Attachment 1

Technical Review of Enbridge's Quantification of Submerged Oil Report (G. Douglas, NewFields)

NewFields

May 7, 2013

Mr. Tom Graan
Weston Solutions, Inc.
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Vernon Hills, IL 60061

RE: Technical Review Of Enbridge Report “Supplement To The Response Plan for Downstream Impacted Areas Commonly Referred As The “Quantification of Submerged Oil Report”

Dear Mr. Graan,

1.0 Introduction

The following is my review of the Enbridge report entitled Supplement to the Response Plan for Downstream Impacted Areas Commonly Referred As The “Quantification of Submerged Oil Report” dated March 21, 2013 (“Report”). The Report consists of approximately twenty five (25) pages of text, two (2) figures, eight (8) tables and seven (7) attachments (A-G). Of the attachments, Attachment G consists of a seven (7) page Technical Memorandum, a Table entitled Line 6B Oil Quantification Summary, and approximately 8000 pages of figures that do not appear to be integrated with the Report. My review is focused solely on environmental chemistry issues as related to the reliable quantification of Line 6B oil in the Kalamazoo Sediments.

Given the complexity associated with reliably quantifying the Line 6B oil in the Kalamazoo River sediments, the application and validation of the interpretive and quantitation methodology is only vaguely discussed in the main body of the Report within Section 3 “Concentration of Oil In Sediment Samples”.[1] Within this Section the “NewFields Model” (Section 3.1) and “ATS Model” (Section 3.2) are examined in less than one page of text. The reader is referred to the NewFields *Technical Memorandum – Determination of Line 6B Oil Concentration in Kalamazoo River Sediments dated March, 2013* (NewFields, 2013). This memorandum provides the U.S.EPA Technical Guidance to be used by Enbridge for the calculation of Line 6B oil in Kalamazoo River Sediments.

Within the Report, Enbridge provides two approaches for the determination of Line 6B oil in Kalamazoo River sediments, the NewFields Method[2] and the ATS Method (ATS 2013).[3] Both methods utilize the chemical relationships provided in a specific group of source/quantitation petroleum related compounds.[4] Because **all of these compounds are ubiquitous in petroleum,**

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[1] Report Pages 17-18.

[2] NewFields 2013

[3] ATS Technical Memorandum - Line 6B Oil Quantification Concentration Term – Update: March 19, 2013.

[4] The primary quantitation compounds include the following: C26,20R- +C27,20S- triaromatic steroid (TAS1), C28,20S-triaromatic steroid (TAS2), 17 β (H),21α (H)-hopane (Hopane), 30,31-Trishomohopane-22S (T30), C3-dibenzothiophenes, and C4-Dibenzothiophenes. Other compounds were considered by Enbridge (Tetrakishomohopane-22R (T33), and moretane but were shown to be unreliable by NewFields.

source and quantitation ratios were developed jointly (TAS1/T30, TAS2/Hopane,[5] TAS1/TAS2) to exploit the chemical differences between the Kalamazoo river sediment background and the Line 6B oil.[6] The primary differences in the two approaches are how these ratios are used to quantify Line 6B oil. The NewFields method incorporates sample specific Line 6B sensitivity[7] into the mixing model calculation and the ATS approach does not. Simply stated, each sediment sample has varying amounts of residual background hydrocarbons (RBH). The response of the Line 6B quantitation ratio (QR) will vary with RBH, for example if 100 mg of Line 6B is added to a sediment with low RBH, the QR will exhibit a greater change (high sensitivity) than if the same amount of oil is added to sediment with high RBH (low sensitivity). Therefore, accurate quantitation of Line 6B oil must recognize and account for the individual sample Line 6B sensitivity for each sample.

Two samples (SEKR0000R024S092112D004-R024, SEKR3510R018S092112D004-MP35.1) were spiked with topped Line 6B oil to provide a calibrated reference samples for quantitation purposes.[8] These calibrations were useful in that they defined the conservative critical values (CV), above which Line 6B is present and below which it is not. The NewFields method generates a Line 6B mixing model for each sample based on the field sample quantitation ratio (e.g., TAS2/Hopane). This approach incorporates differences in Line 6B sensitivity (high and low) within each calculation, and provides a means to evaluate Line 6B detectability for those samples that fall below the defined critical value. The ATS approach directly applies the RFS calibration results to two geographically distinct groups of samples (RFS R024 for MP2-MP16.5 samples, and RFS MP35.1 to MP 18 to MP39.75). This quantification approach will *underestimate* the concentration of Line 6B oil in sediment samples with higher RBH, and is constrained to a maximum Line 6B sediment concentration of 1,500 ppm. This fact is acknowledged by ATS in their report (ATS 2013)[9] when they qualify their RFS calibration based results as the lower bound of Line 6B oil in the sediment.

Both methods also utilize the proportion of petrogenic C3-dibenzothiophenes (C3-DBT) and C4-dibenzothiophenes (C4-DBT),[10] relative to topped Line 6B oil to calculate an upper estimate of Line 6B oil. NewFields uses this value to *constrain* the primary TAS2/Hopane calculations while ATS reports this value as representing the upper bound of Line 6B oil in the sediments. When these values are used for sensitive Line 6B sediment quantitation estimates, the C3-DBT and C4-DBT weathering differences between the Line 6B oil in the sediment and the calibration oil (topped Line 6B oil) must be considered. Percent depletion estimates of representative sediment Line 6B oil samples (e.g., oil-sheens) document that the Line 6B C3-DBTs and C4-DBTs in the sediment samples are degraded relative to the calibration oil (topped cold lake crude). As a result, integration of these results into any additional mass balance calculations must be considered to truly reflect the upper bounds of Line 6B oil in the Kalamazoo River sediment. This was not done and the results reported by ATS based on the C3-DBTs and C3-DBTs is another reason why the ATS results are

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[5] Wang, Z, and Stout, S. 2007. Oil Spill Environmental Forensics – Fingerprinting And Source Identification. Academic Press, Burlington, MA. 2007.

[6] Line 6B oil has a higher proportion of triaromatic sterane (TAS) compounds relative to triterpanes than the background petrogenic hydrocarbons at this site.

[7] Line 6B sensitivity = delta TAS2/Hopane (TAS1/T30)/delta mg of Line 6B oil

[8] These samples are known as the Range Finding Study (RFS) samples.

[9] ATS (2013), Line 6B Oil Quantification Summary Table.

[10] Both groups are corrected for the C3-DBT and C4-DBT sediment concentrations from background non-Line 6B inputs.

biased low for Line 6B oil in Line 6B oil impacted sediments.[11] Application of the NewFields mixing model as directed by the U.S.EPA[12] does not suffer from this low Line 6B oil bias and is not constrained to concentrations less than 1,500 ppm.

Under the U.S.EPA Directive, Enbridge was to apply the Line 6B Quantification Methods as defined in the NewFields (2013) Technical Memorandum and provide the Line 6B concentrations for each Line 6B Quantitation Study sediment sample which would then be used to quantify total Line 6B in the Kalamazoo River Sediment. These analytical results were to be provided by Enbridge in a transparent manner for validation by U.S.EPA during the Report Review. Based on the documents provided by Enbridge in the Report, validation of the U.S.EPA directed quantification data (Tables 5 and 6) is impossible. This is because rather than report the Line 6B concentrations for each individual sample (as they did for their quantification method (ATS 2013), Enbridge has reported the values as *"Layer Weighted Average Core Concentration (mg/kg)"* and *"Average Line 6B Oil Concentration (mg/kg)"* per core.

Finally, this Report is replete with definitive statements that are not supported with any discernible scientific analysis. Specifically, Enbridge states that *"After review and consideration of the U.S. EPA method, Enbridge noted that a modified method would provide a more accurate analysis of the oil concentration."*[13] This statement appears to be the basis for ATS to conclude that their method is a more defensible method than the NewFields (2013) Line 6B quantification method. Other than *"review and consideration"* there is no documentation provided that defines what *"review"* was performed, and what specific scientific variables and proofs were *"considered"* to reach this conclusion. This approach is a common theme throughout the Report and will be discussed in detail below. And although Enbridge provided more than 8,000 graphs in charts in Appendix G, only one figure was identified in the Report as supporting a specific claim. Instead, the reader is forced to search through pages and pages of charts and graphs in an attempt to identify relevant information regarding the conclusions provided in the Report.

2.0 Report Analysis

The following is my analysis of the sections within the Report that are relevant to the quantification of Line 6B oil in Kalamazoo River sediment samples.[14]

1. **Issue:** *"The estimated concentration of Line 6B crude oil in each sediment sample that is calculated utilizing the NewFields method is presented in Table 5 and Table 6."*[15]
   Response: This statement is not true, the concentration of Line 6B oil in each sample is not provided in Table 5 or Table 6. The results are reported on a lumped core basis as the "*Layer Weighted Average Core Concentration (mg/kg)*" and the "*Average Line 6B Oil*

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[11] In addition to the direct application of RFS calibration to field samples.

[12] NewFields (2013)

[13] Report Page 18, Paragraph 2.

[14] These sections include Section 3 Concentration of Oil In Sediment Samples, Section 4.7 Concentration of Line 6B in Sediment, Section 4.8 Estimated Quantity of Line 6B Oil as it relates to individual sediment sample Line 6B estimates, Appendix G, and the raw Alpha Analytical data used estimate Line 6B oil concentrations in the Quantitation Study sediments.

[15] Report Page 18, Paragraph 1.

Concentration (mg/kg)". Presentation of the Line 6B Quantitation Study sediment data in this format makes it impossible to validate the individual sediment sample results.[16]

2. **Issue*:* "***Upon reviewing the U.S. EPA methodology, Enbridge noted that the methods used rely heavily on the use of distinguishing chemical indicators which can be ubiquitous to many sources of potential contaminants other than Line 6B oil."*[17]
   Response: The compounds used by NewFields and ATS are ubiquitous to petroleum and can be derived from sources other than Line 6B. If they were not present in petroleum then they could not be used for Chemical Fingerprinting and petroleum quantification.[18] In addition, these are the standard group of diagnostic compounds that have been used for oil spill investigations since the mid-1970s by both government and industry.[19,20,21,22,23,24,25] The implication that the selected compounds are not appropriate for the Enbridge Oil Spill study are unfounded and not supported by the vast amount of peer reviewed scientific literature. What the authors do not seem to say is that although the individual compounds may be present in many types of petroleum and urban runoff (oil/coal tar/atmospheric combustion sources), it is the ratio of selected compounds such as TAS2/Hopane that provide the source resolution and quantitation power.[26]

3. **Issue: "***Such alternate sources of contaminants have been identified in the Kalamazoo River watershed and include both pyrogenic derived sources (e.g., urban runoff, discharges from historic manufactured gas plant operations, etc.) and petrogenic derived sources (e.g., urban runoff, discharges from commercial/municipal/industrial facilities, etc.)."*[27]
   Response: This statement is true considering that no environment is pristine and is the primary reason oil spill studies rely on the use of Environmental Forensics. For example, chemical fingerprinting and analysis would not be required in these studies if the sediment were not influenced by anthropogenic sources other than the spilled oil. The development of

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[16] This lump sum approach for reporting core sediment concentrations also includes more than 140 samples that were not analyzed for petroleum hydrocarbons making it even more difficult to de-convolute and validate the original sediment Line 6B concentrations.

[17] Page 18, Section 3.2 paragraph 1, first line.

[18] Z. Wang and S.A. Stout. 2007. Oil Spill Environmental Forensics: Fingerprinting and Source Identification. Elsevier Publishing Co., Boston, MA.

[19] Stout**,** S. A.; Uhler, A. D.; McCarthy, K. J. A strategy and methodology for defensibly correlating spilled oil to source candidates. *Environ. Forensics*. **2001,** 2, 87-98.

[20] Wang**,** Z.; Fingas, M; and Page, D. S. Oil spill identification. *J. Chromatogr. A.* **1999**, 842, 369-411.

[21] Federal Register. National Oil and Hazardous Substances Pollution Contingency Plan-Final Rule 40, CFR Parts 9 and 300. **1994.**

[22] Peters, K. E.; Walters, C. C.; Moldowan, J. M. *The Biomarker Guide, Volume 1. Biomarker and isotopes in the environment and human history.* **2005b** Cambridge University Press. Cambridge, UK

[23] Daling, P. S.; Faksness, L. G.; Hansen, A. B.; Stout, S. A.. Improved and standardized methodology for oil spill fingerprinting. *Environ. Forensics*. **2002,** 3, 263-278.

[24] Douglas, G.S.; Bence, A. E.; Prince, R.C.; McMillen, S. J.; Butler, E. L. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technol.* 1996, 30, 2332-2339.

[25] Boehm, P. and Feist, D. 1982. Subsurface distributions of petroleum from an offshore well blowout. The IXTOC Blowout, Bay of Campeche. *Environ. Sci. Technol*. 1982, 16(2):67-74.

[26] Wang, Z., Yang, C., Fingas, M., Hollebone, B., Yim, U., Oh, J. 2007. Petroleum Biomarker Fingerprinting for Oil Spill Characterization and Source Identification. In: 2007. Oil Spill Environmental Forensics: Fingerprinting and Source Identification. Eds. Z. Wang and S.A. Stout. Elsevier Publishing Co., Boston, MA.

[27] Report Page 18, Paragraph 1.

the selected source ratios (e.g., TAS2/Hopane) are designed to discriminate between the observed background and spilled oil.

4. **Issue:** *"In some cases, the pyrogenic derived residuals range in the 1,000s to 10,000 mg/kg (dry weight), while the petrogenic derived residuals were estimated in the 1,000s of mg/kg (dry weight)."*[28]
   Response: Enbridge provides no reference or table to support their claim. There are no examples of pyrogenic sediment residuals of 10,000 ppm identified in the Report.

5. **Issue: "***Thus, use of the U.S. EPA method could cause the concentration to be much higher than actual resulting in the estimated calculated oil volume to be skewed high."*[29]
   Response: Enbridge suggests that the U.S. EPA method developed by NewFields[30] will overestimate the concentration of Line 6B oil in Kalamazoo River sediment samples. As discussed in the Introduction and throughout this review, this is another example of the authors making statements that are not supported by any technical data or analysis. The authors don't provide any scientific analysis or technical proof to support their statement.

6. **Issue: "***After review and consideration of the U.S. EPA method, Enbridge noted that a modified method would provide a more accurate analysis of the oil concentration."*[31]
   Response: This statement is a repeat of the problem that is persistent throughout this Report. Specifically, Enbridge states with authority that the ATS modified method would provide a more accurate analysis (than the NewFields Mixing Model Method) of the oil concentration. Yet they provide no scientific evidence to support their conjecture. Why is the ATS method more accurate? What data were used to determine the accuracy of the respective methods? What samples are affected? The authors have provided no supporting analysis or documentation for the reader to evaluate its validity and impact to the Line 6B Quantitation Study.

7. **Issue:** "*That method, developed by Ann Arbor Technical Services Inc. (ATS) is provided as Attachment G.*"[32]
   Response: The ATS Line 6B quantitation method is vaguely described in Attachment G. The two approaches are summarized as follows.[33] The C3-dibenzothiophenes and C4-dibenzothiophenes present in the sediment and ubiquitous in both the environment and petroleum are corrected for petrogenic inputs used to quantify Line 6B oil relative to the C3-DBT (and C4-DBT) in the topped Cold Lake oil. The second method uses the Range Finding Studies (RFS, spiked with topped Line 6B oil) to generate a Line 6B sediment calibration for background samples SEKR0000R024S092112D004 (R024) and SEKR3510R018S092112D004 (MP35.1). A regression analysis was used to develop a mathematical model that defines source ratio (TAS1/TAS2, TAS1/T30, and TAS2/Hopane) sediment response versus amount of Line 6B oil spiked into the sediment. Enbridge then

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[28] Report Page 18, Paragraph 1.
[29] Report Page 18, Paragraph 1.
[30] NewFields (2013).
[31] Report Page 18, Paragraph 2, First Line.
[32] Report Page 18, Paragraph 2.
[33] Also discussed in Section 1.

applied those calibrations to estimate the amount of Line 6B Oil in the sediment. This method relies on the differences in the source ratios from background to quantify Line 6B oil. For sediments that have the same residual background hydrocarbon (RBH) response, the direct RFS calibration method is a reliable approach. The problem is that most of the sediments have a different RBH than R024 and MP35.1. A few sediments have lower RBH (relative to the RFS calibration used) and the ATS Method will overestimate the Line 6B oil concentration (e.g., field sample SEKR1950C501S042612DX), particularly at low RBH and low Line 6B oil concentrations. Many samples have higher RBH relative to the RFS sediments and the calibrated RFS calculation will **greatly** underestimate the Line 6B oil concentration in the sediment sample (e.g., SEKR1075C702S113012DX).[34]

8. **Issue:** *"The ATS model identified other chemical indicators (e.g., fluoranthene, pyrene) that can be used to develop a correction factor to correct for pyrogenic background contribution from non-line 6B oil sources that used the U.S. EPA chemical indicators as the basis for oil volume calculations."*[35]
   Response: The approach, although not clearly defined in the text, is reasonable. The authors need to provide a Table of the exact reference samples used for the pyrogenic background correction, the associated sediment concentrations and averages used to develop the correction factor used in this report.

9. **Issue:** "*To differentiate petrogenic residues between Line 6B and non-Line 6B sources, several diagnostic ratio indicators were developed using biomarker data (e.g., TAS1/T30, TAS2/T19, and TAS1/TAS2)."*[36]
   Response: Enbridge did not develop these three diagnostic ratios. With the exception of TAS1/T30, these ratios have been used in oil spill studies for the past 20 years and are listed in peer reviewed Journals and well respected oil spill books.

10. **Issue***: "Evaluation of this data suggests that these three diagnostic ratios can be used for direct calibration calculations of Line 6B for samples with hydrocarbon levels up to approximately 1,500 mg/kg. Calculated values for samples beyond 1,500 mg/kg can be considered lower bound estimates for Line 6B concentrations to be used with independently calculated Line 6B concentrations using C3DBT and C4DBT."*[37]
    Response: The usefulness of the TAS1/TAS2 is further limited to below 1,000 ppm.[38] As defined by the authors, the Line 6B quantitation estimates based on the R024 and MP35.1 calibrated RFS studies are clearly biased low.[39] It is unclear why the authors did not examine and critically review the NewField's Mixing Model Line 6B method when this approach does not have the same Line 6B quantitation limitations. The NewFields Mixing Model approach incorporates individual sediment sample Line 6B sensitivity and is not constrained at high Line 6B concentrations.

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[34] See the NewFields March 1, 2013 Technical Memorandum for a more detailed discussion.
[35] Report page 18, Paragraph 2, Line 3.
[36] Report page 18, Paragraph 2, Line 7.
[37] Report Page 18, Paragraph 2.
[38] The R024 RFS calibration curve becomes asymptotic at Line 6B oil concentrations greater than 500 ppm.
[39] See Line 6B Oil Quantification Summary Table, Appendix G, Last Colum *"Lower Bound (TAS1/T30 and TAS2/T19)"*

11. **Issue:** *"The lower bound is calculated using a value of zero for non-detect (ND) and less than the Minimum Detection Limit (MDL) values based on Enbridge evaluation of "chemical reasonableness".*[40]
    Response: Enbridge provides no documentation concerning how the sample specific MDL values were generated; they simply reported that they are based on the Enbridge evaluation of "chemical reasonableness". The authors should define what they mean by chemical reasonableness and specifically how they extrapolated the sample specific MDLs from the R024 and MP35.1 MDL studies to the wide range of sediment samples with varying TPH and Line 6B sensitivities. A table of sample specific MDL values for each Line 6B non-detect (ND) result is required.

12. Issue*: "The oil concentration parameter was developed by ATS to accommodate the overestimating effect of using the chemical indicators suggested by the NewFields model due to alternate sources of background oil containing those same chemical indicators."*
    Response: This statement makes no sense. First ATS has not provided any evidence that the Mixing Model Method overestimates Line 6B oil sediment concentrations. Second, if chemical indicators that are present in background sources are a problem, then it's also a problem for the ATS approach because they use the same compounds and ratios. Finally, the MP35.1 RFS TAS1/T30 calibration method used by ATS most likely overestimates Line 6B oil in Morrow Lake because of a T30 compound petrogenic background depletion relative to Line 6B. This is not true for the NewFields TAS2/Hopane ratio mixing model method.

ATS Technical Memorandum - Line 6B Oil Quantification Concentration Term – Update. Dated March 19, 2013

13. **Issue: "***These two compounds are present in relatively high concentrations in the L6B source oils (330 and 232 ppm respectively in "OLKR"; 425 and 281 ppm respectively in "Topped CL")."*[41]
    Response: Sample OLKR is not a perfect representative Line 6B oil sample because it contains sediment particles, which on a mass basis will artificially lower the C3-DBT and C4-DBT concentrations in the oil. Use of this sample to estimate Line 6B oil based on the sediment C3-DBT and C4-DBT will substantially *overestimate* the Line 6B concentration in the sediment. Conversely, the C3-DBT and C4-DBT in the topped Cold Lake crude oil are less weathered than the field oil-sheen samples. Use of this sample to estimate Line 6B oil based on the sediment C3-DBT and C4-DBT will *underestimate* the Line 6B concentration in the sediment unless the weathering in the field samples is taken into consideration.

14. **Issue:** *"They are relatively minor components in pyrogenic residues found in background sediments of the Kalamazoo River and Battle Creek River. Both compounds have minimal weathering rates for the conditions occurring in these river systems."*[42]

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[40] Report Page 22, Section 4.8.1, Line 3.
[41] ATS (2013) Page 2, Paragraph 4.
[42] ATS (2013) Page 2, Paragraph 4.

Response: In addition to C3-DBT and C4-DBT being minor components in pyrogenic residues, the other biomarker compounds (TAS2, Hopane, TAS1, and T30) are minor components as well. ATS's statement that the weathering rates C3-DBT and C4-DBT are minimal for the conditions occurring in these river systems is another example of the pervasive unsupported statements provided by the authors of this report. Specifically, they have provided no literature reference or data analysis to support their claim, or the potential implications of the amount of weathering that occurred prior to deposition in the sediment. Specifically, the authors ignore that fact that their upper bound C3-DBT/C4-DBT Line 6B calculation will underestimate the amount of Line 6B in a Line 6B-impacted sediment sample.

ATS relies on the absolute concentration of C3-dibenzothiophenes (C3-DBT) and C4-dibenzothiophenes (C4-DBT) to estimate the upper bound of the Line 6B oil in the sediment. The ATS *"upper bound"* Line 6B oil concentration is derived from measured C3-DBT and C4-DBT sediment concentrations[43] relative to the respective C3-DBT and C4-DBT concentrations in the topped oil reference sample CL-6B-072223-092710-JPS-KA-001-33_TOPPED (CLT) to calculate the concentration of Line 6B oil in the sediment. CLT is a laboratory generated topped cold lake oil designed to generally replicate the weathered oil in the sediment. This oil is a reliable reference point, however the C3-DBT and C4-DBT are less weathered in the topped cold lake oil than Line 6B oil identified in the sediment (e.g., oil-sheen samples, Figure 1) and therefore direct use of this reference oil will underestimate the *"upper bound"* Line 6B oil sediment concentration.

Applying the methods found in Douglas et al. [44,45,46] and others[47] the amount of C3-DBT and C4-DBT degradation in the Line 6B sheen samples versus CLT can be quantified. The calculation of C3-DBT and C4-DBT percent depletion relative to the CLT reference oil is calculated as follows.

$$\textbf{\% C3-DBT (C4-DBT) depletion} = [1-(C_1/C_0) \times (H_0/H_1)] \times 100$$

Where:

C_0 = Concentration of C3-DBT (C4-DBT) in the CLT oil.
C_1 = Concentration of C3-DBT (C4-DBT) in the sheen sample.
H_0 = Hopane concentration in the CLT oil.
H_1 = Hopane concentration in the sheen sample.

For sheen samples the range of percent C3-DBT & C4-DBT depletion (Figure 1 red bars) relative to CLT can be substantial. For this reason it is recommended that compounds that are

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[43] Corrected for any pyrogenic C3-DBT and C4-DBT contribution.

[44] Douglas, G.S., McCarthy, K.J., Dahlen, D.T., Seavey, J.A., Steinhauer, W.G., Prince, R.C. and Elmendorf, D.L. 1992. The use of hydrocarbon analysis for environmental assessment and remediation. In: P.T. Kostecki and E.J. Calabrese Eds. Contaminated Soils: Diesel Fuel Contamination. Ann Arbor, MI: Lewis Publishers.

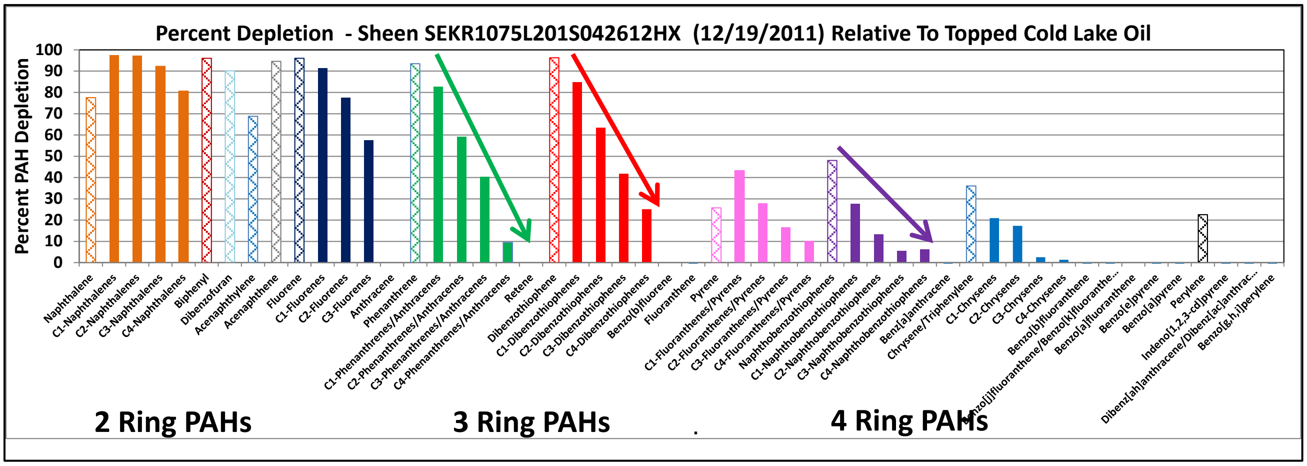
[45] Douglas, G.S., Bence, A.E., Prince, R.C., McMillen, S.J. and Butler, E.L. 1996. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technology,* 30(7):2332-2339.

[46] Douglas, G.S., Hardenstine, J., Owens, E.H., and Prince, R.C. 2002. The OSSA II pipeline oil spill: the character and weathering of the spilled oil. *Spill Science & Technology Bulletin* 7(3-4):135-148.

[47] Peters, K.E., Walters, C.C., Moldowan, M.J. 2005. The Biomarker Guide. Volume 1. Cambridge University Press.

less biodegradable (e.g., naphthobenzothiophenes (purple bars) and triaromatic steranes[48]) also be evaluated and a minimum (e.g., C3-DBT) to maximum (e.g., TAS2) range be used. This will be discussed below in more detail within Issue 23.

Figure 1. Illustration of the relative weathering/biodegradation of un-substituted (parent, hash bars) and substituted (alkylated, solid bars) PAHs and sulfur heterocyclic compounds in sheen sample SEKR1075L291S042612HX relative to topped Cold Lake oil.[49] Three ring phenanthrenes (green) and dibenzothiophenes (red) illustrate the degradation pathway for alkylated compounds within a homologous series. Weathering and biodegradation decrease with increasing ring number and alkylation such that 2 ring > 3 ring > 4 ring > 5 ring > 6 ring, and C0-PAH > C1-PAH > C2-PAH > C3-PAH > C4-PAH as illustrated below in sheen sample SEKR1075L291S042612HX.[50]



15. **Issue:** *"Sediments and other environmental media of the Kalamazoo River contain significant contamination of hydrocarbons from petrogenic sources other than the L6B release."*[51]
Response: ATS has again made a broad technical statement that the sediments contain significant contamination of hydrocarbons from petrogenic sources other than the Line 6B, but do not provide the supporting data they used to reach that conclusion. Which samples represent petrogenic background? What is the range of non-Line 6B oil concentrations in the Kalamazoo River sediment and what is the impact on the calculation of Line 6B oil in sediments? Finally, the authors totally ignore the importance of Environmental Forensics[52]

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[48] Douglas, G.D., Hardenstine, J., Liu, B., Uhler, A.D. 2012. Laboratory and field verification of a method to estimate the extent of petroleum biodegradation in soil. *Environ. Sci. Technology* June 13, 2012. DOI: 10.1021/es203976a

[49] Percent PAH depletion calculated using method described in Douglas, G.S.; Bence, A. E.; Prince, R.C.; McMillen, S. J.; Butler, E. L. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technol.* 1996, 30, 2332-2339.

[50] Elmendorf, D.L., Haith, C.E., Douglas, G.S. and Prince, R.C. 1994. Relative rates of biodegradation of substituted polycyclic aromatic hydrocarbons. In R.E. Hinchee, A.E. Leeson, L. Semprini, and S.K. Ong (eds), *Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbon Compounds.* Ann Arbor, Michigan: Lewis Publishers.

[51] ATS (2013). Page 3, Paragraph 4.

[52] Douglas, G.S., Stout, S.A., Uhler, A.D., McCarthy, K.J., Emsbo-Mattingly, S.D. 2006. Advantages of quantitative chemical fingerprinting in oil spill source identification. *In:* Oil Spill Environmental Forensics: Fingerprinting and Source Identification. Z. Wang and S.A. Stout, Eds. Elsevier Publishing Co., Boston, MA.

in their apparent interpretation of the data. These background petrogenic oils exhibit a specific chemical fingerprint that is easily distinguished from the Line 6B oil, yet there is no indication that they used this approach to distinguish Line 6B oil from other sources in the river sediment. Rather they simply state that the results will be biased high and move on to a different, less robust approach.

16. **Issue:** *"At many locations, these <u>non-L6B petrogenic hydrocarbons</u> are responsible for large percentages of the solvent extractable residue and TPH, often in the thousands of ppm dry weight."*[53]
    Response: ATS again provides no supporting evidence for this statement such as: How many locations? What samples are affected? Where are they located? What is the measured impact to the Line 6B calculation in each sediment sample?

17. **Issue:** *"To date, four compounds have been used for this purpose, T19 (hopane), T30 (30,31-trishomohopane-22S), TAS1 (C26,20R+C27,20S triaromatic steroid) and TAS2 (C28,20S triaromatic steroid). While all four are commonly present in virtually all petroleum sources, including L6B, they occur at different relative abundance depending on the crude oil source."*[54]
    Response: This statement is contrary to the earlier Enbridge statement (Issue 12 discussed above) in the Report where *"The oil concentration parameter was developed by ATS to accommodate the overestimating effect of using the chemical indicators suggested by the NewFields model due to alternate sources of background oil containing those same chemical indicators."* In the first statement they identify the NewFields and ATS list of biomarker compounds that were used in the respective Line 6B quantitation models. In the text cited above, Enbridge state that although these compounds are *"commonly present in virtually all petroleum sources, including Line 6B"* (as are the C3-DBT and C4-DBT compounds) *"they occur at different relative abundance depending on the crude oil source."* This means that the source and quantitation ratios used by ATS and NewFields are defensible, however in the main body of the report they only state the negative (e.g., the diagnostic compounds are present in Line 6B and background petrogenic sources) and do not clarify the utility of the source ratios (e.g. TAS2/Hopane) to reliably identify and quantify the Line 6B oil in Kalamazoo river sediments.

18. **Issue:** *"The two studies verified that within the range of matrices and petrogenic residue concentrations evaluated, the three following biomarker diagnostic ratios were useful to determine low level concentrations of L6B in sediments:"*[55]
    Response: The range finding studies[56] provide a valuable tool for the quantification of Line 6B oil in Kalamazoo River Sediments when applied correctly. The biomarker diagnostic ratios identified by ATS were also used by NewFields. The term "low level" appears to apply to the 100 ppm to 1,500ppm range, above which the ATS approach is inaccurate. It is my

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[53] ATS (2013) Page 3, Paragraph 4.

[54] ATS (2013) Page 4, Paragraph 1.

[55] ATS (2013) Page 4

[56] The range finding studies (RFS) represent an attempt to calibrate Line 6B oil response in two representative groups of Kalamazoo sediment samples, R024 and MP35.1.

professional opinion based on my analysis described above that both lower and upper bounded values reported by ATS (2013) are inaccurate for Line 6B oil quantification.

19. **Issue:** *"Regression analysis statistics from these study results indicate that these three diagnostic ratios can be used for direct calibration calculations of L6B for samples with hydrocarbon background up to approximately 1,500 ppm (Extract Residue Upon Evaporation, mg/kg dry weight)."*[57]
    Response: The RFS calibration approach provides reasonable Line 6B oil quantitation results for sediment samples that have *similar Line 6B sensitivities*. Line 6B sensitivity is a function of the change in the quantitation ratio (e.g., TAS2/Hopane) with the change in Line 6B oil concentration. The resultant sediment quantitation ratio is then compared to the respective RFS calibration curve and the amount of Line 6B is reported. The problem is that there is a broad range and variability of Line 6B sensitivities as documented in the NewFields March 1, 2013 Technical Memo. This means that for a given mass of Line 6B oil added to the sediment, the change in quantitation ratio will vary as a function of both the amount of oil added and the amount and type of background hydrocarbons present in the sample. For this reason, 500 ppm of Line 6B will produce a large change in the quantitation ratio (e.g., TAS2/Hopane) for a relatively clean sample (e.g., R024), but the same amount of Line 6B oil will only produce a small change in the quantitation ratio for sediments with a higher concentrations of RBH.[58] This is the reason that the use of the Line 6B calibration based on sediment sample R024 will under-quantify the amount of Line 6B oil in a sediment with a higher RBH. The mixing model approach that Enbridge was directed to use for the Report takes into account the Line 6B sensitivity in each sediment sample relative to a critical quantitation ratio value as defined by the RFS calibration study.[59] As a result, the direct application of the RFS calibration to Kalamazoo River sediments will produce data that is biased low for Line 6B oil for samples with RBH greater than the calibration sediment.

20. **Issue:** *"As agreed with NewFields, "Topped CL" was used as the L6B reference oil, and its composition was used in these quantitation calculations where a L6B reference was required."*[60]
    Response: In order to have a common reference point between ATS and NewFields, NewFields agreed to use the laboratory generated topped cold lake oil as a surrogate for the oil remaining in the Kalamzoo River sediments. However, ATS was also told by NewFields[61] to consider the impact of differential weathering between the topped cold lake oil and the oil in the sediments when using their C3-DBT and C4-DBT Line 6B calculation method (see Issue 14). This recommendation was apparently rejected and has not been incorporated into the ATS calculations for C3-DBT and C4-DBT Line 6B oil reported in the Line 6B Oil Quantification Summary.

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[57] ATS (2013) Page 5 Last Paragraph
[58] NewFields (2013).
[59] See NewFields Technical Memo dated March 1, 2012 for a detailed analysis of this issue.
[60] ATS (2013) Page 5, Paragraph 2.
[61] November 21 and 26, 2013 conference calls with Enbridge/ATS/AECOM/U.S.EPA/NewFields.

21. **Issue:** *"In our table, the biomarker-derived concentrations (TAS1/T30 and TAS2/T19) should be considered the lower bound estimate of the L6B residual concentration, and the alkyl PAH derived concentrations (C3DBT/C4DBT) should be considered the upper bound estimate of L6B residual concentration."*[62]
    Response: The authors appear to acknowledge the inherent technical problems associated with direct application of the RFS Line 6B calibrations to Kalamazoo River sediment samples and acknowledge that these estimates are generally biased low for Line 6B oil. The authors have not however acknowledged that the C3-DBT and C4-DBT Line 6B upper limit calculations are also biased low due to the weathering differential between the topped cold lake reference oil and the oil-sheen analyses collected from the field.

22. **Issue:** *"There is one instance in our table, SEKR1950C501S042612DX, where the biomarker derived number greatly exceeds the C3DBT/C4DBT number (2,962 versus 459 mg/kg, respectively), and also greatly exceeds the TPH and Extract Residue Upon Evaporation (748 and 1370 mg/kg, respectively). This location is at Mile Post 19.50, downstream from the confluence with the BCR. It is a very good example of why the biomarker data solely should not be relied upon in determining L6B concentrations. The biomarker and APAH cross plots and diagnostic ratio plots for this sample below illustrate this."*[63]
    Response: Sound science is the key to developing a solid understanding of the fate, transport, identification and quantity of spilled oil in complex environmental matrices. The authors have analyzed, processed, charted, corrected and reported data for hundreds of sediment sample analyses associated with the Sediment Quantification Study. Environmental chemistry trends, source relationships, and Line 6B quantitation methods are defined by the complete data set and not individual anomalies. For this reason, I am unable to understand why the authors chose to end their Technical Memorandum with one (1) sample (SEKR1950C501S042612DX) that reflects the weakness in their own technical approach, to undermine the NewFields Mixing Model quantitation method that relies on use of biomarker data (e.g., TAS2/Hopane). Even more astounding is the fact that the authors could not find one of the hundreds of samples that were analyzed as part of the Line 6B Quantification study to make their point, but were forced to reach back to a single sample that is unrelated to the Sediment Quantification Study.

In order to demonstrate the interpretive deficiencies embodied in the ATS Method, I will take this opportunity to discuss in greater detail the analytical results for sediment sample SEKR1950C501S042612DX and show the sound science behind the NewFields interpretive methodology.

First, the paragraph in the ATS Technical Memorandum cited above, exemplifies the problems that are pervasive throughout the Report and Technical Memorandum. Those problems as described above are as follows:

A. This report is replete with definitive statements that are not supported with any discernible scientific analysis are used to add credibility to pre-conceived conclusions. As supporting

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[62] ATS (2013), Paragraph 3

[63] ATS (2013) Page 5 Paragraph 4.

evidence for their conclusion that "*biomarker data solely should not be relied upon in determining L6B concentrations" is a series of* PAH and biomarker crossplots of SEKR1950C501S042612DX.

B. ATS basis its opinion on data that is clearly beyond the usable range of the RFS calibration[64] and then claim that the NewFields reliance on the TAS2/Hopane ratio for Line 6B quantification is suspect "*It is a very good example of why the biomarker data solely should not be relied upon in determining L6B concentrations."*[65]

C. ATS does not include a discussion of the NewFields TAS2/Hopane or TAS1/T30 mixing model results for the same sample even though these results provide a more defensible result.

D. The RFS direct calibration method used by ATS is severely flawed because it does not take into account individual sample Line 6B sensitivity. This is a compounding factor for the over-reporting of Line 6B oil in sample SEKR1950C501S042612DX.

The proof for each of the above statements is as follows:

A. This report is replete with definitive statements that are not supported with any discernible scientific analysis are used to add credibility to pre-conceived conclusions. As supporting evidence for their conclusion that "*biomarker data solely should not be relied upon in determining L6B concentrations." Is a series of* PAH and biomarker crossplots of SEKR1950C501S042612DX

The authors claim that: "*A review of the biomarker cross plots and diagnostic ratio plots (TAS1/T30 and TAS2/T19) suggests the petrogenic residue in this sample is primarily L6B (90+ percent). However, the alkyl PAH cross plots and diagnostic ratios reveal this cannot be the case. They indicate that while L6B is likely present in this sample, it constitutes less than half the petrogenic residue, and significantly less than half the extractable residue. In this way, a match in the biomarker data is a necessary condition to identify L6B residue, but is not necessarily sufficient to conclude the residue is L6B. For the same reason, L6B concentration data based upon biomarkers must be confirmed by other independent lines of evidence.*"[66]

This statement is wrong:

- Analysis of the biomarker plots **confirm** that the dominant oil in this sample is Line 6B. Specifically the TAS2/Hopane (0.75), the TAS1/T30 ratio (3.79-4.18), and the TAS1/TAS2 ratios (1.26-1.27) are consistent with Line 6B oil without any non-Line 6B oil mixing. In addition, direct comparison of the triterpane extracted ion plots between the field sample and Line 6B oil prove with a very high degree of scientific certainty that the oil present in the sandy/gravel sediment sample SEKR1950C501S042612DX (Figure 2) is only Line 6B oil.

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[64] As defined by ATS in the Report Page 18. *"Evaluation of this data suggests that these three diagnostic ratios can be used for direct calibration calculations of Line 6B for samples with hydrocarbon levels up to approximately 1,500 mg/kg."*

[65] For the record the NewFields March 1, 2013 Technical Memorandum clearly states that the C3-DBT and C4-DBT estimated Line 6B oil approach should be used to evaluate the chemical reasonableness of the TAS2/Hopane and TAS1/T30 Line 6B quantitation results.

[66] ATS (2013) Technical Memorandum page 7.

- The PAH distributions represent a mixture of pyrogenic background and Line 6B oil (Figure 3C lower left hand corner). There is no indication of a second petrogenic source.
- The C3-DBT/C3-P[67] versus C4-DBT/C4-P[68] source ratio plot confirms that the oil is Line 6B (Figure 3D, lower right hand corner).[69]
- There is no indication of a second oil in this sample or that the Line 6B oil is less than half of the petrogenic residue.

Figure 2. Photos of sediment sample SEKR1950C501S042612DX (Photo 1) and the sediment sample MP35.1 used to prepare the RFS Line 6B calibration used by ATS (Photo 2).

Photo 1. Course gravel and sand matrix

Photo 2. Fine grained sediment

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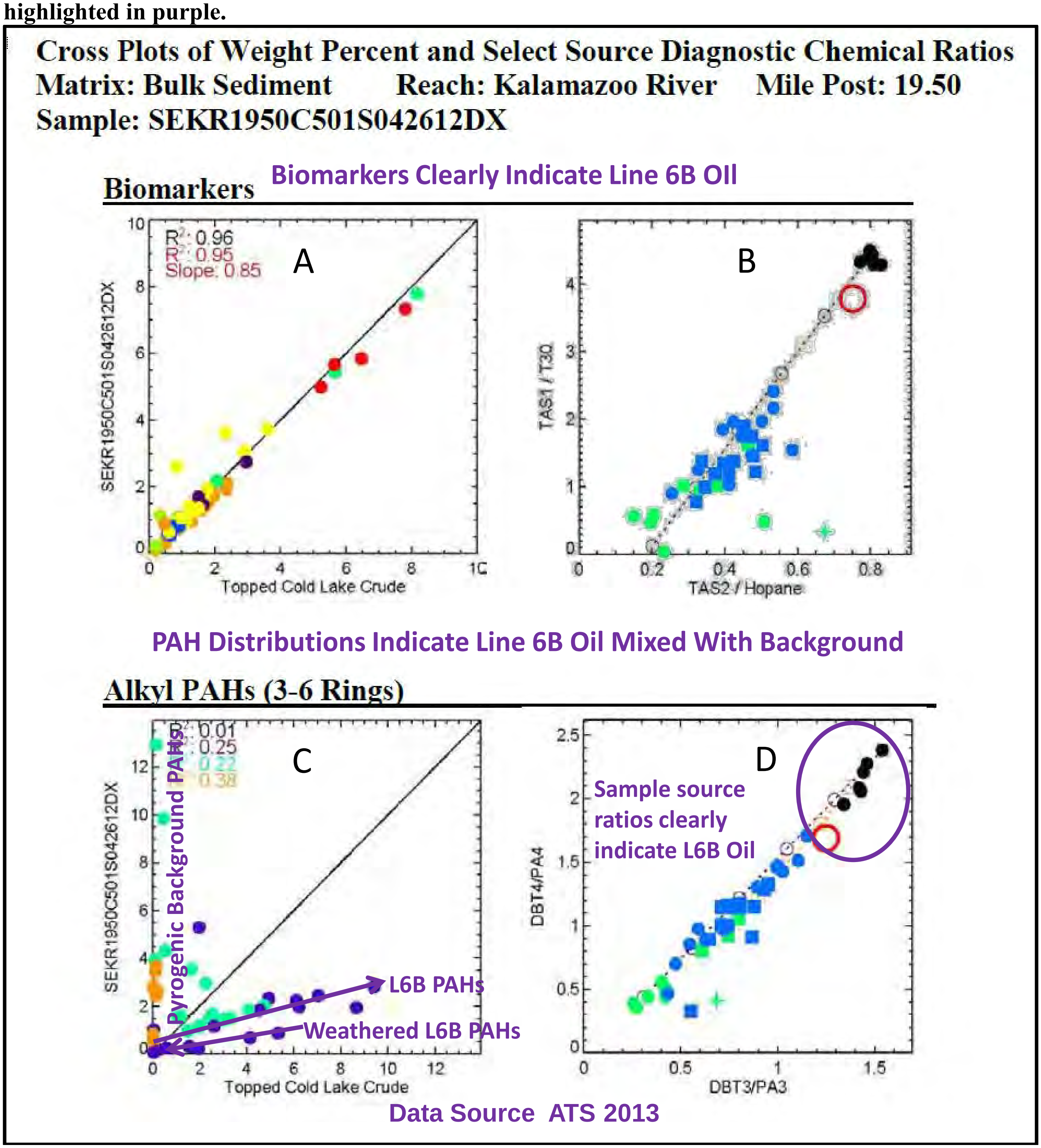
[67] C3-P = C3-phenanthrenes

[68] C4-P = C4-phenanthrenes

[69] Douglas, G.S., Bence, A.E., Prince, R.C., McMillen, S.J. and Butler, E.L. 1996. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technology,* 30(7):2332-2339.

Figure 3. Figure from ATS 2013 Technical Memorandum with NewFields comments highlighted in purple.



Cross Plots of Weight Percent and Select Source Diagnostic Chemical Ratios
Matrix: Bulk Sediment Reach: Kalamazoo River Mile Post: 19.50
Sample: SEKR1950C501S042612DX

Biomarkers

Biomarkers Clearly Indicate Line 6B OIl

PAH Distributions Indicate Line 6B Oil Mixed With Background

Alkyl PAHs (3-6 Rings)

Sample source ratios clearly indicate L6B Oil

Data Source ATS 2013

B. ATS basis its opinion on data that is clearly beyond the usable range of the RFS calibration and them claims that the NewFields reliance of the TAS2/Hopane ratio for Line 6B quantification is suspect "*It is a very good example of why the biomarker data solely should not be relied upon in determining L6B concentrations.*"[70]

The results reported by the authors are derived from the calibration range of the MP35.1 RFS calibration curve that is, by ATS's admission, unreliable and would be expected to be biased high. This fact was not discussed in their critiques of the NewFields biomarker approach, yet they were well aware of the problem *"Regression analysis statistics from these study results indicate that these three diagnostic ratios can be used for direct calibration calculations of L6B for samples with hydrocarbon background up to approximately 1,500 ppm (Extract Residue Upon Evaporation, mg/kg dry weight). Beyond a 1,500 ppm background concentration, L6B concentrations from these biomarker diagnostic ratios cannot reliably be determined without further spiking studies because the spiking level response curves are not linear."*[71]

The plots provided in Figure 4 are an illustration of the direct RFS calibration method used by ATS for sediment sample SEKR1950C501S042612DX showing the quantitation Line 6B concentrations based on TAS2/Hopane and TAS1/T30. Note that the quantitation responses are well beyond the 1,500 ppm calibration range that ATS claims is reliable. None the less, this faulty data is used to claim that the ratio (e.g., TAS2/Hopane) is flawed **"*It is a very good example of why the biomarker data solely should not be relied upon in determining L6B concentrations.*"[70],** when what is flawed is the direct calibration method used by ATS to quantify Line 6B in the Kalamazoo River sediments. The reason that the direct RFS calibration overestimates the Line 6B concentration in sediment sample SEKR1950C501S042612DX is simply because this sample is an example of a high Line 6B sensitivity sediment (Figure 2, see Section D below). Fine grain sediments have a high surface area/mass ratio which act like a magnet for petroleum hydrocarbons (RBH). When these fine grain sediments settle out in depositional basins, they carry with them substantial concentrations of RBH. The opposite is true for coarse grained sediments. Therefore fine grain sediments (e.g., MP35.1) tend to have a higher RBH than coarse grain sediments (e.g., SEKR1950C501S042612DX). Given that the ATS direct RFS calibration is based on the fine grained sediment (MP35.1) with a substantial non-line 6B RBH, the Line 6B calibration based on this sample will overestimate the Line 6B oil concentration in the low RBH and high Line 6B sensitivity sand/gravel sample (Figure 2). Proof of the relative Line 6B sensitivities is provided below in Section D.

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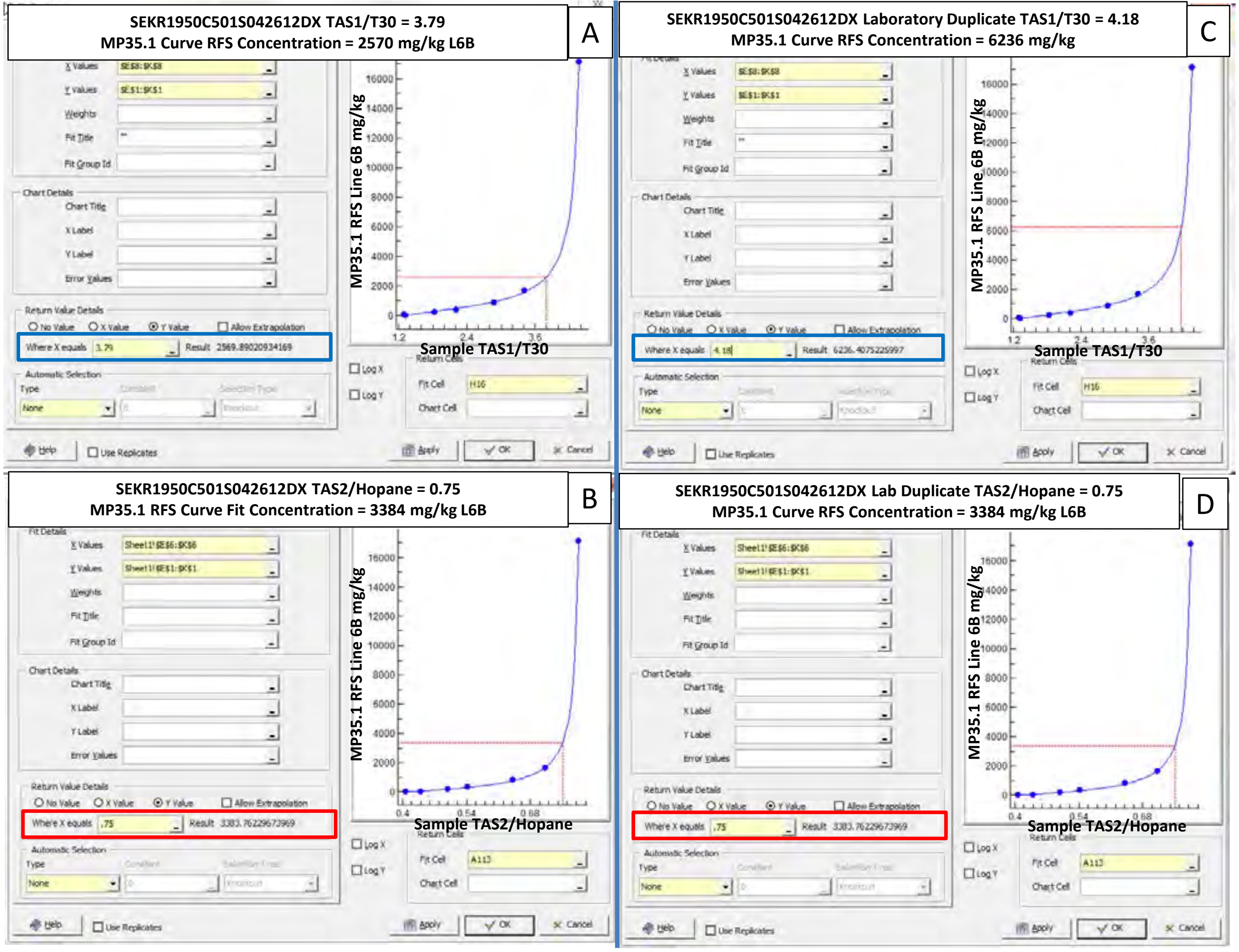
[70] For the record, the NewFields March 1, 2013 Technical Memorandum clearly states that the C3-DBT and C4-DBT estimated Line 6B oil approach should be used to evaluate the chemical reasonableness of the TAS2/Hopane and TAS1/T30 Line 6B quantitation results.

[71] ATS (2013) Pages 4-5.

Figure 4. MP35.1 curve fitting calibration method used by ATS to quantify the amount of Line 6B oil in sediment sample SEKR1950C501S042612DX and its associated laboratory duplicate. A) SEKR1950C501S042612DX TAS1/T30, B) SEKR1950C501S042612DX TAS2/Hopane, C) SEKR1950C501S042612DX TAS1/T30 Lab Duplicate, D) SEKR1950C501S042612DX TAS2/Hopane Lab Duplicate. Calibration curves were determined using the MP35.1 Range Finding Study results and the XLFIT 5 curve fitting program.



A

SEKR1950C501S042612DX TAS1/T30 = 3.79
MP35.1 Curve RFS Concentration = 2570 mg/kg L6B

X Values: $E$8:$K$8
Y Values: $E$1:$K$1
Fit Title: ""
Return Value Details: ○ No Value ○ X Value ● Y Value ☐ Allow Extrapolation
Where X equals: 3.79 Result: 2569.89020934169
Automatic Selection Type: None
☐ Log X
☐ Log Y
Fit Cell: H16
☐ Use Replicates

C

SEKR1950C501S042612DX Laboratory Duplicate TAS1/T30 = 4.18
MP35.1 Curve RFS Concentration = 6236 mg/kg

X Values: $E$8:$K$8
Y Values: $E$1:$K$1
Fit Title: ""
Return Value Details: ○ No Value ○ X Value ● Y Value ☐ Allow Extrapolation
Where X equals: 4.18 Result: 6236.4075225997
Automatic Selection Type: None
☐ Log X
☐ Log Y
Fit Cell: H16
☐ Use Replicates

B

SEKR1950C501S042612DX TAS2/Hopane = 0.75
MP35.1 RFS Curve Fit Concentration = 3384 mg/kg L6B

X Values: Sheet1!$E$6:$K$6
Y Values: Sheet1!$E$1:$K$1
Return Value Details: ○ No Value ○ X Value ● Y Value ☐ Allow Extrapolation
Where X equals: .75 Result: 3383.76229673969
Automatic Selection Type: None
☐ Log X
☐ Log Y
Fit Cell: A113
☐ Use Replicates

D

SEKR1950C501S042612DX Lab Duplicate TAS2/Hopane = 0.75
MP35.1 Curve RFS Concentration = 3384 mg/kg L6B

X Values: Sheet1!$E$6:$K$6
Y Values: Sheet1!$E$1:$K$1
Return Value Details: ○ No Value ○ X Value ● Y Value ☐ Allow Extrapolation
Where X equals: .75 Result: 3383.76229673969
Automatic Selection Type: None
☐ Log X
☐ Log Y
Fit Cell: A113
☐ Use Replicates

C. ATS does not include a discussion of the NewFields TAS2/Hopane or TAS1/T30 mixing model results for the same sample even though these results provide a more defensible result.

NewFields reported the Line 6B concentration in this sample using the more accurate mixing model method. This method is more accurate simply because it incorporates the variance derived by the differential sediment Line 6B sensitivities into the calculation, rather than making the unsupported assumption that the Line 6B sensitivities of the field samples are the same at the calibration sediments (R024 and MP35.1). The NewFields quantified Line 6B concentration in sediment sample SEKR1950C501S042612DX (636 mg/kg Line 6B, Figure 5) is constrained by the range of C3-DBT, C4-DBT, C3-NBT,[72] C4-NBT,[72] TAS1, TAS2, TAS3 maximum Line 6B estimates (Figure 5) and the measured TPH corrected for Line 6B response (748 mg/kg Line 6B, Figure 5). The biodegradability of the reference compounds decreases in a predictable manner from most to least biodegradable as follows:

Most Biodegradable C3-DBT>C4-DBT>C3-NBT>C4-NBT>TAS1≈TAS2≈TAS3 Least Biodegradable[73]

The low constraining value would be C3-DBT with the upper constraining value represented by the TAS compounds. When biodegradation is considered in the field samples relative to the topped Line 6B calibration oil, the range of values is the most defensible approach to evaluate the chemical reasonableness of the Line 6B quantification result.

The NewFields quantified Line 6B is 4.6 times lower than the ATS Line 6B oil estimates because the ATS method does not include the differences in Line 6B sensitivity in the field sample relative to the calibration. Specifically, the quantitation ratio will increase much more rapidly in a gravel/sand sample with a low petrogenic background than a fine grained sediment with moderate petrogenic background (MP35.1, Figure 2). The proof is provided below in Figure 6.

Table 1. Sediment sample SEKR1950C501S042612DX Line 6B diagnostic Data

No.	Parameter	Result	Source
1	TPH (Corrected for Line 6B)	748 mg/kg dry wt.	ATS 2013
2	Extractable Residue	1,367 mg/kg dry wt.	ATS 2013
3	C3-DBT&C4-DBT Max Line 6B	459 mg/kg dry wt.	ATS 2013
4	ATS TAS1/T30, TAS2/T19 (Hopane) Line 6B	2,962 mg/kg dry wt.	ATS 2013
5	NFS Mixing Model TAS1/T30 Line 6B	647 mg/kg dry wt.	NewFields
6	NFS Mixing Model TAS2/Hopane Line 6B	624 mg/kg dry wt.	NewFields
7	NFS Mixing Model Average Line 6B	636 mg/kg dry wt.	NewFields
8	ATS Line 6B – NewFields Line 6B (= ATS overestimate)	2,326 mg/kg dry wt.	

The difference between the ATS Line 6B value (2,962 mg/kg) and the more accurate NewFields Line 6B oil value (636 mg/kg) is because ATS used the inaccurate direct calibration

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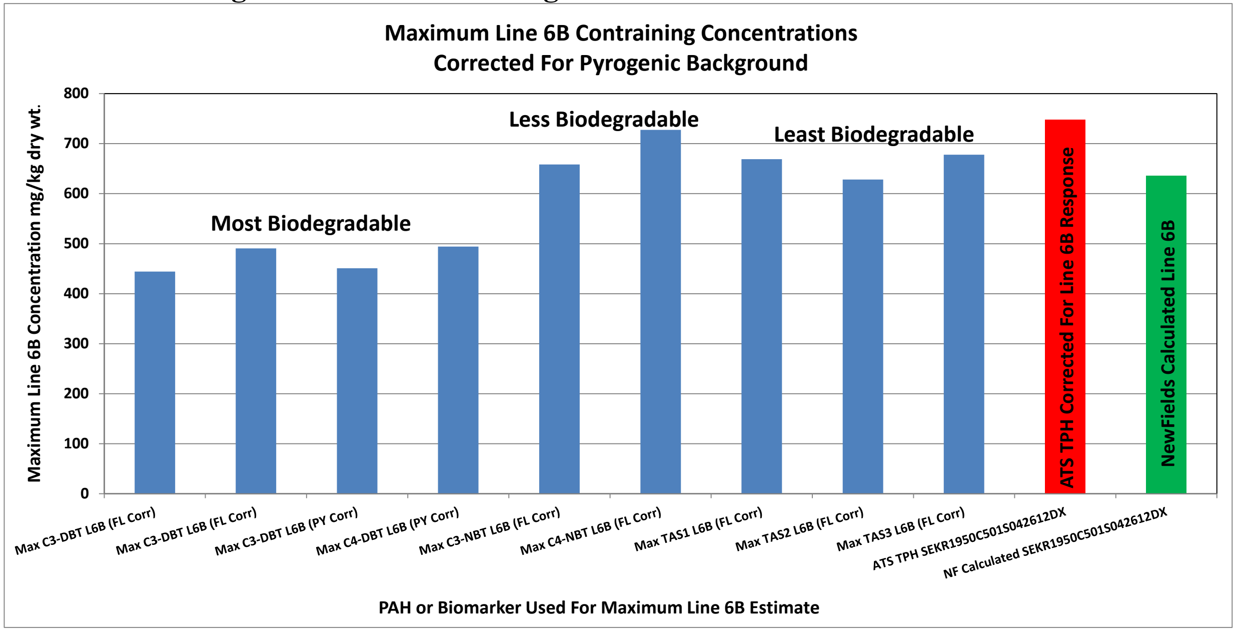
[72] C3-NBT = C3-Naphthobenzothiophenes, C4-NBT = C4-Naphthobenzothiophenes,

[73] Peters, K.E., Walters, C.C., Moldowan, M.J. 2005. The Biomarker Guide. Volume 1. Cambridge University Press.

approach and did not apply the NewFields Mixing Model Method as directed to by the U.S.EPA.[74]

Figure 5. Maximum Line 6B estimates based on biodegradation resistant PAH and biomarker compounds. The estimated Line 6B constraining values increase as biodegradability of the reference compound decrease. The Newfields mixing model Line 6B concentration range fall well between the high and low constraining values and ATS corrected TPH.



D. The RFS direct calibration method used by ATS is severely flawed because it does not take into account individual sediment sample Line 6B sensitivity. This is a compounding factor for the over-reporting of Line 6B oil in sample SEKR1950C501S042612DX.

The direct calibration method used by ATS to calculate Line 6B in Kalamazoo river sediment simply does not work because of the inability of their method to incorporate effects of variable RBH in the sediment samples. The ATS direct calibration method assumes that the Line 6B sensitivity for sediments between MP2-MP15.75 have the same Line 6B sensitivity as the R024 calibration sediments, and that Line 6B sensitivity for sediments between MP16-MP39.75 have the same Line 6B sensitivity as the MP35.1 calibration sediments. This is not true and is the reason that the ATS calculated value for Line 6B oil in sample SEKR1950C501S042612DX makes no sense (Table 1). The reason is not because the NewFields biomarker Line 6B quantification method is flawed. The calculation performed by ATS is to a high degree of scientific certainty flawed because: 1) The ATS value is generated outside the ATS defined usable range of their calibration, and 2) the direct calibration method used by ATS does not incorporate individual sediment sample Line 6B sensitivity. The sample that they used in their example is a gravel/sand (Figure 2 Photo 1) with high Line 6B sensitivity, versus the calibration which is a fine grained silt (Figure 2 Photo 2) has a low Line 6B sensitivity (Figure 6).

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[74] NewFields (2013).

Figure 6. NewFields TAS2/Hopane versus Line 6B oil Mixing Model Plots for reference samples R024 (blue line) and MP35.1 (red line) versus field sediment sample SEKR1950C501S042612DX (green, purple = laboratory duplicate). The R024 and MP35.1 are the RFS base reference sediment samples without Line 6B oil additions. The plots are generated by adding and subtracting topped Line 6B oil to/from the sediment sample using simple algebra to generate new QRs for each addition of oil.

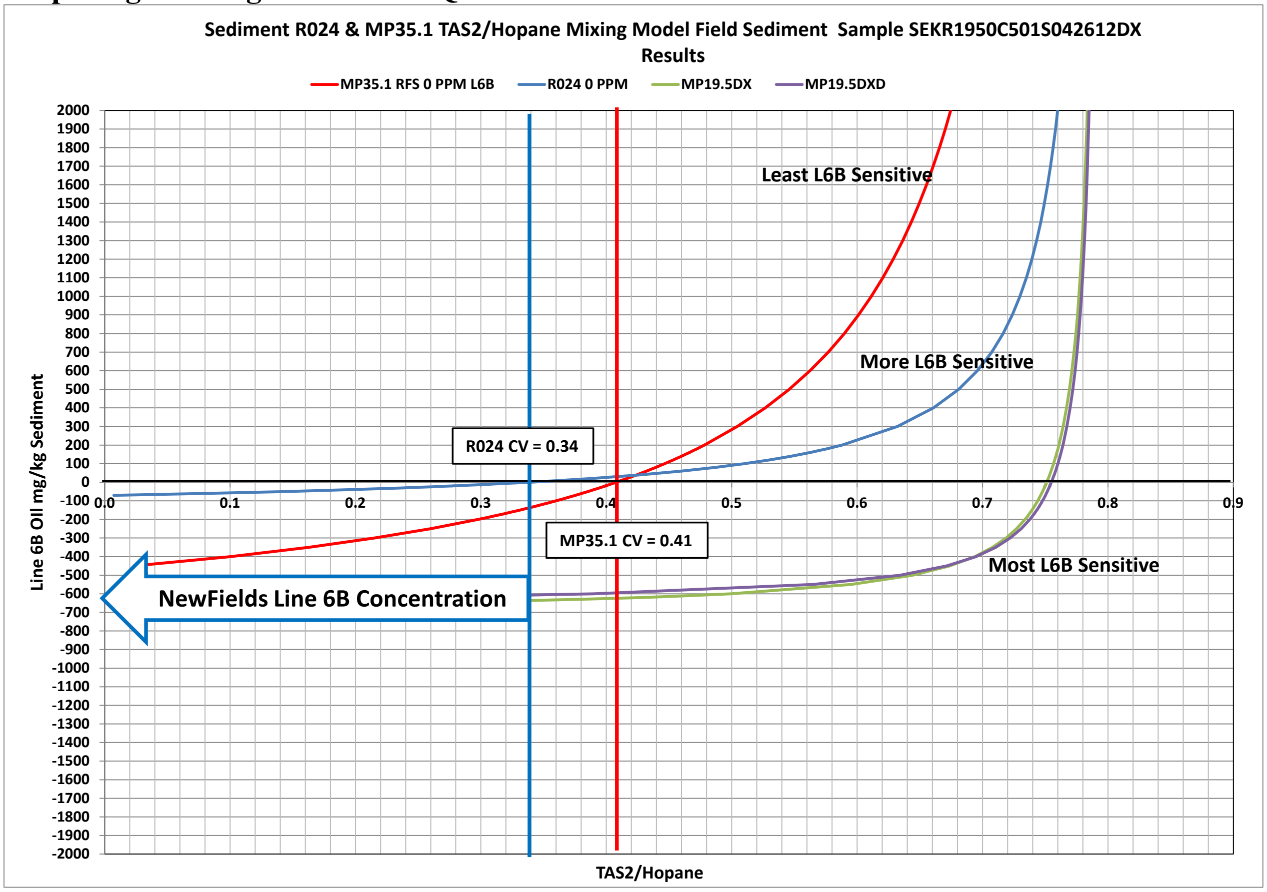

Figure 6 represents the blueprint for the NewFields Line 6B Mixing Model Method. The red sloping line is the Line 6B oil mixing line for RFS sediment sample SEKR3510R018S092112D004-MP35.1, the blue sloping line represents the Line 6B oil mixing line for RFS sediment sample SEKR0000R024S092112D004-R024. Sediment sample SEKR1950C501S042612DX and its associated laboratory duplicate are represented by the green and purple lines respectively. The Y axis is the amount of Line 6B oil mathematically added (positive values) or subtracted (negative values) from the sediment sample and the X axis is the calculated TAS2/Hopane of each mixture. The critical values (CV) are the TAS2/Hopane values where the calibration sediment samples cross the zero Line 6B axis (CV = 0.34 R024, CV = 0.41 MP35.1). The CV is quantified directly from the un-spiked RFS sediment sample. If a field sediment sample had the same Line 6B sensitivity as the calibration samples the mixing model results would fall on the calibration sample curves. The difference in profile and slope of the field samples relative to the calibration samples means that the field sample is highly sensitive to additions to of Line 6B oil (relative to the RFS calibration samples). The highest line 6B sensitivity is between approximately TAS2/Hopane of 0.3 to 0.6 at which point the slope of the curve increases due to the cumulative effects of the added Line 6B oil on the oiled sediment Line 6B sensitivity. At some point (e.g., TAS2/Hopane = 0.7), when more Line 6B is added to a sediment sample, the change in QR (TAS2/Hopane) decreases as it approaches the QR of the Line 6B oil.[75] This proves that the spilled oil itself will alter the Line 6B sensitivity of the field sample and therefore cannot be directly compared to the RFS calibration samples. The only way to overcome this problem is to treat each sample independently with its own unique background RBH.

If the respective calibration curves were used (as they were for the ATS Direct Calibration Method) then the field sample Line 6B oil values were based on the RFS calibrations, the quantified value would be greater than 1,900 mg/kg for the R024 calibration and even greater for the MP35.1 calibration. The most accurate Line 6B value is determined by calculating how much Line 6B oil must be removed from the field sample (SEKR1950C501S042612DX) to reach the zero (0) Line 6B critical value as defined by the reference samples. The results are presented graphically in Figure 6 at 636 ppm Line 6B oil and are well constrained by the PAH and biomarker Line 6B estimates, as well as the ATS corrected Line 6B TPH concentration (Table 1).

23. **Issue:** ADDITIONAL Line 6B CHEMICAL INDICATORS *"Note that we believe that some positively biased results for L6B residuals remain in this data set because of the elevated and significantly variable petrogenic background in both the Kalamazoo River and Battle Creek River sediments. These non-L6B petrogenic residues contain the same alkyl PAHs and biomarkers used in these calculations (C3DBT, C4DBT, T19, T30, TAS1, TAS2) and therefore are included, to varying degrees, in the calculated concentrations of L6B. This results in a positive bias. We currently believe the best way to resolve this positive bias is to add diamonoid biomarker compounds (e.g. adamantanes and diamantanes) in the analysis of sediments, sheens and other media, and incorporate them into the multi-parameter mixing model for calculation of L6B residuals. These diamonoids are found in substantially higher relative abundance in Alberta tar sand crudes as compared to other crude oils, and therefore are much more useful in identifying L6B residues when compared to conventional biomarkers such as hopanes (T19 and T30) and triaromatic steroids (TAS1 and TAS2), which are relatively ubiquitous in crude oils from all sources."*[76]

    Response: ATS provided no evidence (e.g., data or journal reference) that the measurement of diamonoid biomarker hydrocarbons would improve their ability to quantify Line 6B oil in Kalamazoo Sediments. In addition, the authors diminish the reliability of their own quantification methods by suggesting that there is a better path to follow for the Line 6B Quantitation Study. The analytical methods and target compounds used in this study were developed by 100's of government and industry professionals who have worked in the field for the past 30 years and who have also published their work in peer reviewed journals. These methods and target analytes have been successfully applied to the vast majority of significant oils spills (e.g., Exxon Valdez, Cosco Busan, New Carrissa, Selendang, Macondo). If ATS/Enbridge believed that the use of diamonoid biomarkers for the

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[75] The same reduction in Line 6B sensitivity was observed in the RFS studies.

[76] ATS (2013) Page 7, Paragraph 2.

Kalamazoo River Line 6B Quantification Study would produce higher quality results then they should produce the evidence.

3.0 Data Base Issue

In addition to the detailed interpretive analysis of the Report, we have compared the final data files between ATS Technical Memorandum Line 6B Oil Quantification Summary Table to the Enbridge Report Tables 5-8. We find that there are 147 samples (Attachment 1) listed in the Enbridge Report Tables that are not identified in the ATS Line 6B Oil Quantification Table. Further examination of the NewFields data tables and the EQuIS deliverables we received from Enbridge, do not contain these additional samples either. These may be core samples that were not analyzed and the Line 6B concentrations were interpolated from samples above and below. Whatever the reason, their presence in Report Tables 5 and 6 make it even more difficult to validate the analytical results back to the individual sediment samples.

The conclusions in this review are based on currently available data. Should additional data or information become available to me, or if the analytical data is modified as a result of the on-going quality assurance reviews, I reserve the right to update this report as needed.

Please let me know if you have any additional questions concerning this review.

Sincerely,

Gregory S Douglas

Gregory S. Douglas, Ph.D.
Sr. Consultant.

Attachment 1.

List of Sediment Samples Reported In Enbridge Report Tables 5-8 Without Any Associated Analytical Data.

SEKR0400C701S072512D008
SEKR0400C701S072512D013
SEKR0400C701S072512D017
SEKR0400C701S072512D021
SEKR0425C701S072512D011
SEKR0425C701S072512D016
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SEKR0550C701S072612D019
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SEKR0575C702S112712D027
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SEKR0900C702S112712D017
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SEKR1100C701S112912D013
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SEKR1425C701S113012D010
SEKR1425C701S113012D013
SEKR1425C701S113012D016
SEKR1425C701S113012D018
SEKR1475C702S072612D009
SEKR1475C702S072612D013
SEKR1475C702S072612D015
SEKR1475C702S072612D019
SEKR1475C702S072612D020
SEKR1500C701S072612D019
SEKR1500C701S072612D024
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SEKR1850C701S072412D015
SEKR1850C701S072412D020
SEKR1850C701S072412D027
SEKR1950C701S072412D008
SEKR2000C701S072412D016
SEKR2000C701S072412D028
SEKR2025C702S072412D007
SEKR2025C702S072412D011
SEKR2025C702S072412D017
SEKR2025C702S072412D020
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