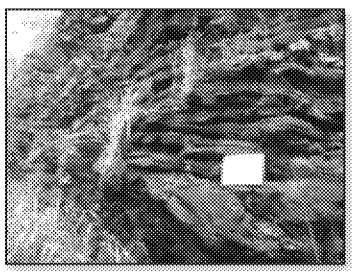
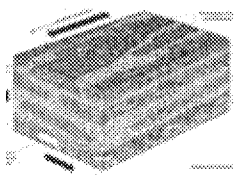
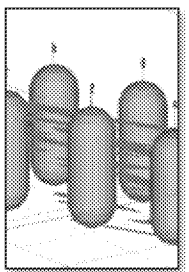
CURRENT CONDITIONS AND CONSERVATIVE SCENARIO EVALUATIONS

Discussion Materials
AOC Parties Technical Working Group Meeting No. 5
April 30, 2018

Preliminary Analyses
Results subject to change with new data/information







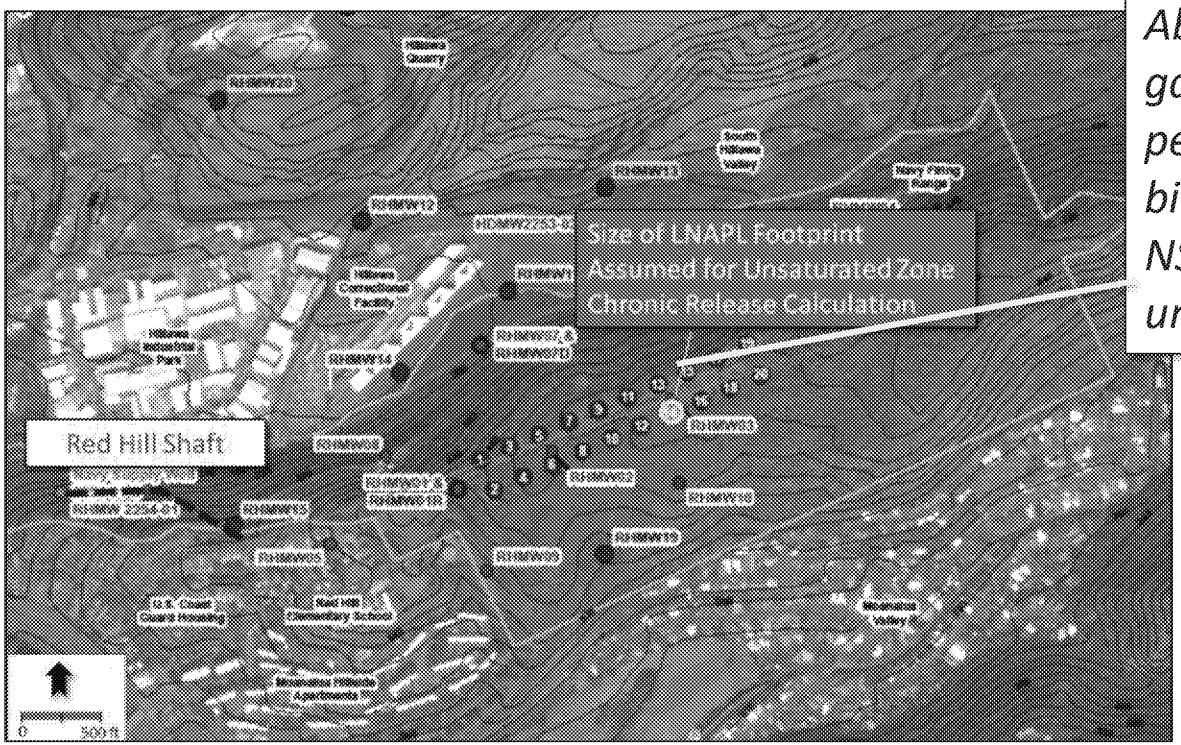
EPA/DOH INITIAL QUESTIONS FOR WG APRIL 4, 2018

- Q1: What happens to small (below detection limit) chronic releases, and where do they go in the environment?
- A1: Based on current data and NSZD studies, the Navy estimates approx. 1,700 gallons/yr/tank could be biodegraded in the unsaturated zone; and 2,500 gallons/yr could be attenuated assuming a large LNAPL lens. Thus, current estimates indicate 4,200 gallons/yr/tank could be attenuated from a chronic release without impacting Red Hill Shaft.
  - See following three slides from previous presentations on LNAPL.

EPA/DOH INITIAL QUESTIONS FOR WG APRIL 4, 2018 (CONTINUED)

Applying current NSZD and MNA data to estimate the acceptable chronic release – results for the unsaturated zone:

- Approx. 1,700 gallons per year per tank (about 4.3 gallons per day) could be biodegraded in the unsaturated zone

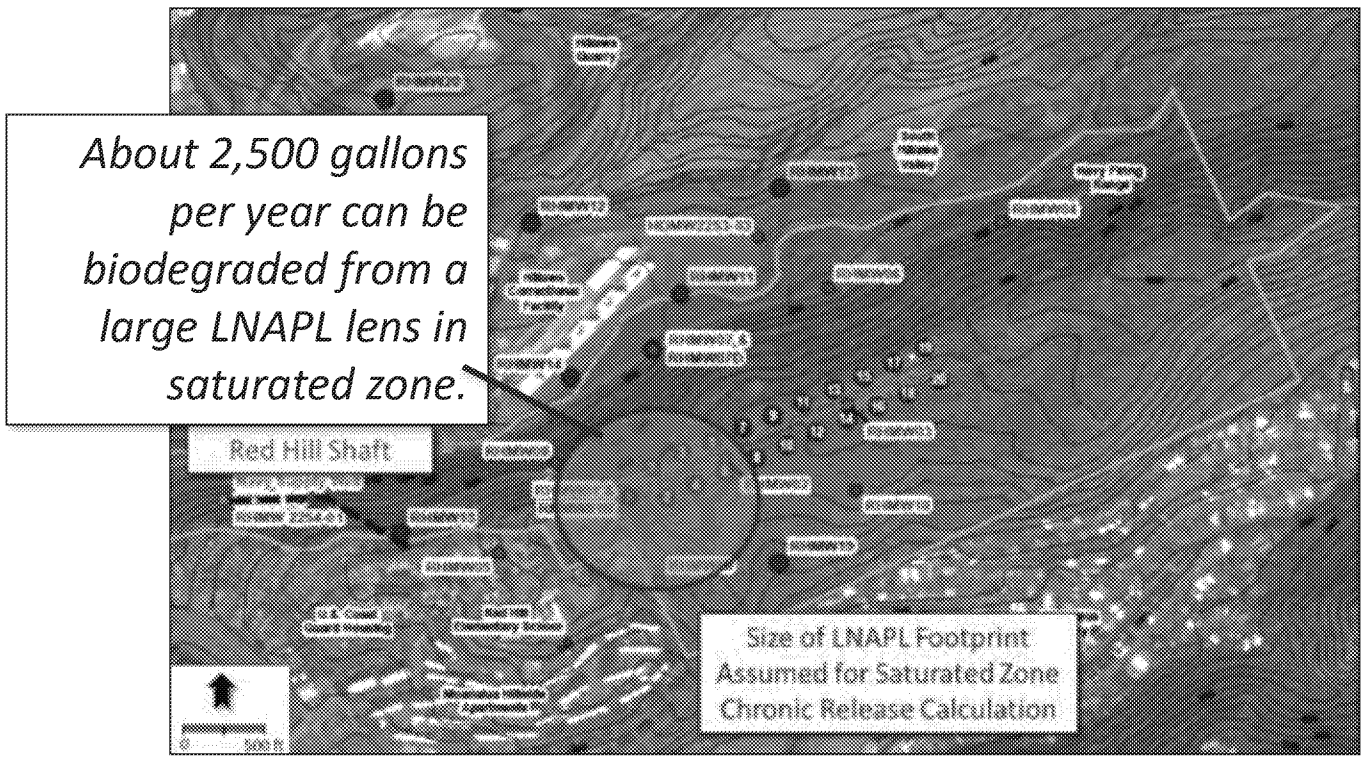


About 1,700 gallons per year per tank can be biodegraded by NSZD in the unsaturated zone.

EPA/DOH INITIAL QUESTIONS FOR WG APRIL 4, 2018 (CONTINUED)

Applying current NSZD and MNA data to estimate the acceptable chronic release – results for the saturated zone:

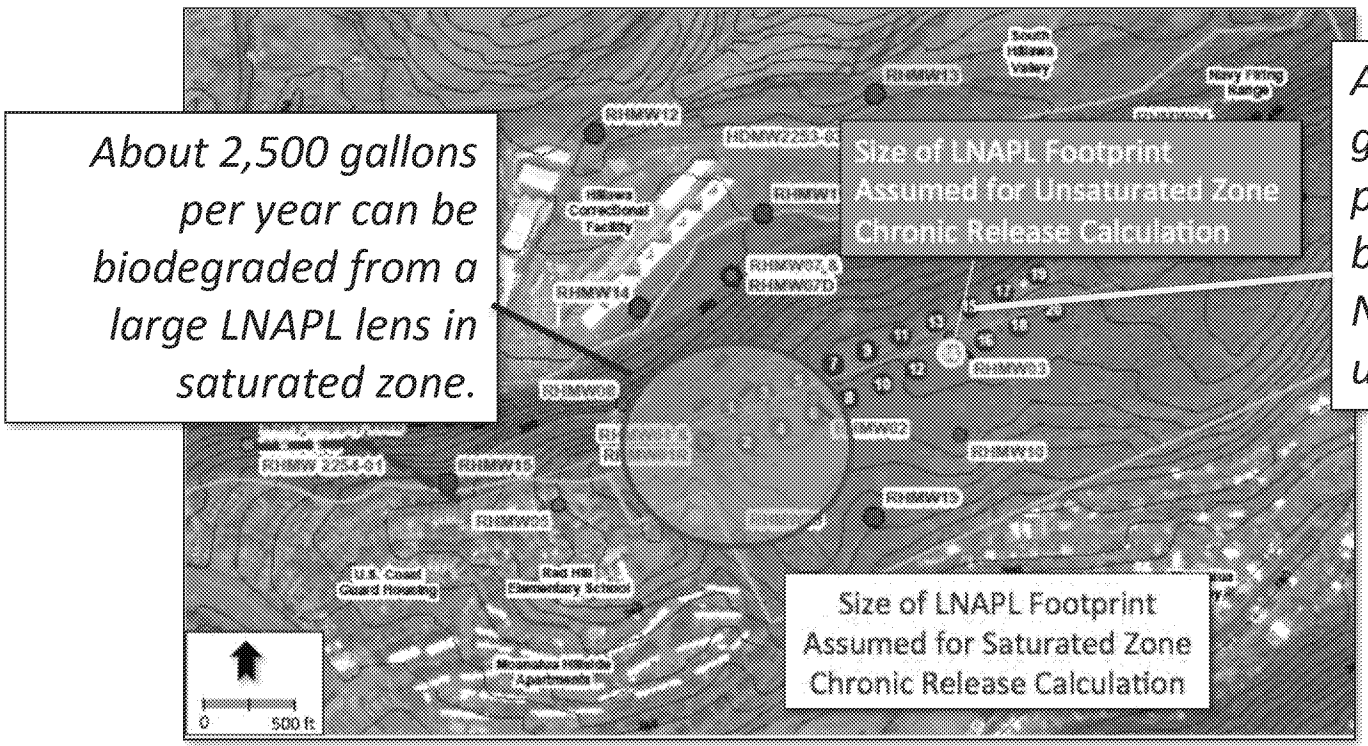
- About 2,500 gallons per year could be attenuated (i.e. controlled by NSZD) assuming a hypothetical, large LNAPL lens



EPA/DOH INITIAL QUESTIONS FOR WG APRIL 4, 2018 (CONTINUED)

Applying current NSZD and MNA data to estimate the acceptable chronic release – results for the unsaturated and saturated zones:

- In total, about 4,200 gallons per year per tank (about 11.5 gallons per day) could be attenuated (i.e. controlled by NSZD) from a chronic release without impacting Red Hill Shaft



About 2,500 gallons per year can be biodegraded from a large LNAPL lens in saturated zone.

About 1,700 gallons per year per tank can be biodegraded by NSZD in the unsaturated zone.

EPA/DOH INITIAL QUESTIONS FOR WG APRIL 4, 2018 (CONTINUED)

- Q2: What happened to the Tank 5 release?
- A2: The Navy believes there is evidence the January 2014 Tank 5 release is likely being retained in the unsaturated zone and has/is being attenuated via NSZD. Based on current data and detailed forensic analyses, the Navy's understanding is that strictly weathered material has been observed within the Red Hill groundwater monitoring network, and COPC concentrations have generally remained within recent historic ranges.
  - This is addressed extensively in Slides 12–39.

EPA/DOH INITIAL QUESTIONS FOR WG APRIL 4, 2018 (CONTINUED)

- Q3 & Q4: If another release of a similar magnitude was to occur from a different tank, what type of environmental response could the Navy have given the information available and monitoring well network? What about a release of hundreds of thousands of gallons?
- A3 & A4: The Groundwater Protection Plan (GWPP) will be followed accordingly. It is important to note that the GWPP will be updated to include all data and evaluations from AOC SOW Sections 6/7. The Navy has processes in place to determine extent of a leak. This determination will identify response actions and procedures. Given current data and the newly expanded monitoring network, there are two potential environmental responses: natural attenuation monitored by expedited and frequent sampling of groundwater and vapor and water treatment.

EPA/DOH INITIAL QUESTIONS FOR WG APRIL 4, 2018 (CONTINUED)

- Q5: Can the Navy predict concentrations at Navy wells and at Red Hill shaft in a release scenario under normal pumping conditions?
- A5: Yes, as previously discussed, the Navy has begun evaluations of hypothetical release scenarios, and presented initial results based on current data for input to the TUA decision process. The Navy has outlined the chronic release and the sudden release conditions that would not cause a risk-based decision criteria (RBDC) exceedance at Red Hill Shaft. These initial calculations were based on estimated normal pumping conditions at Red Hill Shaft, and used a mass flux approach.

RESPONSE TO EPA/DOH CONCERNS IN FEBRUARY 2018 LETTER

- Crosswalk of DOH technical comments per February 2018 letter and Navy responses addressed in this discussion material:

Summary of Select Chemistry and LNAPL Concerns	Response in Discussion Material
"The 2014 release likely impacted groundwater as evidenced by concentration trend increases in some wells following the release (e.g., RHMW01, RHMW02, RHMW03; attached)."	- Updated chemical forensics analyses and TPH - Lines of Evidence Relative to the presence of LNAPL in RHMW02
"Generally elevated and persistent dissolved-phase concentrations at RHMW02 indicate the presence of jet fuel impacts to groundwater over the full period of monitoring (i.e., jet fuel is in contact with groundwater somewhere in the vicinity."	- Updated chemical forensics analyses and TPH - Lines of Evidence Relative to the presence of LNAPL in RHMW02
"Jet fuel sheens and blebs have been reported during some past monitoring events (personal comm., Robert Whittier)."	- Lines of Evidence Relative to the presence of LNAPL in RHMW02 - The Navy requests specific location of this observation
"Given the above, jet fuel has likely impacted groundwater beneath the tank farm and beyond both from the 2014 and prior releases."	- Updated chemical forensics analyses and TPH - Lines of Evidence Relative to the presence of LNAPL in RHMW02

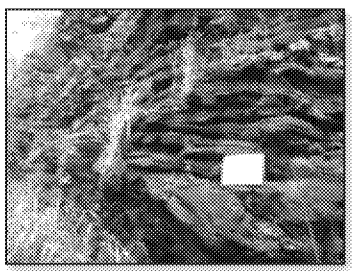
OVERVIEW AND FRAMEWORK FOR ENVIRONMENTAL INPUT TO TUA DECISION

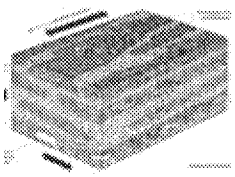
- **Fitting into the Bigger Picture**
  - Addressing uncertainty and resolving technical areas of disagreement
  - Environmental input to TUA decision
  - Investigation & Remediation of Releases and update to the GWPP
- **Current Conditions and Conservative Scenario Evaluations**
  - January 2014 Tank 5 release (i.e. Current Conditions)
  - Hypothetical scenarios with conservative assumptions
    - Environmental impact categories being developed for the TUA decision process
      - ✓ A hypothetical scenario with <u>a leak volume range that does impact groundwater and does not cause an exceedance at Red Hill Shaft</u>
      - ✓ A hypothetical scenario with <u>a leak volume range where LNAPL impacts groundwater and does not cause an exceedance at Red Hill Shaft</u>
      - ❑ A hypothetical scenario with <u>a leak volume range that impacts groundwater and causes an exceedance at Red Hill Shaft</u>

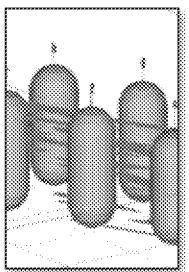
FOCUS OF DISCUSSION MATERIAL

- Discuss current conditions (i.e. Tank 5 release) based on detailed chemical forensics analyses and its application to evaluating potential future conditions
- Discuss groundwater chemistry and hydrocarbon forensics and multiple lines of evidence related to LNAPL from the 2014 JP8 release at Tank 5
  - Major data evaluation limitations: analytical issues and uncertainties
- Discuss evaluations of conservative release scenarios that considers LNAPL impacting groundwater

CURRENT CONDITIONS: UPDATED CHEMICAL FORENSIC ANALYSES AND TPH







ISSUES AND CHALLENGES IN ASSESSMENT OF PETROLEUM HYDROCARBONS IN THE ENVIRONMENT

- Complex mixtures with a range of physical and chemical properties
- Subject to weathering by volatilization, dissolution, biodegradation, etc.
- Assessment of these mixtures is through the estimation of **total petroleum hydrocarbons (TPH)**, an analytical parameter that **is defined by the method used to measure it**
  - Many methods, vary from state to state and even lab to lab
  - Extraction solvents, calibration and carbon ranges are variable
  - Non-petroleum materials and metabolites are also measured
  - Laboratories may assign a name of a product type to anything that elutes within a given carbon range or retention time and results may point to wrong sources
  - Typical acceptance criteria for TPH-d
    - DoD Environmental Data Quality Workgroup (EDQW) - Laboratory Control Sample (LCS) study - summer of 2012, DoD Quality Systems Manual Version 5.1 DOE Quality Systems for Analytical Services Version 3.1, 2017): **36 to 132% (~1800 records)**
    - Performance testing samples from vendor: **30 to 125%** of the spiked concentrations
- Essential to understand what is really being measured as "TPH"
- Most site investigations focus on **individual compounds, which are more definitive and reliable**

WHY DISSOLVED TPH-D IS NOT A GOOD DIAGNOSTIC TOOL TO MONITOR JET FUEL IN GROUNDWATER

- Distribution of Compound Classes in Jet fuels

		Jet A (n=13)	JP-8 (n=11)	JP-5 (n=2)
Total Saturates (Aliphatics)	vol%	80	79	78
Total Aromatics	vol%	20	21	22
- *Monoaromatics (benzene and substituted benzenes)*	vol%	18	19	19
- *Diaromatics (naphthalene and substituted naphthalenes)*	vol%	3	2	3

Source: CRC Report No. 647 (Hadaller and Johnson 2006)
vol%: percent by volume. (n): number of samples

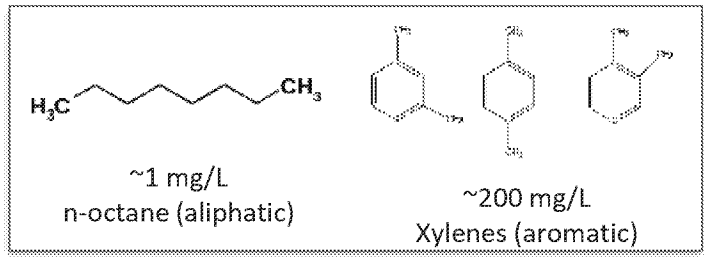
- A small portion of jet fuel (aromatics) is water soluble (<20%) with effective overall water solubility of ~5 mg/L with ~3 mg/L from BTEX alone
- Substituted benzenes and naphthalenes are the rest of the dissolved components

Kerosene	Whole product[a]	Water-soluble fraction[b] 0.5 Hours	17 Hours
Alkanes + cycloalkanes	68.6	4.5	0.5
Benzene + substituted benzenes	13.7	63.5	53.2
Naphthalene+ substituted naphthalenes	5.7	29.6	44.8

[a]Estimated weight percent
[b]Estimated weight percent of constituents dissolved in water after 0.5 or 17 hours of incubation

Source: Coleman 1984

- Saturated/aliphatic hydrocarbons have relatively very low water solubility with respect to aromatic hydrocarbons. For instance, pure xylenes (8 carbons) are >200X more soluble in water than pure n-octane



- Many aromatics (except toluene) do not degrade easily under anaerobic conditions
- TPH-d is not specific, is method/lab dependent and may include naturally occurring organics and biodegradation metabolites

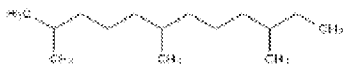
Best to monitor target COPCs

COMPARISON OF UNDEGRADED LNAPL AND BIODEGRADED LNAPL FROM JET FUEL VS BIODEGRADED SOLUBLE JET FUEL COMPONENTS

- Jet fuel vs diesel fuel hydrocarbon distribution
  - n-alkanes are predominant in these fuels

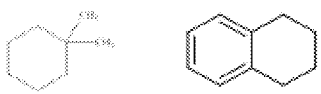
n-dodecane
(amenable to aerobic biodegradation)

- Biodegraded residual jet fuel and diesel hydrocarbon distribution
  - Isoalkanes - branched alkanes



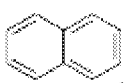
Farnesane (2,6,10-trimethyldodecane)

  - "Complex Mixture" - isoalkanes, cycloalkanes/naphthenes

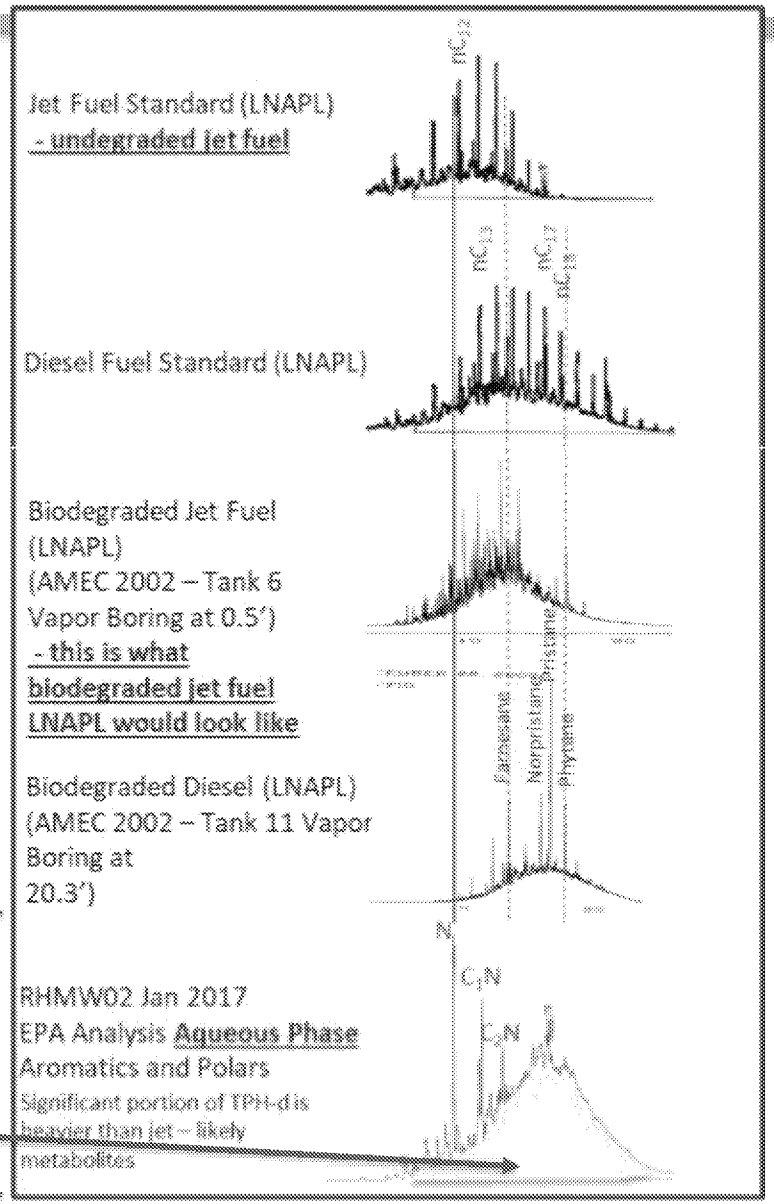


These types of compounds are relatively more resistant to biodegradation

- Dissolved TPH-d in GW from RHMW02
  - Naphthalenes – resolved peaks



  - "Hump" – polar metabolites alcohols, organic acids

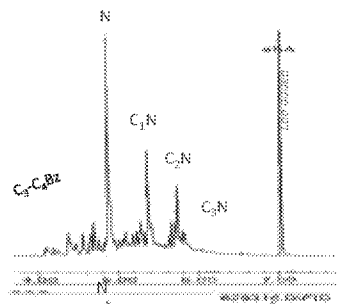


No chromatographic evidence of LNAPL in RHMW02

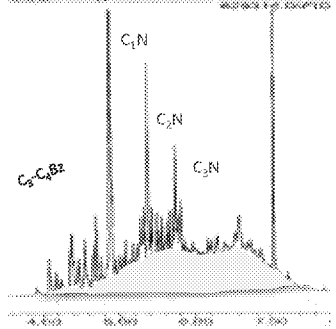
CHROMATOGRAMS FROM ANALYSIS OF RHMW02 (TPH-D WITH AND W/O SILICA GEL TREATMENT)

RHMW02
July 2017
APPL Lab

TPH-d (C10-C24)
Silica Gel Cleanup
(SGC)



TPH-d (C10-C24):



March 2018

	TPH-d µg/L	TPH-d (SGC) µg/L
APPL	1900	640
APPL	1800	460
EPA	2900	430

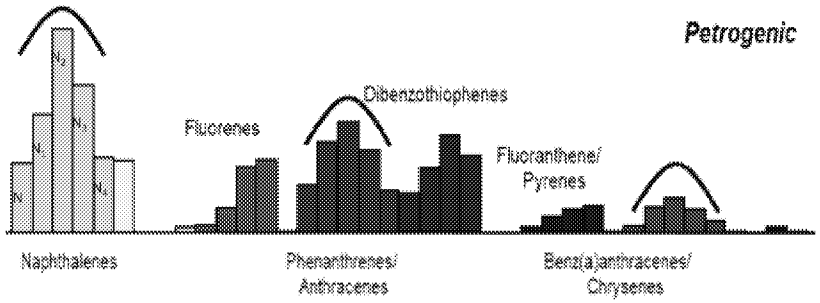
Since TPH-d is >65 to 85 % polar matter, it is difficult to achieve consistent results from lab to lab with these types of biodegraded samples

Mass removed by silica gel is likely polar material

RELATIVE DISTRIBUTION OF NAPHTHALENES IN PETROGENIC MATERIALS

- Alkylated naphthalenes are more abundant in fuels than the parent naphthalene as in all petrogenic materials
  - JP-5: methylnaphthalenes 0.54 wt%, naphthalene 0.22 wt%
  - JP-8: methylnaphthalenes 0.42 wt%, naphthalene 0.16 wt%
- Pure solubility of naphthalene is 31 mg/L and 28 to 25 mg/L for the methylnaphthalenes
- The ratio of alkylated naphthalenes (1-methylnaphthalene and 2-methylnaphthalene) to naphthalene from the calculated ideal effective solubilities are ~2 for both JP-8 and JP-5
- Naphthalene in RHMW02 groundwater samples is more abundant than the methylnaphthalenes:

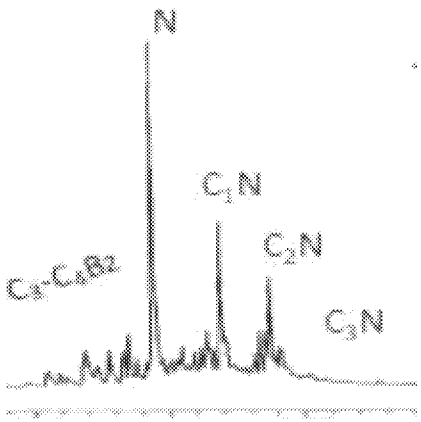
Crude Oil – Relative Distribution of PAHs



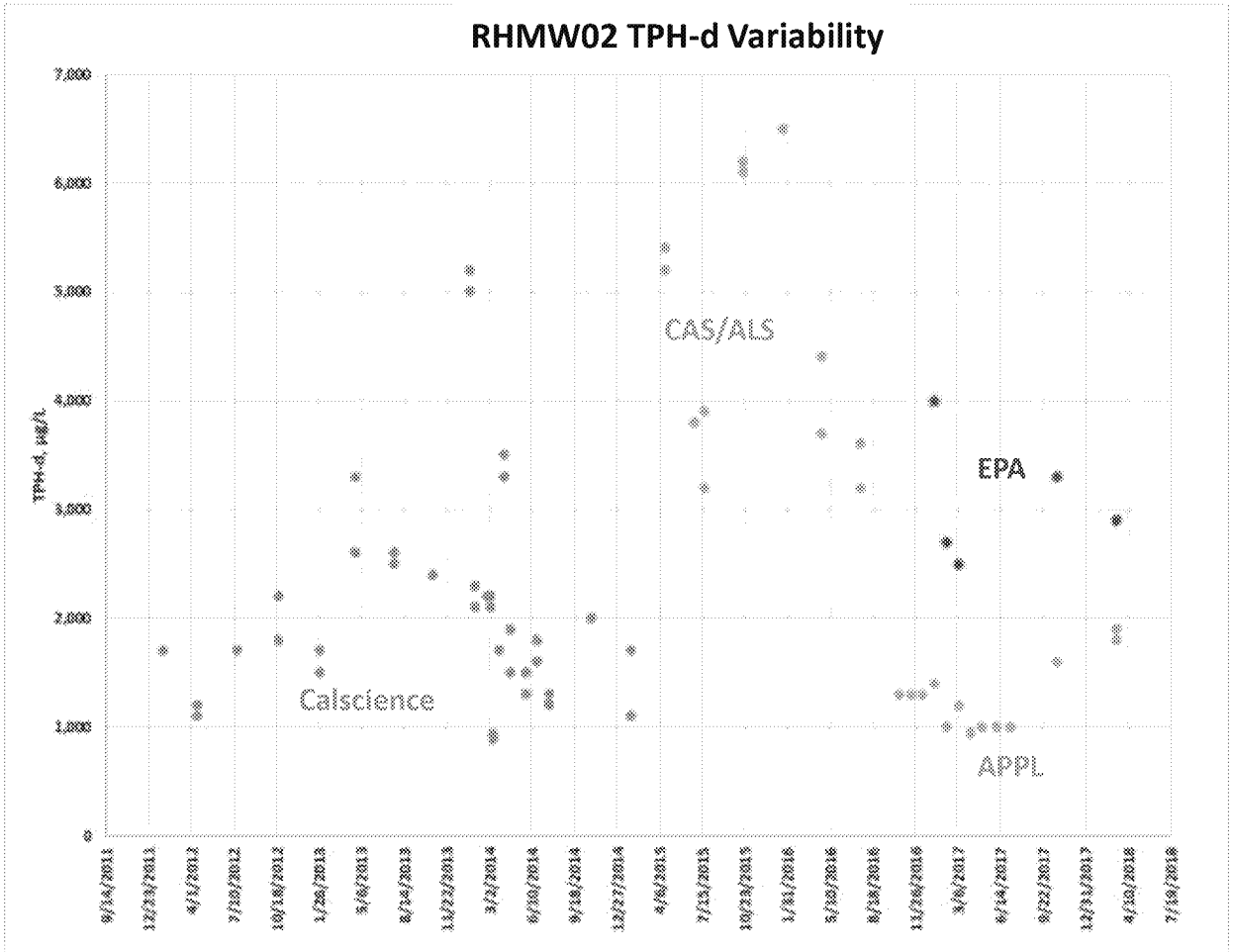
Typical ratios in the fuel and in water (ideal effective solubility) of methylnaphthalenes to naphthalene in JP-5, JP-8 and F-76 are:

JP-5 (avg, 13 samples)		JP-8 (avg, 18 samples)	
Fuel	Water	**Fuel**	Water
2.5	1.9	**2.7**	2.1

Evidence of Biodegradation



TPH-D VARIABILITY – LAB ISSUES



- *Laboratory (Calscience/Eurofins Lab) indicated a mismatch between the calibration standard and the TPH-d chromatographic profile. Mismatches of this type are not uncommon. Even though chromatograms are not part of the standard laboratory package, ESI was able to review the chromatograms from RHMW02 dating back to October 2012. The chromatograms of groundwater samples from RHMW02 did not significantly differ between each event, and did not match a standard chromatogram of JP-8 in water.* (1Q2015 Status Report)

- The difference in relative concentrations between EPA and APPL are just due to different laboratory methods for the same samples

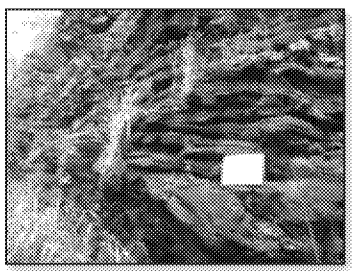
Absolute concentrations alone can NOT be used for trend analyses

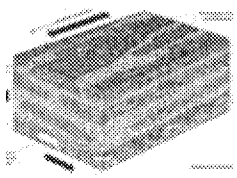
EXCERPTS FROM QUARTERLY REPORTS – LIMITATIONS OF TREND ANALYSES

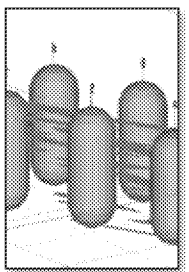
- Comparative analysis of hydrocarbon data should consider the large error inherent in EPA Method 8015 Modified
- Lack of precision, variability in methods and polar/metabolites quantitation issues for TPH-d and TPH-o prevent valid trend analysis based on TPH alone
- Lack of precision in Naphthalene results could falsely indicate an increase in contamination from year to year GW sampling events
- Lower detection limits (2 to 20X lower than other labs) from April 2015 to July 2016 caused appearance of chemicals not observed in previous sampling events
- DOD reporting requirements and resulting data qualifiers may affect graphical analysis of data

Red Hill LTM, 2Q2015 GW Report, page 3-7, August 2015 Inside Tunnel Wells
http://health.hawaii.gov/shwb/files/2016/02/2015-08-2nd-qtr-gw-monitoring-inside-rept.pdf

CURRENT CONDITIONS: LINES OF EVIDENCE RELATIVE TO THE PRESENCE OF LNAPL IN RHMW02







USE OF DISSOLVED CONSTITUENTS FOR EVALUATING POTENTIAL LNAPL IMPACTS TO GROUNDWATER

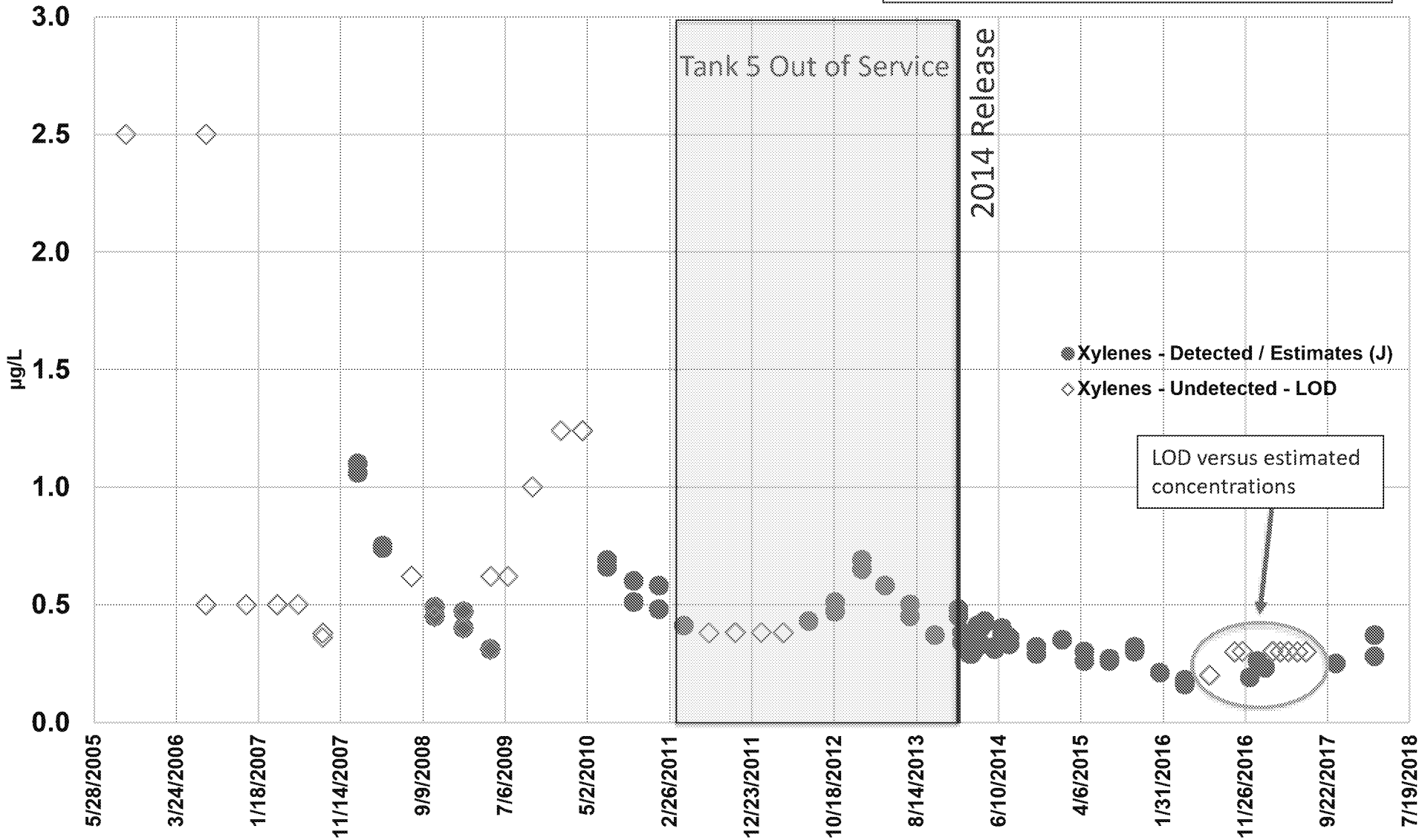
- No reported instances of LNAPL in monitoring wells after the 2014 release
  - An oil/water interface measurement was reported as "<0.01 ft" in monitoring wells RHMW01/RHMW02 in January 2008. This may have been a reporting nomenclature issue, rather than an actual LNAPL occurrence.
- No fingerprint evidence of entrained/emulsified LNAPL seen in available chromatograms
- In order to determine if LNAPL may have reached groundwater in the vicinity of Red Hill monitoring wells, dissolved phase constituents have been evaluated as multiple lines of evidence (LOE)

LINES OF EVIDENCE (LOE): EVALUATION OF DISSOLVED-PHASE CONSTITUENTS AND SOIL VAPOR

1. Xylene
2. Benzene
3. Ethylbenzene
4. Toluene
5. TPH-g
6. Naphthalenes and Methylnaphthalenes to Naphthalene ratio
7. TPH-d
   - *Lab variability – Trend Issues*
   - *TPH-d chromatographic fingerprints*
8. Soil Vapor

LOE 1: RHMW02 Xylene Data

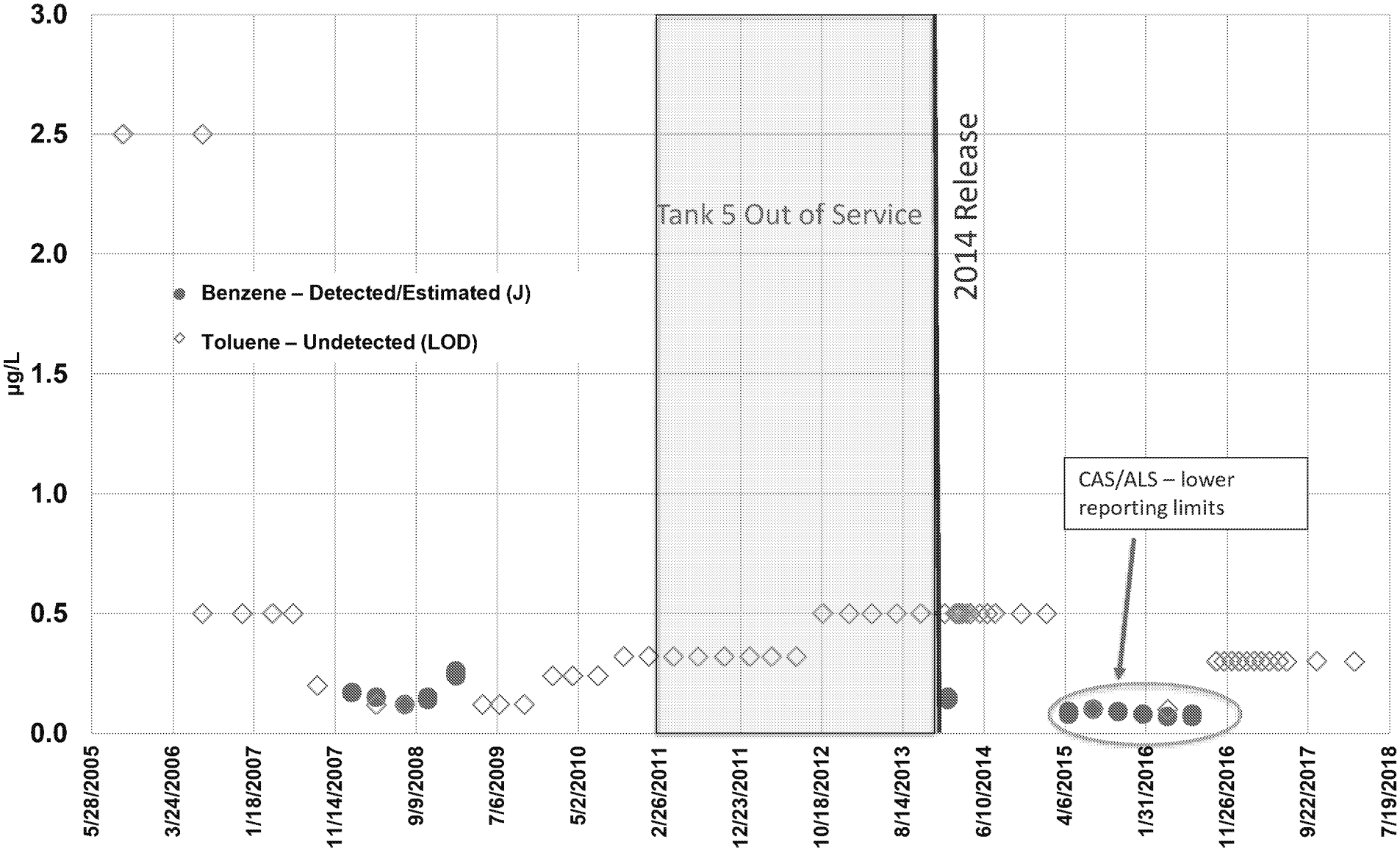
Calculated Ideal Effective Solubility Range (JP-8): 84 to 4100 µg/L
RBDC: 19 µg/L



Key Point: No significant changes in Xylenes after 2014 release

LOE 2: RHMW02 Benzene Data

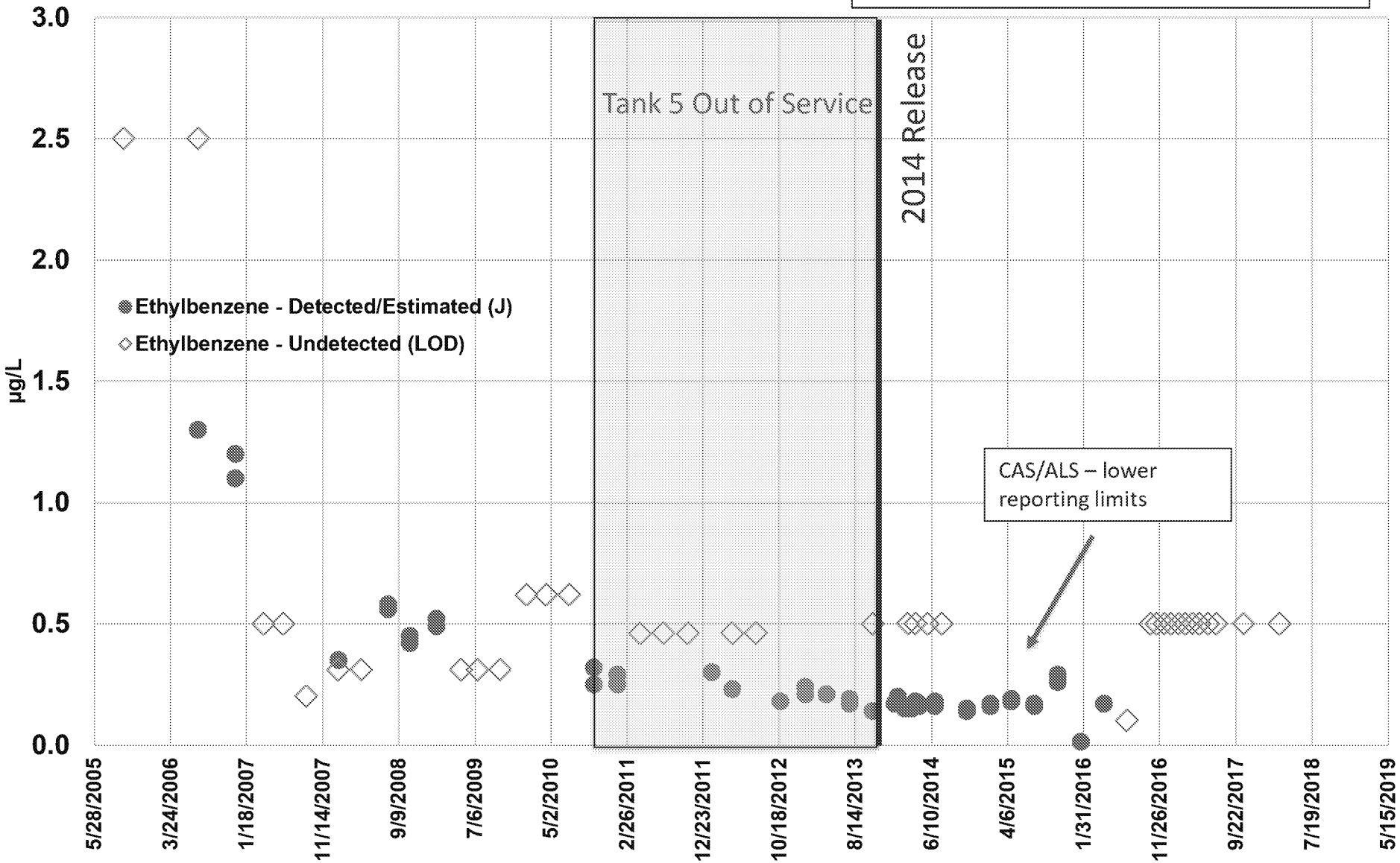
Calculated Ideal Effective Solubility Range (JP-8): 54 to 4520 µg/L
RBDC: 0.46 µg/L



Key Point: No significant changes in Benzene after 2014 release

LOE 3: RHMW02 Ethylbenzene Data

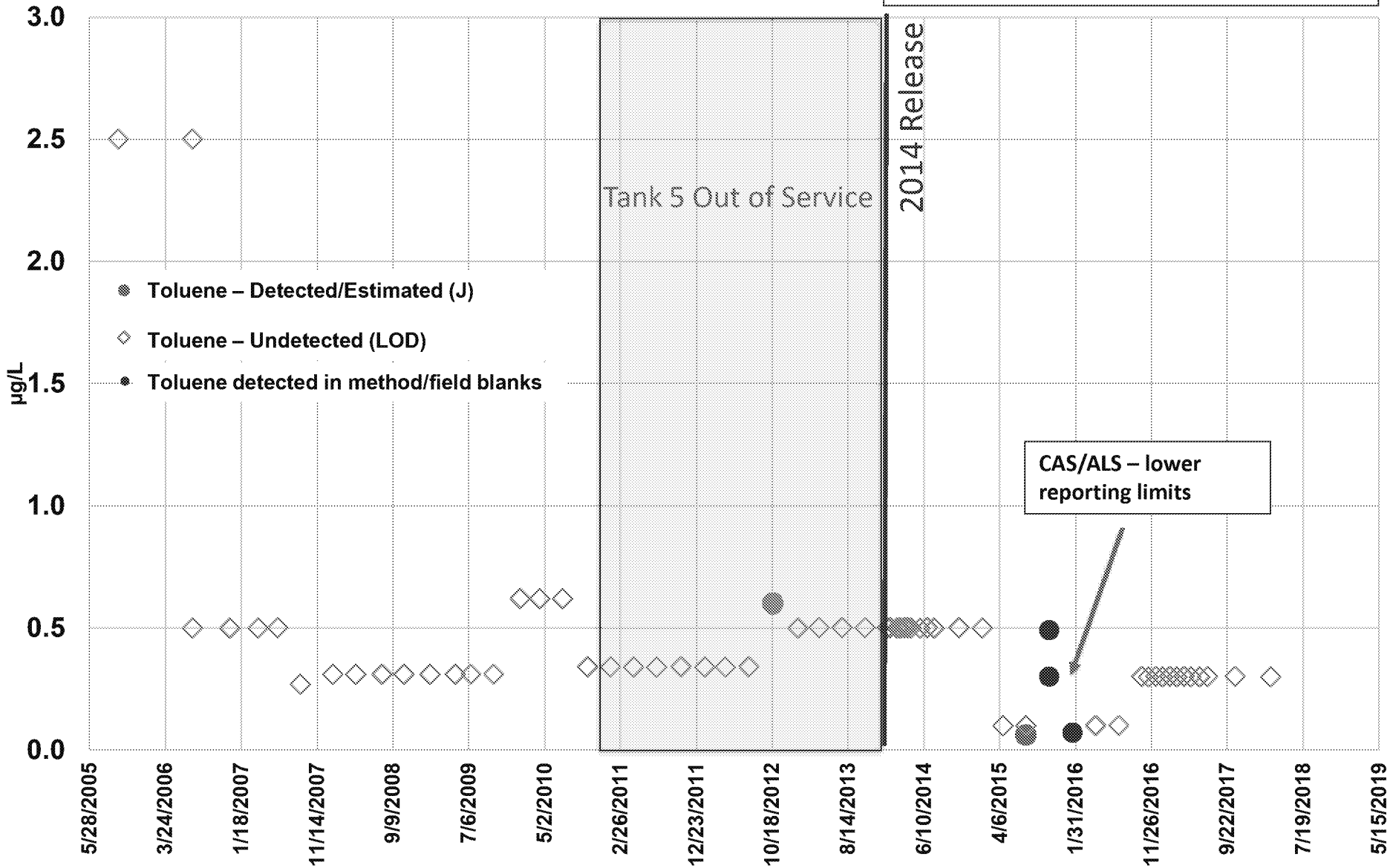
Calculated Ideal Effective Solubility Range (JP-8): 11 to 580 µg/L
RBDC: 1.5 µg/L



Key Point: No significant changes in Ethylbenzene after 2014 release

LOE 4: RHMW02 Toluene Data

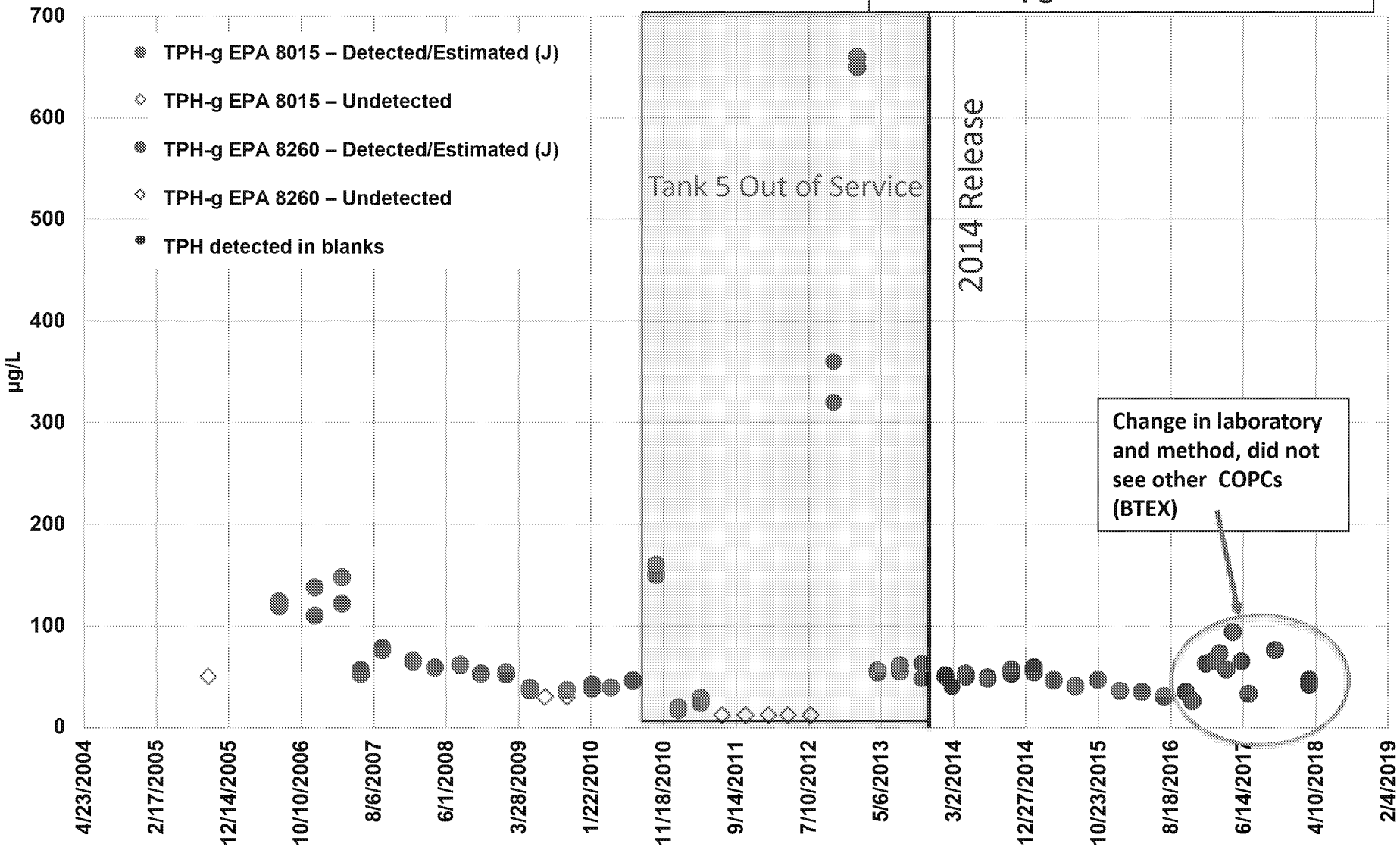
Calculated Ideal Effective Solubility Range (JP-8): 320 to 1530 µg/L
RBDC: 40 µg/L



Key Point: No significant change in Toluene after 2014 release

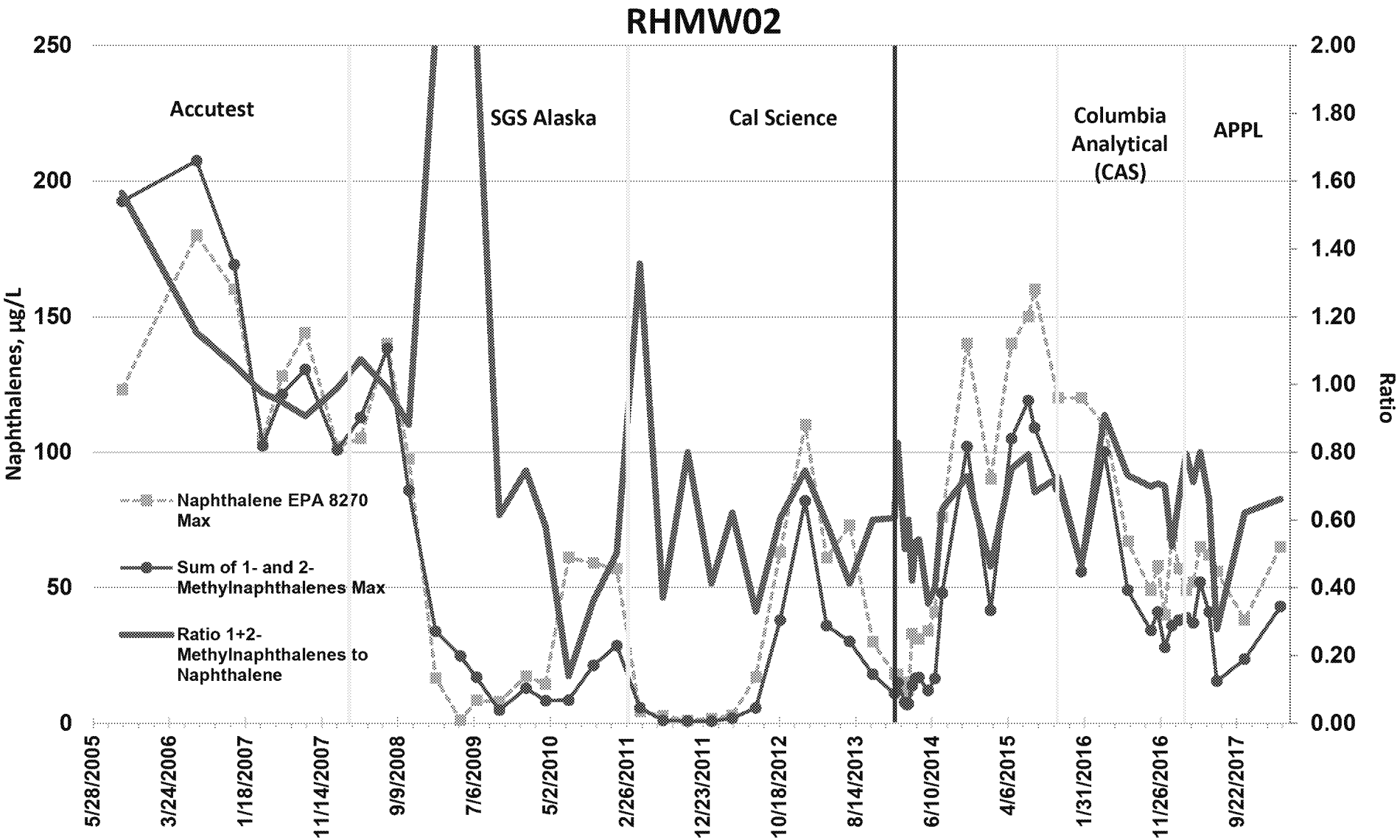
LOE 5: RHMW02 TPH-g Data

Calculated Ideal Effective Solubility Range (JP-8): 84 to 4100 µg/L
RBDC: 19 µg/L



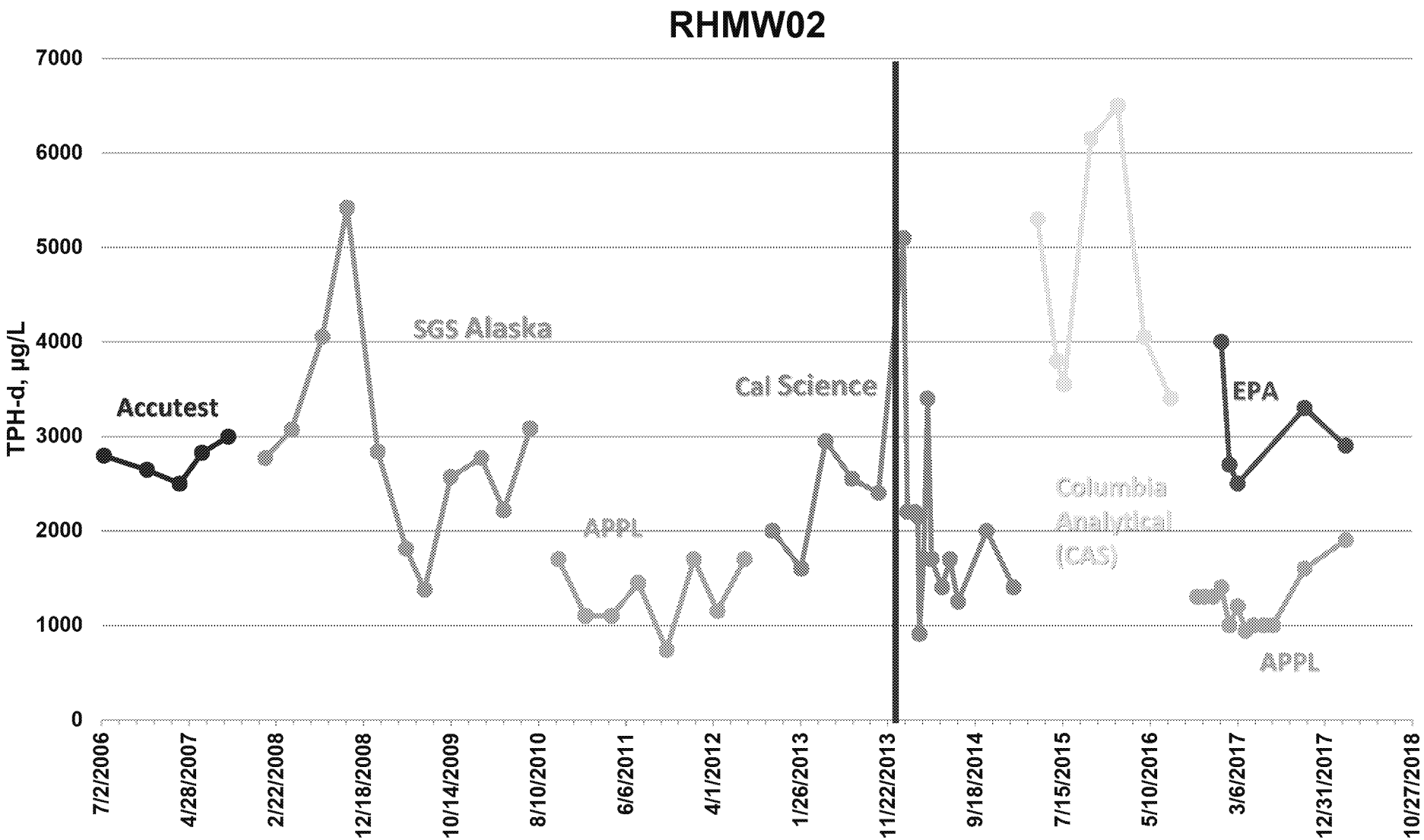
Key Point: No significant change in TPH-g after 2014 release, some variability coincides with change in lab and method, not unexpected for TPH measurements

LOE 6: RHMW02 Naphthalenes and Naphthalene Ratios



Key Point: Ratios of 1+2 Methylnaphthalenes to Naphthalene < 2 indicate a weathered source. Imprecision in Naphthalene results have been observed in previous data validation reports.

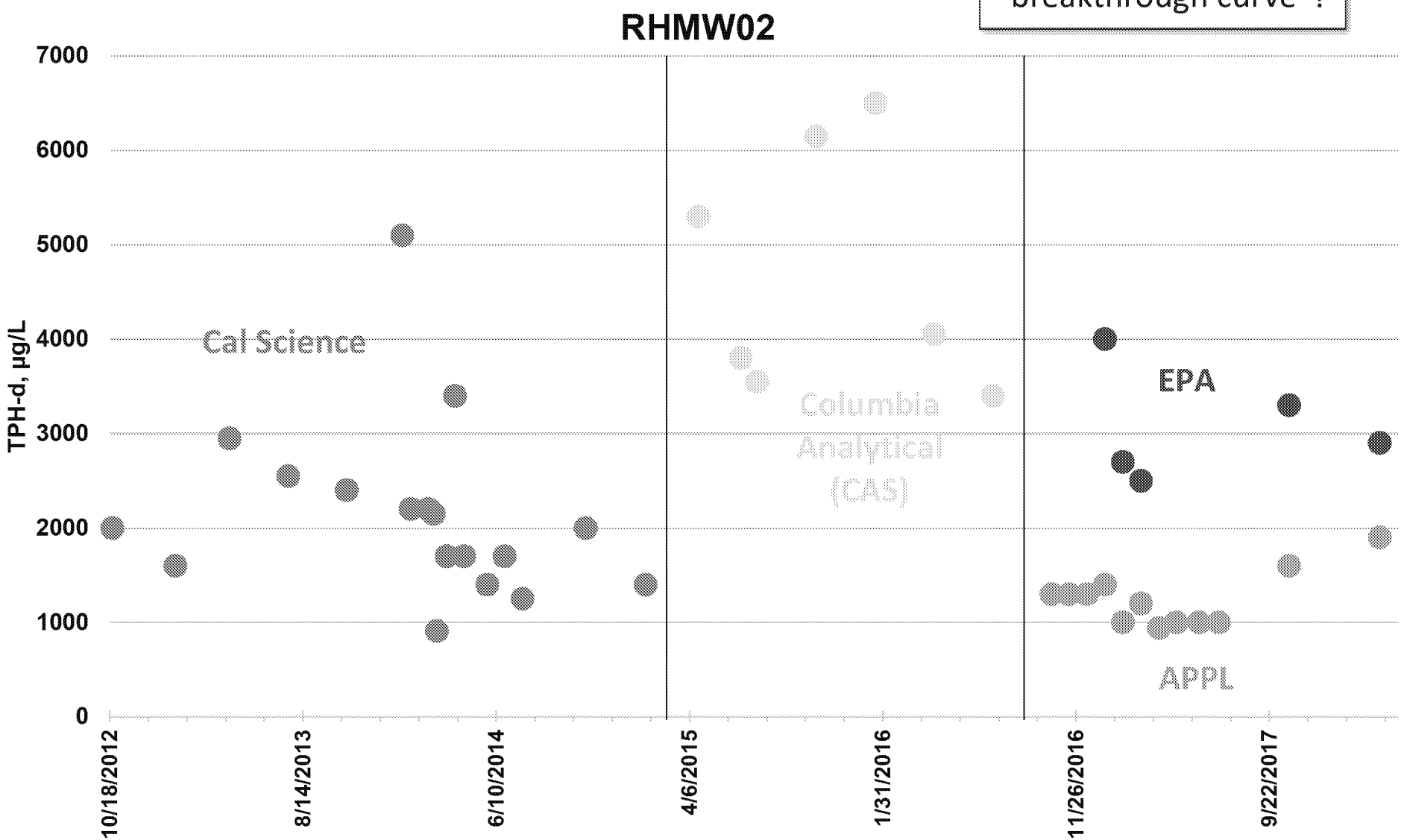
LOE 7: TPH-d Lab Variability



Key Point: Variability for TPH-d from lab to lab precludes reliable trend analyses

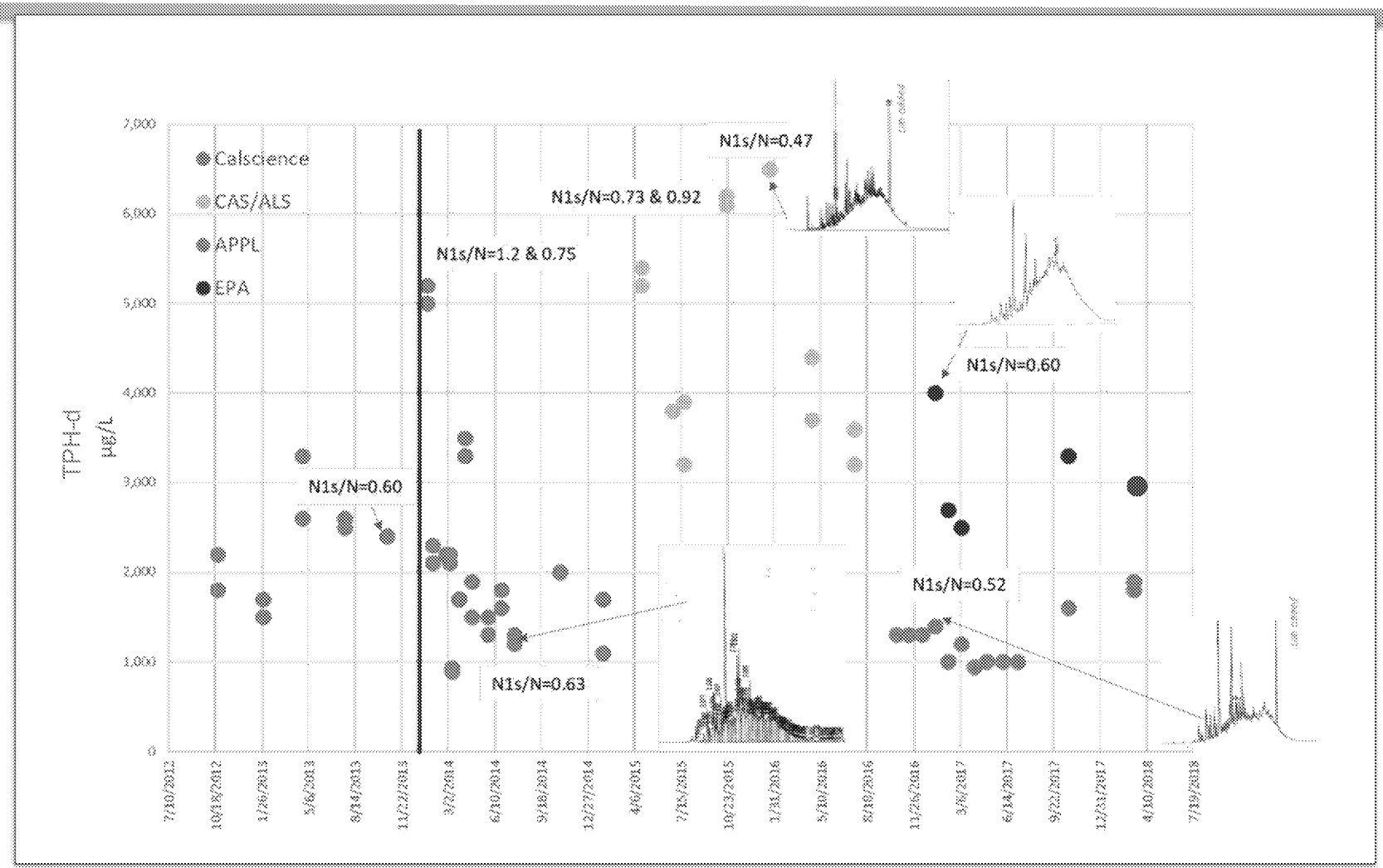
LOE 7: TPH-d Data vs. Changing Labs

Could this be the cause of 2015-2016 "breakthrough curve"?



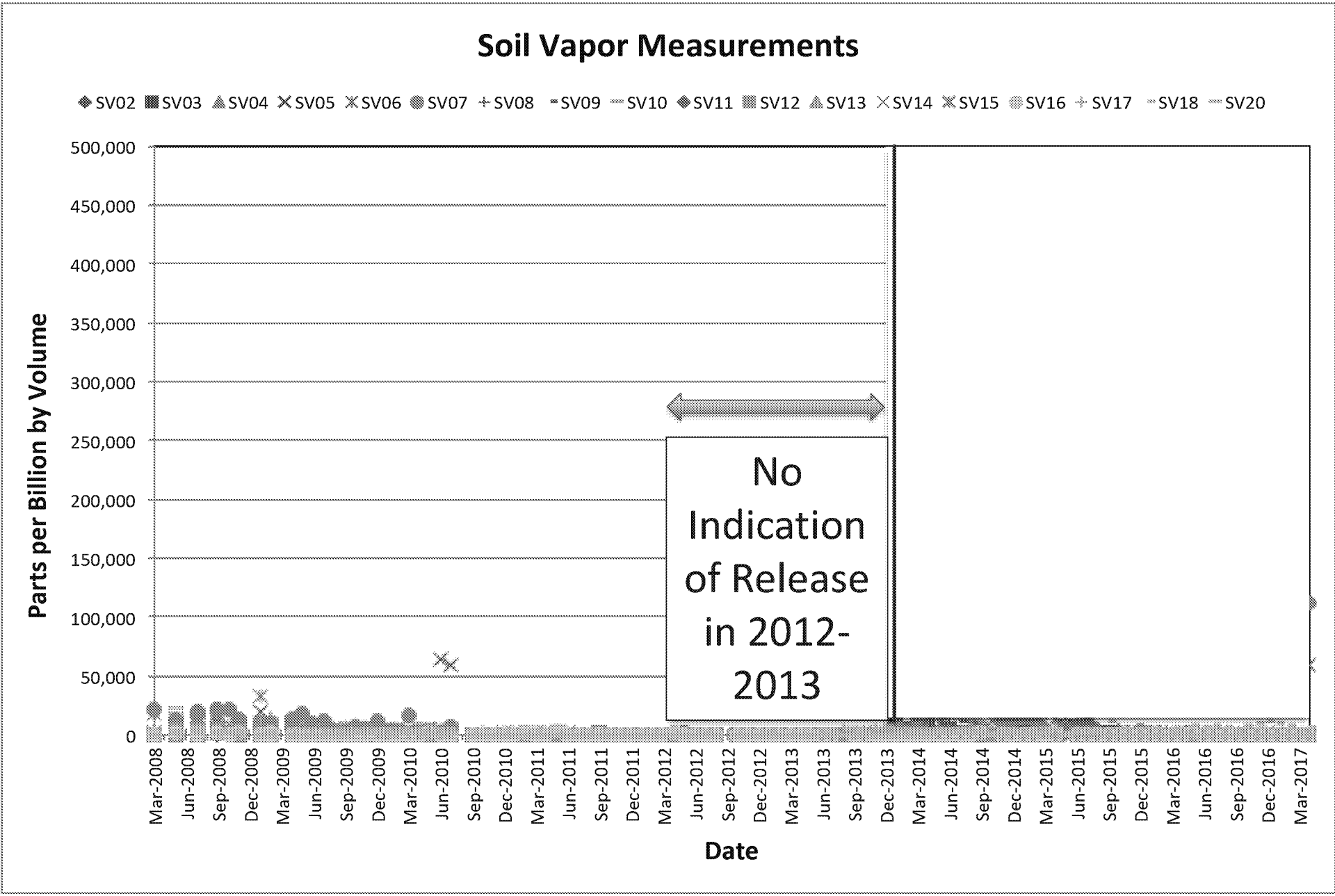
Key Point: Apparent spike in 2015 coincides with a lab change

LOE 7: TPH-D Chromatograms Naphthalene Ratios for Selected Samples



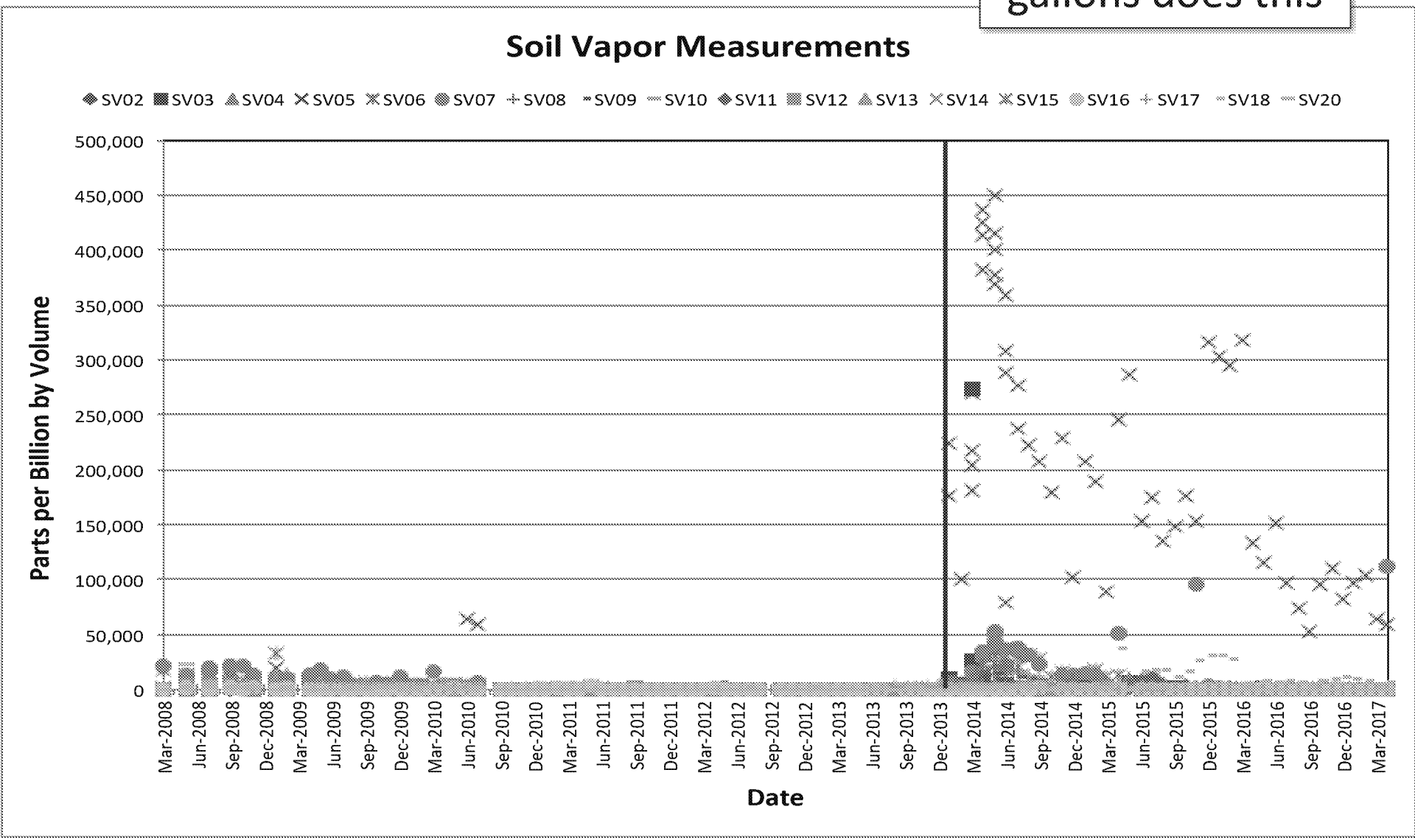
Key Point: Chromatographic profiles and naphthalene ratios show weathered material regardless of concentration changes

LOE 8: Soil Vapor Data



LOE 8: Soil Vapor Data

But 27,000 gallons does this



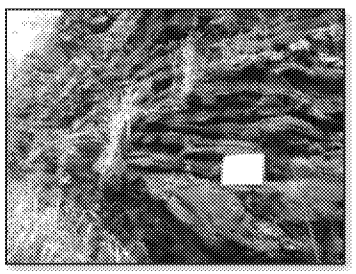
Key Point: LNAPL from 2014 release likely confined to area immediately surrounding Tank 5.

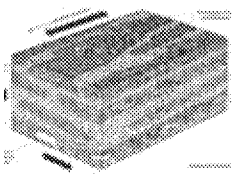
SUMMARY OF LINES OF EVIDENCE: EVALUATION OF DISSOLVED-PHASE CONSTITUENTS AND SOIL VAPOR

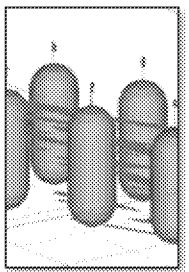
LOE	Description	Key Point	Assessment of LNAPL Impacts
LOE 1	RHMW02 Xylene Data	No significant changes in Xylenes after 2014 release	Not Apparent
LOE 2	RHMW02 Benzene Data	No significant changes in Benzene after 2014 release	Not Apparent
LOE 3	RHMW02 Ethylbenzene Data	No significant changes in Ethylbenzene after 2014 release	Not Apparent
LOE 4	RHMW02 Toluene Data	No significant change in Toluene after 2014 release	Not Apparent
LOE 5	RHMW02 TPH-g Data	No significant change in TPH-g after 2014 release, some variability coincides with lab changes and method variability, not unexpected for TPH measurements	Not Apparent
LOE 6	RHMW02 Naphthalenes and Naphthalene Ratios	Ratios of 1+2 Methylnaphthalenes to Naphthalene < 2 indicate a weathered source. Imprecision in Naphthalene results have been observed in previous data validation reports	Not Apparent
LOE 7	• TPH-d Lab changes • TPH-d Chromatograms naphthalene ratios for selected samples	• Variability for TPH-d from lab to lab precludes reliable trend analyses • Chromatographic profiles and naphthalene ratios show weathered material regardless of concentration changes	Unreliable Not Apparent
LOE 8	Soil Vapor Data	LNAPL from 2014 release confined to area immediately surrounding Tank 5	Not Apparent

➢ *The Navy's assessment of groundwater analytical data currently indicate that strictly weathered material are present in groundwater, and COPC concentrations have generally remained within recent historic ranges.*

RHMW04 ANALYTICAL ISSUES







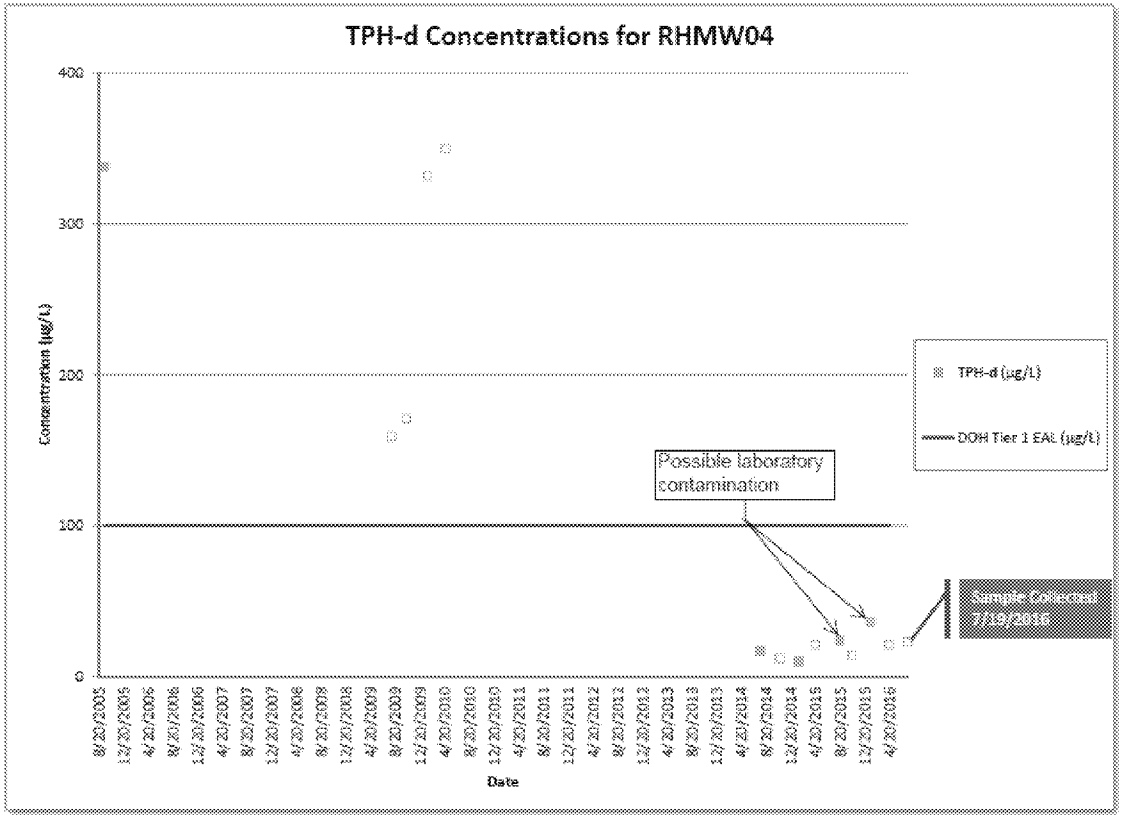
RHMW04 – ANALYTICAL ISSUES

- Past groundwater chemistry data may have been affected by various sampling and analytical issues
- These issues need to be considered when evaluating the data

RHMW04 ANALYTICAL ISSUES

Reviewed available lab and quarterly reports that include results from analysis of samples from RHMW04:

- **No** evidence that supports that this well is impacted by petroleum hydrocarbons
- Known issues related to TPH-d lab analyses
- The initial TPH-d result is an outlier and could be due to contamination from drilling or could be an analytical artifact

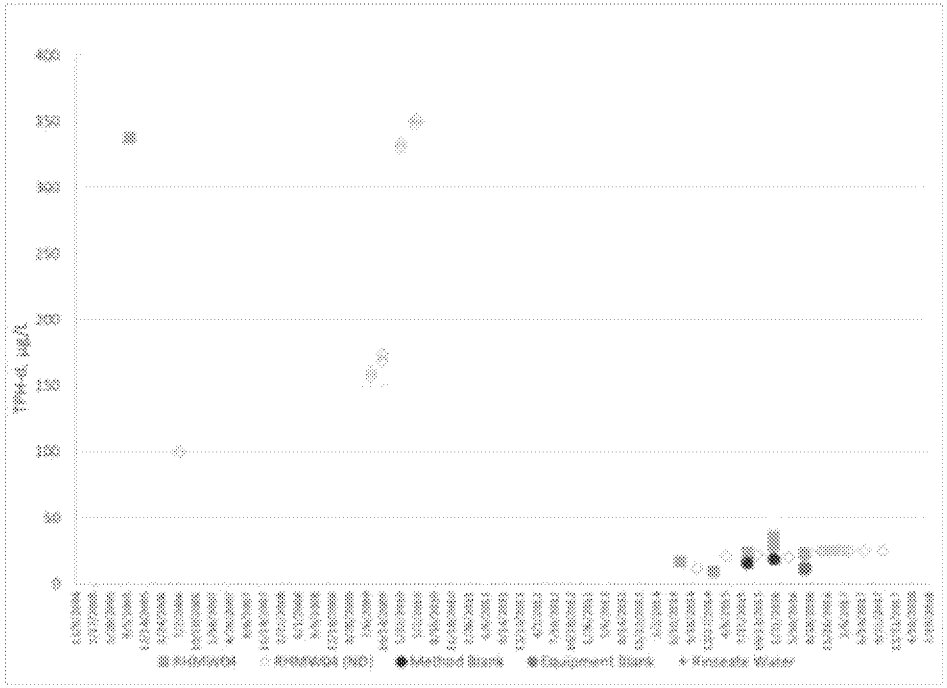


Unfilled boxes indicate non-detections. Several sample results had a chromatographic pattern that did not match the calibration standard. Possible laboratory contamination for 8/20/2015 and 1/19/2016 sampling events

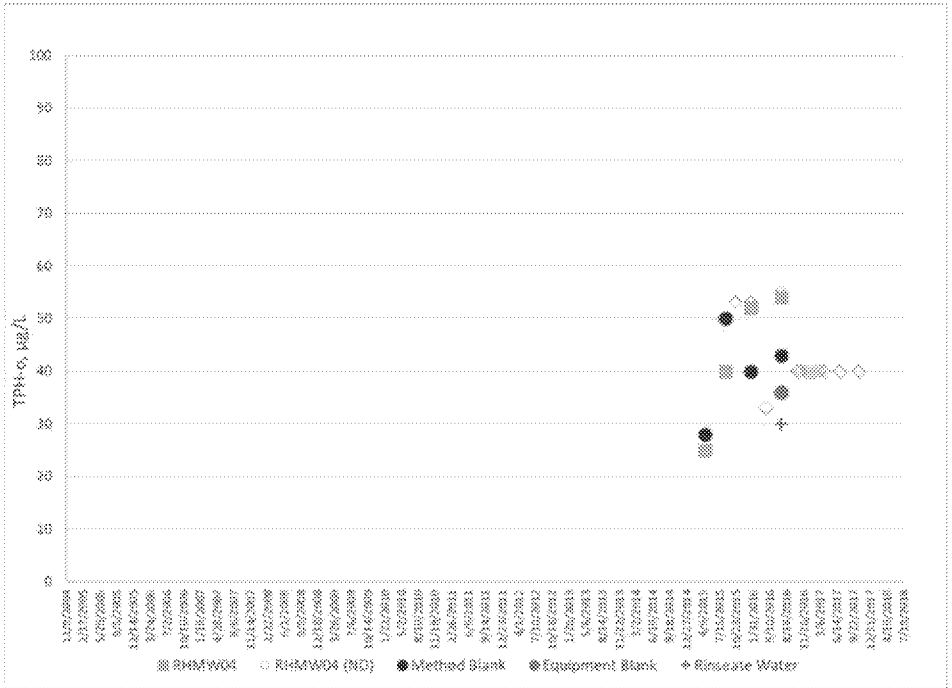
- Very few COPCs reported, most below quantitation limits and many also found in corresponding lab and field blanks indicating potential sample contamination. These few instances coincided with analysis at a laboratory with unusually low reporting concentration levels

TPH QUALIFIERS – RHMW04

TPH-d



TPH-o



After 1/2015
Limit of Quantitation: ~50 µg/L
Limit of Detection: ~20-25 µg/L
Detection Limit: ~11 µg/L

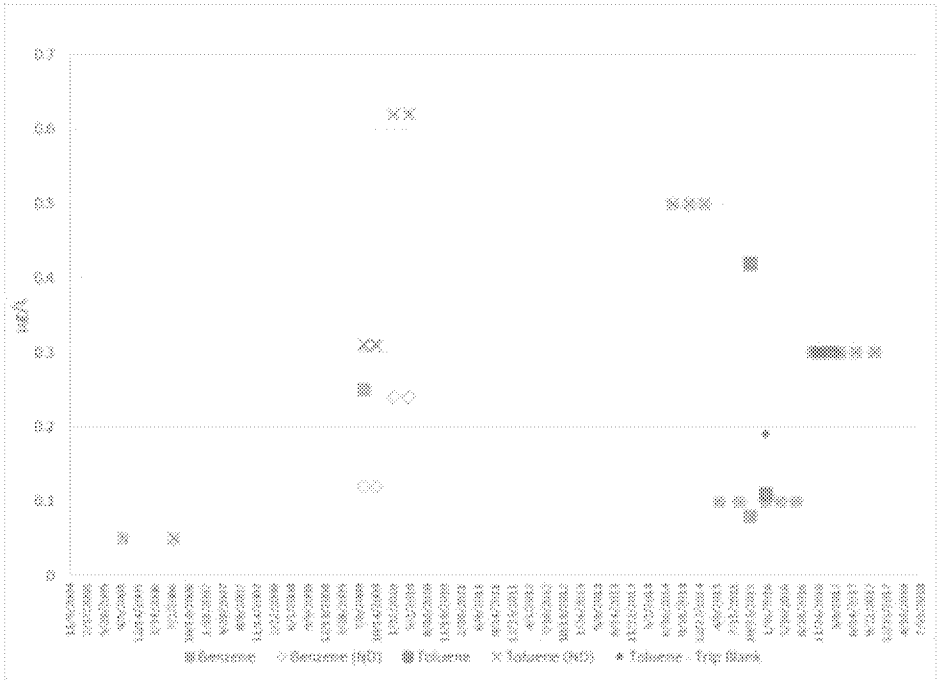
Limit of Quantitation: ~100 µg/L
Limit of Detection: ~40-50 µg/L
Detection Limit: ~20 µg/L

TPH-d and TPH-o Observations:

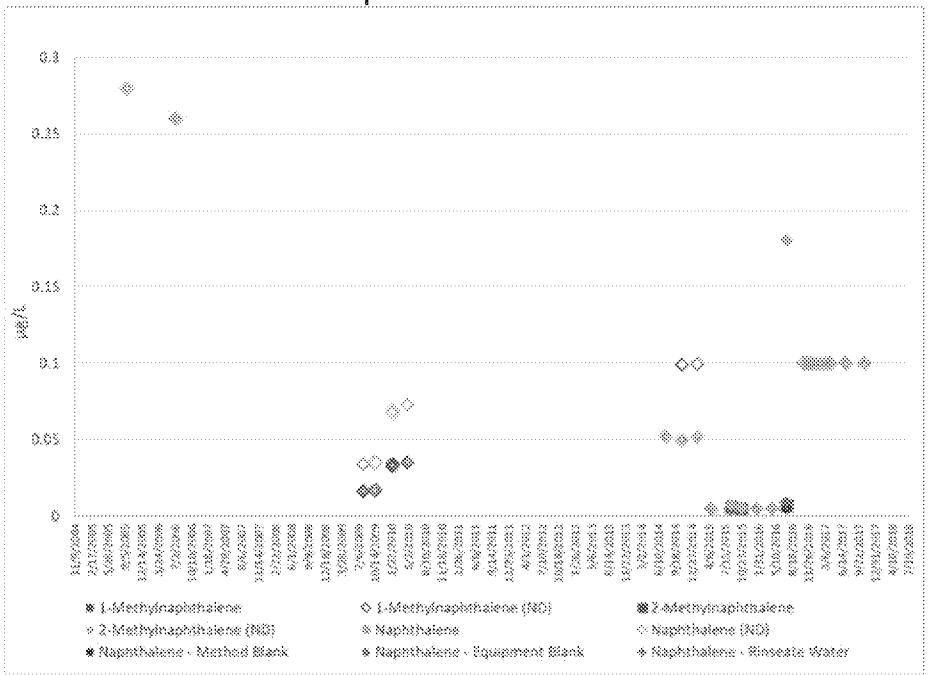
- TPH-d typically not detected or if detected, also in lab method blanks and/or field blanks
- All results are below quantitation limits and are estimates (J flagged)
- Any reported results after mid 2014 are unreliable for trend analyses

BENZENE, TOLUENE AND NAPHTHALENES – DATA QUALIFIERS

Benzene and Toluene



Naphthalenes



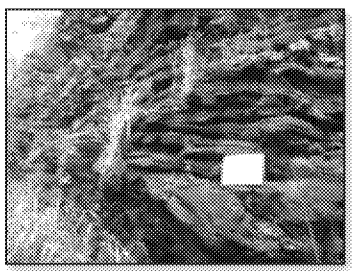
4/2015 to 7/2016
Limit of Quantitation: 0.5 µg/L
Limit of Detection: 0.1 µg/L
Detection Limit: 0.05 µg/L

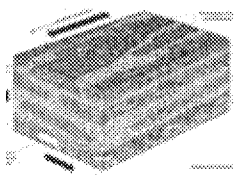
4/2015 to 7/2016
Limit of Quantitation: 0.020 µg/L
Limit of Detection: 0.0050 µg/L
Detection Limit: 0.0038 µg/L

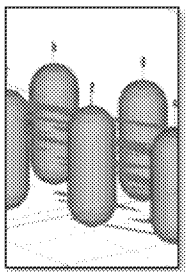
Observations:

- Benzene and Toluene are typically not detected. Some detections are questionable because toluene was also detected in the trip blank at a higher concentration than in the corresponding sample
- All results (except for one for naphthalenes) are below quantitation limits and are estimates (J flagged)
- Any reported results between 4/2015 and 7/2016 are from analysis with lower reporting limits (extremely low for naphthalenes)

CONSERVATIVE SCENARIO EVALUATIONS: LOW- AND HIGH-END ASSUMING HYPOTHETICAL SUDDEN RELEASES REACH GROUNDWATER







EVALUATION OF HYPOTHETICAL FUTURE SUDDEN RELEASES

Challenge: *In considering January 2014 Tank 5 release and current data to support modeling hypothetical future release scenarios, how do we address and account for uncertainty and conservatism regarding potential impacts to groundwater?*

SCENARIO 1: A hypothetical scenario with a leak volume range that does impact groundwater (previously discussed), but does not cause an exceedance of the screening criteria at Red Hill Shaft

- Use as basis for unsaturated zone holding capacity (previously presented approach)
- Evaluation now considers existing residual LNAPL

SCENARIO 2: A hypothetical scenario with a leak volume range where LNAPL impacts groundwater, but does not cause an exceedance at Red Hill Shaft (conservative environmental impact scenario)

- Utilize to evaluate assimilative capacity in GW and is protective of Red Hill Shaft

EVALUATION OF HYPOTHETICAL FUTURE SUDDEN RELEASES

SCENARIO 2: ASSUME LNAPL MIGRATION TO GROUNDWATER

Goal: Evaluate hypothetical future release scenarios protective of Red Hill Shaft

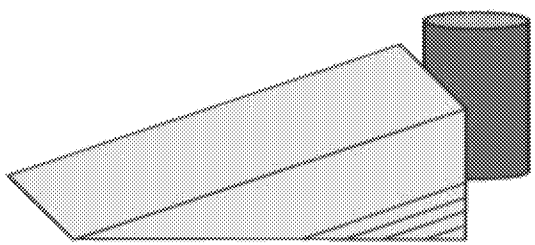
1) Use of Red Hill Shaft monitoring data to evaluate impacts associated with Tank 5 release

2) Use data to develop conservative low-end and conservative high-end hypothetical future release volume protective of Red Hill Shaft

HYPOTHETICAL SCENARIOS FOR INPUT TO TUA DECISION: SCENARIO DIFFERENCES

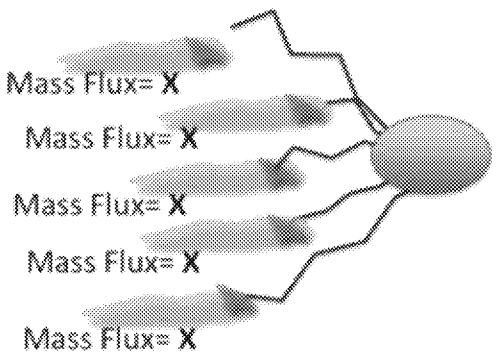
SCENARIO 1

- Calculates holding capacity
- Focuses on hypothetical release from Tanks 1 and 2
- Uses 2014 Tank 5 release to determine specific retention of basalt
- Utilizes geologic zone properties, i.e. clinker and pahoehoe
- Accounts for prior releases
- Accounts for ~11° geologic dip
- Uses a statistical approach



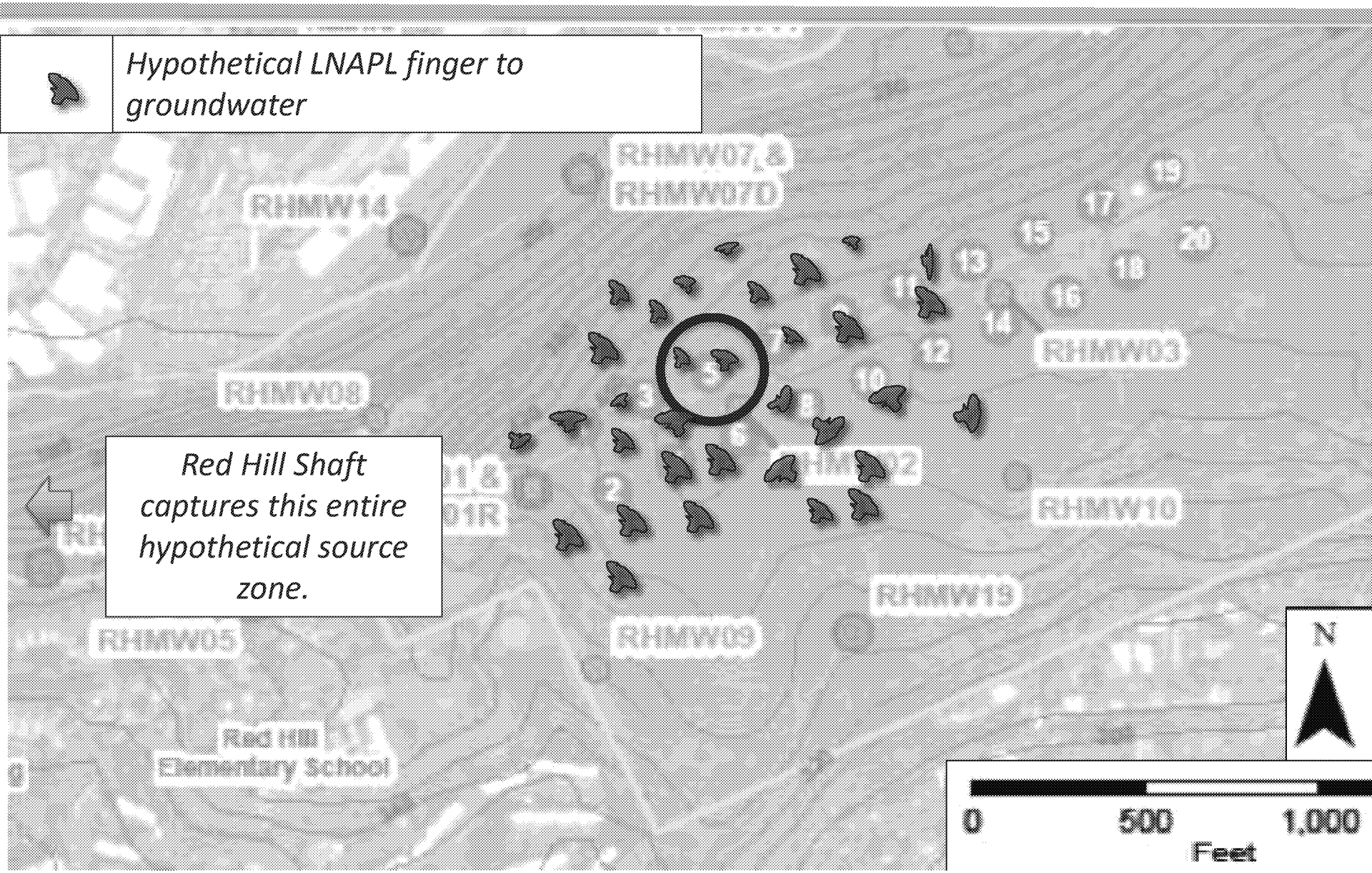
SCENARIO 2

- Assumes all LNAPL reaches GW; no holding capacity
- Mass flux approach
- Based on Red Hill Shaft napthalene concentrations post 2014 Tank 05 release
- No consideration of geology
- Heterogeneous distribution of LNAPL reaching groundwater



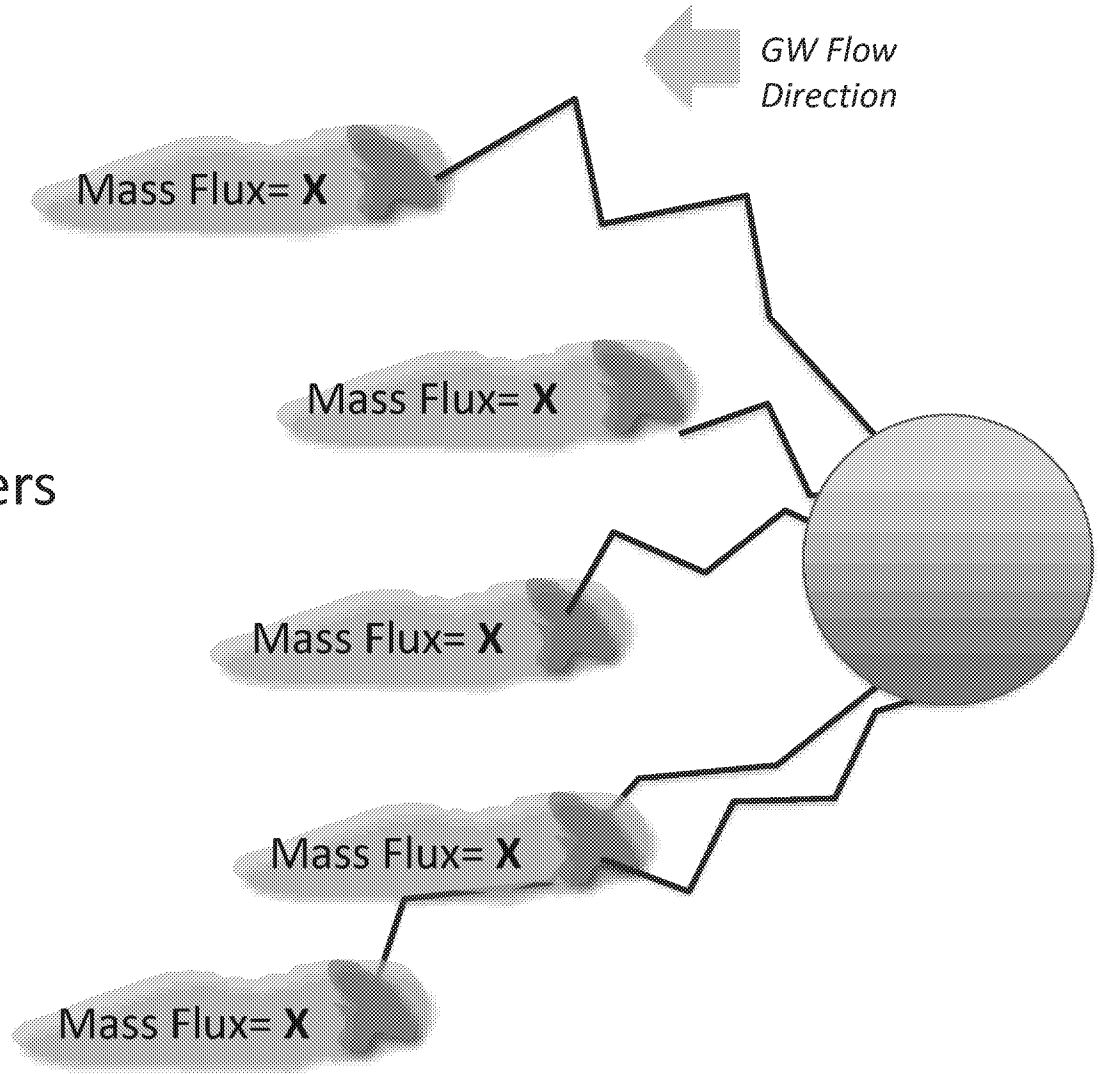
CONSERVATIVE HYPOTHETICAL SCENARIO 2

- Assume no holding capacity in unsaturated zone
- Assume all LNAPL reaches groundwater
- Assume heterogeneous distribution of LNAPL fingers that reach groundwater



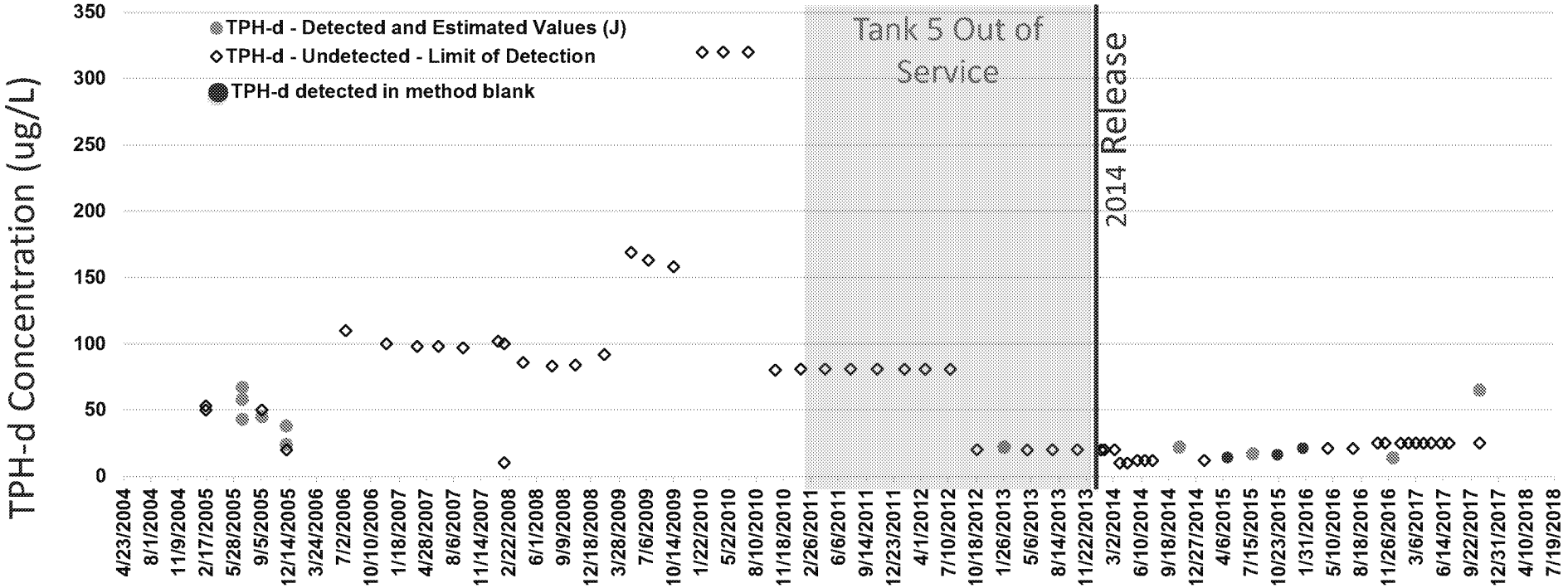
CONSERVATIVE HYPOTHETICAL SCENARIO 2: WHAT IF MULTIPLE LNAPL FINGERS REACHED GROUNDWATER?

Five New Jet Fuel Fingers
Reach Groundwater
Mass Flux= **5X**



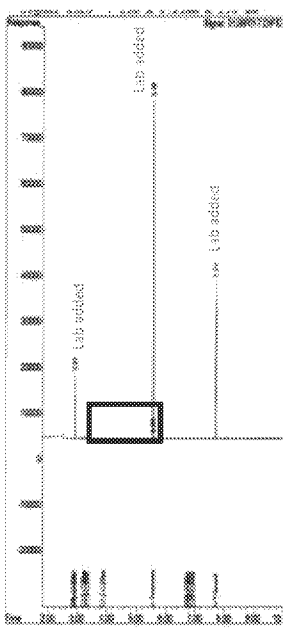
Five Hypothetical LNAPL Fingers

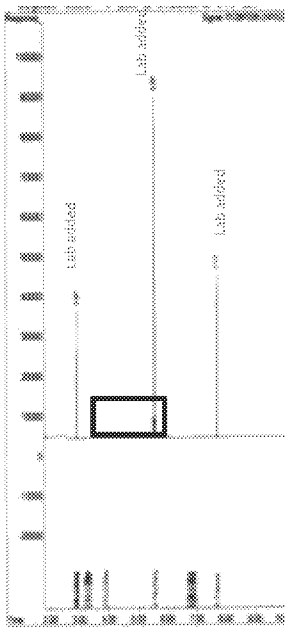
WAS THERE AN IMPACT AT RED HILL SHAFT?
TPH-D DATA AT RED HILL SHAFT

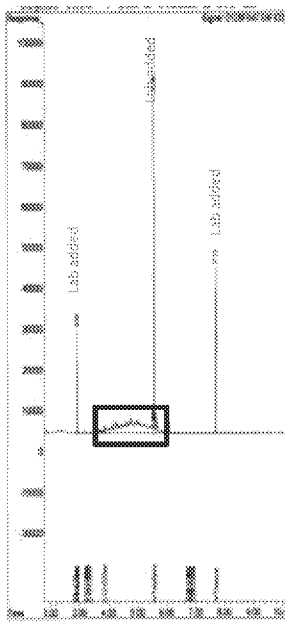


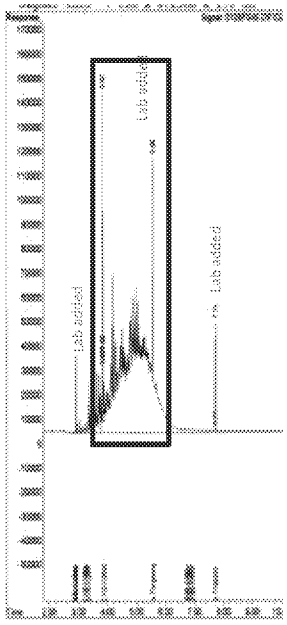
- RHMW2254-01 (Red Hill Shaft)
- Since TPH-d cannot be used for trend analyses, our focus was on Naphthalene

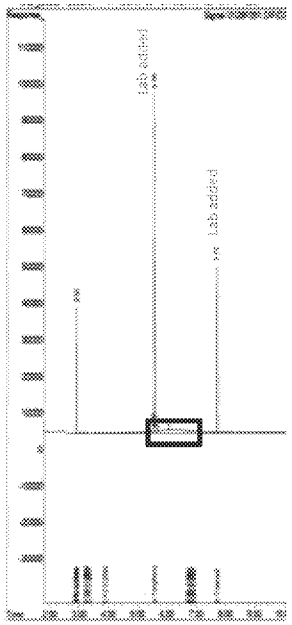
TPH-D DATA: JAN 2016 SAMPLING EVENT
LAB: COLUMBIA ANALYTICAL SERVICES (CAS) NOW ALS

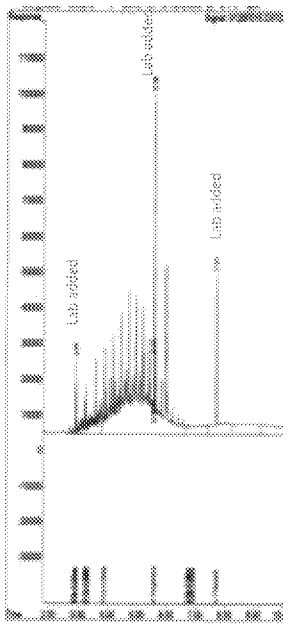












Method Blank
C10-C25 DRO: 22.4 (J) µg/L
C10-C28 DRO: 26.2 (J) µg/L
Diesel Range Organics (DRO): 29.1 (J) µg/L
Residual Range Organics: 39.9 (J) µg/L

Red Hill Shaft
Diesel Range Organics (DRO): 21 (BJ) µg/L
Residual Range Organics: 33 (BJ) µg/L

RHMW01
Diesel Range Organics (DRO): 430 (BY) µg/L
Residual Range Organics: 60(BJ) µg/L

RHMW02
Diesel Range Organics (DRO): 6500 (BY) µg/L
Residual Range Organics: 340 (BL)µg/L

RHMW03
Diesel Range Organics (DRO): 150 (BY) µg/L
Residual Range Organics: 160 (BL) µg/L

Diesel Calb. Std.
C10-C25 DRO: 2510 µg/L
C10-C28 DRO: 2620 µg/L
Diesel Range Organics (DRO): 2640 µg/L
Residual Range Organics: 1390 µg/L

Note: method blank shows same TPH-d levels as sample from Red Hill Shaft
...likely no TPH-d in Red Hill Shaft

Data Qualifiers/Flags
B: Analyte was present in the associated method blank
L, Y: The chromatographic pattern was inconsistent with the profile of the reference fuel standard

CONSERVATIVE HYPOTHETICAL SCENARIO 2: LOW-END SIZE OF THE LARGEST, SUDDEN RELEASE THAT WOULD NOT RESULT IN UNACCEPTABLE RISKS TO GROUNDWATER RECEPTORS

Risk Based Decision Criteria (RBDC)
for Naphthalene = **0.17 µg/L**

- **2013 Average = 0.062 ug/L**
- **2014 Average = 0.052 ug/L**
  (conservative assumption: use ND as actual value)

RHMW-2254-01
(Red Hill Shaft)

Date	Naphthalene (ug/L)
1/29/13	**0.052 J**
4/23/13	*<0.051*
7/23/13	**0.099 J**
10/22/13	**0.036 J**
01/16/2014	**0.046 J**
01/29/2014	**0.049 J**
03/6/2014	**0.081 J**
03/26/2014	*<0.050*
04/22/2014	*<0.049*
05/28/2014	*<0.050*
06/24/2014	*<0.049*
07/22/2014	*<0.048*
10/28/2014	*<0.049*

Key Points:
- Naphthalene did not exceed RBDC
- No indication of 2014 release at Red Hill Shaft

CONSERVATIVE HYPOTHETICAL SCENARIO 2: LOW-END SIZE OF THE LARGEST, SUDDEN RELEASE THAT WOULD NOT RESULT IN UNACCEPTABLE RISKS TO GROUNDWATER RECEPTORS

- **2013 Average = 0.0[illegible] ug/L**

- **2014 Average = 0.052 ug/L**
  (conservative assumption: use ND as actual value)

Date	Naphthalene (ug/L)
1/29/13	**0.052 J**
4/23/13	<0.[illegible]1
7/23/13	**0.095 J**
10/22/13	**0.036 J**
01/16/2014	**0.046 J**
01/29/2014	**0.049 J**
03/6/2014	**0.081 J**
03/26/2014	*<0.050*
04/22/2014	*<0.049*
05/28/2014	*<0.050*
06/24/2014	*<0.049*
07/22/2014	*<0.048*
10/28/2014	*<0.049*

Key Point:
To be ultra conservative assume 100% of 2014 concentration was from Tank 5 release.

CONSERVATIVE HYPOTHETICAL SCENARIO 2: LOW-END SIZE OF THE LARGEST, SUDDEN RELEASE THAT WOULD NOT RESULT IN UNACCEPTABLE RISKS TO GROUNDWATER RECEPTORS

- 2014 Release Volume: 27,000 gallons
- No exceedence of RBDC, no increase in concentrations

- What release volume would result in RBDC at Red Hill Shaft?
  - → 27,000 gallons: *No exceedence*
  - → 30,000 gallons? More?

Key Point: Plenty of holding capacity, attenuation, not close to exceedence even under conservative assumptions

CONSERVATIVE HYPOTHETICAL SCENARIO 2 – LOW-END SIZE OF THE LARGEST, SUDDEN RELEASE THAT WOULD NOT RESULT IN UNACCEPTABLE RISKS TO GROUNDWATER RECEPTORS

- Take Ratio of Ultra Conservative Naphthalene Concentration to RBDC
- Multiply by 27,000 gallons

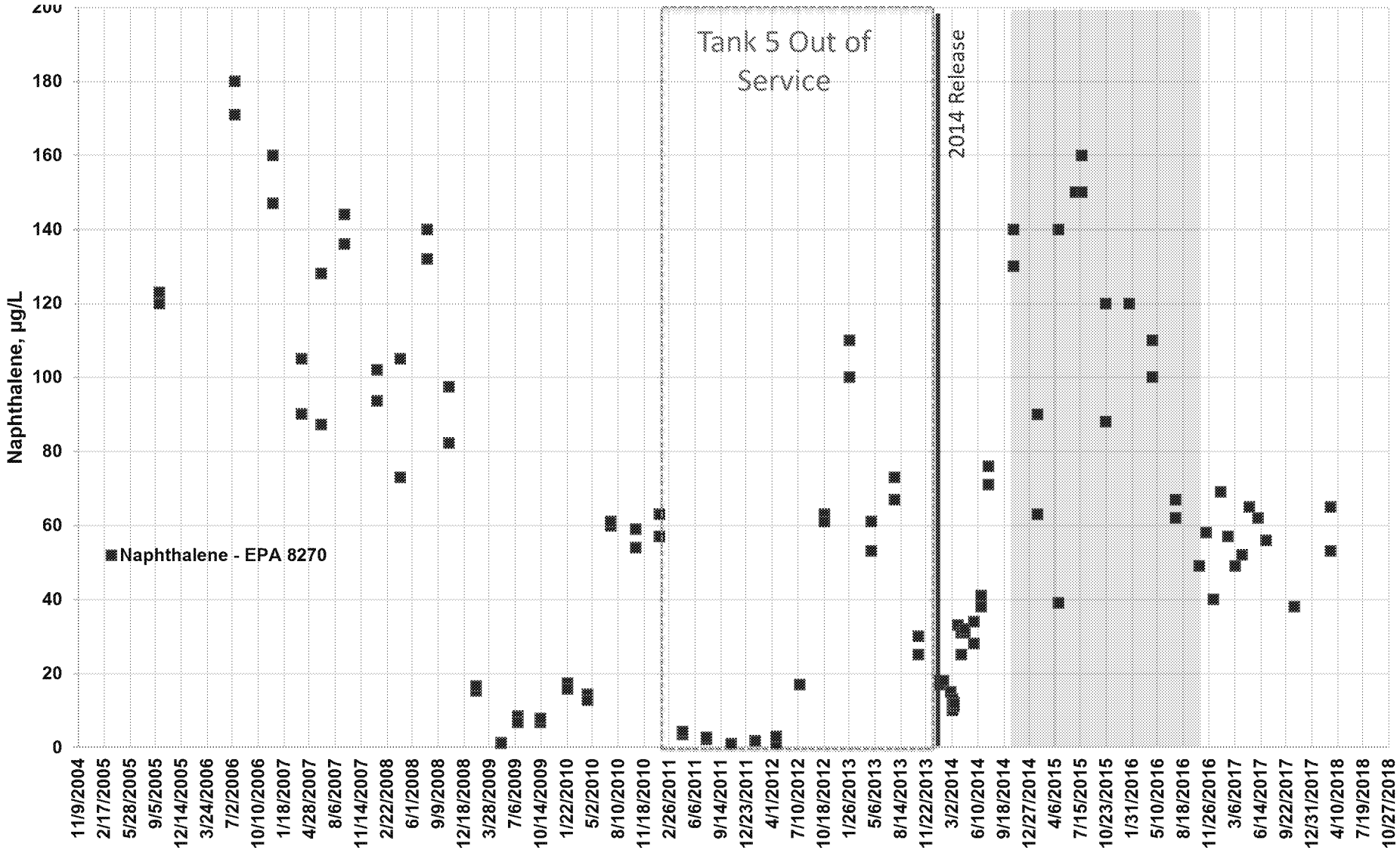
→ RBDC ÷ $C_{avg\ 2014}$ = 0.17 ÷ 0.052 = 3.3 times

→ 3.3 x 27,000 gallons: 88,000 gallons

Extremely Conservative Scenario (Unlikely)
Low End Sudden Release Volume = 88,000 gallons

RHMW02 Naphthalene Data:

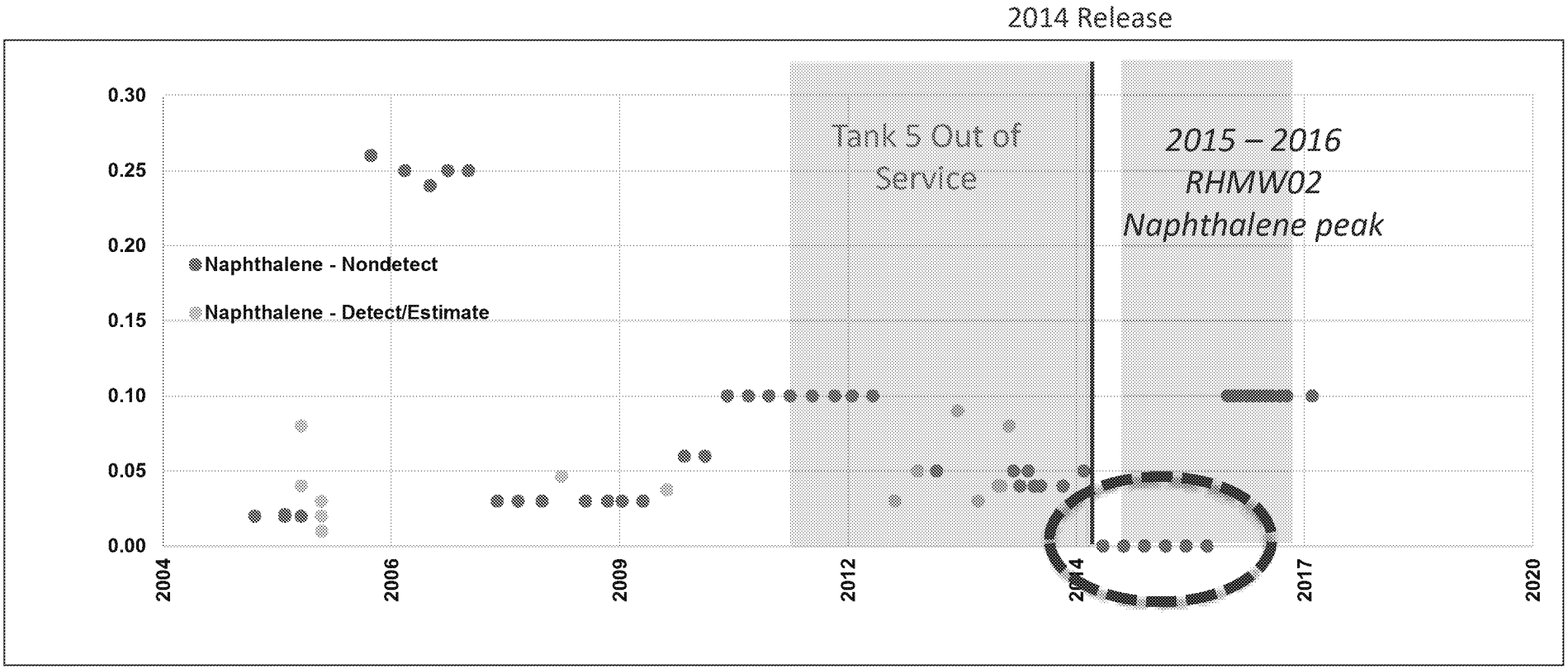
Apparent Breakthrough Curve Peaks in 2015-2106



- The naphthalene ratio was still indicative of a weathered fuel (not a new release)
- Issues with multiple labs

CONSERVATIVE HYPOTHETICAL SCENARIO 2: HIGH-END WAS THERE AN IMPACT AT RED HILL SHAFT?

- **Same "Breakthrough Curve" time period at Red Hill Shaft: Naphthalene is all ND**



QA/QC issues with samples from Red Hill Shaft as previously discussed

CONSERVATIVE SCENARIO – HIGH END

- **This 2015-2016 peak was evaluated at Red Hill Shaft**

Date	Naphthalene Concentration at Red Hill Shaft (µg/L)
4/21/2015	ND <0.005
7/21/2015	ND <0.005
10/20/2015	ND <0.005
1/20/2016	ND <0.005
4/20/2016	ND <0.005
7/20/2016	ND <0.005

- **The average concentration from April 2015-July 2016: <0.0050 µg/L (Using concentration is at detection level is conservative assumption)**
- **The Action Level is 34 times larger than the average during the peak**

  → 34 x 27,000 gallons = 918,000 gallons

Least Conservative Maximum Release Volume = 918,000 gallons

EVALUATION OF HYPOTHETICAL FUTURE SUDDEN RELEASES: INITIAL ANALYSIS (SUBJECT TO CHANGE)

Challenge: *In considering January 2014 Tank 5 release and current data to support modeling hypothetical future release scenarios, how do we address and account for uncertainty and conservatism regarding potential impacts to groundwater?*

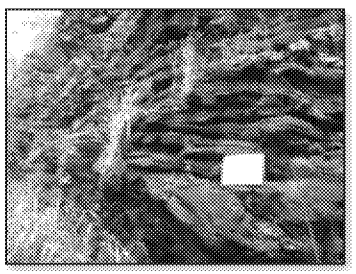
SCENARIO 1: A hypothetical scenario with a leak volume range that does impact groundwater (previously discussed), but does not cause an exceedance of the screening criteria at Red Hill Shaft

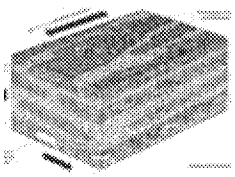
- **Based on unsaturated zone holding capacity and leak location**
- **Low End Analysis:** 65,000 gallons
- **High End Analysis:** 840,000 gallons

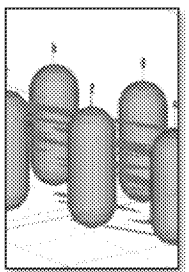
SCENARIO 2: A hypothetical scenario a leak volume range where LNAPL impacts groundwater, but does not cause an exceedance at Red Hill Shaft (conservative environmental impact scenario)

- **Based on Red Hill Shaft data and observed assimilative capacity in groundwater**
- **Assumes no holding capacity in unsaturated zone**
- **Low End Analysis:** 88,000 gallons
- **High End Analysis:** 920,000 gallons

SUPPLEMENTAL SLIDES







DOD CONTROL LIMITS FOR TPH

Appendix C: Laboratory Control Sample (LCS) Control Limits and Requirements

- DoD Environmental Data Quality Workgroup (EDQW) - LCS study - summer of 2012
  - Incorporated the contributions from approximately 50 DoD ELAP and DOECAP accredited/approved laboratories
  - In all, 6.5 million records were analyzed, and LCS limits were set for 23 methods and approximately 1,280 matrix-method-analyte combinations
  - Control limits were calculated as the sample mean (percent recovery) ± 3 sample standard deviations.

Table C-14. Method 8015 (MOD) Water Matrix in Percent

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
303-04	Diesel Range Organics (DRO)	1757	83.7	16	36	132
307-27	Gasoline Range Organics (GRO)	971	99.9	7.3	78	122
307-51	Motor Oil	573	76.9	12.1	41	113

DoD Quality Systems Manual Version 5.1 DOE Quality Systems for Analytical Services Version 3.1, 2017

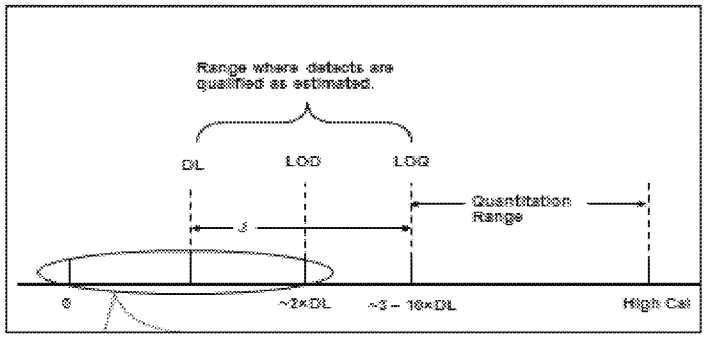
REPORTING CRITERIA FOR DOD QSM

HTTP://WWW.DENIX.OSD.MIL/EDQW/DOCUMENTS/DOCUMENTS

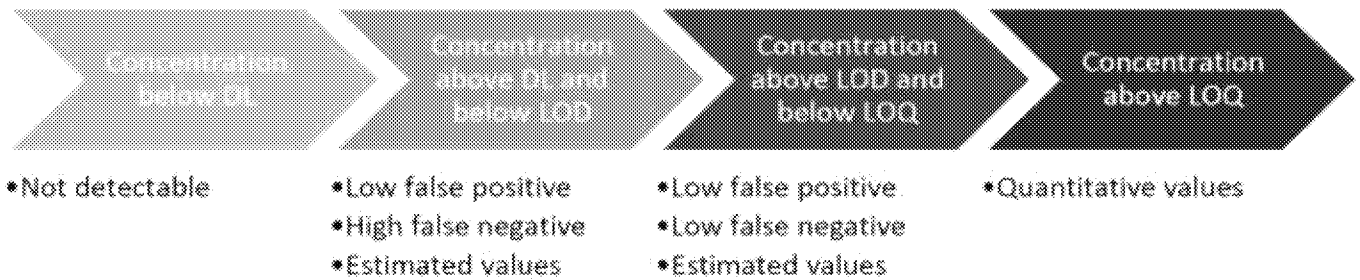
- Report the ND value to the LOD and to report a detect to the MDLs (for detects)
- Report LODs (for non-detects).

Example - TPH-d:
LOQ=50 µg/l, LOD=20 µg/L and MDL=10 µg/L
For a sample has no detection at all, it will be reported at <20 µg/L with "U" flag
If a sample has 12 µg/L, even though it is well below the LOQ and LOD, it will be reported as 12 µg/L with "J" flag

DL < LOD < LOQ



Summary of data quality characteristics below and above DL, LOD, and LOQ



Definitions:

Detection Limit (DL): The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration with 99% confidence. At the DL, the false positive rate (Type I error) is 1%. A DL may be used as the lowest concentration for reliably reporting a detection of a specific analyte in a specific matrix with a specific method with 99% confidence.

Limits of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%. A LOD may be used as the lowest concentration for reliably reporting a non-detect of a specific analyte in a specific matrix with a specific method at 99% confidence.

Limits of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias. For DoD/DOE projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the calibration range.