Analyses – Best for answering specific questions (e.g., bulk hydrocarbon content)**
3. **High TPH-Diesel Concentrations? – Suspect metabolites first, review chromatograms, consider all lines of evidence in conjunction with the CSM**
4. **No adequate justification to treat the bulk metabolites toxicity differently from bulk hydrocarbons**

Same as It Ever Was:
Our Approach to Site Cleanup

1. **Adequate Investigation and Delineation**

   <u>Full disclosure</u>: extractable TPH without SGC to understand the full extent and cumulative effects of petroleum-related contamination

2. **Source Control (removal, treatment, containment)**
3. **Groundwater Plume Remediation (natural attenuation where appropriate) and sufficient monitoring to demonstrate stability**
4. **Institutional Controls when necessary**
5. **Long-Term Stewardship – Data and reports in GeoTracker**

Comments/Questions

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Acknowledgments: Thanks to current and former staff of the regional water board that participated or provided feedback on development of the technical memorandum.

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