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

EXHIBIT
PENGAD 800-631-6989
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Johnson

I. INTRODUCTION AND QUALIFICATIONS

Q. PLEASE STATE YOUR NAME?

A. My name is William P. Johnson

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

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

Q. FOR WHOM ARE YOU TESTIFYING IN THIS PROCEEDING?

A. I am testifying on behalf of Living Rivers.

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

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

II. PURPOSE AND SUMMARY OF TESTIMONY

Q. WHAT IS THE PURPOSE OF YOUR TESTIMONY?

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

Q. WOULD YOU PLEASE SUMMARIZE YOUR TESTIMONY?

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

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

Q. CAN YOU BRIEFLY DESCRIBE D-LIMONENE?

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

Q. CAN YOU DESCRIBE UTAH TAR SANDS COMPOUNDS?

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

Q. WHY ARE YOU CONCERNED ABOUT THE CARCINOGENCITY OF UTAH TAR SANDS COMPOUNDS WITH THE PR SPRING MINE?

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

Q. HOW SO?

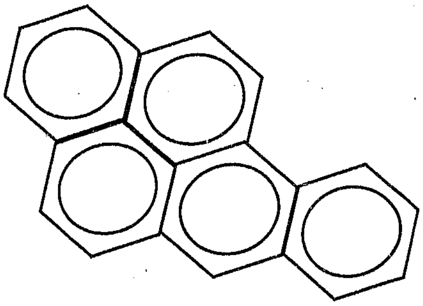
A. Note that these three properties: 1) the semi-solid phase nature of the tar; 2) the very low solubility of the tar compounds; and 3) the very low mobility of the tar compounds are precisely what allow these compounds, under natural conditions, to be considered relatively benign. However, combining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

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

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

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

A. To substantiate these two concerns, the following calculations are provided for a representative PAH compound, namely: (2) the factor by which the solubility of PAH is increased in the presence of d-limonene relative to water; and, (3) the factor by which the transport time of PAH over a given distance is decreased in the presence versus absence of d-limonene. The calculations are made using benzo(a)pyrene as a representative PAH. B(a)P has five fused aromatic rings. The choice of this compound is not critical to demonstrate the changes in transport of tar compounds in response to solubilization by d-limonene. Any PAH compound with four or more rings, and any unsubstituted alkane with approximately ten or more carbon atoms, will show similar effects. Such sizes of compounds (and larger) are expected to dominate the tar (Appendix B).



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

Molecular weight = 252.3 gmol^{-1}

Melting temperature = 176.5 °C

C^{sat}_{w} (s,25^{0}C) = 1.52 μgL^{-1}

C^{sat}_{w} (L,25^{0}C) = 49.19 μgL^{-1}

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

A. I calculated that factor as follows:

The normal solubility of B(a)P dissolving from solid tar in water (C^{sat}_{w}) at room temperature is 1.5 μgL^{-1}. When d-limonene is added to the water, it creates a liquid organic mixture, and this rises the solubility of B(a)P since it is dissolving not from solid tar, but from liquid d-limonene.

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

$$C^{*}_{w} = C^{sat}_{w} + C^{sat}_{w} K^{B(a)P}_{dl} C^{dl}_{w}$$

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

The value for $K^{B(a)P}_{dl}$ can be approximated by the distribution coefficient for B(a)P between water and octanol ($K^{B(a)P}_{ow}$). This value will underestimate the solubility enhancement of B(a)P by d-limonene, since octanol is a somewhat more polar solvent than d-limonene, which makes octanol slightly less ideal than d-limonene for solubilization of the non-polar compound B(a)P. The value of $K^{B(a)P}{}_{ow}$ is available in reference 5, hence:

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

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

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

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

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

Q. WHAT IS THE SIGNIFICANCE OF THIS INCREASED CONCENTRATION?

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

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

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

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

The distribution process is often considered to be near local equilibrium in groundwater because of the relatively slow velocities involved in groundwater flow. Because the tar sands are rich in organic carbon (including tar), and these compounds provide a compatible environment for non-polar compounds such as PAH, the partitioning of PAH between water and sand is driven by the affinity of the PAH compounds for the organic compounds (K_{om}), and the fraction of sediment mass comprised by organic compounds (f_{om}). As a result, the equilibrium constant for distribution of PAH between water and sediment can be calculated as:

$$K_d = K_{om} f_{om}$$

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

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

$$LogK_{om} = 0.81LogK_{ow} - 0.25$$

$$LogK_{om} = 0.81(6.60) - 0.25$$

$$K_{om} = 124{,}738$$

Therefore:

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

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

The retardation factor (R) is obtained from:

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

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

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

$$R = 607$$

Q. WHAT IS THE SIGNIFICANCE OF THIS CALCULATION?

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

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

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

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

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

$$Log K_{om}^{dl} = 0.81 Log K_{ow} - 0.25$$

$$Log K_{om}^{dl} = 0.81(4.2) - 0.25$$

$$K_{om}^{dl} = 1419$$

Therefore:

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

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

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

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

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

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

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

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

Hence:

$$R^* =$$

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

$$R^* = 140$$

Q. WHAT DOES THIS DEMONSTRATE?

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

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

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

Q. WHAT DID YOU CONCLUDE BASED ON YOUR CALCULATIONS?

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

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

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

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

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

Q. WOULD YOU CHARACTERIZE THE PROCESSED SEDIMENT AS "DAMP-DRY"?

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

Q. DOES THIS CONCLUDE YOUR TESTIMONY FOR NOW?

A. Yes.

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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 Department of Geology and Geophysics	Professor (since 2007) Assoc. Professor (2001-2007) Asst. Professor (1995-2001)
1994-1995	University of Arizona at Tucson Department of Hydrology and Water Resources Department of Chemical and Environmental Engineering	Research Assoc.
1993	Water Science, Inc.	Consultant
1990-1993	University of Colorado at Boulder Civil, Environmental & Architectural Engineering	Research Assistant
1987-1990	United States Geological Survey Water Resources Division	Hydrologist
1984-1986	Dartmouth College Department of Earth Sciences	Research Assistant 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.
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.
1980-1983	B.A. degree in Geology. Whitman College, Walla Walla, WA.

HONORS AND AWARDS

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

PROFESSIONAL AFFILIATIONS

Association of Environmental Engineering and Science Professors

American Geophysical Union

American Chemical Society

CURRENT FUNDED PROJECTS

The Ability for Impounded Wetland Sediment to Mobilize Metals, Ammonia and Sulfides and Their Potential Toxicity to Submerged Aquatic Vegetation and Macroinvertebrates, Central Davis Sewerage Improvement District, **05/2011-11/2012**, $40,000, sole PI.

Spatial variation of mercury methylation in the sediment and the deep brine layer of the Great Salt Lake, Utah Department of Wildlife Resources, Division of Forestry, Fire, and State Lands, **09/2011-08/2012**, $28,600, sole PI

Influence of Cell Surface Properties and Structures on Microbial Deposition in Porous Media in the Absence and Presence of Energy Barriers, American Chemical Society Petroleum Research Fund, **01/2011-01/2013**, $100,000, sole PI.

SPLITT-FFF-based detection and monitoring of engineered nanomaterials in aquatic systems, National Science Foundation Chemical, Biological, and Environmental Transport Program and Hydrology Program, **09/2010-08/2013**, $427,500, lead PI of three.

MRI Acquisition: An ICP-MS Facility at the University of Utah, National Science Foundation, EAR-MRI Program, **9/2009-08/2012**, $1,323,400, co-PI of five.

New Filtration Theory via Incorporation of Pore Scale Mechanisms Operating in the Presence of an Energy Barrier, National Science Foundation Chemical, Biological, and Environmental Transport Program and Hydrology Program, **09/2009-08/2012**, $426,000, sole PI.

A Quantitative Assessment of Mercury Influx to the Great Salt Lake, Regional Applied Research Effort (RARE) Program (USEPA Region 8), **09/2010-08/2012**, $200,000, co-PI with three.

REVIEWER FOR

Professional Journals

- Colloid & Surfaces
- Chemical Geology
- Chemosphere
- Environmental Engineering Science
- Environmental Pollution
- Environmental Science & Technology
- Geochimica et Cosmochimica Acta
- Journal of Contaminant Hydrology
- Journal of Colloid & Interface Science
- Journal of Environmental Engineering
- Journal of Environmental Monitoring
- Journal of Environmental Quality
- Journal of Geophysical Research
- Langmuir
- Separation and Purification Technology
- Vadose Zone Journal
- Water Research
- Water Resources Research

Funding agency proposal, panel, and center reviews

- National Science Foundation
  - Hydrologic Sciences Panel 2008-2011
  - Chemical, Biological, and Environmental Transport Panel 2010
  - External reviewer for National Center for Environmental Implications of Nanotechnology (CEINT) 2009 to present
- Department of Energy 1997
- American Chemical Society Petroleum Research Fund

COURSES CREATED AND TAUGHT

Environmental Conflict: Mining and Water Quality in Ecuador, Study Abroad May 2012

Sustainability Practicum

Aqueous Geochemistry for Engineers & Scientists

Subsurface Remediation and Hazardous Waste Management

Contaminant Partitioning for Engineers & Scientists

Architecture of the Earth

STUDENTS/ASSOCIATES ADVISED (Primary Advisor)

2005 to present:

Post-doctoral associates:

Dr. Huilian Ma, Degree: Chemical Engineering, Subject: New filtration theory for colloid retention under unfavorable conditions

Ph.D. recipients/candidates:

Mr, Eddy Pazmino, Degree: Chemical Engineering, Expected completion 2014, Subject: New filtration theory for colloid retention under unfavorable conditions

Mr. Greg Carling, Degree: Geology, Expected completion 2012, Subject: Mercury cycling in the Great Salt Lake Basin

Ms. Wenjie Huang, Degree: Chemical Engineering, Expected completion 2012, Subject: Nanoparticle characterization via field flow fractionation.

Dr. Ximena Diaz, Degree: Environmental Engineering, Completed 2008, Subject: Selenium cycling in the Great Salt Lake, Utah. Present position: Associate Professor of Extractive Metallurgy at the National Polytechnic University, Quito, Ecuador.

Dr. Xiqing Li, Degree: Environmental Engineering, Completed 2006, Subject: Role of fluid drag and energy barrier on colloid retention. Present position: Associate Professor in Resource and Environmental Science, at Peking University, Beijing, China

Dr. Meiping Tong, Degree: Environmental Engineering, Completed 2007, Subject: Role of pore domain geometry and energy barrier on colloid retention in porous media. Present position: Associate Professor in Environmental Science and Engineering, Peking University, Beijing, China

Dr. Pengfei Zhang, Degree: Geological Engineering, Completed 2000, Subject: Immunomagnetic methods for bacterial detection in groundwater and role of fluid velocity and predation on bacterial transport. Present position: Professor at City College of New York, New York.

M.S. recipients/candidates

Mr. Brooks Black, Degree: Geology, 2013, Subject: Mercury and Trace Element Cycling

Mr. Joel Pierson, Degree: Geology, 2013, Subject: Mercury and Trace Element Cycling

Mr. Neil Swanson, Degree: Geology, 2013, Subject: Mercury and Trace Element Cycling

Ms. Eliana Manangon, Degree: Geological Eng., 2012, Subject: Environmental Nanoparticles

Mr. Eddy Pazmino, Degree: Geological Engineering, 2011, Subject: Colloid transport

Ms. Abigail Rudd, Degree: Geological Engineering, 2010, Subject: Mercury methylation

Ms. Kimberley Beisner, Degree: Geology, 2008, Subject: Selenium cycling in the Great Salt Lake

Mr. Wade Oliver, Degree: Geology, 2008, Subject: Selenium sedimentation in the Great Salt Lake

Ms. Mary Ellen Potter, Degree: Civil Eng., 2008, Subject: Phosphorous accum. in Farmington Bay

Ms. Christina Brow, Degree: Environmental Eng., 2004, Subject: Colloid Transport

Mr. Michael Koch, Degree: Public Health, 2004, Subject: Cholera detection in ship ballast

Ms. Margaret McGriff, Degree: Geology, 2002, Subject: Surfactant solubilization of PCE and PAH

Mr. William McIntosh, Degree: Geology, 2002, Subject: Bacterial transport in groundwater

Mr. Ryan Rowland, Degree: Geology, 2002, Subject: U treatment in permeable reactive barrier

Mr. Gaobin Bao, Degree: Geology, 2000, Subject: Surfactant solubilization of PCE and PAH

Mr. Phillip Schmitz, Degree: Geol. Eng., 2000, Subject: Au extraction from carbonaceous ore

Mr. Wynn John, Degree: Geol. Eng., 1999, Subject: PAH solubilization by surfactants and NOM

Mr. Jorn Stenebraten, Degree: Geol. Eng., 1998, Subject: Au extraction from carbonaceous ore

PROFESSIONAL ACTIVITIES

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

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

ADVISORS

Ph.D. advisor: Dr. Gary Amy, U. of Colorado, Civil, Environmental, and Architectural Engineering

Post-doctoral advisor: Dr. Bruce Logan, U. of Arizona, Chemical and Environmental Engineering

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

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BOOK CHAPTERS

W.P. Johnson, **2008**, Mechanisms of Retention of Biological and Non-biological Colloids in Porous Media: Wedging and Retention in Flow Stagnation Zones in the Presence of an Energy Barrier to Deposition, in *Structure, Interactions and Reactivity at Microbial Surfaces*, T. Camesano and C. Mello eds., American Chemical Society Symposium Series 984, 339 pp.

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RECENT INVITED PRESENTATIONS (2010)

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

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

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

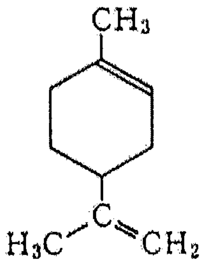
University of Utah Global Change and Ecosystem Center Fall Seminar Series: Ongoing research questions regarding Se and Hg in the Great Salt Lake

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

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

Appendix B: Properties of d-limonene

solubility in water = 13.8 mg/L	ref 1
Koc = 1030-4780 ml/g	ref 2
Half lives: biotic (aerobic) < 14 days, abiotic (in air) < 2 hours	ref 2
Log octanol-water partition coefficient = 4.2	ref 1
Formula: C10H16	ref 3
Molecular weight = 136.24	ref 3
Temp melt: -142.4 F	ref 3
Vapor Pressure:	
2.0 mm Hg	ref 1
1.0 mm Hg at 57.0 ° F	ref 3
5 mm Hg at 104.7° F	ref 3
10 mm Hg at 128.8° F	ref 3
Vapor Density: 4.69	ref 3
Specific Gravity: 0.8411 at 68.0 ° F	ref 3
Boiling Point: 348-349 ° F at 760 mm Hg (NTP, 1992)	ref 3



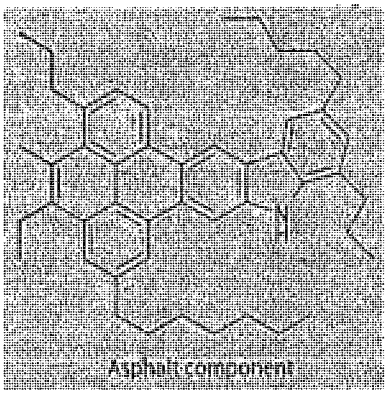
Appendix C: Properties of the tar

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.

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.

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

URL above boils down to: the tar sands are expected to be dominated by asphaltenes. Petroleum-based asphaltenes (as opposed to coal-based) have a significant alkane fraction and contain large aromatic ring systems.

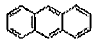
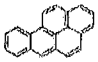
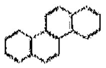
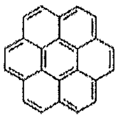
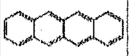
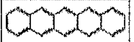
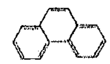
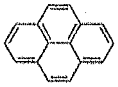
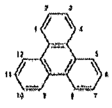
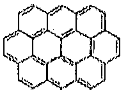


Such molecular structure can be exemplified by the following structure (figure left). Such structures dominated by non-polar bonds characteristically have low water solubilities, e.g. in the μg/L range or less.

Multiple 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

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

(Figure source reference 4)

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

Appendix D - Risk

The cleanup level to meet a given excess carcinogenic risk is obtained by the following equation which determines the intake concentration (in this case in groundwater) corresponding to the acceptable excess carcinogenic risk (set to 1E-6 as default regulatory goal).

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

where:

cleanup level = concentration of compound in groundwater (e.g. mg/L)
R = acceptable excess carcinogenic risk (1E-6 regulatory goal)
BW = body weight (kg)
AT = averaging time (days)
CSF = carcinogenic slope factor for the compound (excess risk per mg/(kg-day))
CR = contact rate (e.g. L/day)
AAF = absorption adjustment factor (usually set equal to unity as default)
EF = exposure frequency (days/year)
ED = exposure duration (years)

Despite being a suspected carcinogen, there is no CSF available for perylene. However, a CSF is available for benzo(a)pyrene, which is another 5-ring PAH expected in crude oil and tar.

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

$$\text{cleanup level} = \frac{(1E-6)(70 kg_{bodyweight})(365 \frac{days}{year} 70 \frac{years}{ave\,time})}{(7.3 \frac{\frac{excess\ risk}{mg_{cmpd}}}{kg_{bodyweight} - day})(2 \frac{L_w}{day})(1)(365 \frac{days}{year})(70 \frac{years}{ave\,time})}$$

cleanup level = 0.00479 μg/L

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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

I. Introduction

Q. Please state your name.

My name is William P. Johnson

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

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

Q. For whom are you testifying in this proceeding?

I am testifying on behalf of Living Rivers.

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

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

Mr. Handl's February 27, 2012 Report

Perry's Chemical Engineer's Handbook, 1999

Perry's Chemical Engineer's Handbook, 1973

(Schwarzenbach R.P., Gschwend P.M., and Imboden D.M., 1993, Environmental Organic Chemistry, Wiley Interscience, New York

Johnson, W.P., and John, W.W., 1999, A Comparison of Humic Substances and Surfactants as Remediation Agents: PCE Solubilization and Mobilization by Commercial Humic Acid, J. of Cont. Hyd., 35, 343-362.

Johnson, W.P., Cabral, K., Lion L.W., and Corapcioglu, Y.M., 1998, Reconciliation of Expressions for the Modified Retardation Factor and Incorporation of Non-linear Effects, J. Cont. Hydr.32, 247-266.

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.

II. Rebuttal to Edward Handl

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

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

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

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

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

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

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

No, Mr. Handl is mistaken when he makes a significant issue out of the fact that I did not account for specific mole fractions in the tar/d-limonene mixture (extract), which are of course needed in order to calculate the specific concentration of a given compound that is achieved in water (raffinate) that is in contact with the residual tar/d-limonene mixture (extract). However, the issue is NOT the specific concentration of benzo(a)pyrene (B(a)P) or any other given bitumen compound in water, because there is an entire class of compounds that are of concern. Specifically, Raoult's Law for compounds dissolving into water for under ideal conditions is:

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

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

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

Furthermore, as I show below, Mr. Handl's incorrect assumption of ideal mixing leads to further underestimation of the value of C_{raf} (the concentration of bitumen compound in the raffinate, which I referred to as $C^{*}{}_{w}$ in my previous testimony). This means that Mr. Handl substantially underestimated the concentration of bitumen compounds in the raffinate because he did not sum the concentrations for all the bitumen compounds of interest that will dissolve into the water phase AND because he did not account for the fact that dissolved d-limonene in the water phase (raffinate) would provide an ideal phase for the bitumen compounds, thereby increasing the concentration of bitumen compounds in the raffinate. Had Mr. Handl summed the concentrations of the many compounds in the tar, and had he accounted for solubilization of bitumen compounds by d-limonene in the raffinate, his calculations would have shown a significantly higher concentration of bitumen compounds in the raffinate.

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

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

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

For the present purposes, the primary issue is the CHANGE in the concentration of bitumen compounds in water before, versus after, the addition of d-limonene. My testimony used partition coefficients (equilibrium coefficients for distribution of an example bitumen compound between water and d-limonene) to demonstrate that the addition of d-limonene to water increases the solubility of bitumen compounds in the water solution by multiple orders of magnitude.

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

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

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

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

$$\mu_o = \mu^0 + RT \ln \frac{\gamma_o X_o P^0(L)}{P^0(L)} \qquad (2)$$

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

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:

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

And re-arranging further yields

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

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.

Q: What do activity coefficients tell us?

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

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

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

What precisely is the value of γ_w in the raffinate is at the heart of the dispute between Mr. Handl and me. Mr. Handl contends that this value is nearly one billion in the raffinate (as in pure water) despite the presence of highly compatible d-limonene in the raffinate. In contrast, my analysis shows that the value in the raffinate drops significantly below that in pure water due to the presence of highly compatible d-limonene in the raffinate. The decreased activity coefficient of bitumen compounds in the raffinate (relative to that in pure water) yields a much higher concentration of bitumen compounds in the raffinate than one would predict for pure water. Mr. Handl's assumption of ideal conditions predicted a concentration of bitumen compounds in the raffinate that approximate the concentration of bitumen in pure water, and ignored the effect of d-limonene dissolved in the water.

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

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

$$\gamma^{sat}{}_w = \frac{1}{X^{sat}{}_w(L)} \qquad (6)$$

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

$$\gamma^{sat}{}_w = \frac{1}{X^{sat}{}_w(L)} = \frac{1}{C^{sat}{}_w(L)}\frac{1}{V_w} \qquad (7)$$

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

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

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

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

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

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

Q: What does this calculation show us?

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

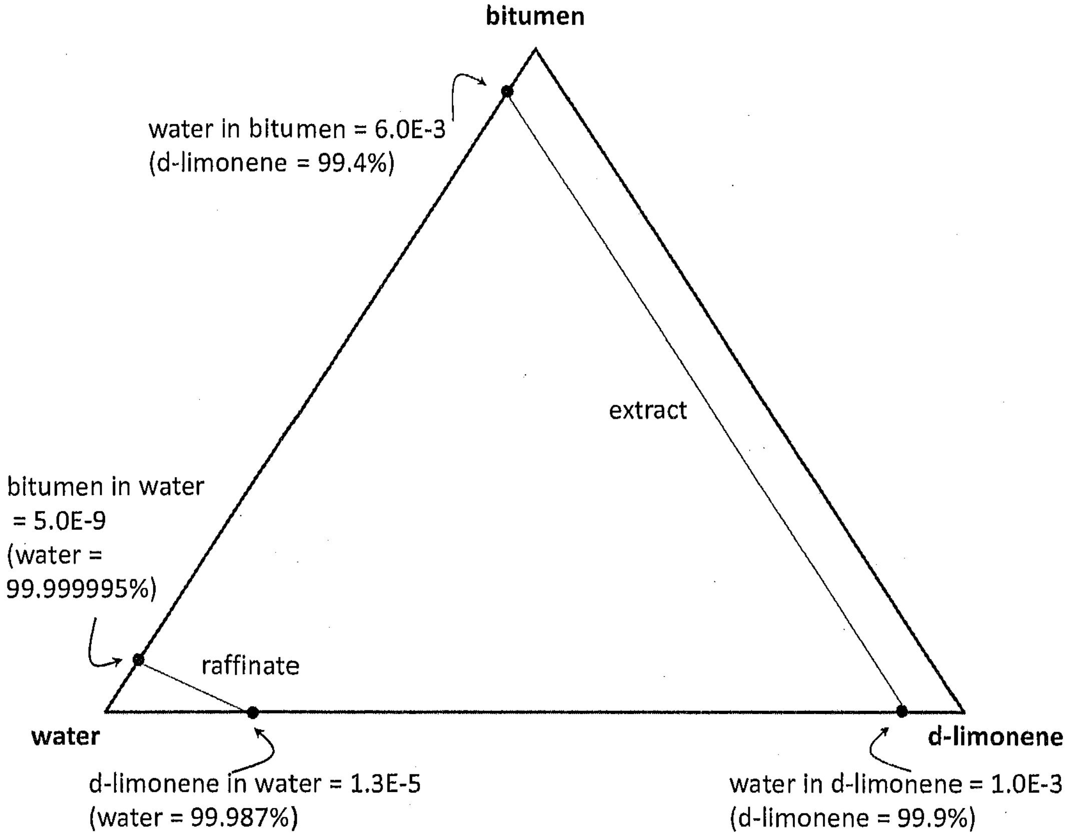
Q: O.K. but before you do, would you summarize your points so far in your testimony?

As indicated above, I demonstrated that Mr. Handl substantially underestimates the concentration of bitumen in the raffinate because he does not sum or add up the concentrations for all the bitumen compounds of interest that will dissolve into the water. I also have further shown that bitumen and water are not an ideal mixture and indeed, are far from ideal. This sets the basis for demonstrating that the non-ideality of interaction between bitumen and water needs to be accounted for. Below I show how this would need to be done using Mr. Handl's ternary phase equilibrium approach, as via thermodynamic relationships.

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

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

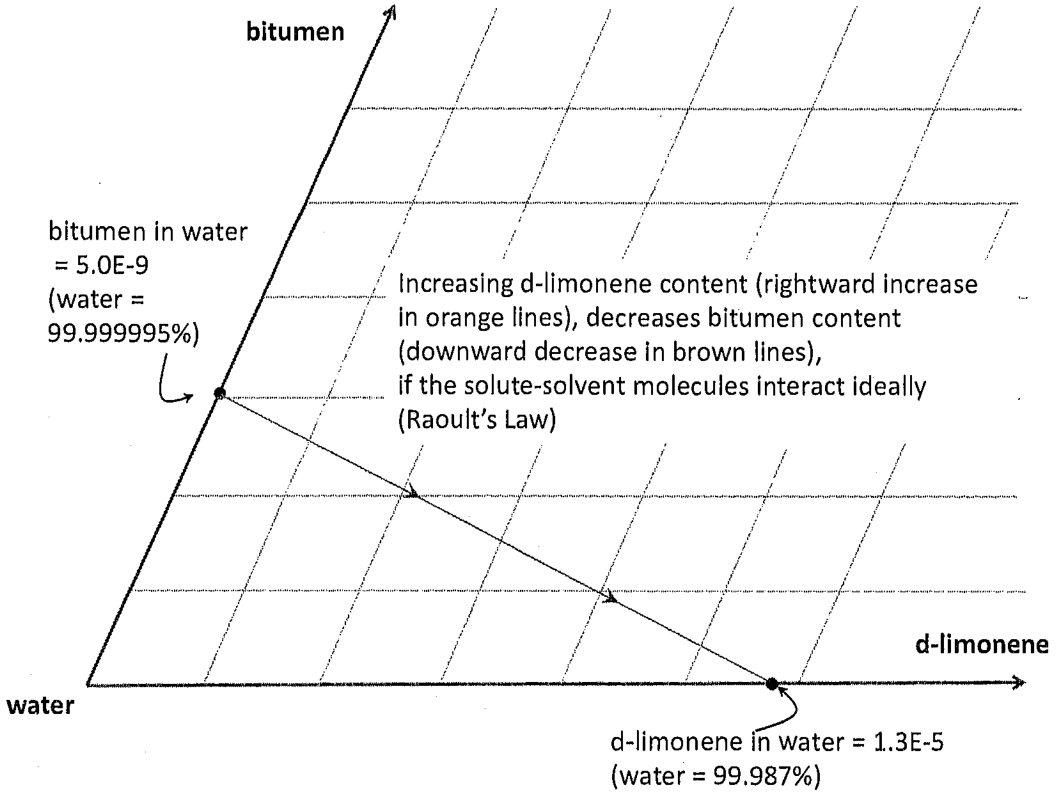
To argue in his response that addition of d-limonene only decreases the concentration of bitumen in water, Mr. Handl's utilizes ternary phase equilibrium analysis, where the solubilities of: 1) water in bitumen; 2) bitumen in water; 3) d-limonene in water; and 4) water in d-limonene are plotted on a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



Mr. Handl correctly points out that these plotted solubilities demonstrate that two separate phases will exist if water comes into contact with the extract (residual tar/d-limonene mixture): a) a water-rich raffinate phase in the lower left; and b) an organic-rich extract phase in the upper/right of the triangle. Mr Handl contends that adding d-limonene to the organic mixture reduces the amount of bitumen compound available to dissolve into water, and while this is correct, as explained further below, this is only part of the picture.

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

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



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

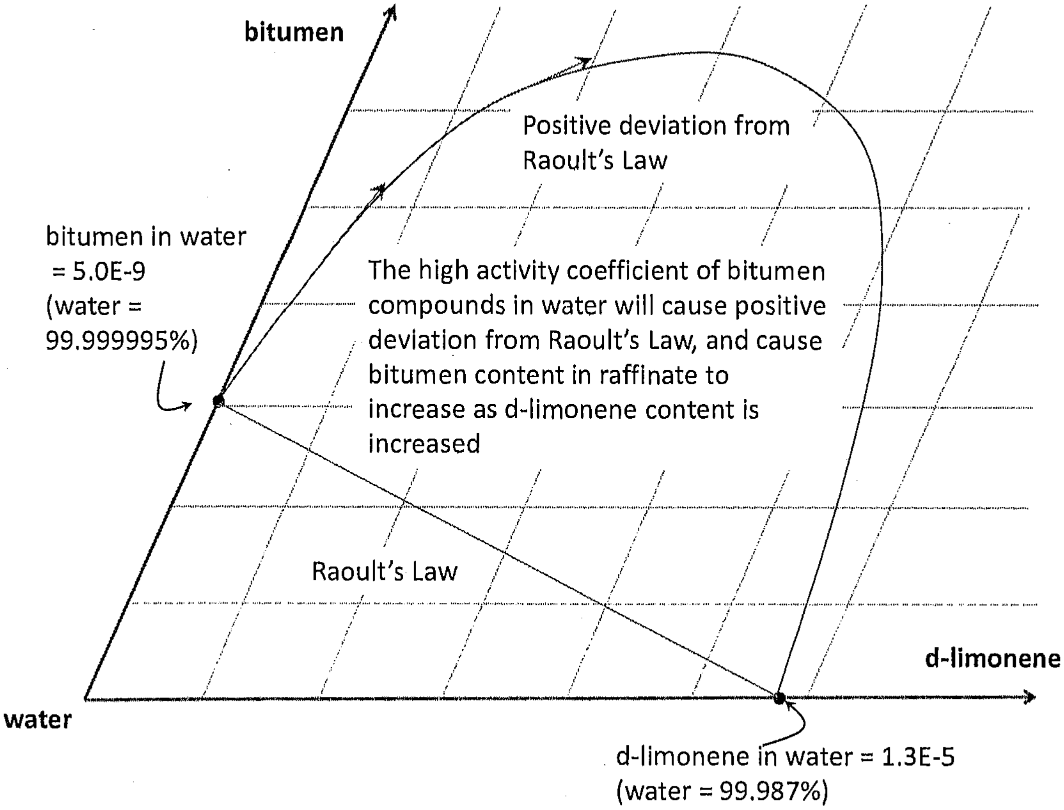
Q: Is Mr. Handl's assertion accurate?

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

$= \gamma^{sat}_{w}$). However, the fact is that the raffinate boundary does not, should not, and cannot follow Handl's assumed line.

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

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



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

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

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

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

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

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

Q: Please summarize the further points you have made.

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

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

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

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

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

Thermodynamics and Non-Ideality – Quantitative

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

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

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

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

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

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

$$\gamma_o X_o P^0(S) = \gamma_w X_w P^0(L) \tag{11}$$

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

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

Q: What does Equation 12 tell us?

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.

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

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

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:

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

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

Yielding:

$$\gamma_{ext}X_{ext} = \gamma_{raf}X_{raf} \tag{15}$$

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

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

Comparing Bitumen Compound Concentrations in the Water Phase in the Presence versus Absence of d-limonene

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

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

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

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

$$\frac{X_o(1-X_{ext}^{d-\lim onene})}{X_{raf}} = \frac{\gamma_{raf}}{1} \qquad (18)$$

Combining (17) and (18) yields:

$$X_o = \frac{X_w \gamma^{sat}{}_w P^0(L)}{P^0(S)} = \frac{\gamma_{raf} X_{raf}}{(1-X_{ext}^{d-\lim onene})} \qquad (19)$$

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

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

Q: What does Equation 20 show?

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

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

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

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

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

$$X_w = \gamma_o X_o X^{sat}{}_w(L) \tag{22}$$

Substituting (22) into (21) yields:

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

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

$$X_{raf} = \gamma_o X_{ext} X^{sat}{}_w(L) \left(\frac{\gamma^{sat}{}_w}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \tag{24}$$

And recognizing that $\gamma_o \sim 1$, $C^{sat}{}_w(L)V_w = X^{sat}{}_w(L)$, $C_{raf}V_{raf} = X_{raf}$, 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:

$$C_{raf} = X_{ext} C^{sat}{}_w(L) \left(\frac{\gamma^{sat}{}_w}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \tag{25}$$

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) $\gamma^{sat}{}_w/\gamma_{raf}$; 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).

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

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

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

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

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

$$\frac{P^o_{(L)}}{P^o_{(S)}} = e^{\left(\frac{\Delta S_{melt}(T_m)}{R}\right)\left(\frac{T_m}{T}-1\right)} \qquad (26)$$

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

Hence:

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

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

Yes. But, the activity coefficient ratio $\gamma^{sat}_w/\gamma_{raf}$ 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 $\gamma^{sat}_w/\gamma_{raf}$ 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.

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

Conversion of the mole fractions to concentrations yields:

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

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:

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

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:

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

Comparing the value of γ_{raf} ($10^{7.45}$ = 11,200,000) to $\gamma^{sat}{}_{w}$ ($10^{8.45}$ = 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 ($\gamma^{sat}{}_{w}$) 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 $\gamma^{sat}{}_{w}/\gamma_{raf}$ and $P^0(L)/P^0(S)$ terms on the concentration of bitumen compound in the raffinate, we can assume that $\gamma^{sat}{}_{w}/\gamma_{raf}$ 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:

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

Q: What does Equation 32 show?

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.

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

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 ($P^0(L)/P^0(S)$) and solubilization of bitumen compounds by dissolved d-limonene in the raffinate ($\gamma^{sat}{}_{w}/\gamma_{raf}$).

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

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.

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

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

Q: Are there any measurements that corroborate your calculations?

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

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

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

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

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

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

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

Q: Please summarize your testimony.

The goal of my testimony is to demonstrate 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 critical question to answer is whether addition of d-limonene will greatly increase the amount of bitumen compounds that will dissolve into water when water comes into contact with the waste piles. My January 20, 2012 testimony used specific values for benzo(a)pyrene (B(a)P) as an example bitumen compound to demonstrate that the presence of d-limonene will greatly increase the concentrations of these compounds that will dissolve into water in contact with the tar/d-limonene mixture. My analysis showed that, in the presence of d-limonene, the concentration of bitumen in water would be 1500 times higher than the concentration would be if d-limonene were not present.

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

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

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

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

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

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

Q: Does this conclude your testimony for now?

Yes.

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