

In the Matter of

PR Spring Tar Sands Project, Ground Water Discharge Permit-by-Rule

No. WQ PR-11-001

PREPARED DIRECT TESTIMONY

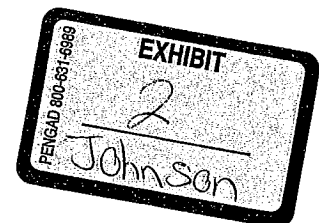
OF

WILLIAM P. JOHNSON, Ph.D

ON BEHALF OF

LIVING RIVERS

January 20, 2012



1 **I. INTRODUCTION AND QUALIFICATIONS**

2

3 Q. PLEASE STATE YOUR NAME?

4 A. My name is William P. Johnson

5

6 Q. BY WHOM ARE YOU EMPLOYED AND WHAT IS YOUR POSITION?

7 A. I am a professor in the department of Geology & Geophysics and an adjunct professor in
8 the department of Civil & Environmental Engineering at the University of Utah.

9

10 Q. FOR WHOM ARE YOU TESTIFYING IN THIS PROCEEDING?

11 A. I am testifying on behalf of Living Rivers.

12

13 Q. WOULD YOU PLEASE SUMMARIZE YOUR EDUCATIONAL AND
14 PROFESSIONAL BACKGROUND?

15 A. Since 1995 I have been a professor conducting research and teaching graduate and
16 undergraduate courses in the subject of contaminant hydrogeology. I have authored, or served as
17 corresponding author, on over 75 peer-reviewed publications, including several specifically
18 regarding organic contaminant solubilization and transport. I serve as a reviewer for more than 15
19 scientific journal and three panels of the National Science Foundation. My doctoral degree is in
20 Civil (Environmental) Engineering from the University of Colorado (1993). More detail on my
21 background is provided in Appendix A.

22

1 **II. PURPOSE AND SUMMARY OF TESTIMONY**

2
3 Q. WHAT IS THE PURPOSE OF YOUR TESTIMONY?

4 A. My testimony will discuss the effect of re-distribution of d-limonene-processed tar sands
5 to the land surface in the area of the PR Spring Mine.
6

7 Q. WOULD YOU PLEASE SUMMARIZE YOUR TESTIMONY?

8 A. My testimony will demonstrate that re-distribution of these sands to the land surface in
9 the area of the PR Spring Mine poses an increased risk of exposure to carcinogenic compounds
10 via two mechanisms: 1) order of magnitude or more increases in the aqueous concentrations of
11 carcinogenic compounds; 2) factor of 4 increases in the rate of transport of carcinogenic
12 compounds in groundwater. The increased aqueous concentration for a tar compound such as
13 benzo(a)pyrene is nearly 1500 times greater than its normal water solubility, and is more than
14 400,000 times greater than the drinking water limit for this compound. Both of these increases
15 (concentration and mobility) result from the mixing of d-limonene with tar compounds. Under
16 natural conditions, the risk of exposure to carcinogenic tar compounds is negligible due to the
17 negligible mobility and low aqueous concentrations of these compounds. However, the
18 combination of tar compounds with d-limonene reverses these characteristics by increasing the
19 aqueous concentration and mobility of the tar compounds. The increase in tar compound
20 concentration and mobility constitutes a significant increase in the risk of exposure, and therefore
21 warrants appropriate down-gradient monitoring for the potential increased concentration and
22 transport of tar compounds emanating from the site.

1 Additionally, I will discuss: 1) why it was inappropriate for DWQ to rely on the MSDS
2 sheets provided by the company in determining the toxicity of the reagent; 2) that DWQ did not
3 require the company to conduct the appropriate tests to assess the potential for leaching of
4 petrochemicals from the processed ore to water; and, 3) that it was inappropriate for DWQ to
5 conclude that the processed sediment is “damp-dry” because it is, in fact, saturated with fluid
6 based on water contents provided by the company.

7
8 Q. CAN YOU BRIEFLY DESCRIBE D-LIMONENE?

9 A. Based on the properties listed in Appendix B, d-limonene is a small molecule that is
10 readily transported to air. Therefore d-limonene by itself will likely vaporize/volatilize readily to
11 the atmosphere.

12
13 Q. CAN YOU DESCRIBE UTAH TAR SANDS COMPOUNDS?

14 A. Based on information regarding Utah tar sand compounds provided in Appendix C, these
15 compounds likely include polycyclic aromatic hydrocarbons (PAH) which are known human
16 carcinogens. The tar exists as a semi-solid, and so has no significant propensity to migrate into
17 the subsurface as a phase. By themselves, the PAH compounds and aliphatic chains comprising
18 the tar are highly insoluble in water, and so despite the significant carcinogenicity of at least some
19 of these component compounds, they are not expected to undergo significant transport in site
20 runoff or site groundwater, greatly limiting the possibility of exposure to these compounds.

21
22 Q. WHY ARE YOU CONCERNED ABOUT THE CARCINOGENICITY OF UTAH TAR
23 SANDS COMPOUNDS WITH THE PR SPRING MINE?

1 A. Concern arises with the PR Spring Mine because the operator of that mine proposes to
2 separate the bitumen from the tar sands using d-limonene, and my concern is the combination of
3 these Utah tar sands compounds as a mixture, i.e. the d-limonene-solubilized tar compounds.
4 The organic mixture of d-limonene and tar compounds has different properties than the two
5 parent mixtures in terms of vaporization, volatilization, and dissolution, and in terms of whether
6 the mixture acts as a semi-solid or a liquid. These altered physicochemical properties yield novel
7 transport properties relative to the parent compounds.

8

9 Q. HOW SO?

10 A. Note that these three properties: 1) the semi-solid phase nature of the tar; 2) the very low
11 solubility of the tar compounds; and 3) the very low mobility of the tar compounds are precisely
12 what allow these compounds, under natural conditions, to be considered relatively benign.
13 However, combining d-limonene with the tar compounds reverses the above attributes.
14 Specifically: 1) the mole fraction of d-limonene in the organic mixture may become sufficiently
15 large that the mixture will act as a liquid rather than semi-solid, thereby increasing the propensity
16 of this liquid mixture to infiltrate directly into the subsurface; 2) mixing with d-limonene will
17 increase the apparent water solubility of the tar compounds by orders of magnitude, far above
18 ambient levels, thereby greatly increasing the potential dose upon exposure for the ecosystem; 3)
19 the solubilization of tar compounds by d-limonene will significantly increase the transport rate of
20 the tar compounds in the pore water underlying the site, thereby greatly increasing the risk of
21 exposure.

22

1 Q. WHY DOES THE D-LIMONENE-SOLUBILIZED TAR COMPOUND HAVE THE
2 PROPENSITY TO INFILTRATE DIRECTLY INTO THE SUBSURFACE?

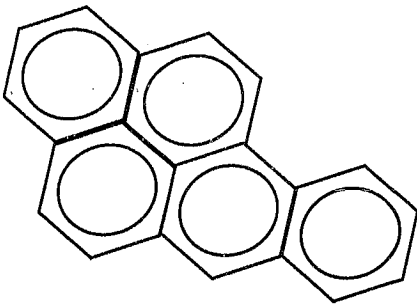
3 A. Let me first note that the residual concentration of d-limonene in re-distributed sediment
4 was not provided to me initially. I therefore first assumed that it was reasonable to expect that
5 the d-limonene content in this d-limonene/tar mixture residual was sufficient to cause the
6 mixture to act as a liquid rather than a semi-solid phase that is characteristic of tar. This
7 assumption was confirmed by information provided by the company to Living Rivers' attorneys.
8 This tendency to act as a liquid rather than a semi-solid phase creates a profound change in the
9 mobility of the tar compound phase by way of two mechanisms: a) by changing their phase from
10 an organic semi-solid to an organic liquid, which is potentially more mobile than the semi-solid
11 phase. The high potential mobility of organic liquids is why disposal of non-containerized
12 hazardous liquids is not allowed in RCRA/CERCLA legislation; b) via vast increases in the
13 groundwater solubility and mobility of the tar compounds in response to equilibration with
14 d-limonene, as demonstrated in the calculations substantiating concerns (2) and (3) below.

15

16 Q. HOW DID YOU GO ABOUT SUBSTANTIATING CONCERN (2) THAT MIXING
17 WITH D-LIMONENE WILL INCREASE THE WATER SOLUBILITY OF THE TAR SANDS
18 COMPOUNDS BY ORDER OF MAGNITUDE, AND CONCERN (3) THAT THIS
19 SOLUBILIZATION WILL SIGNIFICANTLY INCREASE THE TRANSPORT RATE OF THE
20 TAR COMPOUNDS, THUS GREATLY INCREASING THE RISK OF EXPOSURE?

21 A. To substantiate these two concerns, the following calculations are provided for a
22 representative PAH compound, namely: (2) the factor by which the solubility of PAH is
23 increased in the presence of d-limonene relative to water; and, (3) the factor by which the

1 transport time of PAH over a given distance is decreased in the presence versus absence of
2 d-limonene. The calculations are made using benzo(a)pyrene as a representative PAH. B(a)P has
3 five fused aromatic rings. The choice of this compound is not critical to demonstrate the changes
4 in transport of tar compounds in response to solubilization by d-limonene. Any PAH compound
5 with four or more rings, and any unsubstituted alkane with approximately ten or more carbon
6 atoms, will show similar effects. Such sizes of compounds (and larger) are expected to dominate
7 the tar (Appendix B).



8
9 Benzo(a)pyrene data (from reference 5):

10
11 Molecular weight = 252.3 gmol⁻¹

12 Melting temperature = 176.5 °C

13 $C_w^{sat}(s, 25^{\circ}C) = 1.52 \mu\text{gL}^{-1}$

14 $C_w^{sat}(L, 25^{\circ}C) = 49.19 \mu\text{gL}^{-1}$

15

16 Q. HOW DID YOU CALCULATE THE FACTOR BY WHICH THE SOLUBILITY OF
17 PERYLENE IN WATER IS INCREASED?

18 A. I calculated that factor as follows:

19 The normal solubility of B(a)P dissolving from solid tar in water (C_w^{sat}) at room temperature is
20 $1.5 \mu\text{gL}^{-1}$. When d-limonene is added to the water, it creates a liquid organic mixture, and this
21 rises the solubility of B(a)P since it is dissolving not from solid tar, but from liquid d-limonene.

1 The solubility of B(a)P dissolving from an organic liquid is $49.2 \mu\text{gL}^{-1}$, which is more than 30
2 times greater than that dissolving from solid tar. However, this effect is small relative to the
3 further increase in B(a)P concentrations in water that result from d-limonene dissolving into
4 water. Since d-limonene has a strong affinity for B(a)P, and since d-limonene has a much
5 higher water solubility ($13,800 \mu\text{gL}^{-1}$) than B(a)P, the dissolved d-limonene essentially coaxes
6 the B(a)P into the aqueous phase, raising the apparent solubility of B(a)P in the aqueous phase
7 (C_w^*). The extent to which the apparent water solubility of B(a)P is raised relative to its
8 normal water solubility is directly proportional to: 1) the concentration of d-limonene in
9 solution (C_w^{dl}); and, 2) the affinity of B(a)P for d-limonene, as measured by the distribution
10 coefficient for B(a)P between water and d-limonene $K_{dl}^{B(a)P}$. The corresponding equation is:

$$C_w^* = C_w^{sat} + C_w^{sat} K_{dl}^{B(a)P} C_w^{dl}$$

13 The concentration of d-limonene expected in water will vary depending on scenario.
14 Upon re-distribution of the residual tar sand to the land surface, it is reasonable to expect
15 residual d-limonene to dissolve into pore water to a concentration representing its normal water
16 solubility. Solubilities vary with temperature; however, temperature corrections are not made
17 here since the comparison between presence versus absence of d-limonene will be similar
18 regardless of which temperature (e.g. 25 versus 5 Celsius) is used. The room temperature
19 solubility of d-limonene in water is herein used to represent C_w^{dl} (13.8 mg/L).

20 The value for $K_{dl}^{B(a)P}$ can be approximated by the distribution coefficient for B(a)P
21 between water and octanol ($K_{ow}^{B(a)P}$). This value will underestimate the solubility
22 enhancement of B(a)P by d-limonene, since octanol is a somewhat more polar solvent than d-

1 limonene, which makes octanol slightly less ideal than d-limonene for solubilization of the
2 non-polar compound B(a)P. The value of $K^{B(a)P}_{ow}$ is available in reference 5, hence:

3
$$K_{dl}^{B(a)P} \approx K_{oct}^{B(a)P} = 10^{6.50} = 3,162,278$$

4 Inserting the above values into the equation, the apparent solubility in water is calculated:

5
$$C_w^* = \frac{49.2 \mu g_{B(a)P}}{L_w} + \frac{49.2 \mu g_{B(a)P}}{L_w} \left[\frac{3,162,278 L_w}{K_{dl}} \right] \left[\frac{13.8 mg_{dl}}{L_w} \right] \frac{1 kg_{dl}}{10^6 mg_{dl}}$$

6
$$C_w^* = \frac{2196 \mu g_{B(a)P}}{L_w} = \frac{2.2 mg_{B(a)P}}{L_w}$$

7 Hence, the concentration of B(a)P in water will increase in the presence of d-limonene by a
8 factor of over 1440, from 1.5 to 2200 $\mu g/L$.

9

10 Q. WHAT IS THE SIGNIFICANCE OF THIS INCREASED CONCENTRATION?

11 A. To understand the significance of this concentration, a simple risk-based cleanup level in
12 groundwater can be determined (Appendix C). The groundwater concentration supporting a
13 1E-6 excess risk of contracting cancer as a result of drinking groundwater from the site
14 contaminated with benzo(a)pyrene is 0.00479 $\mu g/L$. The expected 2200 $\mu g/L$ concentration is
15 a factor of 458,455 greater than this risk-based concentration. If a 1E-5 risk of contracting
16 cancer were used, the concentration limit would be 0.0479 $\mu g/L$ and the expected
17 concentration would be a factor of 45,845 above this limit. If a 1E-4 risk of contracting cancer
18 were used to define the concentration limit, the concentration limit would be 0.479 $\mu g/L$ and
19 the expected concentration would be a factor of 4,584 above this limit. Therefore, even limited
20 ingestion, or ingestion of diluted groundwater from the site, would be expected to carry
21 significant carcinogenic risk.

1 If no groundwater supply wells exist down-gradient of the site, or if no ingestion of site
2 groundwater by humans is expected, the concern for ecosystem health remains significant since
3 PAHs bioaccumulate through the food chain because they are retained in lipophilic tissues (for
4 the same reason they are solubilized in d-limonene). The result strongly suggests a need for
5 monitoring of site groundwater for elevated PAH concentrations in response to redistribution
6 of sediments containing the d-limonene/tar mixture.

7
8 Q. HOW DID YOU CALCULATE THE FACTOR BY WHICH THE TRANSPORT TIME
9 OF B(A)P IS DECREASED IN THE PRESENCE OF D-LIMONENE?

10 A. The factor by which the transport time of B(a)P is decreased in the presence versus
11 absence of d-limonene is calculated based on the so-called retardation factor for B(a)P
12 transport. The retardation factor represents the ratio of the velocity of an average water
13 molecule relative to the velocity of the average B(a)P molecule in groundwater. For the
14 system with no d-limonene, the retardation factor reflects the partitioning of B(a)P and other
15 PAH compounds between water and sediment (sand). As groundwater moves through the
16 subsurface, B(a)P dissolved in the groundwater partitions between the water and the
17 surrounding sediment according to a distribution constant between water and sediment (K_d).

18 The distribution process is often considered to be near local equilibrium in groundwater
19 because of the relatively slow velocities involved in groundwater flow. Because the tar sands
20 are rich in organic carbon (including tar), and these compounds provide a compatible
21 environment for non-polar compounds such as PAH, the partitioning of PAH between water
22 and sand is driven by the affinity of the PAH compounds for the organic compounds (K_{om}),

1 and the fraction of sediment mass comprised by organic compounds (f_{om}). As a result, the
2 equilibrium constant for distribution of PAH between water and sediment can be calculated as:

$$3 \quad K_d = K_{om} f_{om}$$

4 The value of f_{oc} will be taken to equal 0.1%, i.e., 1 g tar per 1 kg sand. The specific value
5 used for f_{om} will not greatly affect the analysis since the goal is to examine the effect of d-
6 limonene on the retardation of PAH, using B(a)P as an example.

7 The value for K_{om} is obtainable using free energy relationships given in reference 5, for
8 example:

$$9 \quad \text{Log}K_{om} = 0.81\text{Log}K_{ow} - 0.25$$

$$10 \quad \text{Log}K_{om} = 0.81(6.60) - 0.25$$

$$11 \quad K_{om} = 124,738$$

12 Therefore:

$$13 \quad K_d = \frac{124,738 L_w}{Kg_{om}} \frac{1g_{om}}{1Kg_{sand}} \frac{1Kg_{om}}{1000g_{om}}$$

$$14 \quad K_d = 124.7 \frac{L_w}{Kg_{sand}}$$

15 The retardation factor (R) is obtained from:

$$16 \quad R = 1 + \frac{\rho_b}{\theta} K_d$$

17 Where ρ_b and θ are the bulk density and the porosity, respectively, of the sand. Using
18 representative values of ρ_b and θ equal to 1.7 and 0.35, respectively, yields:

$$19 \quad R = 1 + \frac{1.7 Kg_{sand}}{L_{aquifer}} \left[\frac{1L_{aquifer}}{0.35L_w} \right] \left[\frac{124.7L_w}{Kg_{sand}} \right]$$

$$20 \quad R = 607$$

1 Q. WHAT IS THE SIGNIFICANCE OF THIS CALCULATION?

2 A. The significance is that B(a)P will take a factor of 607 times longer than the average
3 water molecule to achieve a given travel distance in groundwater due to partitioning of the
4 B(a)P between sediment tar and groundwater. In other words, if the water takes 1 year to
5 travel 1000 meters, the B(a)P will take 607 years to travel the same distance. This is precisely
6 why the tar compounds do not move appreciable distances from their source in groundwater,
7 and why they are not considered problematic despite their significant carcinogenicities.

8

9 Q. WHAT HAPPENS WHEN YOU ADD D-LIMONENE TO THE SYSTEM?

10 A. However, the addition of d-limonene to the system causes a major change in the transport
11 characteristics of B(a)P and other hydrophobic compounds, and this is discerned in the so-
12 called modified retardation factor (R^*). The modified retardation factor accounts not only for
13 the distribution of B(a)P between water and sediment, but also for the distribution of B(a)P
14 between water and d-limonene (K^{perl}_{dl}), as well as the distribution of d-limonene between
15 water and sediment (K^{dl}_d), as follows:

$$R^* = \frac{1 + \frac{\rho_b}{\theta} K_d + K^{B(a)P}_{dl} C_w^{dl} + K^{B(a)P}_d K^{dl}_d C_w^{dl} \frac{\rho_b}{\theta}}{1 + K^{B(a)P}_{dl} C_w^{dl}}$$

16

17 An approximate value for K^{dl}_d is obtained by applying the linear free energy relationship
18 to determine the partition coefficient for d-limonene between water and sediment organic
19 matter (tar):

$$20 \text{Log} K^{dl}_{om} = 0.81 \text{Log} K_{ow} - 0.25$$

$$21 \text{Log} K^{dl}_{om} = 0.81(4.2) - 0.25$$

$$22 K^{dl}_{om} = 1419$$

1 Therefore:

$$2 \quad K_d^{dl} = \frac{1419L_w}{Kg_{om}} \frac{1g_{om}}{1Kg_{sand}} \frac{1Kg_{om}}{1000g_{om}}$$

$$3 \quad K_d^{dl} = 1.42 \frac{L_w}{Kg_{sand}}$$

4 An approximate value for $K^{B(a)P}_{dl}$ is obtained using linear free energy relationships using
5 the conservative but reasonable assumption that the affinity of B(a)P for d-limonene is similar
6 to the affinity of B(a)P for sediment organic matter:

$$7 \quad \text{Log}K_{dl}^{B(a)P} = 0.81\text{Log}K_{ow} - 0.25$$

$$8 \quad \text{Log}K_{dl}^{B(a)P} = 0.81(6.50) - 0.25$$

$$9 \quad K_{dl}^{B(a)P} = 124,738$$

10 However, the solubilizing capacity of dissolved organic matter tends to be somewhat
11 greater relative to equivalent sorbed organic matter due to conformational effects. Schlautman
12 and Morgan 1990, found the difference to be approximately a factor of two (Reference 6),
13 hence:

$$14 \quad K_{dl}^{B(a)P} = 249,476$$

15 Hence:

$$16 \quad R^* =$$

$$17 \quad R + \frac{\left(\frac{249,476L_w}{Kg_{dl}}\right)\left(\frac{1.38E-5 Kg_{dl}}{L_w}\right) + \left(\frac{124,738L_w}{Kg_{dl}}\right)\left(\frac{1.42L_w}{Kg_{sand}}\right)\left(\frac{1.38E-5 Kg_{dl}}{L_w}\right)\left[\frac{1.7 Kg_{sand}}{L_{aquifer}}\right]\left[\frac{1L_{aquifer}}{0.35L_w}\right]}{1 + \left(\frac{249,476L_w}{Kg_{dl}}\right)\left(\frac{1.38E-5 Kg_{dl}}{L_w}\right)}$$

$$18 \quad R^* = 140$$

19

20 Q. WHAT DOES THIS DEMONSTRATE?

1 A. This demonstrates that d-limonene can be expected to increase the rate of transport of tar
2 compounds by more than a factor of four ($R/R^* = 607/140 = 4.3$). This factor-of-four increase
3 in the transport rate, along with the factor-of-1440 increase in the aqueous concentration of tar
4 compounds in the presence of d-limonene, constitutes a major increase in the potential for
5 exposure to these compounds via groundwater as a result of interaction with d-limonene
6 residual.

7
8 Q. ARE THERE MEASUREMENTS PROVIDED BY THE COMPANY THAT
9 CORROBORATE YOUR CALCULATIONS?

10 A. The reported reagent (TAI) content in the produced fines (averaging 1.8%) (provided to
11 Living Rivers' attorneys by the company) and the reported water content in the produced fines
12 (15.25%) yield a reagent concentration in the fluid equal to 118 mg of reagent per liter of fluid.
13 This concentration is nearly ten times higher than the solubility of d-limonene in water (13.8
14 mg/L) assumed in the calculations above. This discrepancy suggests that the actual increase in
15 tar compound solubility in water as result of mixing with the reagent will be ten times greater
16 than the calculated factor of 1400, i.e, 14,000. Assuming that the reported % bitumen content
17 of the "water" that is mixed with the ore is equivalent to the bitumen content of the residual
18 fluid in produced waste sediment, the bitumen concentration of the residual fluid in the
19 produced waste sediment is 900,000 $\mu\text{g/L}$. Using the normal water solubility (49.2 $\mu\text{g/L}$) of
20 B(a)P, this represents a factor of 18,290 increase in the solubility of the tar compounds due to
21 mixing with the reagent. This is a similar value to the expected factor of 14,000 increase
22 observed in the "water" mixed with the ore. This agreement indicates that solubilization of tar

1 compounds by reagent occurs as expected, and therefore the mobility of the tar compounds will
2 increase as calculated.

3

4 Q. WHAT DID YOU CONCLUDE BASED ON YOUR CALCULATIONS?

5 A. The calculations show clearly that d-limonene enhances the solubility, and facilitates the
6 transport, of tar compounds. It does so because the d-limonene is more soluble than the tar
7 compounds; whereas, the tar compounds have a strong affinity for d-limonene. Although the
8 specific partition coefficients can potentially be refined, the overall finding is correct: the
9 residual d-limonene in the sand creates the potential for increased transport of carcinogenic tar
10 compounds at higher concentrations.

11

12 Q. IS DWQ'S RELIANCE ON THE MSDS SHEETS FOR THE REAGENT
13 APPROPRIATE?

14 A. The two MSDS sheets (d-limonene) provided to DWQ have information pertaining to
15 workplace exposure, and are not specifically intended for assessment of environmental
16 toxicity. However, there is sufficient concern expressed in these MSDS sheets regarding
17 environmental dispersion of the reagent ("may be toxic to aquatic organisms") that additional
18 investigation of potential deleterious consequences of environmental disposal should be
19 investigated.

20

21

1 Q. HAVE THE APPROPRIATE TESTS BEEN CONDUCTED TO ASSESS THE
2 POTENTIAL FOR LEACHING OF PETROCHEMICALS FROM THE PROCESSED ORE?

3 A. Tests should be performed to assess the potential for leaching of tar and terpene compounds
4 into water from the produced sediment. The test that was performed was extraction of non-
5 volatile compounds from ore using hexane, which only assesses how much tar compound can
6 be extracted using a non-polar solvent, and in no way addresses the question of how much tar
7 compound would dissolve into water in contact with produced sediment. In the 2008
8 Demonstration, on page 10, the company makes the curious statement that “the absence of
9 volatile or semi-volatile constituents in the processed material indicates that the organic
10 compounds in the residual material are likely to be no more mobile than the *in situ* tar sands
11 themselves.” This statement completely ignores the fact that the addition of reagent terpenes
12 alters the properties of the tar, as described above.

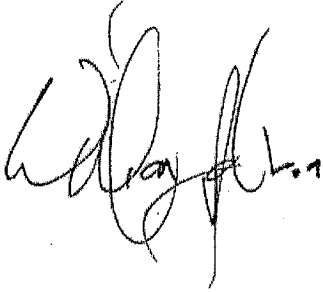
13
14 Q. WOULD YOU CHARACTERIZE THE PROCESSED SEDIMENT AS “DAMP-DRY”?

15 A. A comparison of the % water content in produced sands and fines (provided to Living
16 Rivers by the company) indicates that approximately 511 tons of produced fluid exists in
17 approximately 2763 tons of produced sediment (combined sand and fines). This ratio yields a
18 volumetric ratio of 28.5% of fluid in the sediment, assuming a fluid specific gravity near unity
19 and a sediment bulk density of 1.5 g/mL (reasonable values). This volumetric ratio is close to
20 the expected 30% porosity of the sediment, indicating that the produced rock is saturated and
21 will drain fluid to underlying soil, particularly with additional water added by precipitation.

1 Q. DOES THIS CONCLUDE YOUR TESTIMONY FOR NOW?

2 A. Yes.

3

A handwritten signature in black ink, appearing to read "William P. Johnson". The signature is written in a cursive style with a large initial "W".

4

5

6 William P. Johnson

7 Professor

8 Geology & Geophysics

9 University of Utah

10 115 South 1460 East

11 Salt Lake City, Utah 84112

12 801-664-8289

13

14

Appendix A – Curriculum Vitae

William Paul Johnson, Professor

Geology and Geophysics

Civil & Environmental Engineering Adjunct Professor

University of Utah, 135 South, 1460 East, Salt Lake City, Utah, 84112-1183. (801) 664-8289,
william.johnson@utah.edu.

EXPERIENCE

1995-present	University of Utah	Professor (since 2007)
	Department of Geology and Geophysics	Assoc. Professor (2001-2007)
		Asst. Professor (1995-2001)

1994-1995	University of Arizona at Tucson	Research Assoc.
	Department of Hydrology and Water Resources	
	Department of Chemical and Environmental Engineering	

1993	Water Science, Inc.	Consultant
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1990-1993	University of Colorado at Boulder	Research Assistant
	Civil, Environmental & Architectural Engineering	

1987-1990	United States Geological Survey	Hydrologist
	Water Resources Division	

1984-1986	Dartmouth College	Research Assistant
	Department of Earth Sciences	Teaching Assistant

EDUCATION

1990-1993	Ph.D. in Civil and Environmental Engineering. University of Colorado, Boulder, CO. Dissertation entitled: Facilitated Transport and Enhanced Desorption of Polycyclic Aromatic Hydrocarbons by Natural Organic Matter in Aquifer Sediments.
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1984-1986	M.S. degree in Geology. Dartmouth College, Hanover, NH. Thesis entitled: The physical and magnetic polarity stratigraphy of the Bunthang Sequence, Skardu intermontane basin, northern Pakistan.
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1980-1983	B.A. degree in Geology. Whitman College, Walla Walla, WA.
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1 **HONORS AND AWARDS**

- 2 Leeds Prize in Geology, Whitman College, 1983
3 Dartmouth Fellowship, Dartmouth College, 1984-1986
4 Outstanding Faculty Research Award, Department of Geology & Geophysics (U of U), 2000
5 Outstanding Faculty Research Award, Department of Geology & Geophysics (U of U), 2010

6
7 **PROFESSIONAL AFFILIATIONS**

- 8 Association of Environmental Engineering and Science Professors
9 American Geophysical Union
10 American Chemical Society

11 **CURRENT FUNDED PROJECTS**

- 12 The Ability for Impounded Wetland Sediment to Mobilize Metals, Ammonia and Sulfides and Their
13 Potential Toxicity to Submerged Aquatic Vegetation and Macroinvertebrates, Central Davis Sewerage
14 Improvement District, **05/2011-11/2012**, \$40,000, sole PI.
15
16 Spatial variation of mercury methylation in the sediment and the deep brine layer of the Great Salt Lake,
17 Utah Department of Wildlife Resources, Division of Forestry, Fire, and State Lands, **09/2011-08/2012**,
18 \$28,600, sole PI
19
20 Influence of Cell Surface Properties and Structures on Microbial Deposition in Porous Media in the
21 Absence and Presence of Energy Barriers, American Chemical Society Petroleum Research Fund,
22 **01/2011-01/2013**, \$100,000, sole PI.
23
24 SPLITT-FFF-based detection and monitoring of engineered nanomaterials in aquatic systems, National
25 Science Foundation Chemical, Biological, and Environmental Transport Program and Hydrology Program,
26 **09/2010-08/2013**, \$427,500, lead PI of three.
27
28 MRI Acquisition: An ICP-MS Facility at the University of Utah, National Science Foundation, EAR-MRI
29 Program, **9/2009-08/2012**, \$1,323,400, co-PI of five.
30
31 New Filtration Theory via Incorporation of Pore Scale Mechanisms Operating in the Presence of an
32 Energy Barrier, National Science Foundation Chemical, Biological, and Environmental Transport Program
33 and Hydrology Program, **09/2009-08/2012**, \$426,000, sole PI.
34
35 A Quantitative Assessment of Mercury Influx to the Great Salt Lake, Regional Applied Research Effort
36 (RARE) Program (USEPA Region 8), **09/2010-08/2012**, \$200,000, co-PI with three.
37
38

39 **REVIEWER FOR**

- 40 Professional Journals

- 1 Colloid & Surfaces
- 2 Chemical Geology
- 3 Chemosphere
- 4 Environmental Engineering Science
- 5 Environmental Pollution
- 6 Environmental Science & Technology
- 7 Geochimica et Cosmochimica Acta
- 8 Journal of Contaminant Hydrology
- 9 Journal of Colloid & Interface Science
- 10 Journal of Environmental Engineering
- 11 Journal of Environmental Monitoring
- 12 Journal of Environmental Quality
- 13 Journal of Geophysical Research
- 14 Langmuir
- 15 Separation and Purification Technology
- 16 Vadose Zone Journal
- 17 Water Research
- 18 Water Resources Research
- 19
- 20 Funding agency proposal, panel, and center reviews
- 21
- 22 National Science Foundation
 - 23 Hydrologic Sciences Panel 2008-2011
 - 24 Chemical, Biological, and Environmental Transport Panel 2010
 - 25 External reviewer for National Center for Environmental Implications of Nanotechnology (CEINT)
 - 26 2009 to present
 - 27 Department of Energy 1997
 - 28 American Chemical Society Petroleum Research Fund
- 29

30 **COURSES CREATED AND TAUGHT**

- 31 Environmental Conflict: Mining and Water Quality in Ecuador, Study Abroad May 2012
- 32 Sustainability Practicum
- 33 Aqueous Geochemistry for Engineers & Scientists
- 34 Subsurface Remediation and Hazardous Waste Management
- 35 Contaminant Partitioning for Engineers & Scientists
- 36 Architecture of the Earth

37 **STUDENTS/ASSOCIATES ADVISED (Primary Advisor)**

- 1 2005 to present:
- 2 Post-doctoral associates:
- 3 Dr. Huilian Ma, Degree: Chemical Engineering, Subject: New filtration theory for colloid
4 retention under unfavorable conditions
- 5 Ph.D. recipients/candidates:
- 6 Mr. Eddy Pazmino, Degree: Chemical Engineering, Expected completion 2014, Subject: New
7 filtration theory for colloid retention under unfavorable conditions
- 8 Mr. Greg Carling, Degree: Geology, Expected completion 2012, Subject: Mercury cycling in the
9 Great Salt Lake Basin
- 10 Ms. Wenjie Huang, Degree: Chemical Engineering, Expected completion 2012, Subject:
11 Nanoparticle characterization via field flow fractionation.
- 12 Dr. Ximena Diaz, Degree: Environmental Engineering, Completed 2008, Subject: Selenium cycling
13 in the Great Salt Lake, Utah. Present position: Associate Professor of Extractive Metallurgy at
14 the National Polytechnic University, Quito, Ecuador.
- 15 Dr. Xiqing Li, Degree: Environmental Engineering, Completed 2006, Subject: Role of fluid drag
16 and energy barrier on colloid retention. Present position: Associate Professor in Resource and
17 Environmental Science, at Peking University, Beijing, China
- 18 Dr. Meiping Tong, Degree: Environmental Engineering, Completed 2007, Subject: Role of pore
19 domain geometry and energy barrier on colloid retention in porous media. Present position:
20 Associate Professor in Environmental Science and Engineering, Peking University, Beijing, China
- 21 Dr. Pengfei Zhang, Degree: Geological Engineering, Completed 2000, Subject: Immunomagnetic
22 methods for bacterial detection in groundwater and role of fluid velocity and predation on
23 bacterial transport. Present position: Professor at City College of New York, New York.
- 24 M.S. recipients/candidates
- 25 Mr. Brooks Black, Degree: Geology, 2013, Subject: Mercury and Trace Element Cycling
- 26 Mr. Joel Pierson, Degree: Geology, 2013, Subject: Mercury and Trace Element Cycling
- 27 Mr. Neil Swanson, Degree: Geology, 2013, Subject: Mercury and Trace Element Cycling
- 28 Ms. Eliana Manangon, Degree: Geological Eng., 2012, Subject: Environmental Nanoparticles
- 29 Mr. Eddy Pazmino, Degree: Geological Engineering, 2011, Subject: Colloid transport
- 30 Ms. Abigail Rudd, Degree: Geological Engineering, 2010, Subject: Mercury methylation

1 Ms. Kimberley Beisner, Degree: Geology, 2008, Subject: Selenium cycling in the Great Salt Lake
2 Mr. Wade Oliver, Degree: Geology, 2008, Subject: Selenium sedimentation in the Great Salt Lake
3 Ms. Mary Ellen Potter, Degree: Civil Eng., 2008, Subject: Phosphorous accum. in Farmington Bay
4 Ms. Christina Brow, Degree: Environmental Eng., 2004, Subject: Colloid Transport
5 Mr. Michael Koch, Degree: Public Health, 2004, Subject: Cholera detection in ship ballast
6 Ms. Margaret McGriff, Degree: Geology, 2002, Subject: Surfactant solubilization of PCE and PAH
7 Mr. William McIntosh, Degree: Geology, 2002, Subject: Bacterial transport in groundwater
8 Mr. Ryan Rowland, Degree: Geology, 2002, Subject: U treatment in permeable reactive barrier
9 Mr. Gaobin Bao, Degree: Geology, 2000, Subject: Surfactant solubilization of PCE and PAH
10 Mr. Phillip Schmitz, Degree: Geol. Eng., 2000, Subject: Au extraction from carbonaceous ore
11 Mr. Wynn John, Degree: Geol. Eng., 1999, Subject: PAH solubilization by surfactants and NOM
12 Mr. Jorn Stenebraten, Degree: Geol. Eng., 1998, Subject: Au extraction from carbonaceous ore
13

14 **PROFESSIONAL ACTIVITIES**

- 15 • Symposium co-convener American Chemical Society Colloids & Surfaces Meeting, Johns Hopkins
16 University, June 2012
- 17 • Utah Statewide Mercury Workgroup
- 18 • Symposium co-convener, American Geophysical Union, San Francisco, CA, December, 2011
- 19 • UNESCO IHE Invited Research Director in Kampala, Uganda, Fall 2009
- 20 • National Nanotechnology Initiative Environmental Health and Safety Panel for Research Directions,
21 Fall 2009.
- 22 • National Science Foundation Hydrology Panel Spring and Fall, 2008 to present
- 23 • Sustainability Practicum leader – coordinating students from four colleges with architects and
24 campus operations staff to design and implement 6 projects to increase the environmental
25 performance of the Frederick Albert Sutton Building, U. of Utah
26 (http://www.earth.utah.edu/news_events/news/green07).
- 27 • Field trip developer and coordinator for elementary school field trips to Great Salt Lake for Water,
28 Environment, Science & Teaching (WEST) graduate program (<http://www.earth.utah.edu/west>)

- 1 • Director of the Center for Water, Ecosystems, and Climate Science (CWECS) at the University of
2 Utah, 2004 to 2008. Developer of CWECS ICP-MS facility.
- 3 • Board of Directors, Consortium of Universities for the Advancement of Hydrologic Science, Inc., May
4 2002 to December 2004.
- 5 • Frederick Albert Sutton Building Design Committee, 2006-2009
- 6 • Chair, Geological Engineering Degree Program Committee, 1996-2003
- 7 • Executive committee, Environmental Engineering degree program (1996-present)

8

9 **ADVISORS**

10 Ph.D. advisor: Dr. Gary Amy, U. of Colorado, Civil, Environmental, and Architectural Engineering
11 Post-doctoral advisor: Dr. Bruce Logan, U. of Arizona, Chemical and Environmental Engineering

12

13 **REFEREED PUBLICATIONS (*corresponding author)**

14 Carling G.T., Fernandez D.P., and ***Johnson W.P.**, 2012, Dust-mediated loading of trace and major
15 elements to Wasatch Mountain snowpack, submitted.

16 Ma H., Pazmino E.F., ***Johnson W.P.**, 2011, Surface Heterogeneity on Hemispheres-in-Cell Model Yields
17 All Experimentally-Observed Non-Straining Colloid Retention Mechanisms in Porous Media in
18 the Presence of Energy Barriers, *Langmuir*, <http://dx.doi.org/10.1021/la203587j>.

19 Pazmino E.F., Ma H., ***Johnson W.P.**, 2011, Applicability of colloid filtration theory in size-distributed,
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- 1 Carling G.T., Fernandez D.P., Huang W., Rudd A., Pazmino E., **Johnson W.P.**, 2011, Trace element
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- 11 Dicataldo G, D.F. Hayes, **W.P. Johnson** , W.O. Moellmer , T. Miller, 2010, Effect of dissolved oxygen, pH,
12 and water temperature on diel changes of dissolved selenium and other trace metals in a Great Salt
13 Lake wetland, *Applied Geochem.*, 26, 28-36, doi:10.1016/j.apgeochem.2010.10.011.
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15 Presence of Energy Barriers and Pitfalls of Inferring Mechanisms from Indirect Observations", 2010,
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- 27 **Johnson, W. P.**, X. Li, M. Tong, and H. Ma, 2009, Comment on "Transport and fate of bacteria in porous
28 media: Coupled effects of chemical conditions and pore space geometry" by Saeed Torkzaban et al.,
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2 Micro- Particulates in the Geochemically-stratified Great Salt Lake, *App. Geochem.*,
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5 Great Salt Lake, Utah, *App. Geochem*, 24 , 936-949.
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9 Utah, *Environ. Sci. Technol.*, 43 (1), pp 53–59, DOI: 10.1021/es801638w.
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20 **BOOK CHAPTERS**

- 21 W.P. Johnson, **2008**, Mechanisms of Retention of Biological and Non-biological Colloids in Porous Media:
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25 **REPORTS**

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3

4 **RECENT INVITED PRESENTATIONS (2010)**

5 The Pennsylvania State University Engineering Energy & Environmental Institute (E3I) Fall Graduate
6 Seminar: New filtration theory for predicting retention of *Cryptosporidium* oocysts and other > 2 micron
7 particles in porous media under environmental conditions

8 The Johns Hopkins University Center for Environmental and Applied Fluid Mechanics Fall Seminar Series:
9 Progress and challenges in developing theory for prediction of micro- and nano-particle transport in
10 porous media under environmental conditions

11 Utah State University College of Natural Resources Fall Seminar Series: Ongoing research questions
12 regarding Se and Hg in the Great Salt Lake.

13 University of Utah Global Change and Ecosystem Center Fall Seminar Series: Ongoing research questions
14 regarding Se and Hg in the Great Salt Lake

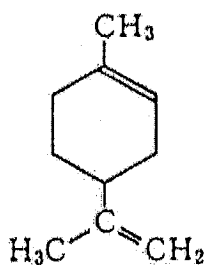
15 EPA Symposium on Ground Water-borne Infectious Disease Epidemiology, Etiologic Agents and
16 Indicators, Washington D.C. Winter 2010, New filtration theory for predicting retention of
17 *Cryptosporidium* oocysts and other > 2 micron particles in porous media under environmental
18 conditions.

19 Panel Presentation at National Nanotechnology Initiative Meeting on Nanomaterials and the
20 Environment & Instrumentation, Metrology, and Analytical Methods, Developing methods to detect
21 nanomaterials and determine exposure routes, Fall, 2009

22

Appendix B: Properties of d-limonene

1		
2		
3	solubility in water = 13.8 mg/L	ref 1
4	Koc = 1030-4780 ml/g	ref 2
5	Half lives: biotic (aerobic) < 14 days, abiotic (in air) < 2 hours	ref 2
6	Log octanol-water partition coefficient = 4.2	ref 1
7	Formula: C ₁₀ H ₁₆	ref 3
8	Molecular weight = 136.24	ref 3
9	Temp melt: -142.4 F	ref 3
10	Vapor Pressure:	
11	2.0 mm Hg	ref 1
12	1.0 mm Hg at 57.0 ° F	ref 3
13	5 mm Hg at 104.7° F	ref 3
14	10 mm Hg at 128.8° F	ref 3
15	Vapor Density: 4.69	ref 3
16	Specific Gravity: 0.8411 at 68.0 ° F	ref 3
17	Boiling Point: 348-349 ° F at 760 mm Hg (NTP, 1992)	ref 3



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Appendix C: Properties of the tar

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Dr. Nick Dahdah (Energy Geosciences Institute, Utah) states that the Eastern Utah tar sands represent recalcitrant compounds dominated by asphaltenes. They contain negligible unsaturated aliphatics and little of the small polycyclic aromatic hydrocarbons (PAHs) such as naphthalene or phenanthrene. However, they may contain significant larger PAHs such as pyrene, chrysene, benz(a)anthracene, benzo(a)pyrene, etc.

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10

Dr. Dahdah says that GC analyses do not resolve the individual compounds in the tar, and so the composition is only generally characterized. He says that Frank Hanson and Milind Deo (UU Chem Eng) examined these compounds prior to retirement.

11

<http://www.docstoc.com/docs/46744779/Asphaltenes-and-Polycyclic-Aromatic-Hydrocarbons>

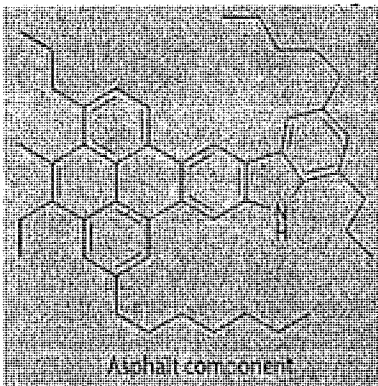
12

URL above boils down to: the tar sands are expected to be dominated by asphaltenes.

13

Petroleum-based asphaltenes (as opposed to coal-based) have a significant alkane fraction and contain large aromatic ring systems.

14



Such molecular structure can be exemplified by the following structure (figure left). Such structures dominated by non-polar bonds characteristically have low water solubilities, e.g. in the $\mu\text{g/L}$ range or less.

22 Multiple

23

aromatic ring structures in the form of polycyclic aromatic hydrocarbons (PAH) (figure right) are well-known carcinogens, although the alkane substituents on asphaltenes may alter their carcinogenicity relative to PAHs

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


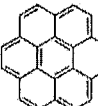






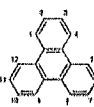

benzo(a)pyrene physical (not necessarily toxicological) properties as an example.

29

30

(Figure source reference 4)

31

Chemical compound		Chemical compound	
Anthracene		Benzo[a]pyrene	
Chrysene		Coronene	
Corannulene		Naphthalene	
Naphthalene		Pentacene	
Phenanthrene		Pyrene	
Triphenylene		Ovalene	

1

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Appendix D - Risk

3

The cleanup level to meet a given excess carcinogenic risk is obtained by the following equation

4

which determines the intake concentration (in this case in groundwater) corresponding to the

5

acceptable excess carcinogenic risk (set to 1E-6 as default regulatory goal).

6

$$\text{cleanup level} = \frac{(R)(BW)(AT)}{(CSF)(CR)(AAF)(EF)(ED)}$$

7

where:

8

cleanup level = concentration of compound in groundwater (e.g. mg/L)

9

R = acceptable excess carcinogenic risk (1E-6 regulatory goal)

10

BW = body weight (kg)

11

AT = averaging time (days)

12

CSF = carcinogenic slope factor for the compound (excess risk per mg/(kg-day))

13

CR = contact rate (e.g. L/day)

14

AAF = absorption adjustment factor (usually set equal to unity as default)

15

EF = exposure frequency (days/year)

16

ED = exposure duration (years)

17

18

Despite being a suspected carcinogen, there is no CSF available for perylene. However, a CSF is

19

available for benzo(a)pyrene, which is another 5-ring PAH expected in crude oil and tar.

20

21

The CSF for benzo(a)pyrene via ingestion is: 7.3 (reference 7)

22

$$\text{cleanup level} = \frac{(1E-6)(70 \text{ kg}_{\text{bodyweight}})(365 \frac{\text{days}}{\text{year}} 70 \frac{\text{years}}{\text{ave time}})}{(7.3 \frac{\text{excess risk}}{\text{mg}_{\text{cmpd}}})(2 \frac{\text{L}_w}{\text{day}})(1)(365 \frac{\text{days}}{\text{year}})(70 \frac{\text{years}}{\text{ave time}})}$$

$$\frac{\text{kg}_{\text{bodyweight}} - \text{day}}$$

23

cleanup level = 0.00479 µg/L

1

2

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In the Matter of

PR Spring Tar Sands Project, Ground Water Discharge Permit-by-Rule

No. WQ PR-11-001

PREPARED SUPPLEMENTAL TESTIMONY

OF

WILLIAM JOHNSON

ON BEHALF OF

LIVING RIVERS

March 16, 2012

1 **I. Introduction**

2 **Q. Please state your name.**

3 My name is William P. Johnson

4

5 **Q. By whom are you employed and what is your position?**

6 I am a professor in the department of Geology & Geophysics and an adjunct professor in
7 the department of Civil & Environmental Engineering at the University of Utah.

8

9 **Q. For whom are you testifying in this proceeding?**

10 I am testifying on behalf of Living Rivers.

11

12 **Q: IN PREPARING THIS SUPPLEMENTAL TESTIMONY, WHAT DOCUMENTS HAVE YOU REVIEWED?**

13 In addition to the documents listed in my direct testimony (and the documents
14 referenced within them), I have reviewed the following:

15 Mr. Handl's February 27, 2012 Report

16 Perry's Chemical Engineer's Handbook, 1999

17 Perry's Chemical Engineer's Handbook, 1973

18

19 (Schwarzenbach R.P., Gschwend P.M., and Imboden D.M., 1993, Environmental Organic

20 Chemistry, Wiley Interscience, New York

21

22 Johnson, W.P., and John, W.W., 1999, A Comparison of Humic Substances and Surfactants as

23 Remediation Agents: PCE Solubilization and Mobilization by Commercial Humic Acid, J. of Cont.

24 Hyd., 35, 343-362.

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Johnson, W.P., and Amy, G.L., 1995, Facilitated Transport and Enhanced Desorption of Polycyclic Aromatic Hydrocarbons (PAH) by Natural Organic Matter (NOM) in Aquifer Sediments: Environmental Science and Technology, 29, 807-817.

Johnson, W.P., Amy, G.L., and Chapra, S.C., 1995, Model Simulation of Facilitated Transport and Enhanced Desorption of Polynuclear Aromatic Hydrocarbons (PAH) by Natural Organic Matter (NOM): ASCE, Journal of Environmental Engineering 121(6), 438-446.

Q. WHAT IS THE PURPOSE OF YOUR SUPPLEMENTAL TESTIMONY?

The goal of my testimony is to predict what will happen when water, such as rain water, contacts the residual tar/d-limonene mixture that will remain in the processed sands returned to the mine and deposited in the waste piles at the PR Spring site. The question to answer is whether bitumen compound would dissolve into that water. In my January 20, 2012 testimony, I determined that the bitumen compounds would indeed dissolve into water and therefore be available for transport. My conservative analysis showed that, in the presence of d-limonene, the concentration of bitumen in water would be 2000 times higher than the concentration would be if d-limonene were not present. The purpose of this testimony is to show the errors in Mr. Handl's analysis of the same issue and to show that my analysis better predicts what could happen when water contacts the processed sands.

1 **II. Rebuttal to Edward Handl**

2
3 **Q: Mr. Handl has filed a response to the testimony you filed in this case on January 20, 2012. Please**
4 **provide a brief summary of Mr. Handl's assertions and your reply to those contentions.**

5 Mr. Handl's February 27, 2012 response to my testimony contends that the only effect
6 of d-limonene on tar (bitumen) compounds in the residual mixture remaining in processed sands
7 is to dilute the bitumen compounds in that organic mixture (referred to as extract), and thereby
8 to simply dilute the compound concentrations in water (referred to as raffinate) that would
9 come into contact with (equilibrate with) the residual mixture. My testimony, in contrast,
10 demonstrates that the role of d-limonene is not merely passive dilution; but rather, that d-
11 limonene dissolved in water serves to "coax" bitumen compounds into the water; thereby
12 greatly increasing the concentration of bitumen compounds in the water that comes into
13 contact with the residual mixture.

14 Mr. Handl's assertion ignores the critical role of dissolved d-limonene in the water,
15 which is to concentrate bitumen in the water by many orders of magnitude relative to bitumen's
16 normal water solubility. In other words, the presence of d-limonene dissolved in water acts to
17 make bitumen more soluble than it would be were the d-limonene not there. The effect of d-
18 limonene on the solubility of bitumen cannot be demonstrated via Mr. Handl's ternary phase
19 equilibrium analysis because he assumes incorrectly that bitumen mixes with water "ideally,"
20 according to Raoult's Law. As I show below, bitumen does NOT mix with water ideally, and this
21 non-ideal interaction between bitumen and water refutes the raffinate boundary that Mr. Handl
22 assumed. Instead, this non-ideal interaction supports a raffinate boundary that in fact
23 demonstrates that bitumen compound concentrations will increase in the water as d-limonene
24 dissolves into the water. Hence, this effect (enhanced dissolution of bitumen compounds into

1 water via d-limonene dissolution into water) is supported both by the partition coefficient
2 approach I provided previously, as well as by a correct ternary phase equilibrium analysis.

3
4 **Q: Is your use of equilibrium partition coefficients standard practice in performing an analysis like the**
5 **one you present in your January 20, 2012 testimony?**

6 Yes. Mr. Handl, in his testimony, calls the use of equilibrium partition coefficients (as I
7 have done) "baffling", and implies that this treatment is unconventional. However, this
8 approach is highly conventional and appropriate, and is well demonstrated in the literature cited
9 below, as well as in the same section of the very text that Mr. Handl cited (Perry's Chemical
10 Engineer's Handbook, 1973); albeit my version of the text seems to be more modern relative to
11 Mr. Handl's version, and has a more extensive treatment of partition coefficients (Perry's
12 Chemical Engineer's Handbook, 1999).

13
14 ***The Problem with Mr. Handl's Use of Mole Fractions and Raoult's Law: Thermodynamics and Non-***
15 ***Ideal Mixtures***

16
17 **Q: Is Mr. Handl correct that the only influence of d-limonene is to reduce the mole fraction of**
18 **bitumen compounds in the extract?**

19 No, Mr. Handl is mistaken when he makes a significant issue out of the fact that I did not
20 account for specific mole fractions in the tar/d-limonene mixture (extract), which are of course
21 needed in order to calculate the specific concentration of a given compound that is achieved in
22 water (raffinate) that is in contact with the residual tar/d-limonene mixture (extract). However,
23 the issue is NOT the specific concentration of benzo(a)pyrene (B(a)P) or any other given bitumen

1 compound in water, because there is an entire class of compounds that are of concern.

2 Specifically, Raoult's Law for compounds dissolving into water for under ideal conditions is:

$$3 \quad C_{raf} = X_{ext} C_w^{sat}(L) \quad (1)$$

4 Applied to the present inquiry, C_{raf} is the concentration of the bitumen compound (e.g.
5 B(a)P or any other compound one might want to consider) in the raffinate (the water phase that
6 is in contact with the extract), X_{ext} is the mole fraction of the bitumen compound of interest in
7 the extract (tar/d-limonene mixture), and $C_w^{sat}(L)$ is the solubility in pure water of the pure liquid
8 form of the bitumen compound of interest. Hence, as Mr. Handl pointed out, the concentration
9 of any given compound in the organic phase would be relatively small (scaled to its X_{ext}).

10 However, there are expected to be many carcinogenic compounds in the organic
11 extract. As a result, to be accurate, one must sum the resulting concentrations for ALL
12 compounds of interest made using Raoult's Law above. In determining the absolute
13 concentration in the raffinate (in his February 27, 2012 response to my testimony), Mr. Handle
14 considered the mole fraction of a single compound only (B(a)P), and obtained a concentration of
15 5.7×10^{-4} $\mu\text{g/L}$ in the raffinate. The sum of the concentrations for all compounds of interest
16 would be considerably higher than the concentration that Mr. Handl calculated. Rather than
17 perform the calculation for a myriad of compounds, I simply represented that class of
18 compounds with B(a)P's water solubility, as my goal was not to obtain the precise concentration
19 of B(a)P in the water phase, but rather to demonstrate the critical effect of d-limonene on the
20 concentration of B(a)P in the water phase.

21 Furthermore, as I show below, Mr. Handl's incorrect assumption of ideal mixing leads to
22 further underestimation of the value of C_{raf} (the concentration of bitumen compound in the
23 raffinate, which I referred to as C_w^* in my previous testimony). This means that Mr. Handl
24 substantially underestimated the concentration of bitumen compounds in the raffinate because

1 he did not sum the concentrations for all the bitumen compounds of interest that will dissolve
2 into the water phase AND because he did not account for the fact that dissolved d-limonene in
3 the water phase (raffinate) would provide an ideal phase for the bitumen compounds, thereby
4 increasing the concentration of bitumen compounds in the raffinate. Had Mr. Handl summed
5 the concentrations of the many compounds in the tar, and had he accounted for solubilization
6 of bitumen compounds by d-limonene in the raffinate, his calculations would have shown a
7 significantly higher concentration of bitumen compounds in the raffinate.

8
9 **Q: For the purposes of further explaining the errors in Mr. Handl's analysis, will you adopt his**
10 **distinction between water and raffinate?**

11 Yes. Mr. Handl's February 27, 2012 response to that testimony refers to the
12 concentration of bitumen compound in the raffinate as " C_w ". However, Mr. Handl's distinction
13 between water and raffinate is useful, and so I have adopted " C_{raf} " to refer to the concentration
14 of bitumen compound in the water phase (raffinate) that is in contact with (equilibrated with)
15 the residual extract (tar/d-limonene mixture). Below I will use the term " C_w " to refer to water
16 that is in contact with tar (but without d-limonene in either phase).

17
18 **Q: In your January 20, 2012 testimony, how did you analyze the effect of d-limonene on the**
19 **concentration of bitumen in water?**

20 For the present purposes, the primary issue is the CHANGE in the concentration of
21 bitumen compounds in water before, versus after, the addition of d-limonene. My testimony
22 used partition coefficients (equilibrium coefficients for distribution of an example bitumen
23 compound between water and d-limonene) to demonstrate that the addition of d-limonene to

1 water increases the solubility of bitumen compounds in the water solution by multiple orders of
2 magnitude.

3
4 **Q: Is Mr. Handl's approach capable of demonstrating the effect demonstrated in your testimony –**
5 **calculating the change in the concentration of bitumen in water caused by the addition of d-limonene**
6 **by using partition coefficients?**

7 Yes, but not under the incorrect assumptions that were made by Mr. Handl. Mr. Handl
8 inexplicably denies the validity of my partition coefficients approach despite its being well
9 established in the literature. Instead, Mr. Handl provides a ternary phase equilibrium analysis
10 that incorrectly assumes the bitumen compound partitioning follows Raoult's Law above for
11 ideal conditions. As a result, he incorrectly concludes that only effect of d-limonene is to dilute
12 the bitumen compounds in the organic residual (extract) and the water phase (raffinate). Mr.
13 Handl's conclusion is wrong because he fails to acknowledge deviation from Raoult's Law for
14 non-ideal interactions, such as those between bitumen compounds and water.

15
16 **Q: Can you show what information is needed to account for the interactions that are not included in**
17 **Raoult's Law?**

18 Yes. To explain further the impact of non-ideal conditions, I show that the above
19 expression of Raoult's Law, equation (1), is derived from a thermodynamic basis by considering
20 chemical potentials (μ_o and μ_w) of the bitumen compound of interest in the organic and water
21 phases, respectively (assuming that both the organic and water phases are liquids):

$$\mu_o = \mu^o + RT \ln \frac{\gamma_o X_o P^o(L)}{P^o(L)} \quad (2)$$

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$$\mu_w = \mu^0 + RT \ln \frac{\gamma_w X_w P^0(L)}{P^0(L)} \quad (3)$$

where μ^0 is the standard chemical potential for the bitumen compound of interest, R is the universal gas constant, T is temperature. The parameters γ_o and γ_w are the activity coefficient of the bitumen compound in the organic and water phases, respectively, and $P^0(L)$ is the vapor pressure of the pure liquid bitumen compound of interest.

At equilibrium, the chemical potentials of any bitumen compound of interest are equal in the organic and water phases ($\mu_o = \mu_w$). Therefore equilibrium is represented by equating the two expressions (2 & 3) above, which boils down to:

$$\gamma_w X_w = \gamma_o X_o \quad (4)$$

And re-arranging further yields

$$X_w = \gamma_o X_o \frac{1}{\gamma_w} \quad (5)$$

Q: What does this equation mean?

What the above expression says is that the concentration of B(a)P (or any other bitumen compound in the water phase) is proportional to its mole fraction in the organic mixture (X_o), its activity coefficient in the organic mixture (γ_o), and the inverse of its activity coefficient in the water phase (γ_w). Here, the organic mixture may be tar (in liquid form), or may be the tar/d-limonene liquid mixture, depending on the context one wishes to address. Both contexts are ruled by the above relationship. This expression is nearly equivalent to Equation 1 (Raoult's Law), but to make this obvious I need to explain further the activity coefficients.

1 **Q: What do activity coefficients tell us?**

2 Activity coefficients represent the compatibility of a compound for a given phase, i.e.
3 the organic mixture and water are the two phases with which the bitumen compound interacts.
4 A cardinal rule is that "like dissolves like." Therefore, polar substances such as water and
5 vinegar dissolve well into each other (are compatible), and non-polar substances such as
6 bitumen and d-limonene dissolve well into each other (are compatible). However, non-polar
7 substances do not dissolve well into polar substances; oil and water do not mix, nor do bitumen
8 compounds mix well into water. This is why the tar remains in the sand after millennia of
9 precipitation; the water does not dissolve the bitumen, and this is why d-limonene is such a
10 great agent for extracting bitumen compounds from the sand; i.e., bitumen and d-limonene are
11 compatible.

12 The activity coefficient for a perfectly compatible substance is 1, and the activity
13 coefficients for incompatible substances are greater than 1, ranging up to around 10^9 (one
14 billion) for large non-polar compounds like those in bitumen when they interact with water.
15 Hence, γ_o (activity coefficient of bitumen compounds in the organic mixture, that is, the non-
16 water phase) is approximately 1 (because they are perfectly compatible or nearly); whereas, the
17 value for γ_w (the activity coefficient of the bitumen compound in the pure water phase) is very,
18 very high (approaching 1 billion).

19

20 **Q: So how do the activity coefficients in water and the organic mixture relate to Raoult's Law and**
21 **ideal versus non-ideal conditions?**

22 What precisely is the value of γ_w in the raffinate is at the heart of the dispute between
23 Mr. Handl and me. Mr. Handl contends that this value is nearly one billion in the raffinate (as in
24 pure water) despite the presence of highly compatible d-limonene in the raffinate. In contrast,

1 my analysis shows that the value in the raffinate drops significantly below that in pure water
2 due to the presence of highly compatible d-limonene in the raffinate. The decreased activity
3 coefficient of bitumen compounds in the raffinate (relative to that in pure water) yields a much
4 higher concentration of bitumen compounds in the raffinate than one would predict for pure
5 water. Mr. Handl's assumption of ideal conditions predicted a concentration of bitumen
6 compounds in the raffinate that approximate the concentration of bitumen in pure water, and
7 ignored the effect of d-limonene dissolved in the water.

8
9 **Q: But still, can you clarify how exactly this relates to Raoult's Law?**

10 This is done by considering pure water in contact with (equilibrated with) a pure liquid
11 bitumen compound, and in this case γ_w is referred to as γ_w^{sat} . From equation 5, recognizing that
12 that γ_o and X_o are each approximately equal to 1 for a drop of pure liquid bitumen compound,
13 the value of γ_w^{sat} can be obtained as the inverse of the solubility of the bitumen compound (in pure
14 liquid form) in water (expressed as a mole fraction):

$$15 \quad \gamma_w^{sat} = \frac{1}{X_w^{sat}(L)} \quad (6)$$

16 Substituting concentration for mole fraction, because solubilities are given as concentrations:

$$17 \quad \gamma_w^{sat} = \frac{1}{X_w^{sat}(L)} = \frac{1}{C_w^{sat}(L) V_w} \quad (7)$$

18 where V_w is the molar volume of water, and where this conversion between mole fraction and
19 concentration is appropriate for dilute concentrations such as for dissolution of bitumen
20 compounds in water.¹

¹ This approach is appropriate because this simple conversion between mole fraction and concentration is accurate only in dilute solutions like the raffinate.

1 Note that equation (6) substituted into (5) gives Raoult's Law in terms of mole fractions,
2 that is: $X_w = \gamma_o X_o X_w^{sat}$. Notice also that substitution of the relationship between mole fraction
3 and concentration given in Equation (7) yields Equation (1): $C_w = \gamma_o X_o C_w^{sat}$, with the
4 understanding that $\gamma_o \sim 1$.

5
6 **Q: O.K. But then where does the deviation from Raoult's Law come in?**

7 To show this I need to first establish the value of the activity coefficient of the bitumen
8 compound in pure water (γ_w^{sat}). Fortunately, this is obtained directly from Equation (7), using
9 B(a)P (again as a representative of many compounds of concern in the bitumen):

10
$$\gamma_w^{sat} = \frac{1 L_w}{1.95E - 7 mol_{B(a)P}} \frac{1 mol_w}{1.8E - 2 L_w} = 10^{8.45} \quad (8)$$

11
12 **Q: What does this calculation show us?**

13 Note that the result of this calculation is $10^{8.45}$, which equals 2.85E8 or 285,000,000.
14 This is a very large activity coefficient, representing highly non-ideal interaction between B(a)P
15 and water. Remember, however, the critical point here is that this value represents the activity
16 coefficient for B(a)P in pure water. It DOES NOT represent the activity coefficient for B(a)P (or
17 other bitumen compounds) in raffinate (water with d-limonene) as was assumed by Mr. Handl.
18 Before quantifying the value of γ_w in the raffinate, I will show conceptually how this analysis
19 relates to the ternary phase equilibrium analysis provided by Mr. Handl.

20
21 **Q: O.K. but before you do, would you summarize your points so far in your testimony?**

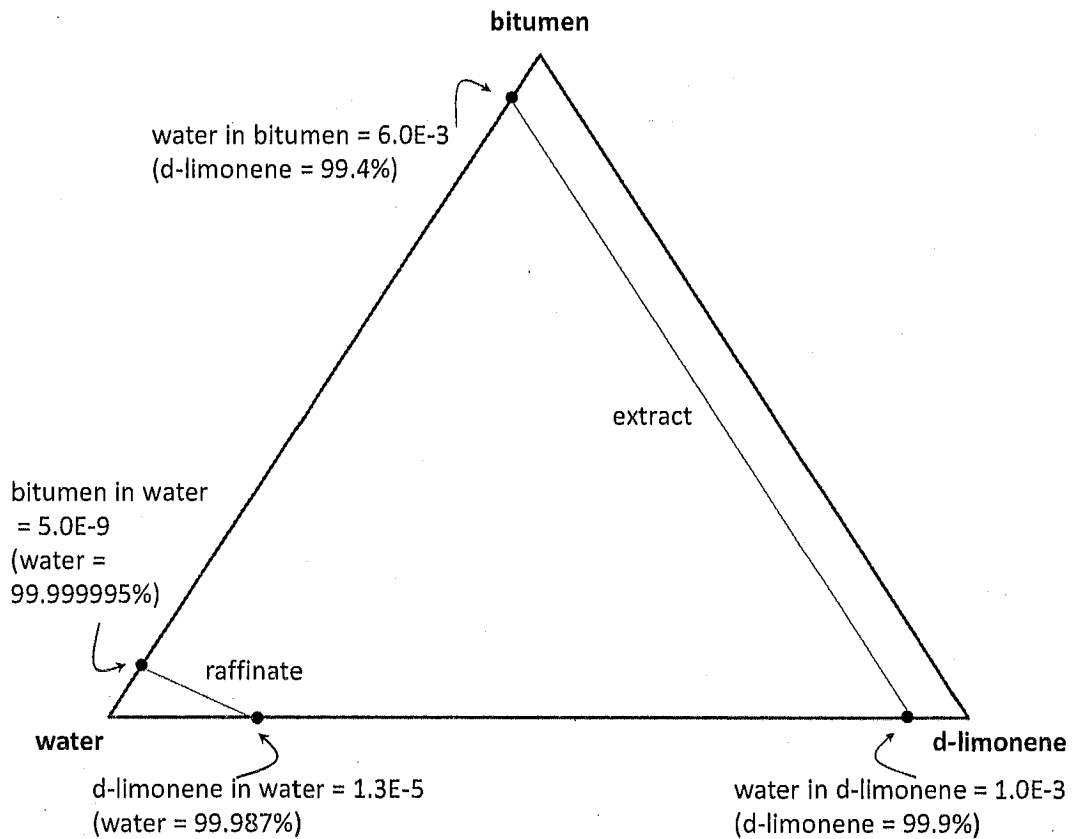
22 As indicated above, I demonstrated that Mr. Handl substantially underestimates the
23 concentration of bitumen in the raffinate because he does not sum or add up the

1 concentrations for all the bitumen compounds of interest that will dissolve into the water. I also
2 have further shown that bitumen and water are not an ideal mixture and indeed, are far from
3 ideal. This sets the basis for demonstrating that the non-ideality of interaction between
4 bitumen and water needs to be accounted for. Below I show how this would need to be done
5 using Mr. Handl's ternary phase equilibrium approach, as via thermodynamic relationships.

6
7 ***The Problem with Mr. Handl's Ternary Phase Equilibrium Analysis***

8
9 **Q: You stated that you would demonstrate how your determination of the that the activity**
10 **coefficient of bitumen (the value of γ_w) in water relates to Mr. Handl's ternary phase equilibrium**
11 **analysis. Please proceed.**

12 To argue in his response that addition of d-limonene only decreases the concentration
13 of bitumen in water, Mr. Handl's utilizes ternary phase equilibrium analysis, where the
14 solubilities of: 1) water in bitumen; 2) bitumen in water; 3) d-limonene in water; and 4) water in
15 d-limonene are plotted on a triangle with water, bitumen, and d-limonene on the vertices, as
16 shown schematically below.



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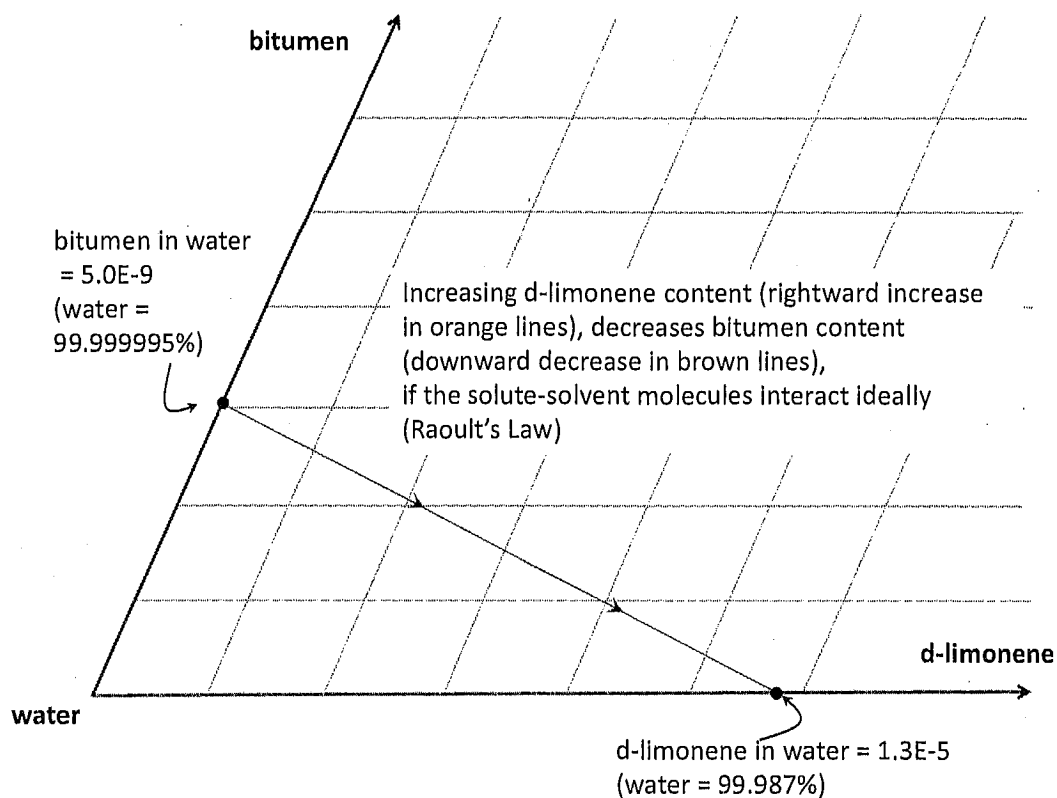
9

Q: How does Mr. Handl depict the effect of d-limonene on the degree to which bitumen will dissolve into the raffinate?

11

12

Mr. Handl's contended effect of d-limonene on dissolution of bitumen compounds into water is shown below:



1
2 Mr. Handl assumes that the relationship between bitumen content and d-limonene
3 content in the raffinate must follow the linear trajectory shown above, and states: "It can thus
4 be seen that Dr. Johnson's assertion that limonene effects to "coax" compounds such as B(a)P
5 into solution, is effectively refuted. In fact, as can be seen from this ternary system analysis, d-
6 limonene will act to suppress the dissolution of other organics (present in bitumen) from the
7 water phase". (Handl response February 27, 2012).

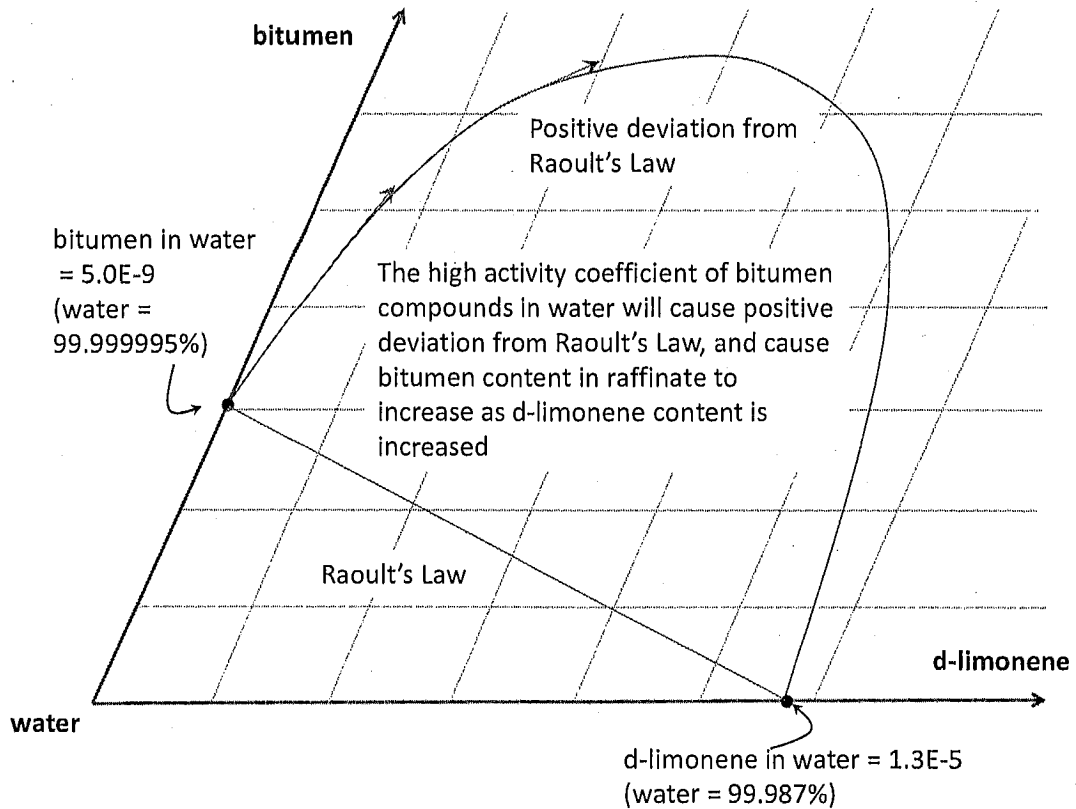
8
9 **Q: Is Mr. Handl's assertion accurate?**

10 No. Mr. Handl reaches this flawed conclusion based on the erroneous assumption that
11 the boundary of the raffinate phase is precisely the line connecting the solubilities of bitumen in
12 water and d-limonene in water. This assumption is further based on the false conclusion that
13 the water-rich solution must be ideal, and therefore follow Raoult's Law (that is he assumed γ_w

1 = γ_w^{sat}). However, the fact is that the raffinate boundary does not, should not, and cannot
2 follow Handl's assumed line.
3

4 **Q: What is the nature of the real boundary that characterizes the raffinate phase?**

5 The boundary is non-linear. This is because a nonlinear boundary arises from the
6 extremely high non-ideal interactions between bitumen compounds and water, and the ideal
7 interactions between bitumen compounds and dissolved d-limonene. The boundary of the
8 raffinate phase is not the line identified by Mr. Handl (reflecting Raoult's Law), but rather a non-
9 linear boundary as shown below (positive deviation from Raoult's Law), which demonstrates
10 that bitumen compound solubility will increase with increasing d-limonene concentration in the
11 raffinate.



12

1 **Q: Is Mr. Handl's assumption of this linear boundary in keeping with what is known about the effects**
2 **of dissolved solvents like d-limonene on extent to which a hydrophobic solute like bitumen will**
3 **dissolve into a water solution?**

4 No. Mr. Handl's assumption and corresponding conclusion conflict with the large body
5 of existing literature regarding co-solvent and co-solute effects (from dissolved solvents like d-
6 limonene) that increase hydrophobic solute (here, the bitumen) dissolution to aqueous (or
7 water) solutions (Schwarzenbach R.P., Gschwend P.M., and Imboden D.M., 1993, Environmental
8 Organic Chemistry, Wiley Interscience, New York).

9
10 **Q: Can you make this more intuitive to a non-expert?**

11 Yes. Note that the diagram above (which uses Mr. Handl's own numbers) shows that
12 the d-limonene (solubility of $1.3E-5$ as mass fraction) is more than four orders of magnitude
13 more soluble in water than bitumen compounds ($5.0E-9$ as mass fraction). This means that
14 there will be a large amount of d-limonene in the water relative to the bitumen. **Because we**
15 **know that d-limonene is an excellent solvent for bitumen, it even makes intuitive sense that**
16 **the dissolved d-limonene in water will create an excellent environment for bringing the**
17 **bitumen into the water, thereby increasing the solubility of bitumen by many orders of**
18 **magnitude.** This is why the non-linear boundary of the raffinate (shown above) must apply.
19 Conceptually it is obvious that the bitumen concentration in the raffinate must increase as d-
20 limonene is added to the system. Below I will use the thermodynamic constructs to rigorously
21 show that this must be the case.

1 **Q: Are there other limitations in Mr. Handl's ternary phase equilibrium analysis?**

2 Yes. Furthermore, the ternary phase equilibrium analysis used by Mr. Handle
3 corresponds to two immiscible or partially miscible LIQUIDS (miscible meaning that they dissolve
4 into one another), and so fails to recognize that tar compounds under ambient (pre-processed)
5 conditions in the vast majority of rock at the site exist in a mixture that is dominated by
6 compounds with melting temperatures above the ambient temperature; i.e. they behave more
7 akin to solids than liquids under ambient conditions.² Hence, for the tar compounds
8 encapsulated in the majority of the rock matrix at the site, mixing with d-limonene (a compound
9 with melting temperature below ambient conditions), causes a profound change in their
10 behavior, as demonstrated below. Mr. Handl's ternary phase equilibrium analysis does not
11 account for this change.

12

13 **Q: Please summarize the further points you have made.**

14 I have pointed out the errors in Mr. Handl's ternary phase equilibrium analysis. I
15 showed that he was mistaken to assume a linear boundary depicts the interactions between
16 bitumen compounds and water. In reality, the boundary is a non-linear boundary. This non-
17 linear boundary indicates that bitumen compound solubility will increase with increasing d-
18 limonene concentration in the raffinate.

19 I also note that Mr. Handl's analysis does not account for the fact that the bitumen
20 being processed acts like a solid before the d-limonene is added; whereas it behaves as a liquid
21 after it is mixed with d-limonene

22

² The exception is at tar seeps where sufficient content of "lighter" liquid petroleum compounds remains to allow the tar to flow.

1 **Q: Can you substantiate this further (beyond a conceptual approach)?**

2 Yes, I can do so using a thermodynamic approach, as follows:

3 ***Thermodynamics and Non-Ideality – Quantitative***

4

5 ***Equilibration of Tar (without d-limonene) and Water (without d-limonene)***

6

7 **Q: You stated that Mr. Handl's analysis does not account for the fact that the bitumen (before it is**
8 **processed) acts like a solid; whereas, addition of d-limonene results in a tar/d-limonene mixture that**
9 **is in a liquid state. Please substantiate this and explain its significance.**

10 The effect of solid to liquid phase transition is easily incorporated into the
11 thermodynamic basis for partitioning, as shown below, where the chemical potential of the
12 representative bitumen compound in the organic phase (semi-solid bitumen) before d-limonene
13 is added is given by μ_o , and the chemical potential of the bitumen compound in pure water is
14 given by μ_w .

15
$$\mu_o = \mu^0 + RT \ln \frac{\gamma_o X_o P^0(S)}{P^0(L)} \quad (9)$$

16
$$\mu_w = \mu^0 + RT \ln \frac{\gamma_w X_w P^0(L)}{P^0(L)} \quad (10)$$

17 In this case, for dissolution of bitumen compound from tar into water (e.g. rainwater)
18 (both lacking d-limonene), the relationship (after equilibration) is:

19
$$\gamma_o X_o P^0(S) = \gamma_w X_w P^0(L) \quad (11)$$

20 Re-arranging gives the mole fraction ratio of bitumen in the tar versus the water (both
21 phases without d-limonene):

$$\frac{X_o}{X_w} = \frac{\gamma_w}{\gamma_o} \frac{P^0(L)}{P^0(S)} \quad (12)$$

2

3 **Q: What does Equation 12 tell us?**

4

5

6

7

8

9

10 ***Equilibration of Extract (tar with d-limonene) and Raffinate (water with d-limonene)***

11

12 **Q: So how does addition of d-limonene to this system change this analysis?**

13

14

15

16

17

This equation shows that the mole fraction ratio is the distribution coefficient for the representative bitumen compound between water and the organic phase (tar), or more simply, the partition coefficient for the bitumen compound between water and tar. This better represents the fact that the bitumen is a tar and therefore in a semi-solid state when exposed to pure water.

In contrast to the above analysis that equilibrated chemical potentials for water interacting with tar, the analysis for equilibrating chemical potentials of organic extract (tar with d-limonene) (μ_{ext}) interacting with raffinate (water with d-limonene) (μ_{raf}), yields the following expressions, where the activity coefficients and mole fractions are defined for the bitumen compound of interested in the extract (γ_{ext}, X_{ext}) and raffinate (γ_{raf}, X_{raf}) phases:

18

$$\mu_{ext} = \mu^0 + RT \ln \frac{\gamma_{ext} X_{ext} P^0(L)}{P^0(L)} \quad (13)$$

19

$$\mu_{raf} = \mu^0 + RT \ln \frac{\gamma_{raf} X_{raf} P^0(L)}{P^0(L)} \quad (14)$$

20

Yielding:

21

$$\gamma_{ext} X_{ext} = \gamma_{raf} X_{raf} \quad (15)$$

1 Re-arranging gives the mole fraction ratios of bitumen compound in the extract and
 2 raffinate (both phases with d-limonene):

$$3 \quad \frac{X_{ext}}{X_{raf}} = \frac{\gamma_{raf}}{\gamma_{ext}} \quad (16)$$

4
 5 **Comparing Bitumen Compound Concentrations in the Water Phase in the Presence versus Absence of**
 6 **d-limonene**

7
 8 **Q: How is this analysis relevant to the present inquiry?**

9 For the case of water in contact with tar (d-limonene absent), we know that $\gamma_o \sim 1$
 10 because the bitumen compounds are compatible with the tar. Substituting the above
 11 information into equation (12) (absence of d-limonene) yields:

$$12 \quad \frac{X_o}{X_w} = \frac{\gamma_w}{1} \frac{P^0(L)}{P^0(S)} \quad (17)$$

13 Likewise, for the case of raffinate in contact with the residual extract (tar/d-limonene
 14 mixture), we know that $\gamma_{ext} \sim 1$ because bitumen compounds are compatible with the tar/d-
 15 limonene mixture. As Mr. Handl pointed out, $X_{ext} < X_o$ (the mole fraction of a given bitumen
 16 compound in the extract is less than that in the tar), and X_{ext} decreases with increasing d-
 17 limonene in the extract. Hence, $X_{ext} = X_o * (1 - X_{ext}^{d-limonene})$. Substituting into (16) (presence of d-
 18 limonene) yields:

$$19 \quad \frac{X_o (1 - X_{ext}^{d-limonene})}{X_{raf}} = \frac{\gamma_{raf}}{1} \quad (18)$$

20 Combining (17) and (18) yields:

$$21 \quad X_o = \frac{X_w \gamma_w^{sat} P^0(L)}{P^0(S)} = \frac{\gamma_{raf} X_{raf}}{(1 - X_{ext}^{d-limonene})} \quad (19)$$

1 Re-arranging yields the mole fraction of a bitumen compound in raffinate (water plus d-
2 limonene) relative to pure water (e.g., rainwater), which is the ratio (X_{raf}/X_w) that quantifies the
3 increase in bitumen compound dissolution into water in the presence versus absence of d-
4 limonene:

$$\frac{X_{raf}}{X_w} = (1 - X_{ext}^{d\text{-limonene}}) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (20)$$

6
7 **Q: What does Equation 20 show?**

8 Equation 20 shows that the ratio of bitumen concentration in the water phase in the
9 presence versus absence of d-limonene scales oppositely to the mole fraction of d-limonene in
10 the extract (as Mr. Handl pointed out in his response to my testimony February 27, 2012).
11 However, Mr. Handl failed to acknowledge that the ratio also directly scales to the ratio of the
12 activity coefficients of the bitumen compound in water relative to raffinate phase (second term
13 on right hand side), which is greater than unity (thereby increasing the ratio of bitumen
14 concentration in the water phase in the presence versus absence of d-limonene). Furthermore,
15 Mr. Handl neglected to confirm that the ratio also directly scales to the ratio of liquid versus
16 solid vapor pressures for the pure bitumen compound (third term on right hand side), which is
17 also greater than unity (thereby further increasing the ratio of bitumen concentration in the
18 water phase in the presence versus absence of d-limonene).

19
20 **Q: But your testimony pointed to equation 1 as representing Mr. Handl's approach. Can you relate**
21 **the above equation to Equation 1?**

22 Yes. To further clarify these omissions by Mr. Handl, re-arrangement of (20) yields:

$$X_{raf} = (1 - X_{ext}^{d\text{-limonene}}) X_w \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (21)$$

By combining (5) and (6), which describes the equilibrium between liquid bitumen and water, we obtain

$$X_w = \gamma_o X_o X_w^{sat}(L) \quad (22)$$

Substituting (22) into (21) yields:

$$X_{raf} = \gamma_o (1 - X_{ext}^{d\text{-limonene}}) X_o X_w^{sat}(L) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (23)$$

Recognizing that $(1 - X_{ext}^{d\text{-limonene}}) X_o = X_{ext}$ (from text prior to equation 18) yields:

$$X_{raf} = \gamma_o X_{ext} X_w^{sat}(L) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (24)$$

And recognizing that $\gamma_o \sim 1$, $C_w^{sat}(L) V_w = X_w^{sat}(L)$, $C_{raf} V_{raf} = X_{raf}$, and that $V_w \sim V_{raf}$, where V_w and V_{raf} are the molar volumes of the water and raffinate phases, we obtain:

$$C_{raf} = X_{ext} C_w^{sat}(L) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (25)$$

Q: How precisely does Equation (25) relate to Equation (1)?

Equation 25 is identical to Equation 1 (Raoult's Law) used by Mr. Handl except for two very important terms: a) $\gamma_w^{sat}/\gamma_{raf}$; and b) $P^0(L)/P^0(S)$. The first of the two terms reflects the influence of non-idealities on dissolution of a bitumen compound in water that contains d-limonene, and the second of the two terms reflects the influence of d-limonene in the residual extract (tar/d-limonene mixture) on the behavior of a bitumen compound (acting as a liquid versus a solid).

1 To account for the latter ratio, my testimony uses the normal water solubilities of solid
2 and liquid B(a)P as a basis for demonstrating the change in B(a)P solubility due to the addition of
3 d-limonene (the ratio of the solid and liquid vapor pressures is equal to the ratio of the solid and
4 liquid solubilities).

5
6 **Q: How does the difference between Equations (1) and (25) explain the differences in your testimony
7 and Mr. Handl's response?**

8 Mr. Handl failed to account for the above two terms in his analysis, and as shown below,
9 both terms greatly increase the amount of a given bitumen compound that will dissolve in
10 water. This means that Mr. Handl's analysis greatly underestimates the concentration of
11 bitumen compounds that will dissolve into water (raffinate) in contact with the residual extract
12 (tar/d-limonene mixture).

13
14 **Q: Can you estimate values that demonstrate the magnitude of these differences?**

15 Yes. We can determine the value for the liquid/solid vapor pressure ratio from the
16 following formula (Schwarzenbach et al., 1993):

$$\frac{P_{(L)}^o}{P_{(S)}^o} = e^{\left(\frac{\Delta S_{melt}(T_m)}{R}\right)\left(\frac{T_m}{T}-1\right)} \quad (26)$$

17
18 Where $\Delta S_{melt}(T_m)$ is the ratio of the entropy of melting (at the melting temperature, T_m), and T is
19 the temperature of interest. The ratio of $\Delta S_{melt}(T_m)/R$ is approximately 6.8 for bitumen
20 compounds (Schwarzenbach et al.), and $(T_m/T)-1$ ranges with the T_m of the compound of
21 interest, which is around 230 °C (~500 K) for bitumen compounds, yielding a $(T_m/T)-1$ value of
22 around 0.78 (assuming a temperature of interest of 10 °C).

23 Hence:

$$\frac{P_{(L)}^o}{P_{(S)}^o} = e^{\left(\frac{\Delta S_{melt}(T_m)}{R}\right)\left(\frac{T_m}{T}-1\right)} \approx e^{(0.78)(6.8)} \sim 200 \quad (27)$$

Q: Can you estimate values that show the effect of the activity coefficient ratio term?

Yes. But, the activity coefficient ratio $\gamma_{wf}^{sat}/\gamma_{raf}$ is not readily estimable for bitumen compounds in the absence/presence of d-limonene, because of limited data. However, this ratio is estimable from data for other compounds that interact with bitumen similarly to the way d-limonene does. Octanol is a reasonable representative for d-limonene in this regard, and data for interaction of octanol with bitumen compounds such as B(a)P is readily available. However, because octanol exhibits more polarity than d-limonene octanol will be more soluble than d-limonene in water, and will have a lower affinity for bitumen than d-limonene. Nevertheless, as demonstrated below, the octanol system will show that the activity coefficient ratio $\gamma_{wf}^{sat}/\gamma_{raf}$ is significantly greater than unity, which means, as Schwarzenbach et al. (1993) acknowledge, that the presence of co-solutes like octanol or d-limonene in water increase the concentration of bitumen compounds in water, in direct contradiction to Mr. Handl's testimony.

In order to obtain the above ratio of activity coefficients for the octanol system, consider a system with dissolved bitumen (e.g. B(a)P) in water that is equilibrated with pure liquid octanol (e.g., octanol being used to extract dissolved B(a)P from the water). Following equilibration (as derived above for d-limonene/tar/water system), the activity of B(a)P in the raffinate (water plus dissolved octanol) (γ_{raf}) relative to that in the octanol droplet (γ_{ext}) is equal to the mole fractions of B(a)P in the octanol (extract) versus raffinate phases.

$$\frac{\gamma_{raf}}{\gamma_{ext}} = \frac{X_{ext}}{X_{raf}} \quad (28)$$

Conversion of the mole fractions to concentrations yields:

$$\frac{\gamma_{raf}}{\gamma_{ext}} = \frac{X_{ext}}{X_{raf}} = \frac{C_{ext} V_{ext}}{C_{raf} V_{raf}} \quad (29)$$

where C_{ext} and C_{raf} are the concentrations of B(a)P in the extract and raffinate phases, and V_{ext} and V_{raf} are the molar volumes of the extract and raffinate phases. Recognizing that C_{ext}/C_{raf} is the well-known octanol-water partition coefficient (K_{ow}), substitution yields:

$$\frac{\gamma_{raf}}{\gamma_{ext}} = K_{ow} \frac{V_{ext}}{V_{raf}} \quad (30)$$

The values of V_{ext} and V_{raf} are well approximated by the molar volumes of octanol and water, 0.16 and 0.018 (L/mol) respectively, because of the low solubility of water and octanol in each other (similar to the d-limonene/water system). The value of K_{ow} is approximately $10^{6.5}$ or 1,250,000 (Schwarzenbach et al.), and the value of γ_{ext} is approximately 1. Substituting the above values into equation 30 yields:

$$\gamma_{raf} = (1250000)(0.16 / 0.018) = 11,200,000 = 10^{7.45} \quad (31)$$

Comparing the value of γ_{raf} ($10^{7.45} = 11,200,000$) to γ_w^{sat} ($10^{8.45} = 285,000,000$), derived above via Equation 8, shows that a small amount of octanol dissolved in water reduces the activity coefficient of B(a)P in the raffinate by one order of magnitude relative to pure water. Recall that whether the value of γ_w in the raffinate (γ_{raf}) is different than that in pure water (γ_w^{sat}) is one major aspect of the dispute between Mr. Handl and me. Clearly these values (11,200,000 and 285,000,000) are very different.

To understand the effect of the $\gamma_w^{sat}/\gamma_{raf}$ and $P^0(L)/P^0(S)$ terms on the concentration of bitumen compound in the raffinate, we can assume that $\gamma_w^{sat}/\gamma_{raf}$ in the octanol system reflects reasonably that ratio in the d-limonene system, and we can substitute (27) and (31) into Equation 25 to obtain:

1
$$\frac{X_{raf}}{X_w} = (1 - X_{ext}^{d\text{-limonene}})(10)(200) = 2000(1 - X_{ext}^{d\text{-limonene}}) \quad (32)$$

2

3 **Q: What does Equation 32 show?**

4

5

6

7

8 **Q: How does this calculation relate to your earlier testimony?**

9

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Q: Would you expect a mole fraction of 0.9995 for d-limonene in the extract?

17

18

19

20

21

22

Equation 32 demonstrates that the concentration of bitumen compounds in water can be expected to be greatly enhanced (by three orders of magnitude) in the presence (X_{raf}) versus absence (X_w) of d-limonene.

This is similar to the ratio I provided in my testimony, but differs because the present approach uses representative values for tar compounds; whereas my testimony used specific values for B(a)P as an example. The above expression further shows that the mole fraction of d-limonene in the extract would need to exceed 0.9995 to cancel the effects of solid/liquid transition ($P^o(L)/P^o(S)$) and solubilization of bitumen compounds by dissolved d-limonene in the raffinate ($\gamma_w^{sat}/\gamma_{raf}$).

No. A mole fraction of 0.9995 for d-limonene in the extract is grossly inconsistent with USOS's claim that d-limonene readily vaporizes from the residual extract. Even if one assumes a mole fraction of d-limonene in the extract of 0.5, then one would still expect that the concentration of bitumen compounds in the raffinate to be 1000 times greater than their concentration in d-limonene-free water.

1 **Q: What is your conclusion based on the analysis above?**

2 Of course the specific values used in these calculations can be disputed, but what
3 cannot be disputed is that the dissolution of bitumen compounds in the raffinate is promoted by
4 the solid/liquid transition ($P^0(L)/P^0(S)$) and by solubilization into dissolved d-limonene ($\gamma^{sat}_{wl}/\gamma_{raf}$).

5
6 **Q: Are there any measurements that corroborate your calculations?**

7 The above calculated effect of d-limonene on the concentration of bitumen compounds
8 in the raffinate is corroborated by the values for percent bitumen content of return water
9 (900,000 $\mu\text{g/L}$) measured by USOS, and reported in documents provided to Living Rivers.
10 Johnson January 20, 2012 Testimony at 14.

11
12 **Q: How do the values measured by USOS equate with Mr. Handl's analysis?**

13 Such a high dissolved concentration of bitumen compounds is impossible to explain
14 using Mr. Handl's analysis. Mr Handl's analysis states that the maximum concentration of
15 combined bitumen compounds in the raffinate should be approximately 1.5 $\mu\text{g/L}$ in the absence
16 of d-limonene, and should decrease below that value as d-limonene is added to the system. In
17 contrast, the USOS data shows a bitumen concentration in the raffinate that is nearly a factor of
18 400,000 (more than five orders of magnitude) higher than the representative concentration 1.5
19 $\mu\text{g/L}$ chosen by Mr. Handl. Clearly Mr. Handl's analysis is greatly at odds with the data provided
20 by USOS.

1 **Q: Therefore, in addition to all of the other reasons stated above, is your analysis more in keeping**
2 **with the USOS findings?**

3 Yes. The data is explained by my analysis above. While my calculation estimated a
4 factor of 2000 increase in bitumen compound concentration (far lower than the observed
5 400,000 increase), my calculation assumed that d-limonene interacted with bitumen similarly to
6 octanol, which likely underestimates solubilization of bitumen compounds by d-limonene.
7 Furthermore, to accurately estimate the full extent of solubilization, my calculations would need
8 to include the mole fractions and vapor pressures of all bitumen compounds. The data provided
9 by USOS supports my claim that d-limonene will greatly increase the concentration of bitumen
10 compounds in water that comes into contact with the residual tar/d-limonene mixture.

11
12 **Q: Is there some test that would actually determine the degree to which the bitumen compounds**
13 **would dissolve into water in the presence of d-limonene?**

14 Yes. Such tests exist. For this reason, it would be prudent for the State of Utah to
15 require leach tests to be performed to quantify the potential for tar compounds to leach into
16 WATER from the residual tar/d-limonene mixture in the processed sand. These measurements
17 are not particularly difficult to perform, and would provide critical understanding of the
18 behavior of the tar compounds should the residual extract come into contact with water. A
19 leach test was previously performed using hexane; however, as recognized by DWQ, this test
20 provides no insight regarding what concentration of bitumen compounds would be expected in
21 water.

1 **Q: Please summarize your testimony.**

2 The goal of my testimony is to demonstrate what will happen when water, such as rain
3 water, contacts the residual tar/d-limonene mixture that will remain in the processed sands
4 returned to the mine and deposited in the waste piles at the PR Spring site. The critical question
5 to answer is whether addition of d-limonene will greatly increase the amount of bitumen
6 compounds that will dissolve into water when water comes into contact with the waste piles.
7 My January 20, 2012 testimony used specific values for benzo(a)pyrene (B(a)P) as an example
8 bitumen compound to demonstrate that the presence of d-limonene will greatly increase the
9 concentrations of these compounds that will dissolve into water in contact with the tar/d-
10 limonene mixture. My analysis showed that, in the presence of d-limonene, the concentration
11 of bitumen in water would be 1500 times higher than the concentration would be if d-limonene
12 were not present.

13 In his February 29, 2012 testimony, Mr. Handl disputes my findings. However, Mr.
14 Handl's analysis makes several errors in attempting to estimate the actual concentration of
15 bitumen in water contacting the residual tar/d-limonene mixture in the processed sands.

16 First, Mr. Handl did not sum the resulting concentrations for ALL compounds of interest
17 made using Raoult's Law. The sum of the concentrations for all compounds of interest would be
18 considerably higher than the concentration Mr. Handl calculates in his testimony.

19 Second, Mr. Handl treats the bitumen and water mixture as though it were ideal, which I
20 showed was improper. This mistaken assumption means that Mr. Handl's simplistic use of
21 Raoult's Law and his ternary phase equilibrium analysis lead to inaccurate results. As a result,
22 Mr. Handl greatly underestimates the effect that d-limonene has on expected concentrations of
23 bitumen compounds in water.

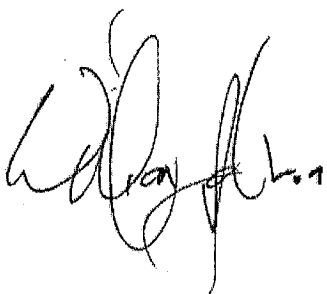
1 Third, Mr. Handl fails to account for the differences in the behavior of tar without d-
2 limonene (a semi solid) and the tar/d-limonene mixture (a liquid). This oversight further causes
3 Mr. Handl's calculation to severely underestimate the increase in the concentration of bitumen
4 compounds that will dissolve into water in the presence versus the absence of d-limonene.
5 I showed these flaws using both Mr. Handl's ternary equilibrium approach as well as an
6 approach using thermodynamic relationships.

7 I also showed that Mr. Handl's approach led to results that were not consistent with
8 USOC's own data and that my analysis more accurately reflect these company-provided results.

9 Finally, I stated that there are tests readily available that would determine the potential
10 for tar compounds to leach into water from the residual tar/d-limonene mixture in the
11 processed sand. I concluded that DWQ should order that such tests be run, reported and
12 analyzed before the agency permits the PR Spring mining operations.

13
14 **Q: Does this conclude your testimony for now?**

15 Yes.

16


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2 Additional References

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