REJOINDER EXPERT REPORT OF JEFFREY W. SHORT, PH.D., REGARDING ACTIVITIES AND ENVIRONMENTAL CONDITIONS IN THE FORMER TEXACO-PETROECUADOR CONCESSION, REPUBLIC OF ECUADOR

In Response to:

Expert Opinion of John A. Connor, P.E., P.G., B.C.E.E. Regarding Remediation Activities and Environmental Conditions in the Former Petroecuador – Texaco Concession, Oriente Region, Ecuador, Response to LBG Report of February 2013, Issued 3 June 2013,

Expert Report by Robert E. Hinchee, Ph.D., P.E, Expert Report Issued 31 May 2013,

and

The Matter of An Arbitration Under the Rules of the United Nations on International Trade law; Chevron Corporation and Texaco Petroleum Company v. The Republic of Ecuador, Claimants' Track 2 Reply Memorial and Annex A

In The Matter of An Arbitration Under the Rules of the United Nations on International Trade law; Chevron Corporation and Texaco Petroleum Company v. The Republic of Ecuador

Prepared for: Winston & Strawn, LLP 1700 K Street N.W. Washington DC 20006-3817 The Louis Berger Group, Inc. -and- 412 Mount Kemble Avenue Morristown, NJ 07962-1946

/Jeffrey W. Short, Ph.D.

Juneau, Alaska U.S.A. Location December 11, 2013 Date

1.0 Introduction¹

This rejoinder report responds to comments on my opinions contained in the *Expert Opinion of Kenneth J. Goldstein, M.A., CGWP and Jeffrey W. Short, Ph.D. Regarding the Environmental Contamination From Texpet's E&P Activities in the Former Napo Concession Area Oriente Region, Ecuador* (hereafter *Louis Berger February 2013 Expert Report*). These comments include the:

- Expert Opinion of John A. Connor, P.E., P.G., B.C.E.E. Regarding Remediation Activities and Environmental Conditions in the Former Petroecuador – Texaco Concession, Oriente Region, Ecuador, Response to LBG Report of February 2013, Issued 3 June 2013 (hereafter <u>Connor June 2013 Rebuttal Report</u>),
- Expert Opinion of Robert E. Hinchee, Ph.D., P.E., In the Matter of an Arbitration under the Rules of the United Nations Commission on International Trade Law Chevron Corporation and Texaco Petroleum Company, Claimant v. The Republic of Ecuador, Respondent, PCA case no. 2009-23 (hereafter <u>Hinchee</u> <u>May 2013 Rebuttal Report</u>), and
- The Matter of An Arbitration Under the Rules of the United Nations on International Trade law; Chevron Corporation and Texaco Petroleum Company v. The Republic of Ecuador, Claimants Reply Memorial, Track 2, Annex A (hereafter <u>Claimants' Memorial Annex A</u>).

I continue to hold my opinions expressed in the Louis Berger February 2013 Expert Report, and provide additional evidence to support these opinions throughout this Rejoinder Report. I have added here supplemental opinions to my original opinions to address issues raised in the three Chevron rebuttal documents listed above.

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2.0 MATERIALS REVIEWED

I have been retained by Louis Berger Group, Inc. (hereafter Louis Berger Group) to review and comment on the above Chevron rebuttal documents. I have also been retained to interpret hydrocarbon data resulting from the chemical analysis of soil and sediment samples collected by the Louis Berger Group from oil contaminated sites within Ecuador's Oriente Concession Area during August through October, 2013. In preparation of this rebuttal report, I have reviewed the above reports, the Republic's

¹ References to exhibits previously submitted to the Tribunal have not been resubmitted with this expert report.

Rejoinder Memorial, the Republic's other rejoinder expert reports (either in final or close-to-final form), and preliminary results of chemical analyses for hydrocarbons produced by Axys Laboratory, Katahdin Laboratory, and Battelle Memorial Institute, provided to me by Louis Berger Group. I have also reviewed the reference and deposition documents that I cite herein, numerous chemical analysis reports produced by Dr. Gregory Douglas at Newfields Environmental Forensics Practice, and associated chemical analysis reports produced by Alpha Woods Hole Group and Severn Trent Laboratories

I am currently an independent consultant offering these opinions, and have never been an employee of Louis Berger Group or of Winston & Strawn LLP.

My opinions in this expert report are given to a reasonable degree of scientific probability. They are based on my education, professional experience, information and data available in the scientific literature, and information and data about this lawsuit made available to me prior to my formulation of these opinions.

I am continuing to review available information, and I reserve the right to amend or supplement this report and the opinions contained in this report on the basis of any subsequently obtained material information.

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3.0 SUMMARY OF REJOINDER OPINIONS

Having reviewed the Connor June 2013 Rebuttal Report and the Hinchee May 2013 Rebuttal Report, I disagree with the method they relied on to assess the extent of hypothetical crude oil degradation occurring once crude oil has been released to the Concession area environment. Contrary to their opinions:

- The method they relied on to characterize the extent of hypothetical crude oil degradation is fundamentally flawed and has grossly exaggerated the extent of actual degradation: their method indicates degradation losses of \sim 50% even for fresh, un-degraded Ecuadorian Oriente crude oils.
- Laboratory analyses of petroleum hydrocarbons from samples of soil and sediments recently collected from the Concession Area (during August through October, 2013) confirm that at least some of the lingering oil in the region is in a state of largely arrested biodegradation, remains mobile, and retains a substantial complement of toxic hydrocarbons.
- The toxicity characteristic leachate procedure (TCLP) used by Chevron to detect and quantify residual soil hydrocarbons fundamentally inappropriate

for such use, and *in principle* cannot, even at undiluted (100%) crude oil concentrations, produce results that exceed a regulatory threshold of 1,000 mg/L through dissolution of contaminants from crude oils into aqueous media.

After review of Claimants' Memorial Annex A, I also disagree, in whole or part, with certain of their statements regarding:

- Assertions made in Claimants' Reply Memorial Annex A disputing the toxicity to fish of alkyl-substituted polycyclic aromatic hydrocarbons (PAHs), which constitute the majority of the toxic PAHs in crude oils. The high toxicity of alkyl-substituted PAHs to fish has been scientifically confirmed by multiple studies, including studies conducted by scientists not affiliated with the US government. These studies were largely ignored by Chevron's experts.
- The supposed absence of regulatory concern regarding the toxicity of alkyl-substituted PAHs.
- The weathering rate and the biodegradation experiments conducted by Dr. Gregory Douglas.

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4.0 REJOINDER OPINIONS

4.1 CHEVRON'S FLAWED CHEMICAL AND DATA ANALYSIS METHODS GROSSLY EXAGGERATE ACTUAL OIL WEATHERING IN THE CONCESSION AREA

Once released into the environment, the composition of spilled crude oil ordinarily begins to change as components evaporate, dissolve into water, are degraded by microbes or are oxidized by sunlight. Collectively, these processes are termed "weathering" and eventually will convert fresh crude oil from a highly fluid liquid to a hardened, immobile asphalt-like material that is depleted of toxic hydrocarbons. The rates of these processes determine how long spilled oil remains a toxic threat to biota. While it might seem that the warm temperatures of the Ecuadorian Oriente would accelerate these weathering processes, other counteracting factors -- including (i) the unavailability of oxygen, oil-degrading microbes and nutrients necessary to sustain oil degradation, and in particular (ii) the relatively small surface area to volume ratio of the oil itself -- are more important².

² Louis Berger, 2013, p. 61 – 62

Both Connor³ and Hinchee⁴ rely substantively on results presented in a scientific paper published by O'Reilly and Thorsen⁵ as the basis for their opinion that petroleum could not "... migrate to impact groundwater, surface water, or other areas beyond the well platform – which is physically impossible"⁶ This conclusion might seem plausible premised on O'Reilly and Thorsen's claim that half the oil-contaminated soil samples they considered had lost 87 percent or more mass from weathering, and three-fourths of the samples had lost 80 percent mass.⁷ However, the O'Reilly and Thorsen results actually reflect a large bias derived from inappropriately equating chemical measurements of (a) "total petroleum hydrocarbons" (TPH) with (b) the actual amount of all residual crude oil present. As applied to soil samples from the Concession Area, the chemical measurements of TPH will only account for about half the mass (weight) of residual crude oil actually present. The supposedly "missing" mass not appearing in the TPH measurement was mistakenly attributed to weathering losses rather than to the true cause -- the inappropriate analytic method used.

<u>Conclusion</u>: Exaggerated estimates of oil weathering, combined with a failure to adequately address the toxicity associated with the alkyl-substituted PAHs, has led Chevron's experts to dramatically underestimate the potential for contamination of receiving waters in the Concession Area caused by release of toxic hydrocarbons from residual oil attributable to Texpet operations.

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4.1.1 OVERVIEW OF CHEVRON'S FLAWED TESTING AND EVALUATION OF CRUDE OIL WEATHERING

Oil weathering processes gradually reduce the mass of released crude oil. The proportion of initial mass lost is frequently used as an index for characterizing the extent of weathering. This "weathering index" (Wx) is simply the difference between the initial mass M_i and final mass M_f , as a proportion of the initial mass:

$$Wx = \frac{M_i - M_f}{M_i} = 1 - \frac{M_f}{M_i}$$
(1)

³ Connor, 2013, p. 22

⁴ Hinchee, 2013, p. 9

⁵ O'Reilly, K. and Thorsen, W., 2010, Impact of Crude Oil Weathering on the Calculated Effective Solubility of Aromatic Compounds: Evaluation of Soils from Ecuadorean Oil Fields, *Soil and Sediment Contamination*, 19:391 – 404

⁶ Connor, 2013, p. 22

⁷ O'Reilly and Thorson, 2010, p. 397

The weathering index, *Wx*, will have a value of "zero" if no mass was lost (*i.e.* no weathering has occurred), and will approach "1" as the loss of mass from weathering becomes extreme. While conceptually and arithmetically straightforward, derivation of true *Wx* requires careful application of consistent analytical methods.

The initial mass, M_{i} of crude oil is usually inferred from measurement of a conserved component compound and knowledge of the initial composition of the source oil. A "conserved" component compound is one that has little tendency to evaporate, dissolve, biodegrade or photo-oxidize, so that its mass will have changed by a negligible amount after the crude oil has been released. If (a) the initial (*i.e.* date of release) ratio of a conserved component to a unit mass of the released crude oil is known, and (b) if the ratio of the same conserved component to a unit mass of the same crude is measured post-release, then the Wx of the post-release sample can be easily calculated.

The conserved component usually used for calculating crude oil weathering indexes is called *hopane* (*HP*), a 5-ringed alicyclic hydrocarbon that is relatively abundant in most crude oils. If the same amount of *HP* is left in the weathered unit mass, M_{f_i} as was present in the initial unit mass, M_i , then equation 1 can be re-written as:

$$Wx = 1 - \frac{\frac{M_f}{HP}}{\frac{M_i}{HP}} = 1 - \frac{[HP]_i}{[HP]_f}$$
(2)

because the numerator and denominator terms in the middle part of this expression are just the inverses of the corresponding concentrations, denoted by the brackets on the right. Hence, the weathering index can easily be calculated by comparing measurements of (a) the later concentration of *HP* in the exposed crude oil field sample to (b) its earlier concentration in the corresponding source crude oil sample. Obviously, the integrity and validity of this measurement assumes that the concentrations are measured *in exactly the same way in both cases*.

Exactly this approach was used by Dr. Gregory Douglas in his 1996 scientific publication on petroleum hydrocarbon source and weathering ratios.⁸ He clearly pointed out the requirement of making consistent measurements when applying equation (2) above with the statement:

"The concentration of hopane in the weathered oil (H_1), *measured on an oil weight basis*, relative to its initial concentration in the source oil (H_0) is a function of the amount of oil degraded..."⁹ (emphasis added).

⁸ 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, *Environmental Science and Technology* 30:2332-2339

⁹ Ibid., at p. 2334

Dr. Douglas confirmed the requirement to make measurements *consistently* on an *oil weight basis* in his deposition:

"This percent depletion refers to total oil depletion in the sample, and in that case total oil depletion in the sample --in an oil sample, for example, or a weathered oil sample would be measured on an oil weight basis.."¹⁰

But the O'Reilly and Thorsen methodology violates this consistency requirement. Instead of basing the *HP* concentration of field samples on an oil weight basis, obtained by (for example) separating the oil from the inorganic material present in a soil or sediment sample and then weighing it, they inappropriately relied on results from USEPA Method 8015, which on an oil weight comparison basis can only measure about half the weight of Ecuadorian Oriente oils actually present in field soil samples.

<u>Conclusion</u>: Because the method used by Chevron's experts to measure the hopane concentration in field samples of weathered crude oil involves inappropriate use of USEPA Method 8015, they introduced a large bias that grossly exaggerated the magnitude of the weathering index, as calculated by the O'Reilly and Thorsen methodology.

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4.1.2 INCONSISTENT METHODS USED TO EVALUATE CRUDE OIL WEATHERING

Hopane is routinely measured by gas chromatography-mass spectrometry (GCMS), using USEPA Method 8270 or similar. This method begins with a known mass of crude oil that is diluted in an organic solvent, and then fractionated on a liquid chromatography column into aliphatic and other fractions. After separation from other components in the gas chromatographic column, the hopane constituent is measured at a specific mass:charge ratio (= m/z 191) in the mass spectrometer detector. The response of the mass spectrometer is calibrated with standards of authentic hopane. Finally, the concentration of hopane is computed as the ratio of the amount of hopane measured by the GCMS and the initial sample mass of crude oil. While this procedure is straightforward for measuring hopane concentrations in a <u>laboratory sample</u> of pure source oil, where the initial oil mass is determined by simply weighing it, collecting and measuring the equivalent mass of crude oil in a <u>field sample</u> is not so easily determined.

¹⁰ Douglas Dep. at 172

Samples of weathered crude oil collected from the field usually involve some admixture with inorganic particles (*e.g.*, sand, mud, clay etc.) and water. Legitimate application of equation (2) above requires accurate measurement of the mass of oil in the sample, net of other extraneous material. One common way to do this would be to dissolve the weathered crude oil in a strong organic solvent such as dichloromethane, remove the extraneous material by filtration through a hygroscopic salt, evaporate the solvent from the filtrate, and weigh the remaining residue. Instead, O'Reilly and Thorsen inappropriately used USEPA Method 8015 to measure TPH in the field samples.¹¹ But this method does not account for the full range of the constituents of the crude oil mass actually present in a field sample.

USEPA Method 8015 was designed to measure TPH from refined petroleum products such as gasoline, diesel or lubricating oils mixed with some environmental matrix such as soils or water.¹² As a result, it only accounts for those organic petroleum components which are in the gasoline (GRO) and diesel (DRO) ranges of molecular weight. The method involves extraction of the environmental soil or water sample by an organic solvent, followed by filtration and dehydration and then injection of a portion of the concentrated extract into a gas chromatograph equipped with a flame ionization detector (FID). The FID detector is non-specific, and responds to combustion products of all organic compounds that pass through the gas chromatograph column. And here is the heart of the flaw: in contrast with highly refined petroleum products like gasoline or diesel oil, only about half the mass of crude oil is able to pass through the gas chromatograph column and into the FID. The amount of petroleum components that cannot pass through -- approximately 50 percent -- has been mistakenly attributed by O'Reilly and Thorsen to loss from "weathering."

¹¹ O'Reilly and Thorsen, 2010, p. 394

¹² U.S. Environmental Protection Agency, 1996, Test Methods for Evaluating Solid Waste – Physical/Chemical Methods, SW-846, Revised Methods, 3rd edition, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC

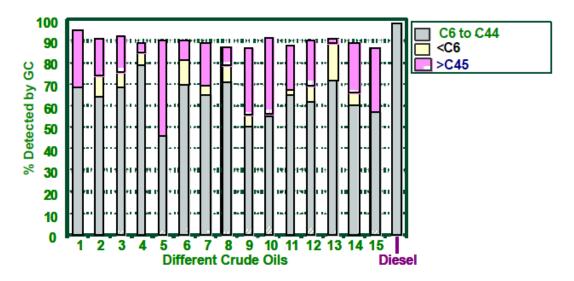


Figure 1. Typical proportions of un-weathered crude oils detected by methods based on gas chromatography, such as USEPA Method 8015 and TNRCC methods 1005 & 1006.¹³ Note that at best these methods only cover the carbon range (in molecular weight) from C6 through C44.

The proportion of oil by weight that is not detected by USEPA Method 8015 and similar gas chromatographic methods increases with the molecular density of crude oil components. Most Ecuadorian Oriente crude oils have API "gravities" (roughly, an inverse measure of density) between 24.4° and 30.5°, corresponding to proportions of "vacuum residua" (*i.e.*, heavy material that cannot be detected by gas chromatographic methods) ranging from 20 percent to 50 percent for fresh, unweathered crude oils (Fig. 2). As oil weathers, the proportion of the weathered oil that is not detectable as TPH by gas chromatographic methods, including USEPA Method 8015, increases, because the oil components amenable to gas chromatographic analysis are preferentially lost during weathering.

¹³ McMillen S., Rhodes I., Nakles D.V., and Sweeney R.E. 2001. Application of the total petroleum hydrocarbon criteria working group (THPCWG) methodology to crude oils and gas condensates. Chapter 4 in: McMillen, S.J., Magaw, R.I. and Caravillano, R.L., eds.; Risk-Based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites. US Department of Energy, National Energy Technology Laboratory, National Petroleum Technology Office, One West Third Street, Tulsa, OK 74103-3519, at p. 66

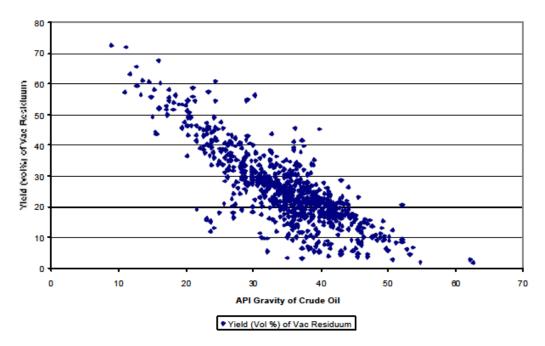


Figure 2. Yield of vacuum residuum for 800 crude oils at oil densities as measured by API gravity¹⁴.

The bias toward underestimating the amount of residual crude oil in a field sample, based on TPH as measured by USEPA Method 8015, is well understood by Chevron's own experts. In the course of reviewing various methods for determining TPH in field samples based on gas chromatography, they note that up to half the mass of oil may not be detected¹⁵ (*e.g.*, oil sample 5 in Fig. 1).

<u>Conclusion</u>: Analysis for TPH by gas chromatographic methods including USEPA Method 8015 are subject to well-known biases that underestimate the concentration of total crude oil actually present in a field sample. This bias (low) under-reports concentrations on the order of 50% for fresh, un-weathered Ecuadorian Oriente crude oils, and under-reports concentrations even more in weathered crude oil, because the field samples will have lost their lighter and more detectable components during weathering.

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4.1.3 RELIANCE ON USEPA METHOD 8015 MISLED CONNOR'S ASSESSMENT OF CRUDE OIL WEATHERING

¹⁴ McMillen et al., 2001, p. 66

¹⁵ McMillen et al., 2001, p. 65

In his reply report, Connor states that:

"As discussed in my prior report (Connor, 2010), Chevron experts analyzed the mobility of the residual hydrocarbons found in petroleum-impacted soils by means of physical inspection, soil leachate tests, chemical fingerprinting analyses, and residual saturation tests. These data showed the residual hydrocarbons to consist of insoluble resins and asphaltenes that are immobile in the soil matrix. LBG suggests that these petroleum residuals could migrate to impact groundwater, surface water, or other land areas beyond the well platform – which is physically impossible (Newell, 2005; O'Reilly and Thorsen, 2010)."¹⁶

Connor did not actually test the oil to determine whether it contained only immobile asphaltenes and resins. Instead, Connor relies exclusively upon the O'Reilly and Thorsen weathering index to support his assertion that the residual hydrocarbons consist of insoluble resins and asphaltenes. To determine the extent of weathering in 107 Oriente soil samples, O'Reilly and Thorsen in turn cite Douglas et al. 1996 as their authority¹⁷ for applying exactly the same formula for computing the weathering index, *Wx*, that Douglas had presented in his 1996 scientific paper on oil weathering, namely:

"Wx = 1 - (HPo/HPs)

(3)

Where:

HPo= concentration of HP in fresh oil (mg HP/kg fresh oil). HPs = concentration of HP in soil TPH (mg HP/kg soil)/(mg TPH/kg soil)"¹⁸

Note that their statement of their equation (3) appears similar to equation (2) above, but with a key difference: *the hopane (HP) concentration in their field soil sample is not on an oil weight basis.* Instead, the hopane concentration in the soil sample is on a TPH basis, where TPH is determined by USEPA Method 8015, as O'Reilly and Thorsen stated explicitly.¹⁹ As shown in Section 4.1.2 above, their method does not account for all of the oil weight present in a soil sample, which results in a "bias high" of the weathering index.

This "bias high" weathering index calculation (based on the inverse "bias low" calculation of TPH from use of USEPA Method 8015) inherent in O'Reilly and Thorsen's method is exacerbated by O'Reilly and Thorsen's restriction of TPH to the sum of only gasoline range organics (GRO) and diesel range organics (DRO), leaving out other hydrocarbon molecular weights commonly found in crude oil that **do** pass

¹⁶ Connor, 2013, p. 22

¹⁷ O'Reilly and Thorsen, 2010, p. 394

¹⁸ Quoted verbatim from O'Reilly and Thorsen, 2010, p, 394

¹⁹ O'Reilly and Thorsen, 2010, p. 394

through the gas chromatograph.²⁰ Thus, in addition to omitting all the crude oil components that cannot pass through the gas chromatograph, O'Reilly and Thorsen's limitation of DRO to the C10 – C25 carbon window omits even more TPH components associated with carbon numbers greater than C25 (Figure 3).

FID Chromatogram of Lingering Crude Oil in Soil at Site Guanta 06 – SL10 After More than 20 Years

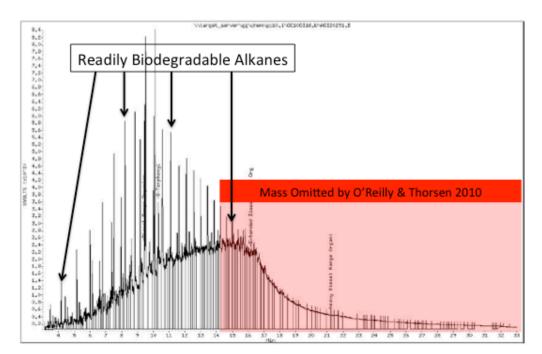


Figure 3. Chromatogram of oil components produced by USEPA Method 8015 of a slightly weathered sample of crude oil collected by Louis Berger personnel during August through October 2013 at site Guanta 06-SL010. The pink-shaded area shows a portion of the oil components omitted by O'Reilly and Thorsen's restriction of DRO components to C10 through C25, shown in the un-shaded portion of the chromatogram. Also note the regular sequence of sharp peaks indicating abundant and readily degradable *n*-alkanes in this sample, four of which are indicated by black arrows, confirming arrested biodegradation soon after this oil was released to the environment (see Sec. 4.2 below).

This additional "bias high" weathering calculation factor introduced by O'Reilly and Thorsen's method is clearly illustrated by its application to un-weathered crude oil. Taking Lago Agrio reference oil sample denoted LA-N-JI-OIL1 as a specific and

²⁰ O'Reilly and Thorsen, 2010, p. 394

typical example, the Alpha Woods Hole Group analysis found that the DRO fraction²¹ accounts for 400,000 mg/kg of Lago Agrio crude²². The GRO of Lago Agrio crude is about 152,000 mg/kg crude.²³ Together the GRO and DRO account for 552,000 mg/kg crude, or 55.2 percent of the crude's total mass. The hopane concentration of sample LA-N-JI-OIL1, also reported by the Alpha Woods Hole Group, is 160 mg/kg crude²⁴. Inserting these numbers into the formula above used by O'Reilly and Thorsen to compute their weathering index gives:

 $Wx = 1 - \frac{\frac{160 \text{ mg hopane}}{\text{kg fresh oil}}}{\frac{160 \text{ mg hopane}}{0.552 \text{ kg TPH}}} = 0.448$

Conclusion: O'Reilly and Thorsen's flawed methodology thus leads to the inherently incredible conclusion that this fresh un-weathered crude oil sample has already lost 44.8% of its mass to weathering before its release to the environment! This is a serious bias.

It is small wonder then that O'Reilly and Thorsen (2010) erroneously conclude that half the samples they evaluated had a weathering index, Wx, of 0.87 or more, since their inappropriate combination of chemical analysis methods (equating TPH results by USEPA Method 8015 with crude oil weight) ensures that **all** of their samples begin life with a weathering index value of ~0.4. This misuse of analytical methodology ensured a systematically gross exaggeration of the actual weathering state of all crude oil samples they evaluated, and hence their results for their weathering index must be completely discarded.

Conclusion: The crude oil weathering index, Wx, as determined by O'Reilly and Thorsen (2010), grossly overstates loss of mass due to "weathering" because they used analytic methods that were clearly not appropriate for that purpose. Reliance on this index by Connor led him to estimate erroneously that residual crude in the Concession Area is far more weathered than is actually the case; hence, all of his arguments regarding the extent of oil weathering based on O'Reilly and Thorsen (2010) and premised on "extensively degraded oil" should be disregarded.

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²¹ This includes a somewhat greater range of components, from C10 – C28, than was used by O'Reilly and Thorsen, who only included components through C25, exacerbating their underestimation bias

 $^{^{22}}$ Alpha Woods Hole Group, total hydrocarbon summary C10 – C28 DRO at GSD037626

²³ Alpha Woods Hole Group, laboratory sample number 0406054-04 at GSD 305118, identified as Lago Agrio oil at GSD 207000

²⁴ Alpha Woods Hole Group, hopane concentration at GSI_0589009

4.1.4 INAPPROPRIATE USE OF USEPA METHOD 8015 TO MEASURE CRUDE OIL CONTAMINATION IN ENVIRONMENTAL MEDIA

Chevron's experts made widespread and inappropriate use of USEPA Method 8015 to assess crude oil contamination in environmental media. While I noted this concern in the Louis Berger February 2013 Expert Report²⁵, additional data that have since become available confirm my concerns. In our February report, Goldstein and I noted that, in the relatively few instances then available to us where measurements for TPH were performed on the same sample by both USEPA Methods 418.1 and 8015, the results by Method 418.1 were consistently higher by a factor ranging from 4 to 8. This is not surprising because Method 8015 was primarily designed to detect refined oils, gasoline and diesel fuel in particular²⁶. In contrast, as explained above crude oils contain innumerable compounds that cannot pass through the gas chromatograph column employed by Method 8015, and hence simply were not measured by that method (Fig. 1). Moreover, of those compounds that were detected, the ones that fall within the upper end of the carbon range (*i.e.* are heavier than the DRO range) also were not measured. Consequently, TPH as measured by Method 8015 (i.e., by accumulating only GRO and DRO molecular weights) only detects a portion of the actual amount of crude oil present in a sample.

The "bias low" limitation of USEPA Method 8015 for crude oil weight is again clearly evident by examining its application to fresh un-weathered crude oil. An accurate method would consistently account for all or most of the mass of oil present. But as the results of Chevron's own analyses of fresh un-weathered crude oils vividly demonstrate, USEPA Method 8015 is only capable of detecting about 50 percent of the mass initially present in the crude oils of the Ecuadorian Oriente (Figs. 1 – 3, and Sec. 4.1.3 above). Consequently, USEPA Method 8015 cannot be relied upon for quantitative estimates of the intensity of oil contamination within the Concession Area. This contrasts with Method 418.1, which measures the number of carbonhydrogen bonds in a sample extract regardless of what compounds are present.

While Method 418.1 may also detect traces of organic non-petroleum hydrocarbon compounds, this is a negligible concern when characterizing the soils and sediments of an oilfield where the concentration of *heavily contaminated* media (*i.e.* > 1000 mg/kg, or > 0.1 percent oil) is the primary focus of concern. For soils containing a typical natural burden of total organic non-petroleum carbon compounds of 1 percent or less, natural sources of hydrocarbons that could increase hydrocarbon concentrations measured by Method 418.1 would be less than about 200 mg/kg, and then only if the organic carbon were entirely composed of highly interfering natural sources such as pine needles. TPH in pine needles have been measured at

²⁵ Louis Berger, 2013, p. 35 – 37

²⁶ USEPA, 1996

19,000 mg/kg by Method 418.1²⁷, so assuming a soil sample contains 1 percent by mass pine needles, the TPH concentration by Method 418.1 would be $0.01 \times 19,000$ mg/kg = 190 mg/kg. Even this highly unusual degree of interference is no more than a moderate bias at most when heavily contaminated media are the focus of concern.

Results from use of USEPA Method 8015 become progressively less accurate as oil weathers, exacerbating the discrepancy between the mass of oil components detected and the larger mass of oil components actually present. This is because the oil components most readily detected by USEPA Method 8015 consist mainly of those most vulnerable to weathering losses.²⁸ Hence, as weathering proceeds, USEPA Method 8015 detects an ever smaller proportion of the crude oil components remaining. This progressively worsening inaccuracy is the reason why TPH by GRO/DRO (Method 8015) yields lower mass concentrations that detected by USEPA Method 418.1 by a factor of from four to eight, as noted in the Louis Berger February 2013 Expert Report.²⁹

Conclusion: USEPA Method 8015 is poorly suited for evaluating the extent of oil contamination in the Concession Area because it only detects approximately half of the oil components present in fresh un-weathered Ecuadorian Oriente crude, and the proportion of crude components that it is able to measure decreases as the crude weathers.

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4.2 PRELIMINARY HYDROCARBON ANALYSIS RESULTS OF SOILS AND SEDIMENTS SAMPLED IN THE CONCESSION AREA IN 2013 CONFIRMS LIMITED WEATHERING OF SOME RESIDUAL OIL

Members of Louis Berger visited the Concession Area of the Ecuadorian Oriente during August through October 2013 to collect samples from selected well sites considered to be "Texpet-only," meaning unaffected by subsequent oil production operations conducted by those other than Texpet. Any oil lingering in soils or in stream sediments at these sites would therefore have had well over 20 years to biodegrade or otherwise weather. I have reviewed some of the preliminary chemical analysis for hydrocarbons in 68 samples of soil or sediments collected from these sites, and the results are sufficiently clear to support my following opinions, to a reasonable degree of scientific certainty:

²⁷ McMillen et al., 2001, p. 59

²⁸ *Ibid.* at p. 60

²⁹ Louis Berger, 2013, p. 36

- Based on the results for petroleum biomarker compounds determined for 14 of the 68 samples, it is clear that the source of the hydrocarbon contamination in all these 14 samples is Ecuadorian Oriente crude oil. It is also likely that Ecuadorian Oriente crude oil is the source of hydrocarbon contamination in all 54 of the remaining samples, based on the similarity of the alkyl-substituted PAH distributions. Finally, it is likely that the oil contamination in the upland soil (including platform and pit areas) and stream sediment samples at each site all came from the same oil source within that site.
- Comparing distributions of alkane hydrocarbons and PAHs, including alkyl-substituted PAHs, permits tentative assignment of the same weathering index used by Dr. Gregory Douglas when evaluating the weathering state of soil and sediment samples collected from the Concession Area nearly a decade ago. Most of the samples evaluated by Dr. Douglas had Kaplan and Galperin weathering states³⁰ of from 5 to 7.³¹. This range of weathering states typical of the mid-2000's is similar to the preliminary range of states evident in the 68 samples collected by LBG in July 2013, which mostly also range in weathering states from 5 7 along the same scale (Table 1). This similarity of weathering state over the last decade strongly re-confirms Louis Berger February 2013 Expert Report's assertion that "Data produced by Chevron for the JI process confirms the largely arrested state of oil biodegradation beneath the upper meter of soil."³²
- Alkyl-substituted PAH compounds account for the overwhelming majority of total PAHs remaining in the samples. In particular, the USEPA "priority pollutant" PAHs usually only account for about 2 percent of the total PAHs present (Table 1). This is consistent with distribution patterns of unsubstituted and alkyl-substituted PAHs typical of crude oils generally.³³
- Finally, at least two of the oil samples recently collected were remarkably well preserved, with weathering states of 3 or 4. The first of these was from a soil depth of 30 40 cm outside the pit at Guanta 06 and still contained a substantial complement of alkane hydrocarbons that are easily biodegraded,

³⁰ Kaplan, I.R., and Galperin, Y., 1996, Patterns of Chemical Changes during Environmental Alteration of Hydrocarbon Fuels, *Groundwater Monitoring and Remediation* 113 – 114

³¹ Douglas, Summary of Forensic Analysis of Crude Oil Weathering, at GSI-0529074 – GSI-0529530. The Kaplan and Galperin weathering scale depends on progressive losses of different hydrocarbon classes, and so is not vulnerable to misapplication of chemical analysis methods that affected the O'Reilly and Thorson weathering index as discussed above in Sec. 4.1

³² Louis Berger, 2013 at 62

³³ Canadian Council of Ministers of the Environment, 2010, Canadian Soil Quality Guidelines, Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs), (Environmental and Human Health Effects), Scientific Criteria Document, National Guidelines and Standards Office, Environment Canada, 200 Sacre-Coeur Blvd. Gatineau, Quebec K1A 0H3, at p. 11

confirming scant biodegradation in the field after more than 20 years (Fig. 3). The second was from about 3 m soil depth inside the pit at Lago Agrio 02 and also contained the easily degraded alkane hydrocarbons but at lower levels. According to Louis Berger staff, the Lago Agrio 02 pit was closed by Chevron in 1990, so this oil remaining inside the pit has persisted with only quite modest biodegradation for 24 years. These results are not surprising, as oil that seeped into oxygen-starved sediments has been shown to persist for decades elsewhere.³⁴

A comparison of results for the 16 USEPA priority pollutant PAHs with the alkylsubstituted PAHs and dibenzothiophenes in Guanta Reference Oil is presented in Figure 4. The 16 USEPA priority pollutant PAH compounds account for about 8 percent of total PAHs (including dibenzothiophenes) contained in this oil, and this proportion is typical of other oils produced from the Concession Area. Once spilled, weathering losses reduce this proportion to about 2 percent (Table 1), as illustrated in Figure 4, which represents results for sample SD010 from site Guanta 6, collected from stream sediments nearly 0.5 km downstream of the pit at this site. The total PAH concentration of 180 mg/kg sediment in this sample confirms the heavy oil contamination present, implying well above 10,000 mg/kg of whole oil remaining in sediment, or more than three times the actual TPH (by DRO) measured by US EPA Method 8015 for this sample. This sample clearly demonstrates that crude oil that escaped from the pit migrated a considerable distance beyond the pit to contaminate stream sediments, which still retain a substantial burden of toxic PAHs compounds as of 2013.

Conclusion: These results (1) illustrate how restricting consideration of toxic PAHs to the 16 US EPA priority pollutant PAHs leads to considerable underestimation of the toxic potential of the crude oils still present in the Concession Area, and (2) confirm the visual evidence of heavy lingering oil contamination found by Louis Berger personnel during their 2013 site inspection.

³⁴ Short, J.W., Irvine, G.V., Mann, D.H., Maselko, J.M., Pella, J.J., Lindeberg, M.R. Payne, J.R., Driskell, W.B. and Rice, S.D. 2007. Slightly Weathered Exxon Valdez Oil Persists in Gulf of Alaska Beach Sediments after 16 Years. *Environmental Science and Technology* 41:1245 – 1250.

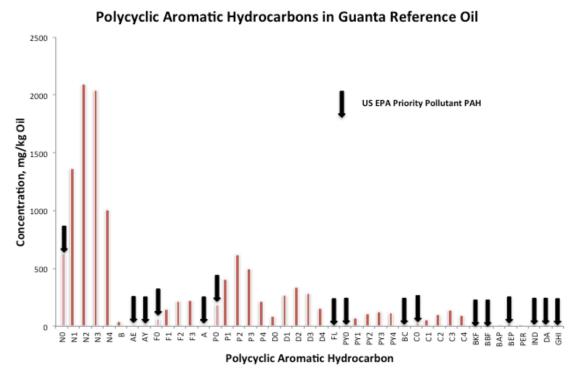


Figure 4. Unsubstituted and alkyl-substituted PAHs and dibenzothiophenes in Guanta Reference Oil.³⁵ The 16 US EPA "priority pollutant" PAHs used by Chevron's experts to assess toxicity are indicated by solid black arrows. Abbreviations for these compound classes are as follows: N=naphthalene, B=biphenyl, AY=acenaphthylene, AE=acenaphthene, F=fluorene, A=anthracene, P=phenanthrene, D=dibenzothiophene, FL=fluoranthene, PY=pyrene, BA=benzo[a]anthracene, C=chrysene, BBF & BFK=benzofluoranthenes, BEP=benzo[e]pyrene, BAP=benzo[a]pyrene, PER=perylene, IND=indenopyrene, DA=dibenzoanthracene, GHI=benzoperylene; numbers following PAH abbreviations indicate the number of carbon atoms of alkyl substituents.

³⁵ Data from Alpha Woods Hole Group, Analytical Report at GSD-202387 – GSD-202389

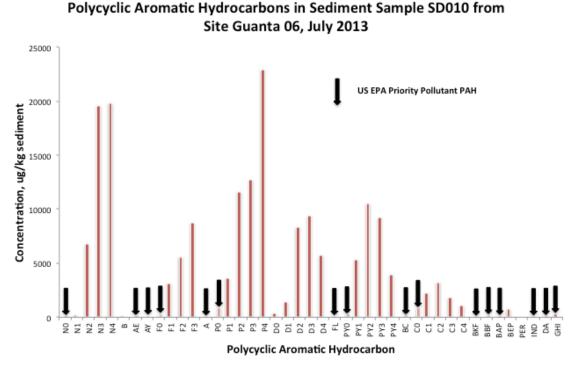


Figure 5. Un-substituted and alkyl-substituted PAHs and dibenzothiophenes in sample GU06-SD010, from stream sediments ~0.5 downstream from the Guanta 06 reserve pit.³⁶ The 16 US EPA "priority pollutant" PAHs used by Chevron's experts to assess toxicity are indicated by solid black arrows. Abbreviations for these compound classes are given in Figure 3 above.

Table 1. Preliminary hydrocarbon analysis results for 68 soil (-SLXXX) and sediment (-SDXXX) samples collected from the Ecuadorian Oriente Concession Area during July 2013. Concentrations are ug/kg for PAHs and mg/kg for diesel range organics (DRO), both on a dry mass basis. TPAHs = total PAHs. Preliminary weathering state assignments are based on the Kaplan and Galperin 1996 scale.

| | Total PAHs ³⁷ | EPA16 PAHs | | DRO | Weathering |
|------------|--------------------------|------------|---------------------------|------------------|------------|
| Sample ID | (ug/kg) | (ug/kg) | EPA16/TPAHs ³⁸ | (mg/kg) | State |
| GU06-SD001 | 1,300 | 23 | 0.020 | 95 | 7 |
| GU06-SD002 | 37,000 | 580 | 0.018 | 2,200 | 7 |
| GU06-SD003 | 800 | 21 | 0.030 | 16 | 7 |
| GU06-SD004 | 280,000 | 5,100 | 0.021 | 12,000 | 5 |
| GU06-SD005 | 17,000 | 240 | 0.016 | 170 | 5 |
| GU06-SD006 | 190,000 | 3,100 | 0.019 | NA ³⁹ | 5 |
| GU06-SD007 | 73,000 | 910 | 0.014 | 2,700 | 5 |
| GU06-SD009 | 690 | 8.0 | 0.014 | 30 | 7 |

³⁶ Data from Alpha Woods Hole Group, Analytical Report at GSD-202387 – GSD-202389

³⁷ Includes dibenzothiophenes but not perylene, a naturally-occurring PAHs

³⁸ Excluding dibenzothiophenes and perylene in TPAHs

³⁹ NA: Data not yet available

| | Total DAILs | EDA1C DAIL | | DBO | Moothowing |
|-------------|-------------|------------|-------------|---------|------------|
| Comula ID | Total PAHs | EPA16 PAHs | | DRO | Weathering |
| Sample ID | (ug/kg) | (ug/kg) | EPA16/TPAHs | (mg/kg) | State |
| GU06-SD010 | 180,000 | 3,100 | 0.019 | 3,500 | 5 |
| GU06-SL001 | 1,200 | 21 | 0.022 | 49 | 5 |
| GU06-SL002 | 19,000 | 260 | 0.016 | 620 | 5 |
| GU06-SL003 | 230 | 24 | 0.125 | 7.9 | 7 |
| GU06-SL004 | 40,000 | 1,000 | 0.029 | 800 | 5 |
| GU06-SL005 | 86 | 8.0 | 0.108 | 10 | 7 |
| GU06-SL006 | 1,200 | 26 | 0.026 | 57 | 7 |
| GU06-SL007 | 930 | 40 | 0.047 | 11 | 7 |
| GU06-SL009 | 350 | 15 | 0.055 | 13 | 8 |
| GU06-SL010 | 17,000 | 380 | 0.025 | 300 | 3 |
| GU06-SL014 | 410 | 13 | 0.038 | 10 | 8 |
| LA02-SD001 | 72,000 | 450 | 0.009 | 2,200 | 5 |
| LA02-SD002 | 27,000 | 180 | 0.010 | 940 | 5 |
| LA02-SD003 | 240 | 12 | 0.057 | 7.8 | 5 |
| LA02-SD004 | 14,000 | 120 | 0.010 | 740 | 6 |
| LA02-SD005 | 88,000 | 560 | 0.009 | 3,200 | 5 |
| LA02-SL001 | 33,000 | 200 | 0.007 | 520 | 5 |
| LA02-SL002B | 710,000 | 12,000 | 0.019 | 9,400 | 5 |
| LA02-SL002B | 690,000 | 10,000 | 0.013 | 10,000 | 5 |
| LA02-SL003 | 80,000 | 500 | 0.007 | 630 | 5 |
| LA02-SL004 | 690,000 | 9,600 | 0.015 | 7,900 | 5 |
| LA02-SL005 | 510,000 | 9,000 | 0.013 | 6.400 | 5 |
| | 270 | , | | 13 | |
| LA02-SL007 | | 11 | 0.051 | | 8 |
| LA02-SL008 | 220,000 | 3,400 | 0.017 | 2,500 | 5 |
| LA02-SL009 | 470,000 | 7,800 | 0.019 | 4,500 | |
| LA02-SL010 | 940,000 | 14,000 | 0.017 | 5,500 | 5 |
| LA02-SL011 | 910,000 | 18,000 | 0.021 | 8,800 | 5 |
| LA02-SL012 | 360 | 54 | 0.201 | 12 | 8 |
| LA02-SL013 | 2,000,000 | 46,000 | 0.025 | 25,000 | 5 |
| LA02-SL014 | 350,000 | 6,400 | 0.021 | 3,500 | 4 |
| LA02-SL015 | 1,600,000 | 26,000 | 0.018 | 19,000 | 5 |
| LA02-SL016 | 12,000 | 120 | 0.012 | 230 | 7 |
| SSF25-SD001 | 32,000 | 200 | 0.007 | 420 | 5 |
| SSF25-SD003 | 110,000 | 1,300 | 0.014 | 4,200 | 7 |
| SSF25-SD004 | 300,000 | 3,000 | 0.012 | 9,000 | 7 |
| SSF25-SL001 | 26,000 | 280 | 0.013 | 370 | 6 |
| SSF25-SL002 | 4,900 | 26 | 0.006 | 7.5 | 7 |
| SSF25-SL003 | 210 | 10 | 0.056 | 7.6 | 7 |
| SSF25-SL004 | 180,000 | 3,500 | 0.023 | 2,800 | 5 |
| SSF25-SL005 | 410,000 | 10,000 | 0.030 | 6,900 | 5 |
| SSF25-SL006 | 440,000 | 10,000 | 0.026 | NA | 5 |
| SSF25-SL007 | 85 | 5 | 0.071 | 6.7 | 8 |
| SSF25-SL008 | 85 | 6 | 0.080 | 3.4 | 8 |
| SSF25-SL009 | 75 | 6 | 0.098 | 3.8 | 8 |
| SSF25-SL010 | 51 | 2 | 0.059 | 6.9 | 8 |
| SSF25-SL011 | 58 | 5 | 0.108 | 3.5 | 8 |
| SSF25-SL012 | 73 | 6 | 0.104 | 7.0 | 8 |
| SSF25-SL012 | 65 | 9 | 0.156 | 7.0 | 8 |
| SSF25-SL013 | 510,000 | 12,000 | 0.028 | 9,800 | 5 |
| SSF25-SL014 | 290 | 7 | 0.028 | 4.1 | 8 |
| SSF25-SL015 | 160 | 8 | 0.029 | 7.2 | 8 |
| YU02-SD001 | | | | | 6 |
| | 800,000 | 11,000 | 0.017 | 34,000 | |
| YU02-SD002 | 130,000 | 1,500 | 0.015 | 4,000 | 5 |
| YU02-SD004 | 150,000 | 1,600 | 0.013 | 4,100 | 5 |
| YU02-SL001 | 170 | 16 | 0.139 | 42 | 8 |
| YU02-SL002 | 56 | 11 | 0.298 | 4.2 | 8 |
| YU02-SL003 | 1,600 | 50 | 0.038 | 150 | 7 |
| YU02-SL004 | 130,000 | 1,300 | 0.012 | 2,700 | 5 |
| YU02-SL005 | 170,000 | 1,600 | 0.012 | 5,900 | 6 |
| YU02-SL006 | 1,000 | 28 | 0.019 | 130 | 5 |

4.4 INAPPROPRIATE USE OF THE TOXICITY CHARACTERISTIC LEACHATE PROCEDURE (TCLP) TO ASSESS MOBILITY OF CRUDE OIL COMPONENTS IN SOILS

As noted in the Louis Berger February 2013 Expert Report⁴⁰, the Toxicity Characteristic Leachate Procedure (TCLP), as modified to evaluate the adequacy of RAP remediation in the Concession area, was inappropriately applied for that effort. The regulatory threshold for this test seems to have been arbitrarily established at 1,000 mg/L TPH, but this unrealistically high threshold could not even have been approached by soils saturated with crude oil, and certainly never by dissolution of oil compounds into soil pore water. Hence, it is difficult to understand why this method and associated regulatory threshold were ever adopted in the first place. It was truly "failure proof" (from Texpet's point of view) as a remediation standard.

Also as noted in the Louis Berger February 2013 Expert Report⁴¹, the modification adopted for the TCLP as employed in RAP remediation involved substitution of gravity filtration for pressure filtration. Being less dense than water, crude oil is unlikely to be separated from soils unless the soils contain so much crude oil that the crude oil itself flows out of the soils and through the filter following water drainage. This would only happen for extremely oiled soils that contain much more than 1,000 mg/L TPH.

The only other way that crude oil components could move into the acidic water used in the TCLP test would be through dissolution. Although in general oil and water simply do not mix, some constituent compounds of crude oil are slightly soluble in water. As presented in Louis Berger February 2013 Expert Report⁴², crude oils may be considered as mixtures of four major classes of compounds: saturates, aromatics, resins and asphaltenes. Ecuadorian crude oils from the Oriente region contain about 35 percent, 45 percent, 10 percent and 10 percent of these major compound classes, respectively⁴³. Of these, the most soluble in water are the aromatics.

The most soluble aromatics are the so-called "BTEX" compounds – benzene, toluene, ethylbenzene and xylene. The maximum concentrations that these compounds can attain in water by dissolving from crude oil are closely approximated by the octanol-water partition coefficient, K_{ow} , which is the ratio of the concentration of a

⁴⁰ Louis Berger, 2013, pp. 55 - 57

⁴¹ *Ibid.* at p. 52

⁴² *Ibid.* at p. 1 of Appendix B

⁴³ Douglas et al., The Calibration and Field Verification of a New Method for Estimating the Extent of Petroleum Biodegradation in Soil, at REH-057077

compound in octanol (which stands as a surrogate phase for crude oil) to its concentration in water:

$$K_{ow} = \frac{[A]_o}{[A]_w} \tag{4}$$

The square brackets in equation 3 denote the concentration of compound "*A*", and the subscripts "*o*" and "*w*" stand for oil and water. For example, benzene, the aromatic hydrocarbon most soluble in water, will always be about 130 times more concentrated in oil than in water when the two are at equilibrium at room temperature, so K_{ow} has the value of 130 for benzene⁴⁴. These values increase as the molecular weight of aromatic hydrocarbons increases, as illustrated in Table 2 for several mono-aromatic hydrocarbons.

| | | Concentration in Oriente Crude Oil | Equilibrium Water Concentration |
|-------------------------------|---------------------|---------------------------------------|------------------------------------|
| Compound | Kow | (mg/L) | (mg/L) |
| Benzene | 130 | 1,100 | 8.3 |
| Toluene | 440 | 3,600 | 8.1 |
| Ethylbenzene | 1,400 | 1,400 | 1.0 |
| Xylenes | 1,400 | 5,300 | 3.8 |
| | | | |
| Sum | | 11,400 | 21 |
| Trimethybenzene | 4,500 | | |
| | | | |
| Remaining Oil Constituents | 4,500 ⁴⁵ | 800,000 | 179 |
| Grand Total | | | 200 |

Table 2. Octanol-water partition coefficients (*K*_{ow}), crude oil concentrations andequilibrium aqueous concentrations of monocyclic aromatic hydrocarbons.

The K_{ow} values presented in Table 2 can be combined with concentration values for BTEX compounds in crude oil to establish an upper limit on the total concentration of these compounds that could dissolve into water. Typical composition values for BTEX compounds in Oriente crude oils⁴⁶ are listed along with the associated K_{ow} values⁴⁷ in Table 2. By equation (4), the ratio of the concentration of a compound in

⁴⁵ Nearly all remaining oil constituents have *K*_{ow} values considerably lower than this

⁴⁶ Douglas, G., BTEX, Polycyclic Aromatic Hydrocarbon, Trace Metal Content and Bulk Properties of Crude Oils from Ecuador, at MacKay-00058044

⁴⁴ MacKay, D., Shiu, W.Y., and Ma, K.C., 1992, Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Vol. I., CRC Press, Lewis Publishers

⁴⁷ MacKay et al., 1992

the oil and its K_{ow} value gives its corresponding equilibrium concentration in water, also listed in Table 2. Note that the sum of the BTEX equilibrium concentrations in water amounts to about 21 mg/L. After the BTEX compounds, the next most soluble aromatic hydrocarbons in crude oil are benzenes that have three alkyl carbon atoms attached to them (i.e., trimethylbenzenes), which have Kow values of about 4500.23 Even assuming that all the remaining compounds in crude oil were equivalently soluble — which they are not, they are actually much less soluble — and that these compounds collectively account for 80 percent of the mass of crude oil, their combined concentrations in water at equilibrium would be about 179 mg/L. The remaining 20 percent of crude oil consists of resins and asphaltenes that have negligible solubility in water. So adding the 179 mg/L to the 21 mg/L from the BTEX compounds gives a maximum solubility of crude oil components in water of approximately 200 mg/L. It is thus clear that the upper limit concentration for hydrocarbons dissolved from crude oil into water can never exceed 200 mg/L, and realistically cannot even come close to that because nearly all the remaining hydrocarbons in crude oil are actually much less soluble than trimethylbenzenes.

Conclusion: the only way the modified TCLP test used by TexPet would result in TPH concentrations greater than the artificial threshold of 1,000 mg/L would require soil so contaminated with crude that the oil could ooze out of the soil and seep through the filtration apparatus en masse.

* * * *

4.5 EMBRYOTOXICITY OF ALKYL-SUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBONS TO FISH

Contrary to the assertion in Claimants' Memorial that the toxicity of alkylsubstituted PAHs is "...not grounded in valid science..."⁴⁸, convincing evidence for the toxicity of these compounds was clearly established decades ago. The toxicity of PAHs arises from the chemical reactivity of the aromatic bonding electrons⁴⁹. This reactivity and the toxicity that results may be enhanced or impaired by substitution of an alkyl-group for a hydrogen on the aromatic ring system of a parent (*i.e.* unsubstituted) PAHs, depending on the location of the substitution ⁵⁰. As stated by Hecht et al. in 1985:

⁴⁸ Claimants' Memorial Annex A, 2013, p. 22

 ⁴⁹ Jerina, D.M., and Daly, J.W., 1974. Arene Oxides, a New Aspect of Drug Metabolism, Science, 185:573
– 582

⁵⁰ Hecht, S.S., Radok, L., Amin, S., Hule, K., Melikian, A.A., Hoffmann, D., Pataki, J., and Harvey, R. G., 1985, Tumorigenicity of 5-Methylchrysene Dihydrodiols and Dihydrodiol Epoxides in Newborn Mice and on Mouse Skin, Cancer Research, 45:1449-1452

"Methylated PAHs, particularly those with a methyl group in the same bay region as the epoxide ring of a putative dihydrodiol-epoxide metabolite, are often more carcinogenic than their parent hydrocarbons or other methyl isomers..."⁵¹

PAHs compounds impair the development of fish embryos at concentrations near one part per billion (*i.e.*, 1 μ g/L). Fish embryos exposed to part-per-billion concentrations of PAHs soon after fertilization fail to develop normal circulatory systems⁵² which lead to a manifold of functional deficits in fish that are not killed outright. This toxicity mechanism was first proposed and confirmed on the basis of fish embryos exposed to PAHs that dissolved out of crude oil, which studies I personally participated in during my tenure at NOAA⁵³.

Claimants' Reply Memorial also asserts that these studies are "...highly controversial..."⁵⁴, when in fact the results have been confirmed elsewhere by researchers at independent institutions, including those in countries outside the United States. A clear demonstration that alkyl-PAHs induce defects in developing fish embryos was presented by Turcotte et al., who showed that a controlled-release exposure of 9 μ g/L retene, an alkyl-substituted phenanthrene found in Oriente source oils, caused developmental defects in 50 percent of exposed Japanese medaka (*Oryzias latipes*) embryos⁵⁵. Furthermore, this research team also presented convincing evidence that the toxicity of the alkyl-substituted phenanthrenes increased with the degree of alkyl substitution. This study was not vulnerable to any of the supposed confounding effects alluded to in Claimants' Reply Memorial⁵⁶.

Conclusion: alkyl-substituted PAHs that are found in and leach from lingering Oriente crude oils in soils may be harmful to developing fish embryos in receiving waters if concentrations exceed even a per billion. This is a much lower threshold of concern than was applied on the basis of human drinking water standards.

⁵¹ *Ibid.* at p. 1449

⁵² Incardona, J. P., M. G. Carls, Teraoka, H., Sloan, C.A., Collier, T.K., and Scholz, N.L., 2005, Aryl Hydrocarbon Receptor-Independent Toxicity of Weathered Crude Oil during Fish Development, *Environmental Health Perspectives* 113:1755 – 1762

⁵³ Carls, M.G., Rice, S.D., and Hose, J.E., 1999, Sensitivity of Fish Embryos to Weathered Crude Oil: Part I. Low-Level Exposure During Incubation Causes Malformations, Genetic Damage, and Mortality in Larval Pacific Herring (*Clupea pallasi*), Environmental Toxicology and Chemistry, 18:481 – 493, and Heintz, R.A., Short, J.W., and Rice, S.D., 1999, Sensitivity of Fish Embryos to Weathered Crude Oil: Part II. Increased Mortality of Pink Salmon (*Oncorhynchus gorbuscha*) Embryos Incubating Downstream from Weathered Exxon Valdez Crude Oil, Environmental Toxicology and Chemistry, 18:494-503 ⁵⁴ Claimants' Memorial Annex A, 2013, footnote 306 at p. 44

 ⁵⁵ Turcotte, D., Akhtar, P., Bowerman, M., Kiparissis, Y., Brown, R.S., and Hodson, P.V., 2011,
Measuring the Toxicity of Alkyl-Phenanthrenes to Early Life Stages of Medaka (*Oryzias latipes*) using
Partition-Controlled Delivery." Environmental Toxicology and Chemistry, 30: 487-495.
⁵⁶ Claimants' Memorial Annex A, 2013, footnote 306 at p. 44

4.6 REGULATORY CONCERNS REGARDING ALKYL-SUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBONS

* * * *

While concerns regarding the toxicity of alkyl-substituted PAHs in soils have been clearly articulated by regulatory authorities⁵⁷, evaluating their combined toxicity is technically challenging. As noted by the Canadian Council of Ministers of the Environment:

"Possible concern over alkylated PAH derives from both the routine occurrence of relatively high concentrations in hydrocarbon-contaminated environmental samples and the potential for adverse effects on living organisms."⁵⁸

Toxicity studies on alkyl-substituted PAHs are hampered by the large numbers of different compounds to evaluate, and to date efficient means of doing so have not been widely available. However, those studies that have been conducted indicate that concerns regarding the toxicity of these compounds are warranted.

At my deposition I was asked to identify a regulatory body that recommends routine monitoring for alkyl-substituted PAHs. I could not identify such a regulatory body because of the technical challenges involved⁵⁹, not absence of regulatory concerns. But in cases where contaminant sources are rich in alkyl-substituted PAHs, such as with Ecuadorian crude oils, monitoring these compounds is simple common sense based on the known toxicity of the parent PAHs and the known toxicity of the alkyl-substituted PAHs to fish and possibly other biota.

Conclusion: the absence of regulations for alkyl-substituted PAHs should not be taken as indications of their environmental safety or lack of toxicity.

* * * *

4.7 APPLICABILITY OF BIODEGRADTION STUDIES CONDUCTED ON ECUADORIAN ORIENTE CRUDE OILS BY DR. GREGORY DOUGLAS

⁵⁷ Canadian Council of Ministers of the Environment, 2010, p. 14

⁵⁸ *Ibid.* at p. 11

⁵⁹ Short Dep. at 147-155

While the biodegradation studies conducted by Dr. Gregory Douglas⁶⁰ demonstrate that some components of Ecuadorian Oriente crude oils are subject to biodegradation under ideal laboratory conditions, these conditions do not always hold in the field. In particular, absence of oxygen dramatically retards biodegradation, but Dr. Douglas did not include anaerobic test conditions in his laboratory tests⁶¹. Lack of significant oxygen is one of the most significant factors to explain the lack of biodegradation that has occurred in the Oriente.⁶²

Conclusion: the laboratory biodegradation tests conducted by Dr. Gregory Douglas merely indicate the potential extent of biodegradation under ideal conditions, which often are not present in the field, especially at locations where oil has now been shown to persist for decades without evidencing advanced degradation.

⁶⁰ Douglas et al., An Assessment of Intrinsic Petroleum Biodegradation in soils at Exploration Sites in Ecuador, at REH-057032

⁶¹ Douglas Dep. at 115

⁶² See § 4.2 discussing fact that weathering is mostly arrested in the Oriente.