Forensic Identification and Quantification of Oil Sands-Based Bitumen Released Into a Complex River Environment The Kalamazoo River Oil Spill

National Environmental Monitoring Conference – Forensic Chemistry

NewFields

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"The views expressed herein do not necessarily represent the views of the U.S. EPA or the United States."

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The objective of this work was to develop a scientifically defensible approach for the identification and quantification of Line 6B oil (DILBIT) in discrete Kalamazoo River sediment samples after the Line 6B Oil Spill on July 26, 2010.

Spill Zone

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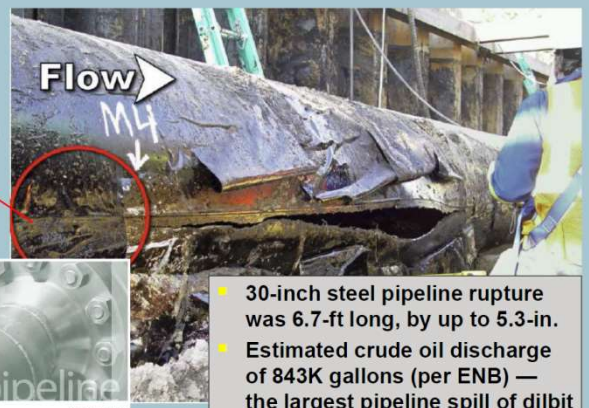
Enbridge Line 6B Incident Site



- 30-inch steel pipeline rupture was 6.7-ft long, by up to 5.3-in.
- Estimated crude oil discharge of 843K gallons (per ENB) — the largest pipeline spill of dilbit into inland U.S. waters.

KALAMAZOO
DIVISION E
MORROW LAKE
DIVISION D
BATTLE CREEK
DIVISION C
MARSHALL
DIVISION B
DIVISION A
Talmadge Creek

FOR OFFICIAL USE ONLY

N W E S
0 0.4 0.8 1.6 Miles

Prepared for:
U.S. EPA REGION V
Contract No.: EP-S5-06-04
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KALAMAZOO RIVER/ENBRIDGE SPILL OVERVIEW MAP - 08/06/2010
MARSHALL OIL ER
MARSHALL, KALAMAZOO AND CALHOUN COUNTIES, MICHIGAN
CREATED: AUGUST 6, 2010

File: \\10.1.1.5\planning\epa_share\gis_data\Marshall_Oil_ER\GIS\MXD\20100806\Overview_Map_20100806.mxd, 06-Aug-10 10:51, Dell

DILBIT Sank To Sediments

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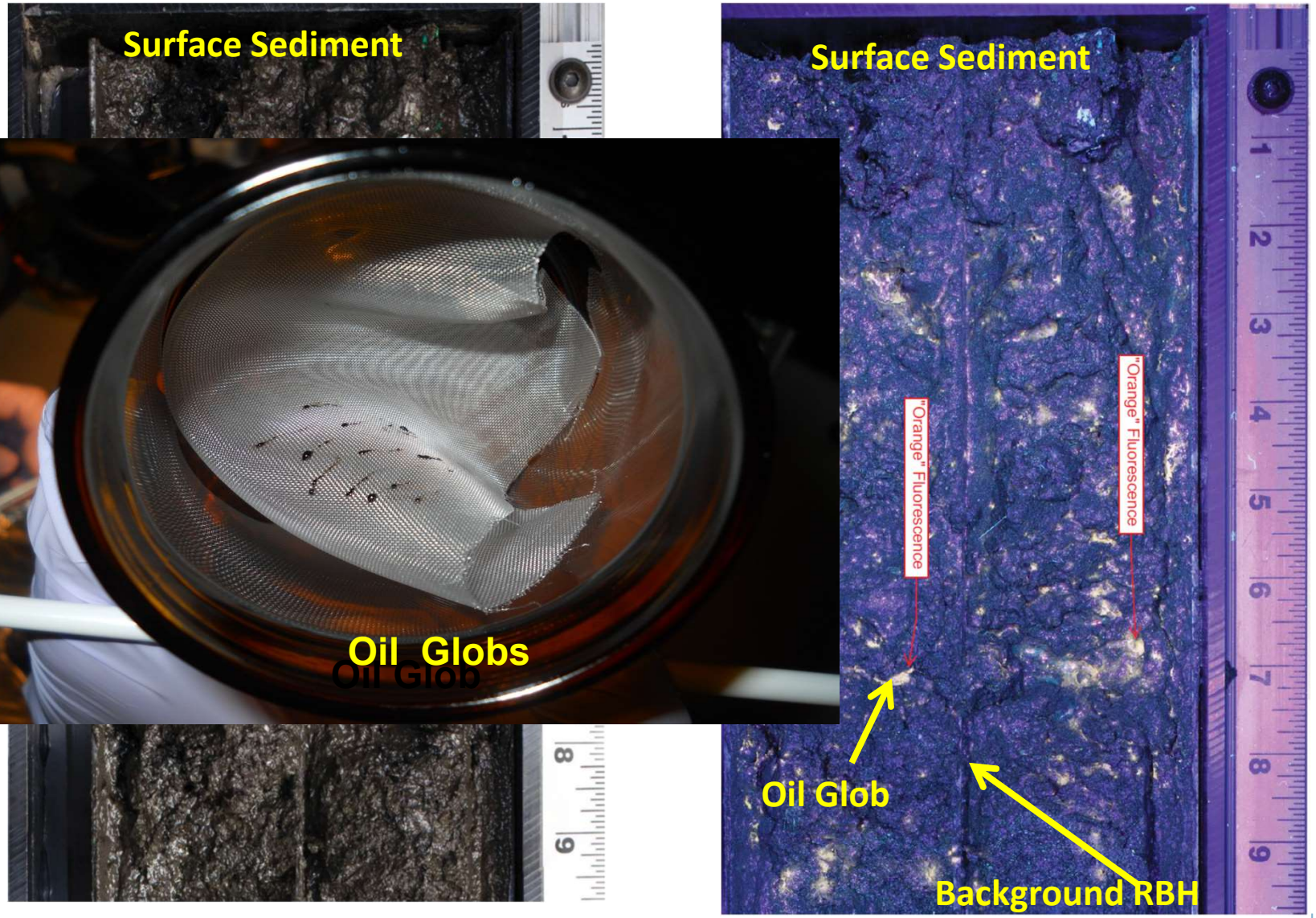
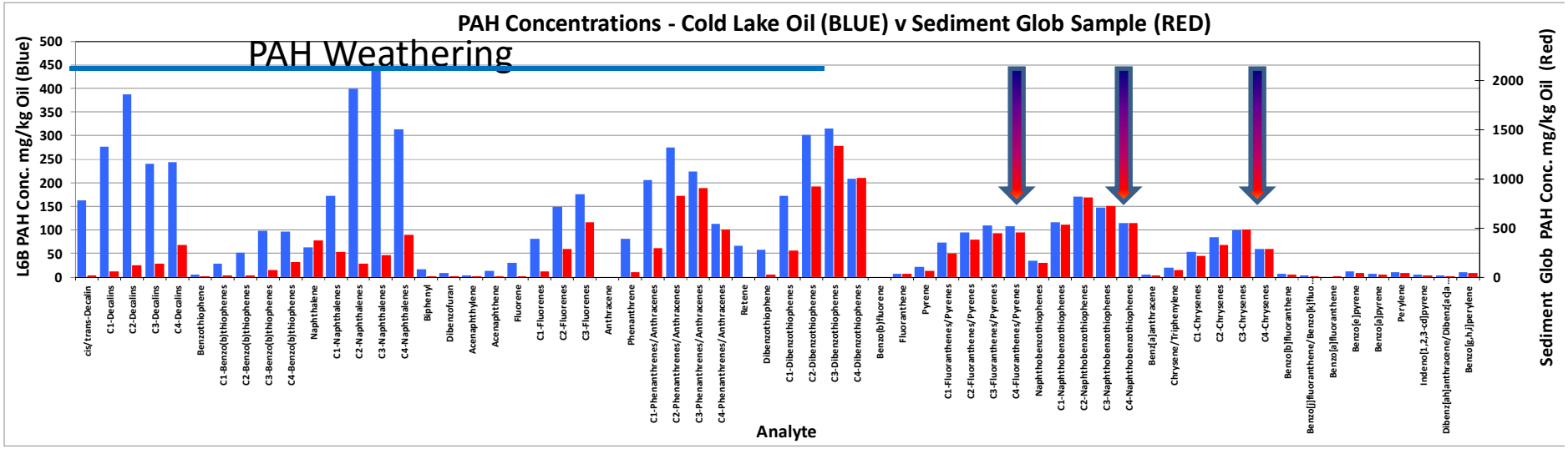
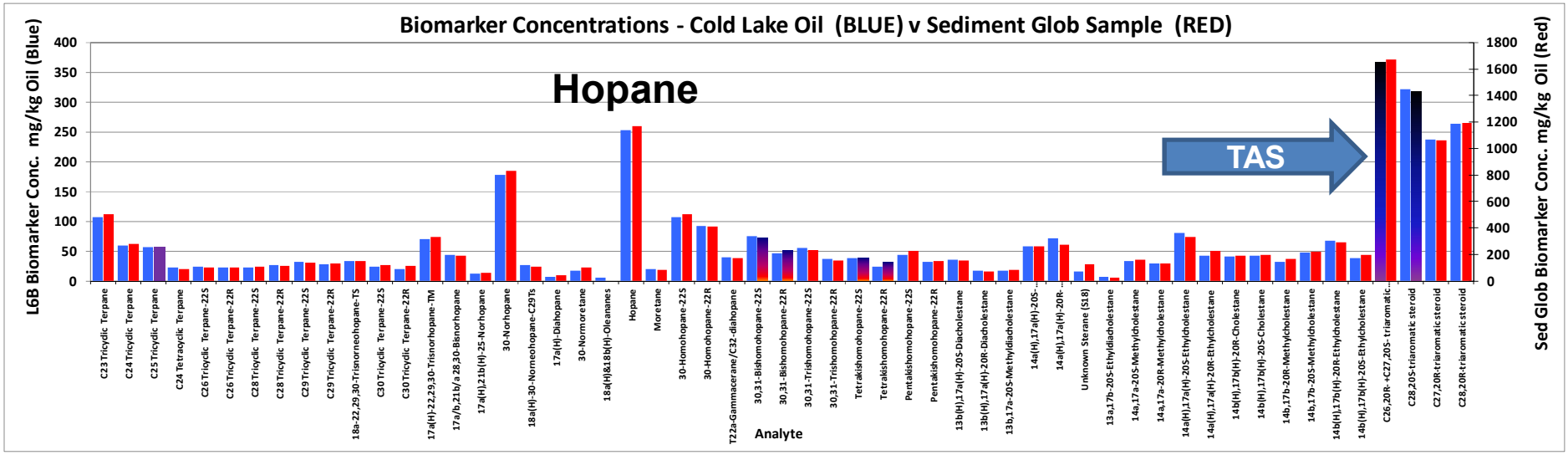
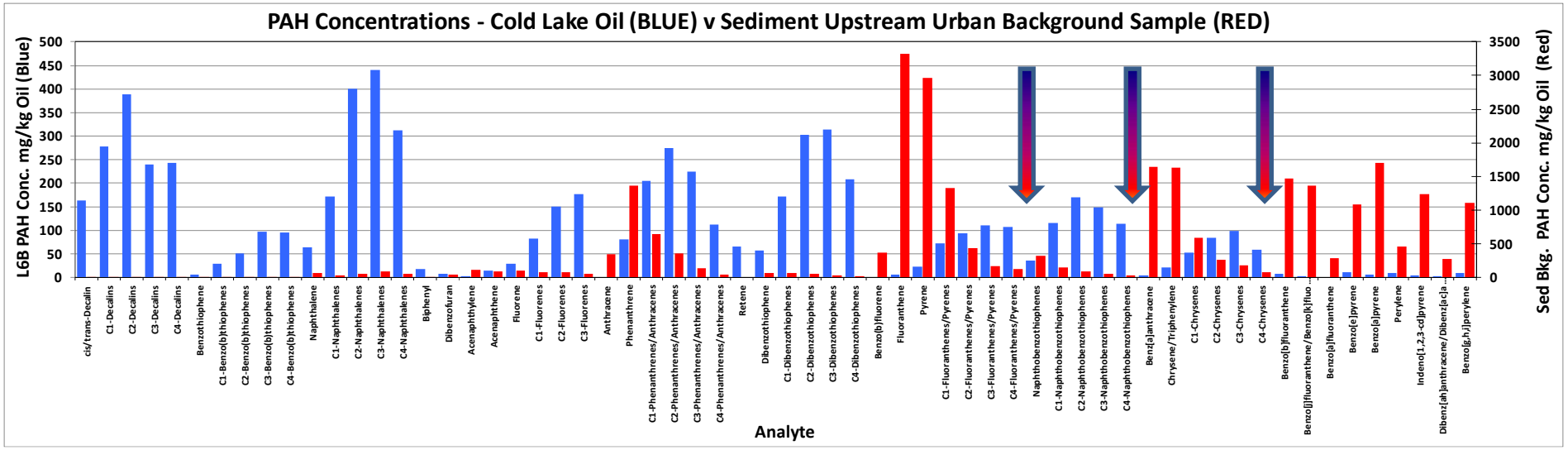


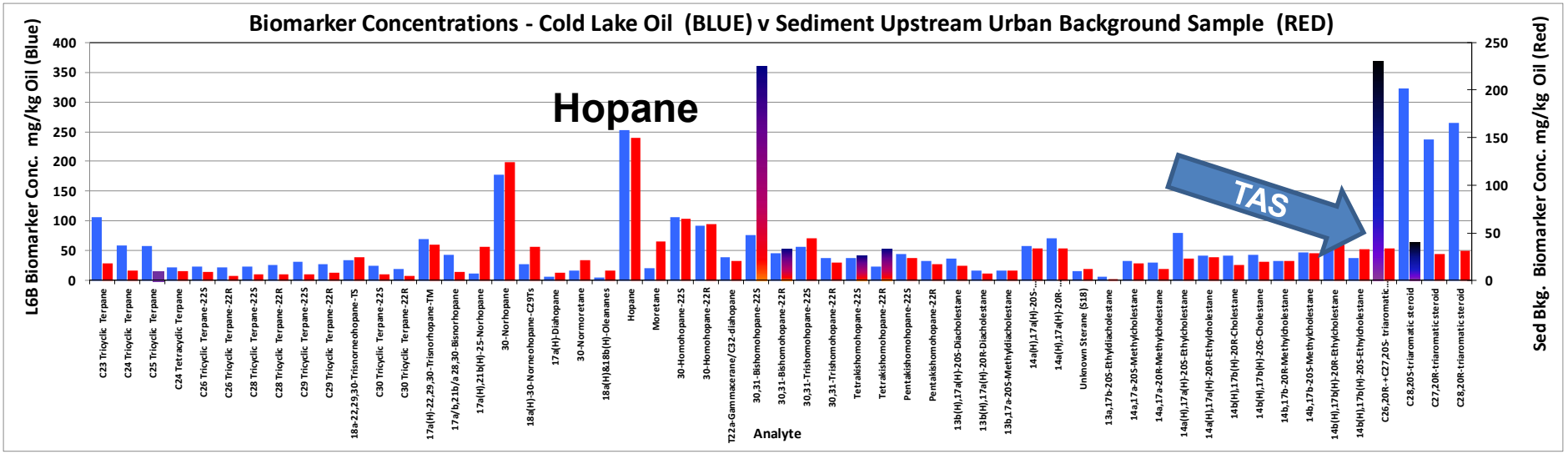
Chemistry of Spilled Line 6B Oil



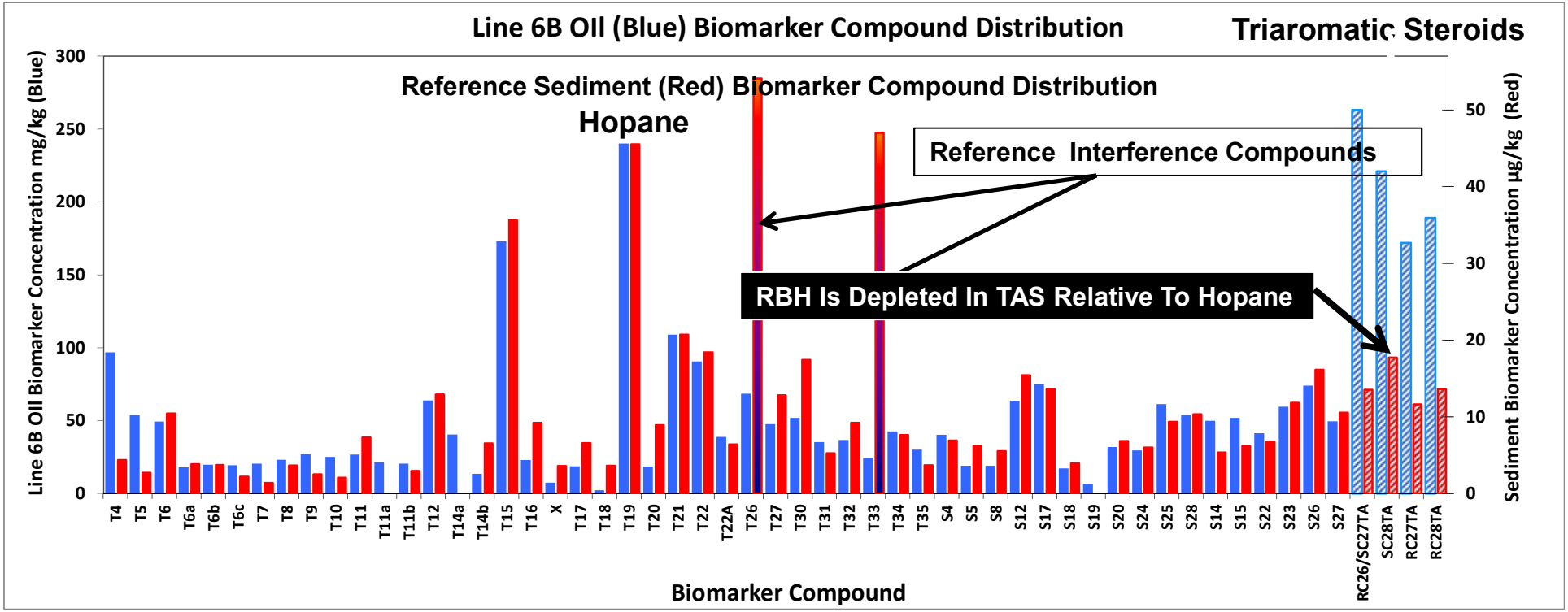


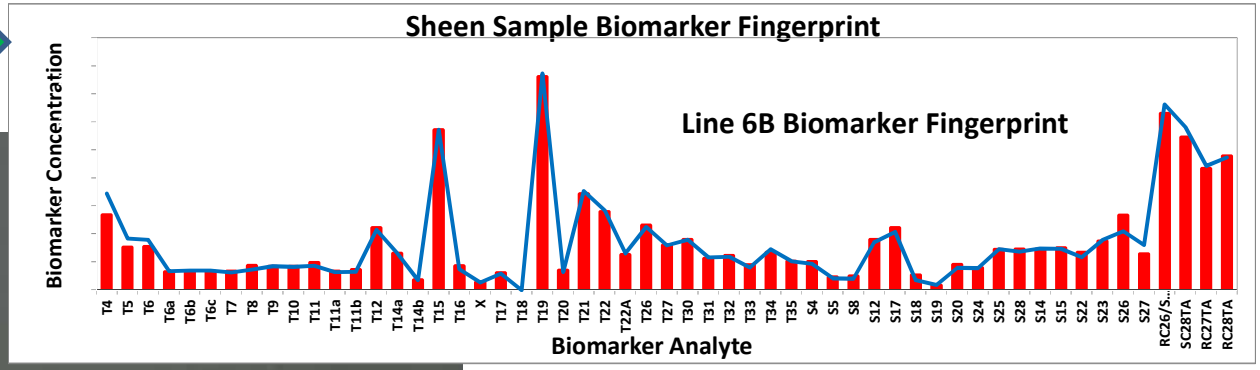
Chemistry of Background

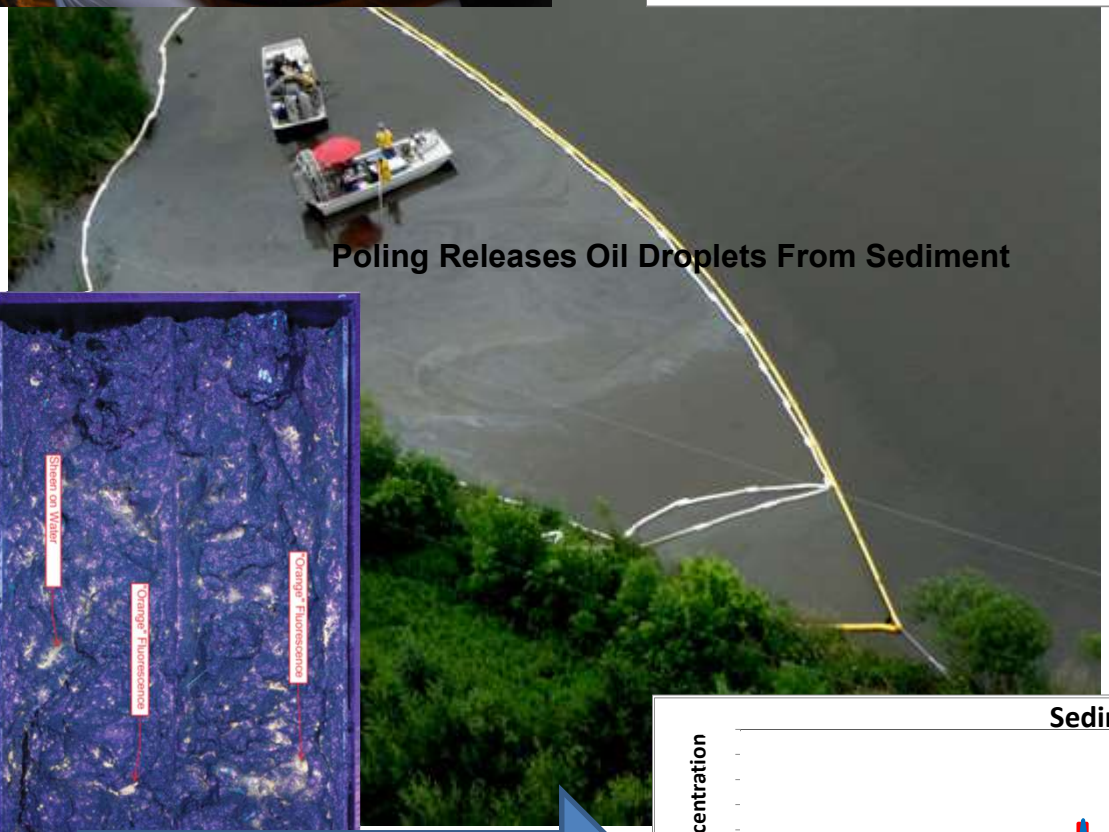




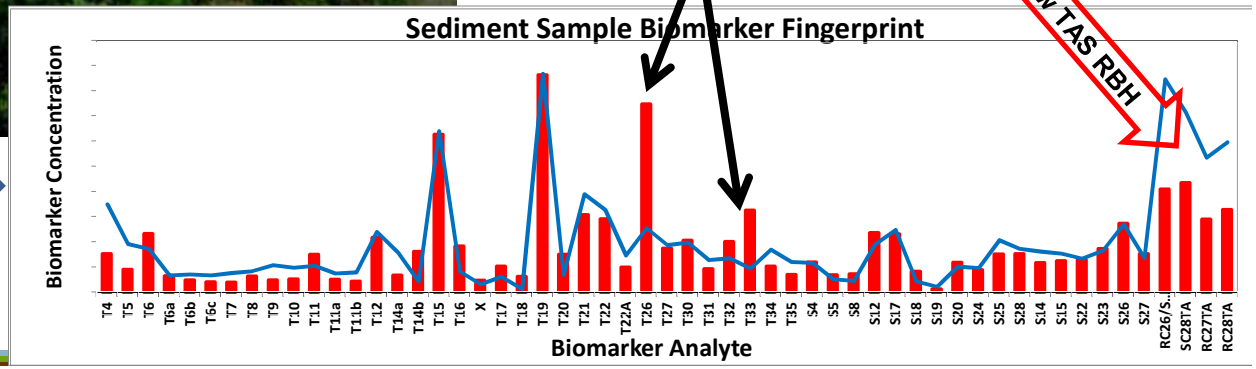
Biomarker Patterns Used To Identify RBH And Quantify Line 6B



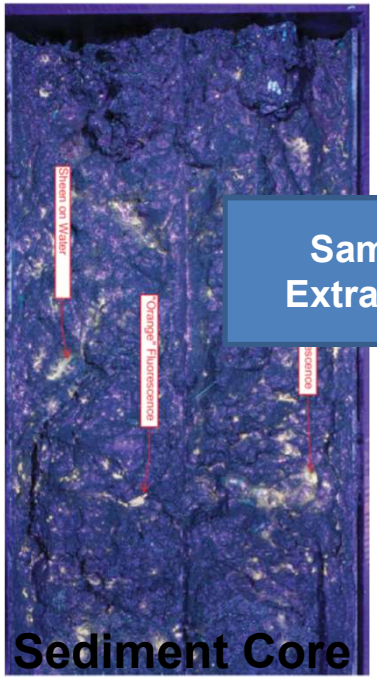




Because of the of physical/chemical properties of DILBIT poling releases Line 6B oil from the sediment matrix where it is collected with a sheen sampling net. This whole oil sample is then analyzed without the sediment background interferences and Line 6B is identified with a high degree of confidence.



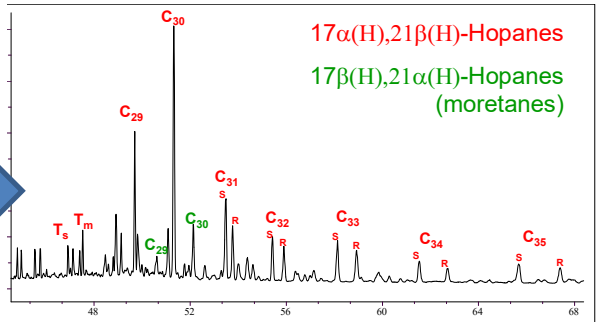
Final Technical Approach



Sample Extraction

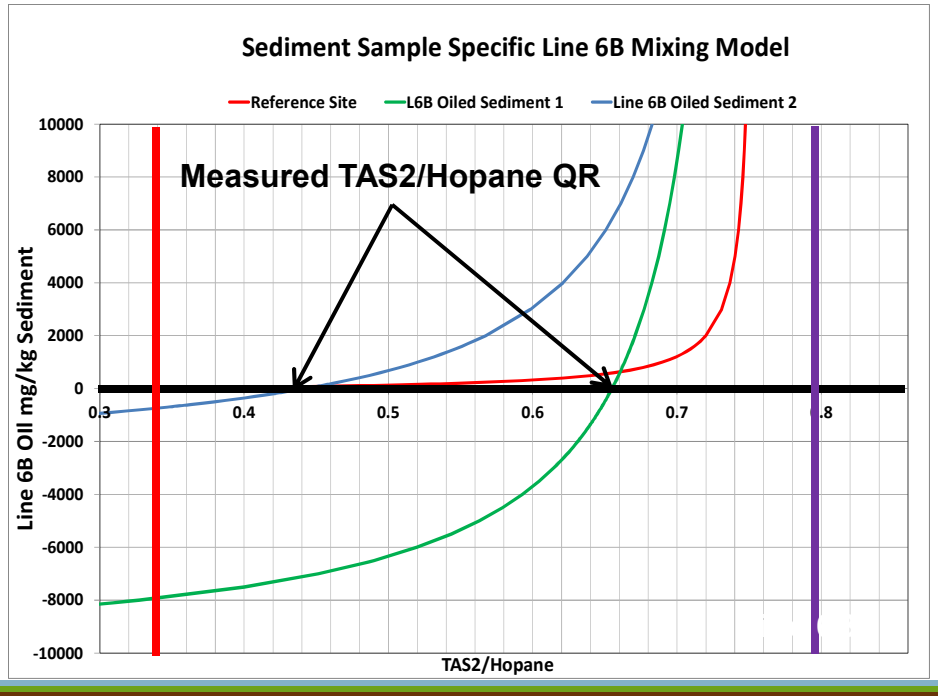
GC/MS Analysis

Forensic Chemistry Analysis



Data Analysis

How Much Line 6B Oil Must Be Removed From The Field Sample For The TAS2/Hopane Ratio To Equal The Sediment Reference Value?



1. Kalamazoo River Sediment samples have different amounts of RBH (TAS2 and Hopane).
2. The more RBH a sediment sample contains (higher TAS2 and Hopane Concentrations) the less TAS2/Hopane response for a given quantity of Line 6B Oil.
3. The same concentration of Line 6B can have different QR values.

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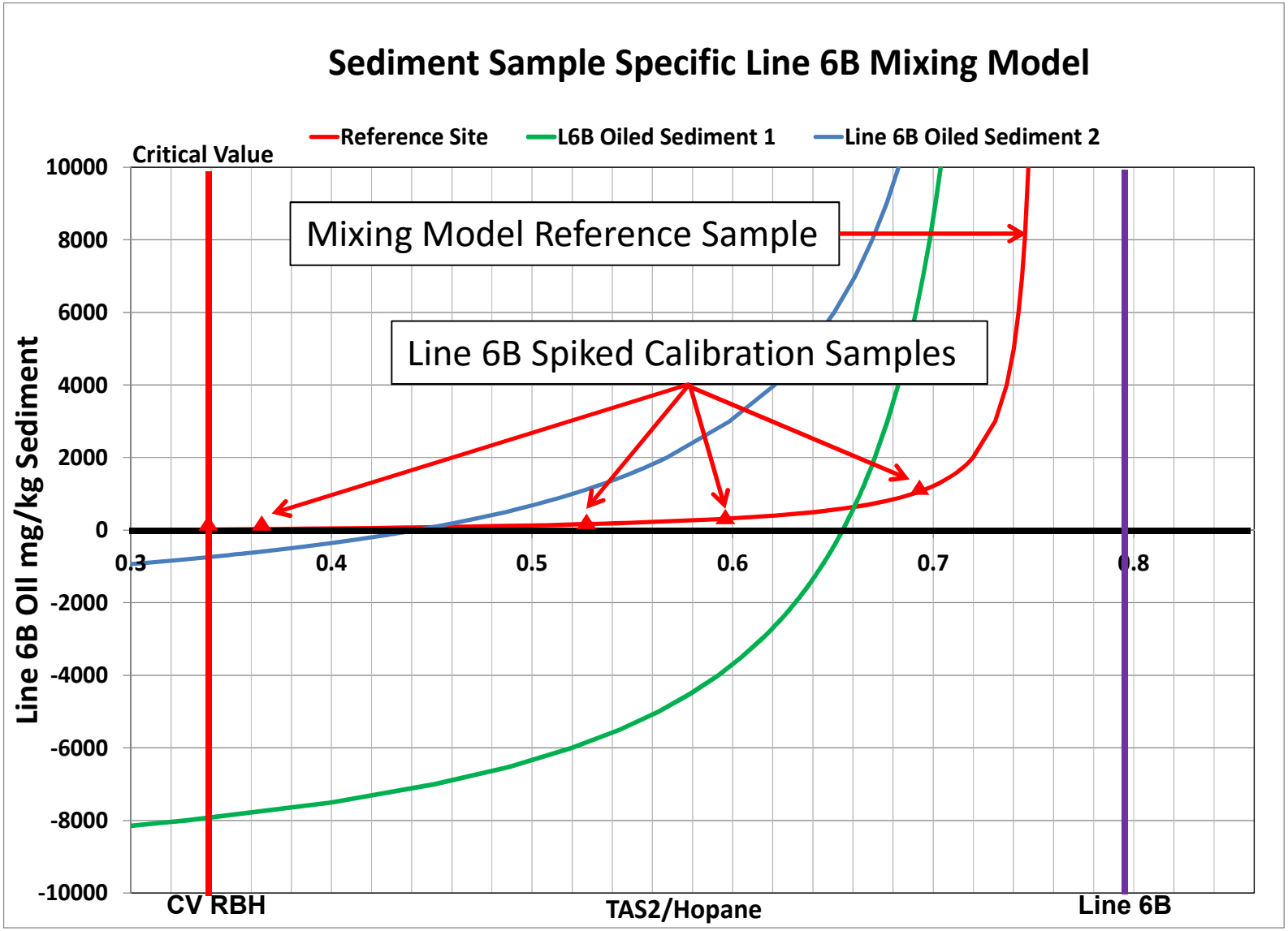
DILBIT Quantification

1. Critical TAS2/Hopane Value (CV) determined from reference samples,
2. Reference sediment spiked with Line 6B oil,
3. Mixing model curve calculated for reference soil,
4. Used reference calibration to quantify field sample,
5. Results greatly underestimated Line 6B oil concentration?
6. Why?

Background RBH Defined For Each Sample – Line 6B Mixing Model



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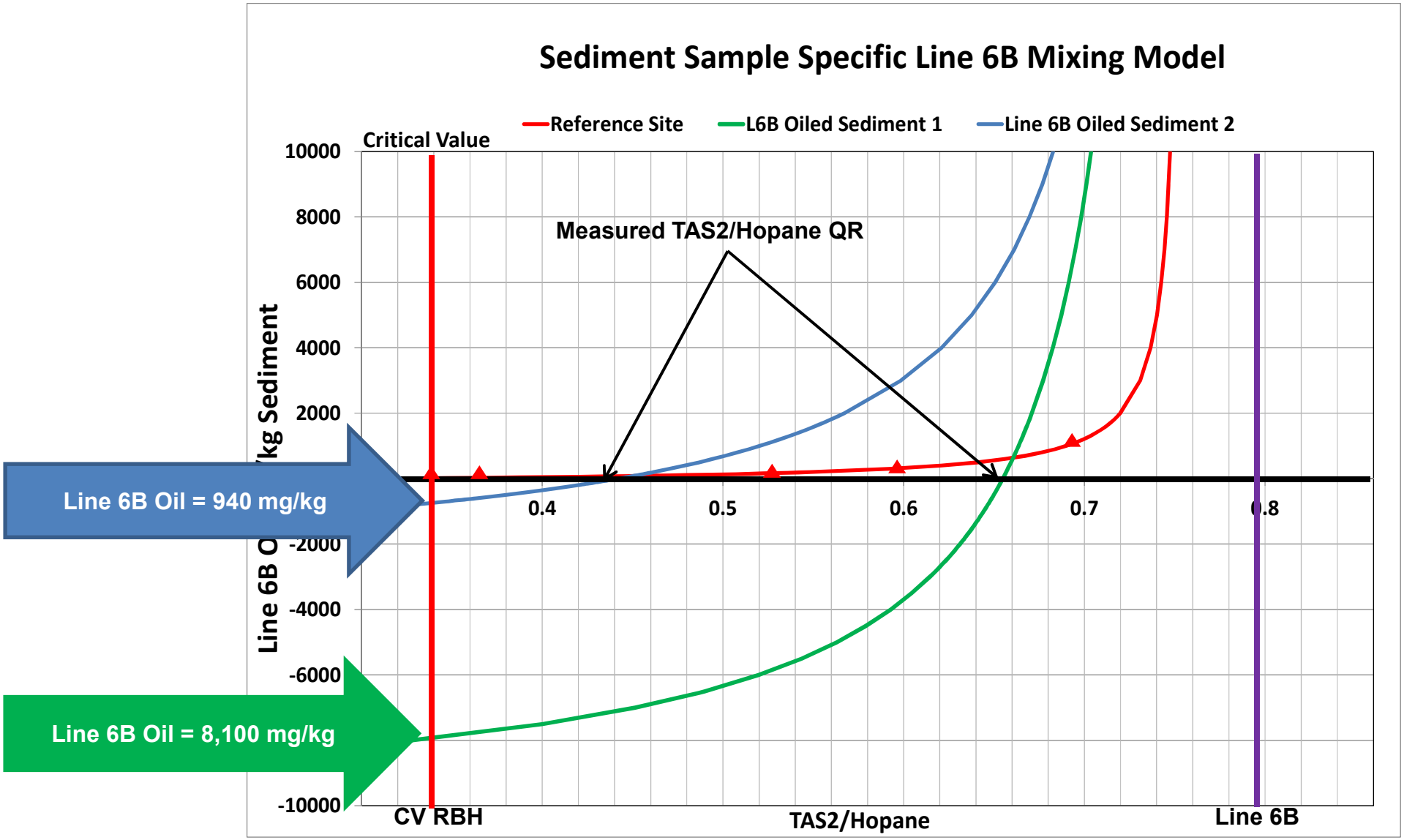
DILBIT Quantification

1. Because the field samples have difference amounts of background TAS2/Hopane,
2. Line 6B sensitivity is different for each sample,
3. However background CV constant for upper spill zone,
4. Cannot use external calibration, must adjust for Line 6B sensitivity in every sample,
5. Mathematically add/subtract Line 6B oil from field sample, the curve represents Line 6B sensitivity,
6. Line 6B oil calculated as the amount of Line 6B oil that must be removed to achieve the Critical Value (CV).

Background RBH Defined For Each Sample – Line 6B Mixing Model



Conclusion

The Final Technical Approach Provided a Reliable Method to Identify Line 6B Oil and to Quantify it in the Presence of a Substantial RBH.